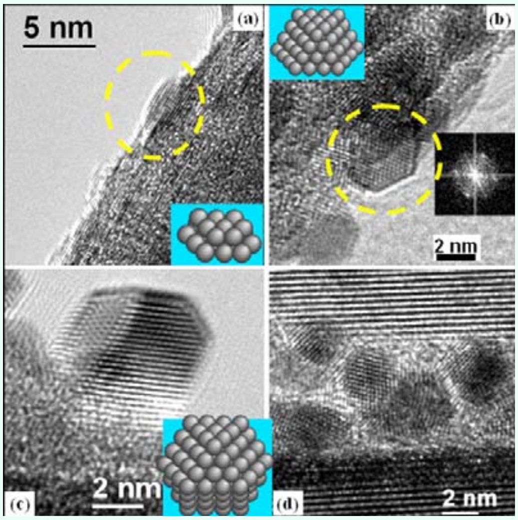
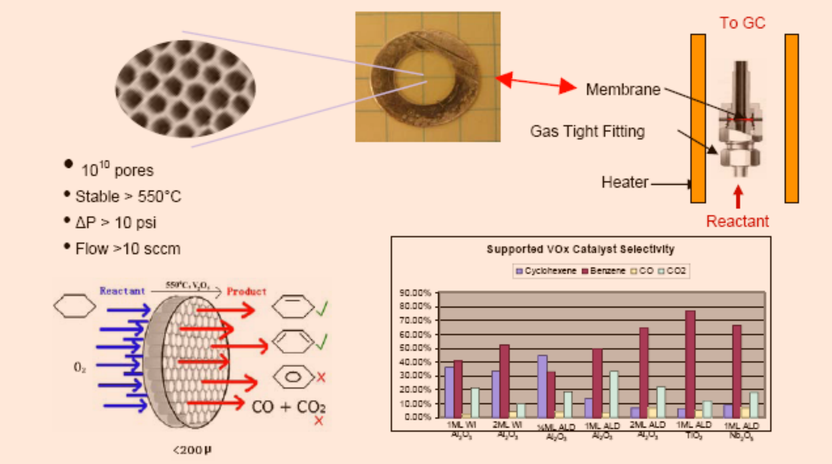
Frontiers in Interfacial and Nano Catalysis





Meeting of the Catalysis and Chemical Transformations Program
Chemical Sciences, Geosciences and Biosciences Division
Office of Basic Energy Sciences
U.S Department of Energy
Wintergreen, VA
May 23-26, 2007

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Cover figures (clockwise):
1. Nuzzo, R., et al.: HRTEM of oxygen-treated Au particles with various sizes and shapes
2. Liu, M.: Potential energy profiles for the interactions of O_2 and LaSrMn electrolyte
3. Stair, P.: Oxidative dehydrogenation on VO_x over nanostructured membranes

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FOREWORD

The 2007 Catalysis and Chemical Transformations Program Meeting is sponsored by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences (OBES), U.S. Department of Energy. It is being held on May 23-26, 2007, at the Wintergreen Resort, Wintergreen, VA. The main purpose of the meeting is to discuss the advances made by the program PIs over the past two years, to discuss the future directions for the program and catalysis, and to foster exchange of ideas and cooperation among participants. This year's meeting will encompass projects in heterogeneous catalysis, surface science and electrochemistry, and some of the projects recently started in nanoscience, biocatalysis, hydrogen fuel initiative, and chemical imaging.

Catalysis activities within OBES emphasize fundamental research aimed at understanding and controlling the chemical reactivity of fluid and condensed matter. The long-term goal of this research is to discover the fundamental principles and develop the techniques to predict structure-reactivity relations. Such knowledge, integrated with advances in synthesis, instrumentation, characterization, and theory, will help us to control chemical reactions along desired pathways. Ultimately, this new knowledge will result in chemical and materials processes to efficiently convert fossil and renewable resources, or to generate, convert and store energy, with minimum impact to our environment.

Special thanks go to our invited speakers, who will relate to us recent advances in their fields, to the program investigators and their students, postdocs, and collaborators, for their dedication to the continuous success and visibility of the OBES Catalysis and Chemical Transformations Program, and to the session moderators, for their invaluable help. We also thank the Oak Ridge Institute of Science and Education staff, Ms. Sophia Kitts, Ms. Deborah Garland, Ms. Camella Mitchell, Ms. Deborah Grubb, and Ms. Angie Lester, for the logistical and web support and the compilation of this volume.

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MEETING OVERVIEW

2007 Meeting of the DOE/BES Catalysis and Chemical Transformations Program

May 23 – 26, 2007 Wintergreen, VA

Time	Wednesday, May 23	Thursday, May 24	Friday, May 25	Saturday, May 26
7:00 AM		**Continental breakfast** *Skyline*	**Continental breakfast** *Skyline*	**Continental breakfast** *The Edge*
8:00				
8:30		**Thursday morning session** *Skyline*	**Friday morning session** *Skyline*	**Saturday morning session** *Skyline*
9:00				
10:00				
11:00				
11:30				**Lunch buffet** *Skyline*
noon		**Lunch buffet** *Skyline*	**Lunch buffet** *Skyline*	
12:30 PM				
1:00				**Meeting adjourns**
2:00				
3:00	**Poster set-up begins** *Commonwealth Ballroom*			
4:00	**Registration** *Mountain Inn Lobby*			
5:00		**Posters** *Commonwealth Ballroom*	**Posters** *Commonwealth Ballroom*	
5:30				
6:00	**Registration concludes for the day** **Dinner buffet** *Skyline*	**Dinner buffet** *Blue Ridge Terrace*	**Dinner buffet** *Skyline*	
7:15	**Wednesday evening session** *Skyline*	**Thursday evening session** *Skyline*	**Friday evening session** *Skyline*	
9:00	**Posters** *Commonwealth Ballroom*			
9:30		**Posters** *Commonwealth Ballroom*	**Posters** *Commonwealth Ballroom*	

2007 Meeting of the DOE/BES Catalysis and Chemical Transformations Program
May 23-26, 2007 – Wintergreen, Virginia

Poster Presentations – Commonwealth Ballroom
Oral Presentations – Skyline

Meeting Agenda

Wednesday, May 23, 2007

06:00 p.m. Dinner

Evening Sessions – Chair: Steve Overbury

07:30 p.m. **Keynote:** Can Li - *UV Raman Spectroscopic Studies on Catalytic Materials: Active Sites and Active Phases*

08:30 p.m. Nick Camillone – *Towards time- and space-resolved chemical imaging: ultrafast and chemically-specific STM*

09:10 p.m. Poster Session

Thursday, May 24, 2007

Morning Sessions – Chair: Fabio Ribeiro

07:30 a.m. Breakfast

08:30 a.m. **Keynote:** *Molecular Transformations, Catalysis and Modeling in Support of Catalyst Development in the Context of Conversion of Canadian Bitumen to Transportation Fuels*

09:30 a.m. Lanny Schmidt - *Renewable Hydrogen and Chemicals at Millisecond Contact Times*

10:10 a.m. Break

10:40 a.m. Jim Dumesic - *Catalytic Conversion of Carbohydrates to Liquid Fuels*

11:20 a.m. Victor Lin - Multifunctional Mesoporous Silica Nanoparticles for Selective Catalysis and Conversion of Bio-based Feedstocks to Biodiesel and Valueadded Chemicals

12:00 p.m. Lunch

Evening Sessions – Chair: Judith Yang

05:00 p.m. Poster Session (Continues)

06:00 p.m. Dinner

07:30 p.m. Abhaye Datye - *Nanostructured Catalysts for Hydrogen Generation from Renewable Feedstocks*

08:10 p.m. Perla Balbuena - *Analysis of reactivity and stability against dissolution of bimetallic nanocatalysts*

08:50 p.m. Jinguang Chen - *Novel properties of monolayer bimetallic surfaces*

09:30 p.m. Poster Session (Continues)

Friday, May 25, 2007

Morning Sessions – Chair: Francisco Zaera

07:30 a.m. Breakfast

08:30 a.m. **Keynote:** Johannes Lercher - *Catalytic conversion of alkanes by bifunctional catalysis*

09:30 a.m. Susannah Scott - *Explorations of amorphous oxide surfaces and their role in activating organometallic catalysts*

10:10 a.m. Break

10:40 a.m. Annabella Selloni - *Defects at TiO_2 surfaces*

11:20 a.m. *Mike Henderson - Radical* thinking about photocatalysis on TiO_2

12:00 p.m. Lunch

Evening Sessions – Chair: Talat Rahman

05:00 p.m. Poster Session (Continues)

06:00 p.m. Dinner

07:30 p.m. Matt Neurock – *First Principles Insights in the Influence of Alloying on Metal Catalyzed Oxygenate Synthesis*

08:10 p.m. Cynthia Friend - *The Surface Chemistry of Oxidation Reactions on Au*

08:50 p.m. Mike White - *Characterization and reactivity of metal compound clusters prepared by size-selected deposition*

09:30 p.m. Poster Session (Continues)

Saturday, May 26, 2007

Morning Sessions – Chair: Charles Campbell

07:30 a.m. Breakfast

08:30 a.m.	Chuck Peden - *Early Transition Metal Oxides as Catalysts: Crossing Scales from Clusters to Single Crystals to Functioning Materials*
09:10 a.m.	John Vohs - *Structure-Activity Relationships for the Reaction of Thiols and Alkyl Sulfides on Metal Oxide Surfaces*
09:50 a.m.	Jonah Erlebacher - *Mesoporous Metals with Monolayer-Thick Precious Metal Electrocatalyst Skins*
10:30 a.m.	Break
11:00 a.m.	Discussion on Future Directions
12:00 p.m.	Lunch
01:00 p.m.	Adjourn

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Poster Presentations

Poster Presentations Addendum

UV Raman Spectroscopic Studies on Catalytic Materials: Active Sites and Active Phases

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UV Raman spectroscopy is becoming a powerful characterization technique for chemistry, physics, biology, materials science as well as many other fields, mainly because it can avoid the fluorescence interference occurred in visible Raman spectra and concurrently can enhance the Raman signal owing to the short wavelength of the excitation laser and resonance Raman effect. This opens up the possibility for Raman spectroscopy to characterize a wide range of catalytic materials, particularly nanomaterials, such as metal oxides, microporous and mesoporous materials, and functional materials under working conditions.

This lecture presents a brief introduction of UV Raman spectroscopy and the recent advances in the characterizations of catalytic materials using the UV Raman spectroscopy, including the characterization of transition metal oxides highly dispersed at atomic, molecular as well as nano scales; metal ions incorporated in the framework of microporous and mesoporous materials; and the surface phase evolution of metal oxide materials in the preparation process. In particular, this lecture focuses on the structural characterization of catalytically active sites, like transion metal ions in porous materials and active phases of transition metal oxide catalysts such as ZrO_2 and TiO_2. The active sites and the active phases characterized by UV Raman spectroscopy are well correlated with their catalytic performance. The present work also further demonstrates that the characterization of catalytic materials at molecular and nano levels are essentially important to develop more active and selective catalysts.

Contractor No. FWP CO-023 **Nicholas Camillone III**
Peter Sutter

Ultrafast and Chemically Specific Microscopy for Atomic Scale Imaging of Nano-Photocatalysis

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Goal

The objective of this multidisciplinary program is to develop and apply new techniques that advance the understanding of atomic-scale mechanisms of photocatalytic reactions at nanostructured surfaces. We explore novel experimental approaches that probe light-induced nonequilibrium charge populations with combined sub-picosecond temporal and sub-nanometer spatial resolution. When combined with a chemically-selective probe that can quantitatively assess reactant and product populations, such a novel tool has the potential for unprecedented insight into the mechanisms of photocatalytic reactions on nanostructured surfaces. To map photoinduced electronic excitation dynamics in individual nanostructures, we are implementing a two-pulse correlation technique, shaken pulse pair excitation STM, which couples scanning tunneling microscopy (STM) with femtosecond laser excitation. In addition, we are developing energy-filtered STM (EF-STM) as a chemically-selective technique to image catalytic centers and track adsorbed reactants and products. Ultimately SPPX-STM and EF-STM will be combined to study photocatalysis on single supported nanoparticles.

DOE Interest

Photocatalytic chemical transformations on supported nanoparticles are important to solar photoconversion and photocatalytic environmental remediation chemistries. Because heterogeneous sensitized photoreactions depend on the transfer of charge or energy from the photoexcited catalyst to a ground-state adsorbate molecule, their efficiency depends strongly on the rate of hot carrier relaxation near the binding site. Basic investigations of nanoparticle-based photocatalysis pose two fundamental challenges: (i) probing hot-carrier dynamics for individual nanostructures with sub-picosecond temporal resolution, and (ii) tracking changing populations of active sites and reaction species. Measurements characterizing dynamical events with space, time, and energy resolution at the single molecule level coincide with emerging opportunities in the area of nanophotocatlysis on supported nanoclusters.

Recent Progress

This project is in the initial development phases now focused on the installation of a new laser system and STM. Early work addresses the technical challenges associated with coupling laser pulses into the microscope, and aims at the implementation of SPPX-STM in a well-defined environment (ultrahigh vacuum) on a model material system.

Experimental Design, Purchase and Construction: The experiments use a new, state-of-the-art, commercial Besocke-type STM system for operation at low temperatures (5 K). This system is on schedule to be installed at Brookhaven's Center for Functional Nanomaterials in April of 2007.

Time-resolved correlation measurements require coupling the output of an ultrafast laser into the STM tunneling gap. For this purpose a new, sub-60-fs, ultrafast Ti:sapphire laser system and associated pulse diagnostics have been purchased and are being installed. Optics, optomechanics and electronics are being designed or purchased to assemble an optical system suitable for stable introduction of the beam into the STM tunneling gap and manipulation of the pulses for the correlation measurements.

Surface Preparation and Nanoparticle Deposition: Initial work on the proposed model surface, rutile $TiO_2(110)$, has established sample preparation and the imaging of well-ordered TiO_2 surfaces by UHV-STM. Methods for deposition of metals (*e.g.*, Pd, Au) by physical-vapor deposition have been developed, and are now being optimized to yield well-defined populations of oxide-supported nanoparticles required for this program. These are necessary building blocks as we move toward the initial time-resolved STM experiments which are to be conducted on both metal films and nanoparticles supported on the $TiO_2(110)$ surface.

Future Plans

In the near term, the work will follow two parallel tracks: (i) development of ultrafast two-pulse correlation STM and (ii) development of energy-filtered STM for chemical imaging of molecular adsorbate states.

Spatially-Resolved Ultrafast Carrier Dynamics: The possibility of achieving spatially-resolved measurements of sub-picosecond carrier dynamics will be explored, initially based on an approach recently described by Shigekawa and coworkers [H. Shigekawa, *et al.*, *Sci. Tech. Adv. Mater.*, **6**, 582 (2005)]. With the STM tip held stationary above a point of interest on the sample, a mode-locked Ti:Sapphire laser ($\lambda = 800$ nm, $\Delta t < 100$ fs) is tightly focused onto the sample surface under the tip, and the time-dependent electron energy distribution is probed by measuring photoinduced changes in tunneling current (Fig. 1). Because the STM electronics are far too slow to capture transients on a sub-picosecond timescale, a two-pulse correlation (2PC) method is employed. Each excitation pulse is split into two pulses separated by a variable delay time, t_d. The observed signal is the result of the nonlinear dependence of the tunneling current on t_d and reflects the characteristic relaxation times of the electron energy distribution. To minimize parasitic effects (*e.g.*, due to thermal expansion) which have historically hindered progress in photoexcited STM, a high repetition-rate (80 MHz) laser and a long time constant in the STM feedback loop are employed. To enhance sensitivity, the time delay is modulated and lock-in detection is used; thus the method is referred to as shaken-pulse-pair-excited STM (SPPX-STM).

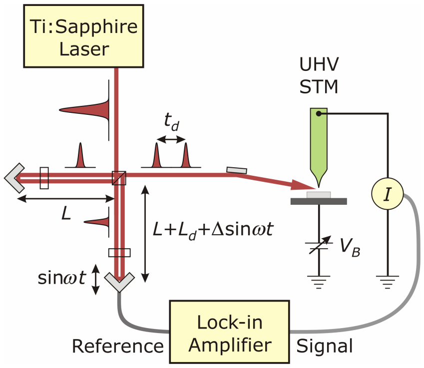

FIG. 1. Schematic of the shaken-pulse-pair-excited STM experiment.

Energy-Filtered STM for Atomic-Level Chemical Imaging: Complementing our work on SPPX-STM outlined above, we will develop energy-filtered STM (EF-STM) for molecular-level spectroscopic mapping of photocatalytic reactions at surfaces. We have recently demonstrated this new pathway toward spectroscopic STM that is inherently fast and thus applicable to surface reaction kinetics [P. Sutter, P. Zahl, E. Sutter, and J.E. Bernard, *Phys. Rev. Lett.*, **90**, 166101

(2003), Fig. 2]. The technique replaces the conventional metal STM probe with a semiconductor tip to achieve efficient energy filtering of the tunneling current in constant-current STM, which can be used to selectively image individual localized electronic states at surfaces. A logical extension of EF-STM for atomic-scale chemical mapping is its development for species-specific imaging of molecules adsorbed on metal or semiconductor substrates. If different molecules give rise to localized states with characteristic energies, such electronic signatures can be used to selectively map different adsorbates or different binding sites of the same molecular species. In addition to avoiding the complex modulation techniques used in conventional tunneling spectroscopy, EF-STM has the potential to provide generic fingerprinting of adsorbed molecules and of a wide range of other surface species that give rise to localized electronic states, such as defects or substituted surface atoms. This approach would enable the mapping of complex chemical reactions in unprecedented detail.

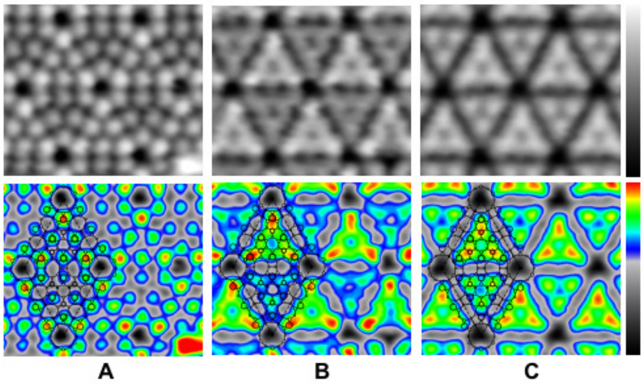

FIG. 2. Demonstration of state-selective imaging in filled-state EF-STM on Si(111)-(7x7). **a)** Preferential adatom imaging (bias: 1.0 V). **b)** Simultaneous imaging of adatom and rest-atom surface states (bias: 1.7 V). **c)** Preferential rest-atom imaging (bias: 2.0 V).

Primary Milestones: Extended semiconductor, metal single crystal, and thin film surfaces will be used for the first 2PC measurements. Our goals will be: (i) to unambiguously identify laser-induced tunneling signals and establish a clear link between the optical excitation and the tunneling signal, (ii) explore the dependence of these signals on STM operating parameters and incident laser characteristics (*e.g.*, polarization, pulse width, pulse energy, repetition rate) with the goal of identifying conditions (*e.g.*, field-enhancement effects) that provide a superior signal-to-noise ratio, (iii) gain a fundamental understanding of the physical mechanism(s) responsible for the observed effect(s). We anticipate that a significant effort will need to be invested in identifying — and developing methods to suppress — possible parasitic effects, such as thermal expansion of sample and tip, or multiphoton photoemission. In addition, an important component at this stage will be calculations aimed at simulating the STM current with the purpose of identifying and understanding the mechanism responsible for the observed signals and guiding our experiments. The number of adjustable experimental parameters is large; a model that can predict system responses to changes in even some of these parameters at a qualitative or semi-quantitative level will greatly aid the development of our experimental methods.

A major milestone of the project will be the demonstration of combined sub-picosecond temporal and sub-nanometer spatial resolution in our STM-based 2PC technique. Our plan is to apply SPPX-STM to the measurement of carrier dynamics in and around individual supported metal nanoparticles on wide-gap semiconductor substrates such as TiO_2. The selective excitation of nanoparticles will provide a clear means for testing the spatial resolution of the technique, and thus provide proof of simultaneous spatial and temporal resolution not achieved in previous experiments. The experiments will be performed in UHV and at temperatures low enough to provide the stability necessary to maintain the STM tip at a fixed location for extended time periods. By measuring the SPPX-STM response directly above a nanoparticle, as a function of distance from the nanoparticle center, and eventually above the bare substrate, we will be able to carefully characterize the lateral resolution of the technique.

Molecular Transformations, Catalysis and Modeling in the Context of Conversion of Canadian Bitumen to Transportation Fuels

J. Govindhakannan, H. Yang and Z. Ring
Canadian National Centre for Upgrading Technology (NCUT)

Canada has reserves of oil-sand hydrocarbons that are second only to Saudi Arabia. The oil-sands-derived bitumen and synthetic crude hydrocarbons are very cyclic (aromatic/cycloparaffinic) in nature and special technologies are needed for upgrading and refining of those materials in North America.

In order to solve this problem and add value to bitumen-derived streams, NCUT has been exploring two directions involving the development of:

- selective ring-opening catalysts (ring-opening with minimal reduction of the molecular weight) to improve the cetane number of middle-distillates and the quality of heavy distillates as fluid-catalytic-cracking feedstocks;
- sulphur-resistant noble-metal catalyst component to enhance the hydrogenation activity of commercial hydrotreating catalysts.

NCUT has engaged several Canadian universities, Canadian government research institutes and, most recently, US DOE PNNL laboratory in a research program aiming at the development of catalytic processes tailored for bitumen-derived materials and including catalyst design, characterization, pilot-plant testing and quantum-chemistry computational studies to understand the fundamental science behind selective ring-opening.

Experimental studies show that the endocyclic cracking of carbon-carbon bonds of naphthenic rings proceed at a much slower rate than cleaving carbon-carbon bonds. Consequently, selective ring-opening is very difficult due to secondary cracking reactions. NCUT together with the Canadian National Institute for Nano-Technology (NINT) has been exploring computationally various fundamental mechanistic aspects of ring-opening reactions occurring on solid acid catalysts. The elementary steps involved in the ring-opening of cyclohexane on a solid acid catalyst are studied using Hartree-Fock (HF) and density functional (DFT) theories. Cluster models are used to simulate the catalyst surface with a Bronsted acid site and the potential energy surface is scanned to identify various energy minima and transition states to construct the reaction pathways. This work will help understand the detailed mechanisms of ring opening of various naphthenic molecules that, in turn, will help rational design of ring-opening catalysts.

DOE DE-FG02-88ER13878 **Lanny D. Schmidt**

Autothermal Reforming of Renewable Fuels

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Abstract

In reforming of renewable fuels we have quantified ethanol reforming and published a manuscript on this topic. We have also compared reforming of small alcohols from methanol to propanol. We also have compared small carbohydrates up to glycerol. A manuscript on reforming of esters is in preparation.

The reforming of heavy fuels that cannot be vaporized without decomposition into carbon is the major topic currently being explored. Experiments in progress involve glucose-water mixtures and soy oil and solids from cellulose to aspen wood.. We use flash vaporization in milliseconds to break up molecules without dehydrogenation.

A final project involves periodic operation of millisecond reactors and measurement of spatial profiles within the reactor. We observe unexpected structure in the profiles for methane and ethane partial oxidation.

Renewable Fuel Reforming

We have examined simple prototype biomass sources: alcohols, carbohydrates, and biodiesel. For alcohols we have examined methanol, ethanol, 1-propanol, and 2-propanol. For carbohydrates $(CH_2)_n$ we have examined methanol, ethylene glycol, and glycerol which are carbohydrates with n=1, 2, and 3.

The alcohol comparison paper has been published, a paper with extensive results on ethanol reforming has been published, and a paper comparing carbohydrates in the subject of a PhD dossier by Paul Dauenhauer and will be submitted for publication next month.

We have been examining the autothermal reforming of simple esters. These have the formulas RCOOR' with R and $R'=CH_3$, C_2H_5, and C_3H_7, as well as some simple olefinic esters. These are all fairly volatile (bp<300°C) so they can be rapidly vaporized and mixed with air without forming coke or catching fire. We have approximately half of the required data for this project and hope to complete a manuscript by the end of the summer.

A major and exciting part of this program is the conversion of nonvolatile fuels into syngas or into olefins. This is a challenge because the fuels cannot be vaporized without decomposition because under normal situations they will not boil without decomposition. We have constructed flash vaporization capabilities that convert the liquids at room temperature into fine mists that can impact the glowing catalyst at ~1000°C within ~0.01 seconds. Flash decomposition appears to convert all of the liquids into small stable molecules with no carbon formation.

Transients, Lightoff, and Spatial Profiles

The examination of transients and spatial profiles in millisecond reactors is an ongoing part of this program. We have been working on this project for several years, and several recent publications are listed below.

We have recently devised a method to measure spatial and temporal profiles within an active catalyst without interfering with the species or temperature fields. At the end of this report we enclose an abstract of a recently submitted paper and a figure (in color) of the variations in time and position of several variables in a transient experiment in which the C/O ratio is varied periodically with a 20 second period. The overshoots and undershoots observed with methane partial oxidation suggest that this technique will capture many features of millisecond reactors that are not yet observed or understood.

Publications 2005-present

K. A. Williams, C. A. LeClerc, and L. D. Schmidt, "Rapid Lightoff of Syngas Production from Methane: Transient Product Analysis, *AIChE Journal* **51** (1), 247-260 (2005).

R. Subramanian and L. D. Schmidt, "Renewable Olefins from Biodiesel by Autothermal Reforming", *Angewandte Chemie* **44**, 302-305 (2005).

K. A. Williams and L. D. Schmidt, "Catalytic Autoignition of Higher Alkane Partial Oxidation on Rh-Coated Foams," *Applied Catalysis A: General*, **299**, 30-45 (2006).

E. Wanat, B. Suman, and L. D. Schmidt, "Partial Oxidation of Alcohols to Produce Hydrogen and Chemicals in Millisecond Reactors", *Journal of Catalysis*, **235**, Issue 1, 18-27, (2005).

L. D. Schmidt, R. Subramanian, J. R. Salge, and G. A. Deluga, "Hydrogen and Chemicals from Renewable Fuels by Autothermal Reforming", *Indian Chemical Engineer* **47**, 100-105 (2005).

J.R. Salge, G.A. Deluga, and L.D. Schmidt, "Catalytic Partial Oxidation of Ethanol Over Noble Metal Catalysts", *Journal of Catalysis* **235**, 69-78 (2005).

J.R. Salge, G.A. Deluga, and L.D. Schmidt, "Catalytic partial oxidation of ethanol over noble metal catalysts", Journal of Catalysis, **235**, 1, 69-78, (2005).

B.J. Dreyer, I. Lee, J.J. Krummenacher, and L. D. Schmidt, "Autothermal Steam Reforming of Higher Hydrocarbons: n-decane, n-hexadecane, and JP-8" *Applied Catalysis A: General* **307** 184-194 (2006).

G. J. Panuccio, K. A. Williams, and L. D. Schmidt "Contributions of heterogeneous and homogeneous chemistry in the catalytic partial oxidation of octane isomers and mixtures on rhodium foams," *Chemical Engineering Science* **61**, 4207-4219 (2006).

N.J. Degenstein, R. Subramanian, L.D. Schmidt, "Partial Oxidation of n-Hexadecane at Short Contact Times: Catalyst & Washcoat Loading and Catalyst Morphology," *Applied Catalysis, A: General* **305**, 146-159 (2006).

R. Horn, K.A. Williams, N.J. Degenstein, L.D. Schmidt, "Syngas by catalytic partial oxidation of methane on rhodium: Mechanistic conclusions from spatially resolved measurements and numerical simulations," *Journal of Catalysis* **242** (2006) 92-102.

R. Horn, N.J. Degenstein, K.A. Williams, L.D. Schmidt, "Spatial and temporal profiles in millisecond partial oxidation processes," *Catalysis Letters* **110** (2006) 169.

G.J. Panuccio, L.D. Schmidt, "Increasing olefins by H_2 and CH_4 addition to the catalytic partial oxidation of n-octane," Applied Catalysis A: General **313** (2006) 63-73.

P.J. Dauenhauer, J.R. Salge, L.D. Schmidt, "Renewable hydrogen by autothermal steam reforming of volatile carbohydrates," Journal of Catalysis **244** (2006) 238-247.

J.R. Salge, B.J. Dreyer, P.J. Dauenhauer, L.D. Schmidt, "Renewable Hydrogen from Nonvolatile Fuels by Reactive Flash Volatilization," Science 314 (2006) 801-804.

R. Horn, K.A. Williams, N.J. Degenstein, L.D. Schmidt, "Mechanism of H2 and CO formation in the catalytic partial oxidation of CH4 on Rh probed by steady-state spatial profiles and spatially resolved transients," Chemical Engineering Science 62 (2007) 1298-1307.

DE-FG02-84ER13183 **James A. Dumesic (PI)**

Fundamental Studies of the Reforming of Oxygenated Compounds over Supported Metal Catalysts

Postdocs: Ricardo Soares
Students: Dante Simonetti, Ed Kunkes, Juben Chheda, Jeppe Hansen
Collaborators: Manos Mavrikakis (University of Wisconsin), George Huber (now at the University of Massachusetts), Randy Cortright (Virent Energy Systems)
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Goal

The goal of this project is to elucidate the fundamental surface chemistry involved in the catalytic conversion of renewable biomass resources to produce energy. The primary focus of this work has been the catalytic production of H_2:CO_2 or H_2/CO gas mixtures by aqueous-phase reforming of biomass-derived oxygenated hydrocarbons over supported metal catalysts. The objectives of our work during the past year have been (i) to understand how the aqueous-phase reforming process can be operated to produce H_2:CO gas mixtures at high rates and at low temperatures (e.g., 548 K), (ii) to study the potential coupling between aqueous-phase reforming and alkane synthesis, and (iii) to understand how the synthesis of liquid alkanes from H_2:CO gas mixtures is affected by oxygenated hydrocarbon intermediates that are produced during the aqueous-phase reforming process.

Recent Progress

During the past year, we have studied the factors that control the CO:CO_2 ratio of the gas stream that is produced during aqueous-phase reforming. We have shown that the first step in aqueous-phase reforming is the production of CO and H_2, followed by the water-gas shift reaction (i.e., $CO+H_2O \rightarrow CO_2 + H_2$) to produce CO_2 and H_2. This latter reaction can be suppressed by decreasing the concentration of water in the aqueous feed stream (e.g., increasing the concentration of the organic reactant from 30 to 80 wt%), and by decreasing the overall pressure of the reforming process. This second effect is caused by the fact that the reforming rate is a negative function of pressure (caused by adsorption of CO on the catalyst surface), whereas the rate of water-gas shift is a weaker function of pressure. We have determined that the rate of water-gas shift is promoted over metal oxide catalyst supports, such as alumina, zirconia, ceria, and magnesia. Therefore, to suppress the rate of water-gas shift, we have developed a series of carbon-supported metal catalysts.

The potential coupling between aqueous-phase reforming and alkane synthesis is a promising approach for the production of liquid transportation fuels. To take advantage of this coupling, however, it is necessary to lower the temperature of the reforming process to that commensurate with effective alkane synthesis. In this respect, we have determined that the rate of the reforming process is controlled by the strength of CO adsorption. Accordingly, we have developed several bimetallic catalysts (e.g., Pt-Re supported on carbon) that show high rates of aqueous-phase reforming at temperatures (e.g., 548 K) and pressures (e.g., 15 bar) where high selectivities for the production of liquid alkanes can be achieved. In our most recent work, we have started to explore how the rates and selectivities for producing various alkanes are affected by the presence of oxygenated hydrocarbon intermediates that are produced in significant quantities during aqueous phase reforming. For the specific case of glycerol reforming, the most abundant intermediates are ethanol, acetone, and acetol; and, while ethanol and acetone have minor effects on the rates of alkane production, the addition of acetol to synthesis gas leads to an increase in the selectivity to heavier hydrocarbons. This desirable effect indicates that the coupling between aqueous phase reforming and alkane synthesis may have synergistic effects beyond the advantage of heat integration between these endothermic and exothermic processes.

DOE Interest

Environmental and political problems created by our dependence on fossil fuels, such as global warming and national security, combined with diminishing petroleum resources are causing our society to search for new renewable sources of energy and chemicals. Accordingly, renewable biomass resources are promising options for the sustainable production of hydrogen and fuels in an age of diminishing fossil fuel reserves. Our recent work is focusing on the conversion of biomass resources to liquid alkane fuels.

Future Plans

In our future work we plan to study in greater detail how the binding energy of CO on Pt-based catalysts can be decreased such that these catalysts can be operated at lower temperatures or at high pressures for the conversion of glycerol to synthesis gas. In this respect, we plan to study our promising Pt-Re/C catalysts to probe the oxidation state of Re in the catalyst at various reaction conditions. These studies will involve microcalorimetric and TPD measurements for catalysts that have been subjected to various oxidation and reduction conditions. We also plan to study in greater detail the coupling between glycerol conversion and Fischer-Tropsch synthesis to produce liquid alkanes from renewable biomass resources. Importantly, it appears that some of the intermediates from glycerol (*e.g.*, acetol) are beneficial for Fischer-Tropsch synthesis, suggesting that glycerol conversion to synthesis gas and Fischer-Tropsch synthesis may be synergistic processes, and we plan to study this possible synergy in detail.

Publications for 2006

Aqueous-phase Reforming of Ethylene Glycol over Supported Pt and Pd Bimetallic Catalysts, Applied Catalysis B Environmental **62**, 226 (2006), with G. W. Huber, J. W. Shabaker, and S. T. Evans.

An Overview of Aqueous-phase Catalytic Processes for Production of Hydrogen and Alkanes in a Biorefinery, Catalysis Today **111**, 119 (2006), with G. W. Huber.

Glycerol as a Source for Fuels and Chemicals by Low-temperature Catalytic Processing, Angewandte Chemie International Edition **45**, 3982 (2006), with R. R. Soares and D. A. Simonetti.

Gas-phase conversion of glycerol to synthesis gas over carbon supported platinum and platinum-rhenium catalysts, accepted in the Journal of Catalysis, with D. A. Simonetti and E. L. Kunkes.

Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals, accepted in Angewandte Chemie International Edition, with J. N. Chheda and G. W. Huber.

AL-03-380-011 **Victor S.-Y. Lin and Marek Pruski**

Selective and Efficient Catalysis in 3-D Controlled Environments

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Goal

Develop and characterize multifunctionalized mesoporous silica materials with well-defined pore/particle morphology and surface properties for heterogenization of single-site catalysts, and study the selectivity, reactivity and kinetics of these catalytic systems.

Recent Progress

Synthesis of Multifunctional Mesoporous Silica Materials with Controlled Morphology: We have developed synthetic approaches[6,18] that allow efficient *multi-functionalization* with precise control of the relative concentrations of functional moieties, and provide means to modify the particle and pore morphology. As depicted in **Figure 1**, our method involves the utilization of organotrialkoxysilanes with various anionic, hydrophobic, or hydrophilic functional groups that can provide different non-covalent interactions, e.g., electrostatic attractions, hydrophobic interactions, with the cationic CTAB surfactant micelles in a NaOH-catalyzed condensation reaction of tetraethoxysilane (TEOS).[6,18] By carefully designing the interfacial interaction between the surfactant head groups and the desired organic functional group precursors, we have reported that the extent of organic functionalization as well as the particle shape and size of mesoporous silica nanoparticles (MSNs) can be controlled and fine-tuned.[6,18] A series of

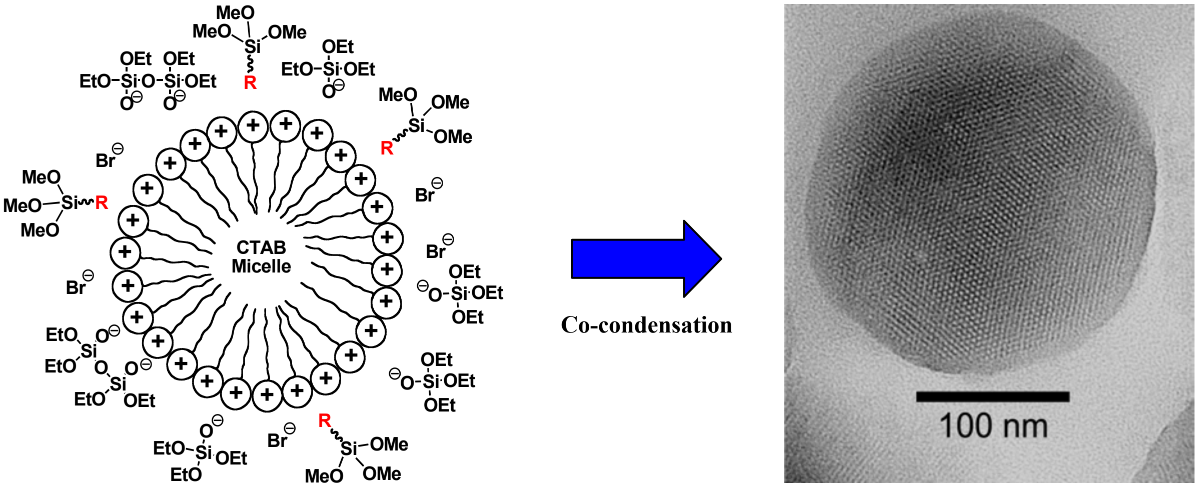


Figure 1. Schematic representation of the utilization of various organoalkoxysilanes (R~Si(OMe)$_3$, R = anionic, hydrophobic, and hydrophilic organic groups) for controlling the functionalization of the MSN materials. The MCM-41 type mesoporous structure is illustrated by the hexagonally packed light-colored dots shown in the TEM micrograph of an organically functionalized MSN material.[18]

organically functionalized MSN materials with spherical, tubular, and rod-like particle morphologies and narrow particle size distributions could be easily synthesized via our method.[6,18]

***Control of the Orientation and Activity of Tethered Organic Catalysts*:** We have successfully synthesized and characterized a new nucleophilic catalytic system comprised of dialkylaminopyridine-functionalized mesoporous silica nanosphere (DMAP-MSN)[20] as depicted in **Figure 2**. The structure of the organic functionality was detailed by solid-state ^{1}H-^{13}C heteronuclear correlation (HETCOR) NMR spectroscopy. Successful functionalization of DMAP on mesoporous silica surfaces has never been reported prior to our study. This could be attributed to the undesired protonation of the pyridyl group of various trialkoxysilyl-derivatized dialkylamino pyridines by the surface silanol groups during the conventional post-synthesis grafting reaction. We have demonstrated that the DMAP-MSN material is an efficient, selective and recyclable heterogeneous catalyst for Baylis-Hillman, acylation, and silylation reactions.[20] We envision that this material can also serve as an effective heterogeneous catalyst for many other catalytic nucleophilic reactions.

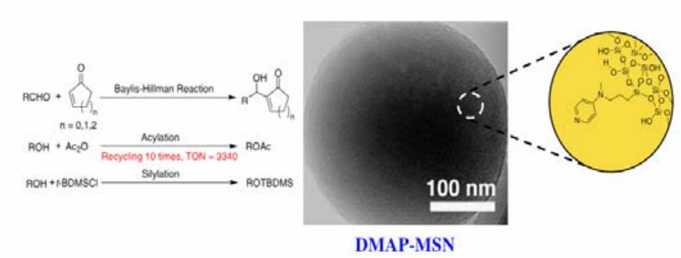


Figure 2. TEM micrographs of dialkylaminopyridine-functionalized mesoporous silica nanosphere (DMAP-MSN) material. The DMAP-MSN can serve as a catalyst for Baylis-Hillman, acylation, and silylation reactions with good reactivity, product selectivity, and recyclability.[20]

***Template removal and thermal stability of organically functionalized MSN's*:** The MCM-41-type MSN materials, functionalized using a co-condensation method with 2,2'-bipyridine (BPY), 4-dimethylaminopyridine (DMAP) and pentafluorobenzene (PFP), were studied using ^{13}C and ^{29}Si solid-state NMR following a series of heat treatments between 100 and 400 °C.[8] The spectra showed that the structures and concentrations of functional groups remained unaffected in this temperature range (**Figure 3a**). Furthermore, CTAB could be effectively removed by such treatment (**Figure 3b**), without disrupting the chemical accessibility and reactivity of organic functionalities. We expect that this process can be further developed into an economical and environmentally friendly method for surfactant-removal from various organically functionalized mesoporous silicas.

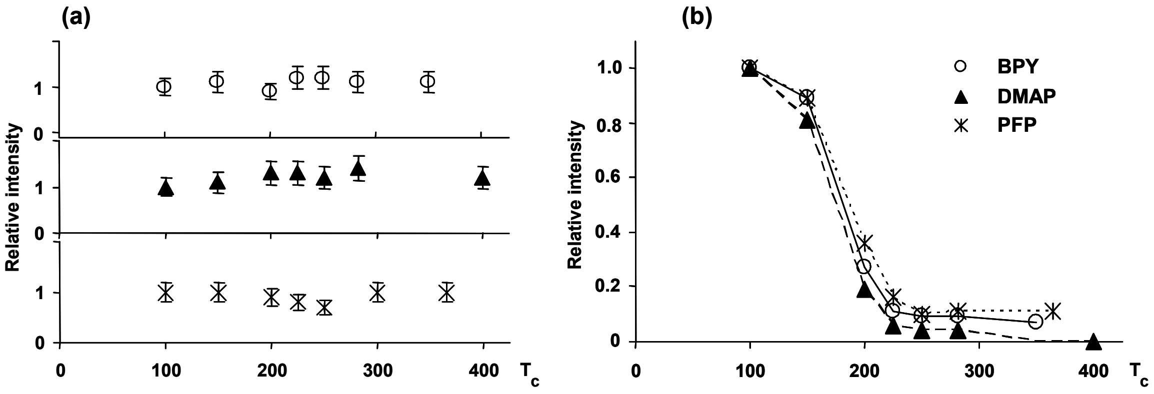


Figure 3. Concentrations of the organic functional groups (a) and CTAB (b) versus the temperature of the thermal treatment T_c in samples functionalized with BPY, DMAP and PFP. The experimental points represent integrated intensities of all ^{13}C resonances for each species.[8]

***Cooperative Acid-Base Catalysis by Bifunctionalized Mesoporous Silica Nanoparticles*:** We have developed a new cooperative catalytic system comprised of a series of bifunctionalized mesoporous silica nanoparticle (MSN) materials with various relative concentrations of a general acid, ureidopropyl (UDP) group, and a base, 3-[2-(2-amino-ethyl-amino)ethylamino]-propyl (AEP) group.[14] As depicted in **Figure 4**, three bifunctional AEP/UDP-MSN catalysts with the initial molar ratio of the organoalkoxysilane precursors, AEP/UDP = 2/8, 5/5, and 8/2, were synthesized via our previously reported co-condensation method[6,18] and thoroughly characterized by solid-state NMR.[14,19] These AEP/UDP-MSN bifunctional materials were employed as catalysts for aldol, Henry and cyanosilylation reactions. We have demonstrated that the general acid group, UDP, could cooperatively activate substrates with the base group, AEP, in catalyzing these reactions that involve carbonyl activation.[14] By fine-tuning the relative concentrations and proper spatial arrangements of different cooperative functional groups, we were able to regulate the turnover numbers of these important reactions.[14]

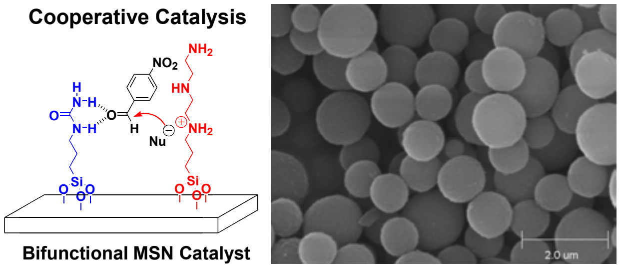
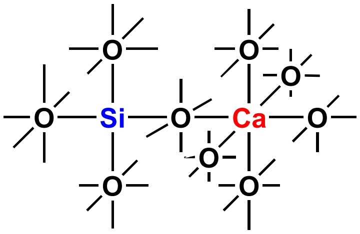


Figure 4. A new cooperative catalytic system which consists of a series of bifunctionalized mesoporous silica nanosphere (MSN) materials with various relative concentrations of a general acid, ureidopropyl (UDP) group, and a base, 3-[2-(2-aminoethylamino)ethylamino]propyl (AEP) group.[14]

***Synthesis of Acid-Base Mesoporous Mixed Oxide Catalysts for Cooperative Catalysis*:** The rapid consumption of petroleum and the soaring oil price have increased the demand of new catalysts that can work with complex molecules as feedstocks for many applications. Nature uses multiple functional groups to interact with reactants with complicated structures and the synergy between multiple catalytic groups leads to the high activity and selectivity for many reactions. For example, enzymes engaged in carbonyl chemistry often employ both general acid and base catalytic residues to cooperatively activate specific substrates. The presence of electron acceptor (acidic) and electron donor (basic) sites in modern heterogeneous metal oxide catalysts also plays a pivotal role in C-H and C=O activation. Designing a new generation of cooperative catalysts that possess both acidic and basic sites would be important to further advance the field of catalysis.

Recent progress, including our own,[6,18] in the synthesis of organic/inorganic hybrid mesoporous silica materials with control over the particle and pore morphology as well as the loading of multiple organic functional groups have yielded a series of mesoporous materials for cooperative catalysis, i.e., acid-base catalysis.[14] Given the fact that many mixed metal oxide materials exhibit unique and often superior catalytic performances in comparison with those of the parent metal oxides, it would be desirable to develop mesoporous mixed metal oxide materials with ordered porous structures and synergistic catalytic activities. However, progress in developing synthetic methods for preparing ordered mesoporous mixed oxide materials has been slow compared with those of mesoporous silica and alumina.

We developed a new synthetic method for the preparation of mesoporous acid-base mixed oxide catalysts with ordered structures.[10] The central idea is to combine a strong basic metal oxide with a weak acid oxide, so that the acidity of the weak acid oxide would be enhanced. For example, in the case of calcium silicate mixed oxide, substituting Ca atoms with Si atoms at the high coordination environment (octahedral) of calcium oxide (strong base) sites will create a



Si atoms occupy Calcia sites:
The 4 positive charge of Si are distributed to 4 bonds.
The 2 negative charge of O are distributed to 6 bonds.

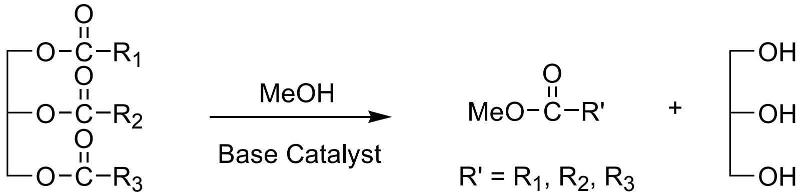
Net Charge difference = $(+\frac{4}{4}-\frac{2}{6})\times 4=+\frac{8}{3}$

Therefore, Si atoms are Lewis acidic

"positive" charge difference in comparison with the pure CaO material as illustrated below. Therefore, the silica sites of this type of mixed oxide materials would be Lewis acidic, whereas the calcia sites would be basic.

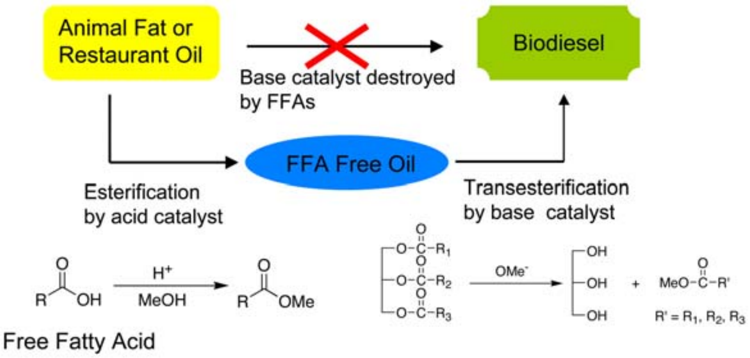
By using this strategy, we have recently synthesized and characterized a mesoporous calcium silicate mixed oxide material that can serve as an efficient and recyclable heterogeneous catalyst for biodiesel synthesis. Currently, the feedstock for biodiesel production is limited to soybean and other vegetable oils with low free fatty acid (FFA) contents. As depicted in **Scheme 1**, the conventional conversion of triglyceride to a mixture of methyl esters (biodiesel) and glycerol is catalyzed by a homogeneous base, sodium methoxide. Other more economical oil feedstocks, such as animal fats and restaurant waste oils, cannot be used because of the high FFA content. The FFAs in these oils will destroy the base catalyst.

Scheme 1



To circumvent this issue and to avoid using a pretreatment catalyst for the elimination of FFAs, we have synthesized an integrated "acid-base" calcium silicate mixed oxide catalyst.[10] Bulk calcium oxide was added to an aqueous solution of CTAB and TEOS at pH 1.5. After 30 min of stirring, the pH of the mixture was adjusted to 11 to yield a mixed oxide material. The as-synthesized sample was calcined at 600 ºC for 8 h to yield the desired mesoporous calcium silicate catalyst with a high surface area (640 m^2/g). It is interesting to note that this material can catalyze the conversion of both soybean oil and poultry fat with 5-15% FFA quantitatively to biodiesel within 24 h at 60 ºC and atmospheric pressure. In contrast to the pure CaO, where the catalytic activity was completely lost after 7 and 3 runs with soybean oil and poultry fat, respectively, the calcium silicate catalyst can be recycled 20 and 7 times without any decrease in its initial catalytic activity. Apparently, the acidic sites (silica) of our mixed oxide catalyst can efficiently catalyze the esterification of FFAs to biodiesel, while the basic sites (calcia) catalyze the transesterification of triglyceride to biodiesel as depicted in **Scheme 2**. The results indicated that the acidity of silica has been significantly enhanced by

Scheme 2



the formation of calcium silicate mixed oxide.

In contrast to other literature-reported mixed oxides, where the different oxides are usually distributed in domains and separated from each other, our mesoporous calcium silicate mixed oxide catalyst shows a homogeneous distribution of calcium and silicon oxides as confirmed by solid-state ^{29}Si NMR spectroscopy and powder XRD measurements. In fact, our calcium silicate catalyst contain a structural unit that is similar to a crystalline calcium silicate, 1.4 nm tobermorite, which is a composite layer composed of a distorted central Ca–O sheet that is ribbed on either side with single dreierketten, i.e., silicate chains that repeat at intervals of three silicate tetrahedral as depicted in **Figure 5a**,**b**. Unlike other calcium silicate hydrate gels, where water and calcium cations exist between layers of 1.4-nm tobermorites (**Figure 5b**,**c**), the bridging silicate tetrahedra (Q^2 silicons) of our catalyst material are connected and formed Q^3 type of Si atoms (**Figure 5d**).[10] The overall material exhibits a spherical particle morphology with wormhole-like mesopores. As determined by the spin counting of ^{29}Si NMR spectroscopy, this unique structure gives rise to a high Ca/Si ratio of 1.8, which is very different from the value (0.83) of tobermorite in common calcium silicate hydrate gels. The observed high Ca/Si ratio further support the aforementioned "Charge Difference" hypothesis that the enhanced Lewis acidity can be attributed to the replacement of Ca atoms with silicons at sites with high coordination numbers of oxygens.

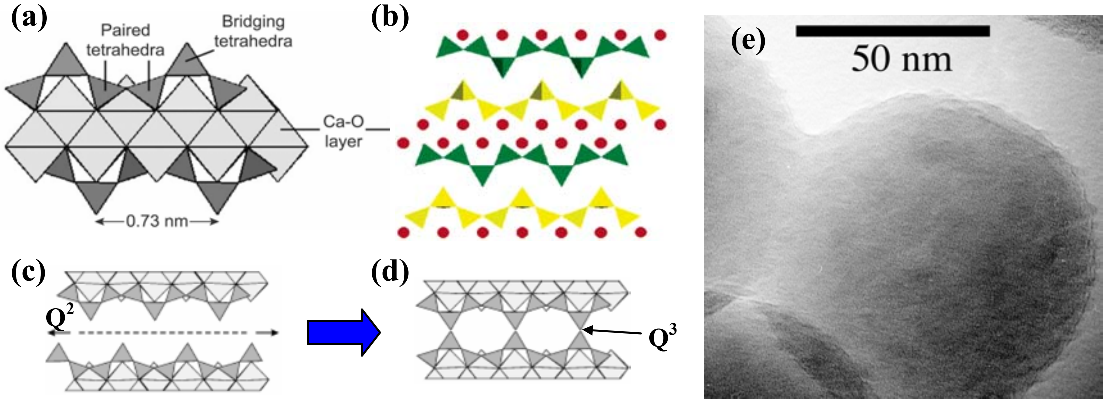


Figure 5. Single layer of 1.4-nm tobermorite seen along **(a)** [210] illustrating the Ca–O main layer (light gray) with attached dreierketten (dark gray). **(b)** Layers of tobermorite in which a central Ca–O sheet is flanked on both sides by rows of single dreierketten, together with interlayer Ca atoms and water molecules. Water molecules and Ca atoms present in the interlayer spaces are omitted. Schematic representation of the difference in interlayer spacing of tobermorite between common calcium silicate hydrate gels **(c)** and our acid-base mixed oxide catalyst **(d)**. **(e)** The TEM micrograph of the acid-base calcium silicate nanoparticle catalyst. Wormhole-type of mesoporous structure with a BJH average pore diameter of 3 nm.

Solid-state NMR characterization of non-functionalized and functionalized mesoporous material**:** We have used solid-state NMR spectroscopy as a primary tool for characterization of structural features of non-functionalized and functionalized MSN's[1-5,8-10,12-14,16,20] and developed new NMR methods for such studies.[7,11,15,22]

(a) ***Non-functionalized materials*****:** A systematic NMR study of the surface of MCM-41-type MSN's prepared under low surfactant concentration was carried out.[7] The samples were studied after acid extraction of the CTAB surfactant, followed by various thermal treatments between 30 and 500 ˚C. The structures and concentrations of various species present during these processes were detailed with one-dimensional (1D) and two-dimensional (2D) ^{1}H, ^{13}C and ^{29}Si NMR techniques which utilized MAS rates of up to 45 kHz.

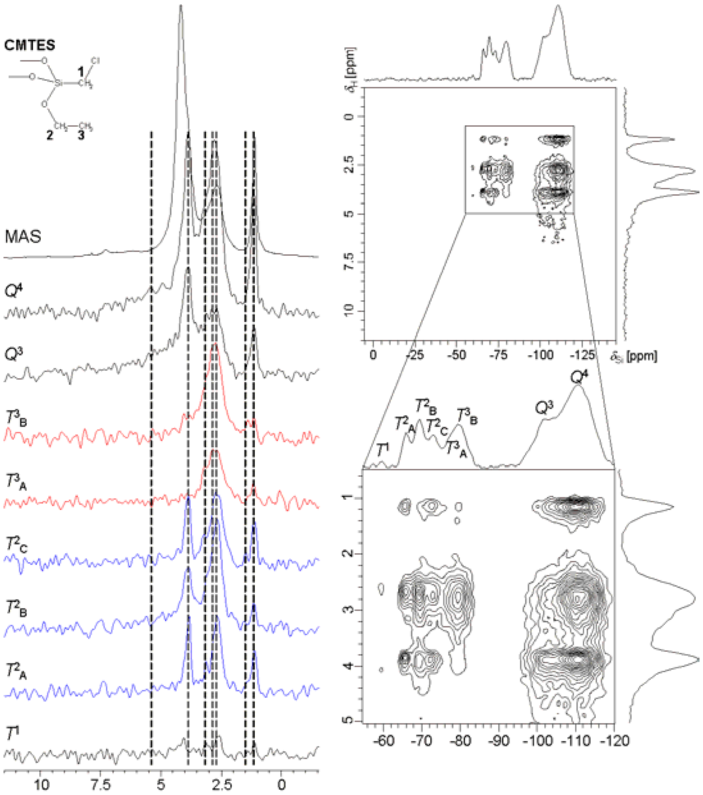
After acid extraction, CTAB molecules were identified in the concentration corresponding to 1 molecule per 3 nm of the channel length. These molecules were located in prone positions along the channel walls. CTAB was found to decompose at around 250 ˚C and its head section was removed first from the mesopores. At the high level of hydration, all SiOH groups were involved in the rapidly exchanging SiOH-$(H_2O)_n$ species, whose structures were postulated based on the observed chemical shifts and spectral intensities. The dehydration involved the removal of relatively mobile water (at 30 to 90 ˚C), followed by gradual dehydroxylation at higher temperatures. After thermal treatment of MCM-41 silicas at 500 ˚C, water that readsorbed inside the pores was mainly in the form of mobile SiOH-H_2O species and a strongly adsorbed form yet to be determined. The reconstruction of silica surface inside the pores, which occurred during the initial calcination, was permanent.[7] The molecular dynamics, chemical exchange and spin diffusion processes associated with these transformations were probed by ^{1}H-^{1}H double-quantum (DQ) and exchange NMR.

There is intense interest in our program in the development of catalytically active mesoporous frameworks composed of mixed oxides. In addition to characterizing the calcium silicate mixed oxide described below, we have applied ^{27}Al-^{29}Si double resonance NMR to probe a mesoporous aluminum silicate (Al-MS) material synthesized via a base-catalyzed co-condensation reaction.[5] The newly developed RAPT-CPMAS-CPMG NMR experiment provided first direct evidence that all Al atoms are surrounded by Si atoms forming Al-O-Si bonds in the framework. The silicon to aluminum atomic ratio at the surface $(Si/Al)_s$ was estimated at around 100, which exceeded the overall Si/Al ratio of 60. A related study involving ^{43}Ca nuclei in ^{43}Ca-enriched Ca-silica catalysts is underway. Similar techniques will be further developed and exploited to characterize other mesoporous scaffolds composed e.g. of MgO, MnO, and SrO.

(b) ***Solid-state NMR studies of organically functionalized MSN's*****:** 1D solid-state NMR methods, such as ^{1}H MAS and/or ^{1}H CRAMPS, ^{29}Si MAS, and ^{1}H-X CPMAS, where X included ^{13}C, ^{29}Si, ^{31}P, ^{27}Al, and other nuclei, were applied for basic characterization of functionalized supports/catalysts. For example, ^{1}H-^{13}C CPMAS spectra were used to identify the structure and measure the concentrations of organic moieties.[2,4,8,14-16,20] The differences in CP dynamics yielded information about the motion of functional groups. The same studies used ^{29}Si NMR to identify and quantify the silicon functionalities. In MSN's these include Q^4 sites ($(\equiv SiO)_4\mathbf{Si}$), which comprise typically 50-60% of silicon atoms. In non-functionalized materials, silica surfaces are terminated by the silanol groups forming Q^3 sites and Q^2 sites. The Q^n sites are described by a general formula $(\equiv SiO)_n\mathbf{Si}R_m(OH)_{4-n-m}$, where m = 0. Surface functionalization yields silicon atoms in positions denoted as T^n (m = 1; n = 0,1,2,3) and D^n (m = 2; n = 0,1,2), whose resonances are shifted by up to 100 ppm toward higher frequencies with respect to Q sites.[4]

We have also demonstrated numerous applications of advanced 2D methods in these studies. For example, we employed the recently developed fast MAS in ^{1}H-^{1}H homonuclear and ^{1}H(or^{19}F)-X HETCOR NMR of functionalized silicas (where X represents nuclei with low magnetogyric ratio γ, such as ^{13}C or ^{29}Si).[4,15,16,20] MAS at rates $\geq$ 40 kHz can provide adequate ^{1}H-^{1}H decoupling in the silica-bound species to allow unambiguous identification of proton chemical functionalities via the fingerprint of the chemical shift. Additional advantages of this approach include easy setup, lack of scaling factors, and ease of acquisition of sideband-free spectra. The loss of sensitivity due to small rotor volume (less than 10 μL), is offset by the relaxed requirements for the RF magnetic field homogeneity within the sample compared to that utilizing CRAMPS for homonuclear decoupling.[20]

The utility of these methods is demonstrated in **Figure 6**, for MCM-41-type silica functionalized with CMTES.[4] In this experiment, we applied the CPMG train of refocusing π pulses to the ^{29}Si spins, which increased the sensitivity by about one order of magnitude (or shortened the measurement by *two orders of magnitude*). The acquisition of the ^{1}H-^{29}Si HETCOR of such spectrum would have required 60 days without this method. The detailed peak assignments can be made by examining the cross sections of ^{1}H-^{29}Si HETCOR spectra in ^{1}H and ^{29}Si dimensions. The corresponding ^{1}H-^{1}H and ^{1}H-^{13}C correlation experiments were also carried out (spectra not shown). Taken together, these 2D methods allow for characterization of the structure and conformation of functional groups inside the pores with unprecedented resolution and sensitivity, also in materials functionalized with relatively complex molecules.[4,15,16,20]



re 6. ^{1}H cross-sections of the ^{1}H-^{29}Si HETCOR spectrum of mesoporous silica functionalized with chloromethyltriethoxysilane $(EtO)_3Si(CH_2Cl)$. See reference 4 for details.

DOE Interest

Developing catalytic systems that can coherently unite the best features of the homogeneous and heterogeneous areas of catalysis has been a key interest of the DOE. By controlling the structure, reactivity and morphology of the mesoporous solid support and its interaction with the active sites, these studies provide truly unique opportunities for the design of a new generation of highly efficient and selective catalysts. This research can also provide new fundamental knowledge about catalysis in general by deconvoluting the key factors that affect selectivity, reactivity and kinetics.

Future Plans

- *Influence of the mesopore environment on catalyst selectivity and activity.*[10] Our ability to anchor two types of groups on mesopore walls allows us to tether not only the catalyst but also other functional moieties. The influence of these auxiliary groups will be directed toward achieving various catalyst functions, such as enantioselectivity. These studies will use the concept of gatekeepers, which will be tested in the development of catalysts for the stereochemically controlled polymerization, selective hydrolysis, etc.
- *Cooperative catalysis inside mesopores.* To study how various functional groups could synergistically catalyze a reaction in a 3-D controlled environment, we will functionalize the surface of mesopores with two to three different types of catalytically active moieties and vary the relative ratio and spatial distribution of these functionalities. As a proof of

principle, functional groups that can serve as general acid and base will be introduced to study the selective carbon-carbon bond formation in, for example, aldol, Diels-Alder, and hetero-Diels-Alder (HDA) reactions that involve carbonyl activation.

- *Control of the orientation and activity of tethered transition metal complex catalysts.* In order to understand the activity and selectivity of metal complex catalysts tethered on the walls of mesopores, we will characterize and control the location and the exact structure of the tethered catalysts on the surface.
- *Catalyst characterization*. Solid-state NMR techniques will be further developed to better characterize the catalytic surfaces, especially to probe the spatial organization of the surface species and to provide key dynamic information about catalysts that will be prepared and tested during the next stages of this research. We will focus on further development of 2D methods, exploitation of J-spectroscopy, detection of low-gamma nuclei, and studies of solid-liquid interfaces.
- *Theory, modeling and simulation of transport and reaction in mesopores.* Theoretical and computational tools will be developed to allow analysis of electronic structure and dynamics for the complex silica surface + functional group + reactant + solvent systems. Second, statistical mechanical models will be proposed for the relevant many-particle transport and reaction processes in silica nanopore geometries, ideally utilizing energetic and dynamic information from the above electronic structure studies.

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Nanostructured Catalysts for Hydrogen Generation from Renewable Feedstocks

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Goals

This research program focuses on the development of highly active and selective catalysts for the production of hydrogen from alcohols. Alcohols, which can be produced from biomass or corn, have the potential to be an important renewable source of energy and may help to reduce our dependence on dwindling foreign and domestic oil supplies. Alcohols can be reformed to produce hydrogen, which can then be used in highly efficient energy conversion devices such as fuel cells. Metal particle size, composition and support structure play a major role in modifying the activity and selectivity of a catalyst. The underlying mechanisms are not well understood. Achieving the highest activity for reforming, while maintaining CO_2 selectivity (and suppressing CO formation) remains a major challenge. The specific objectives of this research program are to achieve advances in the design, synthesis, and characterization of catalysts for H_2 generation.

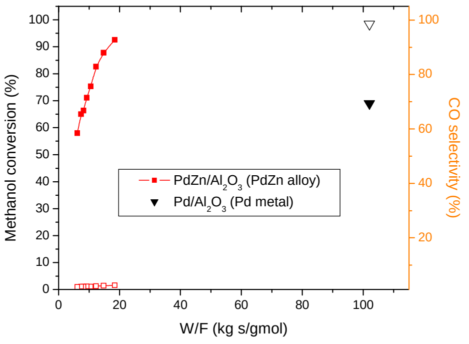
Research Plan

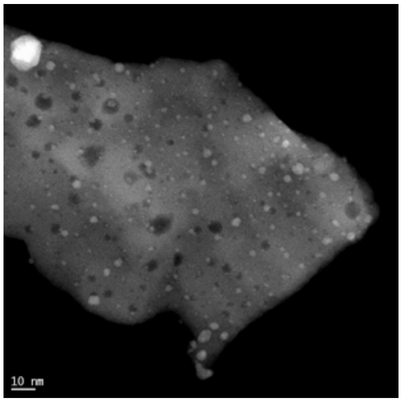
The project involves collaboration between two university groups and one national lab. Our work over the past 18 months has been directed at understanding the role of various factors that influence activity and selectivity for H_2 formation, while minimizing the byproduct CO formation. Pd-Zn alloys have been shown to possess high selectivity towards CO_2 during methanol steam reforming, compared with monometallic Pd. It is commonly assumed that PdZn alloy formation is essential to achieve high selectivity towards CO_2. The simplest method to form a PdZn alloy is to treat a Pd/ZnO catalyst at elevated temperatures in H_2, which transforms Pd to PdZn, but also leads to particle growth. This makes it difficult to assess independently the role of particle size and composition on selectivity. We have used alternative activation treatments in order to vary independently the particle size and extent of alloy formation to understand the origins of selectivity. By using organic Pd precursors, we avoid the dissolution and etching of the ZnO substrate. The work on supported catalysts is complemented with studies of Pd deposited on ZnO(0001) surfaces. These model catalyst studies show clearly how Pd and Zn interactions modify the selectivity for steam reforming of methanol.

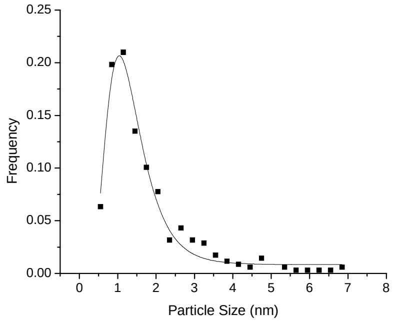
Progress Report

Effect of Pd-Zn alloying

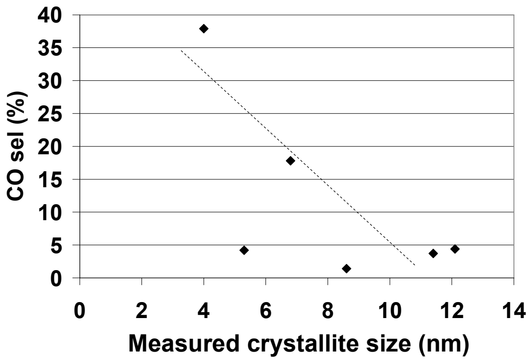
Monometallic Pd/Al_2O_3 leads to decomposition of methanol to form CO + H_2, while Pd-Zn on alumina completely shuts off the decomposition route, in favor of the reforming to produce CO_2 + H_2. The figure on the left shows this dramatic shift in selectivity (1). What is most surprising is that the Pd-Zn is far more reactive than the monometallic Pd catalyst (note the high conversion of methanol at low W/F ratios on the Pd-Zn catalyst). Previous work in the literature has been performed on ZnO supported Pd. The role of the ZnO support, the extent of alloy formation and the particle size, are not well understood. We therefore performed a detailed study of a co-precipitated Pd/ZnO catalyst. By choosing appropriate treatment conditions, it was possible to generate separate Pd and PdZn nanoparticles coexisting on the support, with the extent of alloy formation ranging from 25% PdZn to 100% PdZn. The catalysts were characterized using HAADF imaging and the extent of alloying analyzed via EDS as well as XRD Reitveld refinement. While the lowest CO selectivity was generally achieved with increasing alloy content, the relationship was not monotonic. For any given extent of alloying, the lowest CO selectivity was achieved only when the smallest particles (<2nm), such as those seen in the figure below, had been eliminated.



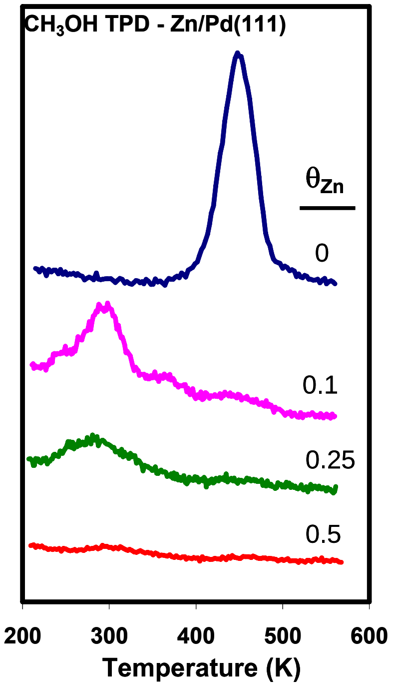




Size effects

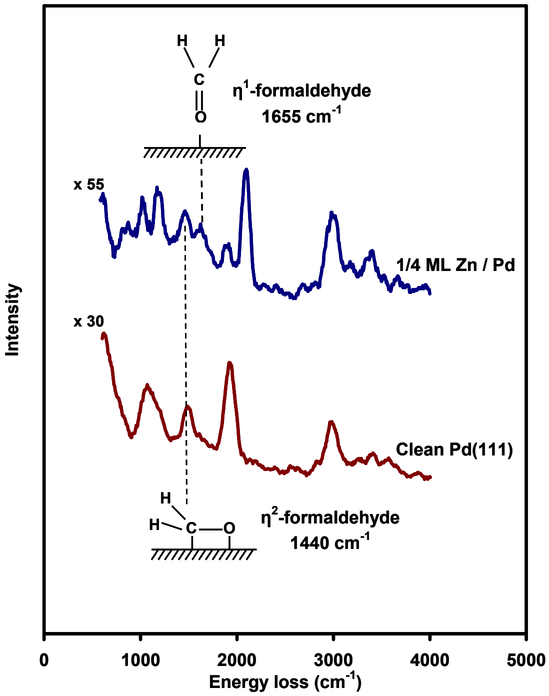


It appears that small particles are responsible for the formation of CO (which is undesirable since CO poisons the fuel cell electrocatalyst). The figure on the right shows a typical catalyst containing a large fraction of particles under 2 nm in diameter. We found that such catalysts always exhibited high CO selectivity. As the catalyst was treated at progressively higher temperatures, the Pd transformed into PdZn, but we also eliminated the smallest particles. Increasing extent of alloying to form PdZn was accompanied by an increase in mean particle size. It was therefore difficult to separate the two effects, the role of alloying and that of increasing particle size. By using carefully designed pretreatments, it was possible to retain small particle sizes. To our surprise, the smaller PdZn particles did not result in higher reactivity. Catalysts with a mean diameter of 9nm were just as reactive as those with mean diameter of 34nm. These results suggest that the support ZnO could be playing a significant role in the methanol steam reforming reaction and deserves more careful study. One problem with catalysts prepared with acidic Pd precursors is that the ZnO dissolves, leading to complete loss of ZnO morphology. Therefore, in order to understand the nature of particle size effects, free of these dissolution effects, it is essential to study the deposition of Pd from organic precursors using a non-aqueous route. Pd/ZnO catalysts were prepared (2) using an organic preparation method allow evaluation of the effects of PdZn alloy crystallite size without the complication of ZnO morphology change typically occurring during conventional aqueous impregnation. Using this approach, we have been able to confirm that the size of PdZn alloy crystallites plays an important role in determining the CO selectivity (see figure on the previous page). Large sized PdZn crystallites dramatically suppress CO selectivity while providing high activity for methanol steam reforming.



Model Catalysts

It is clear that model catalyst studies are needed to unravel some of the complexities in this system. Two separate model systems have been the focus of the work at UPenn: (1) Pd and PdZn films and particles supported on ZnO(0001) and (2) Pd(111) surfaces covered with submonolayer amounts of Zn.



Pd/ZnO(0001)

Model catalysts consisting of vapor deposited Pd films supported on ZnO(0001) were investigated. XPS and LEED studies showed that the Pd film growth at 300 K proceeds via a two-dimensional island growth mechanism (2DI). Pd films grown in this manner are meta-stable, however, and agglomerate into particles upon heating but remained oriented with respect to the ZnO surface. Heating above 500 K was also found to induce reaction of the Pd with the ZnO surface to form a PdZn alloy. The reaction of CH_3OH on the Pd/ZnO(0001) model catalysts was characterized using temperature programmed desorption(TPD) as a function of Pd coverage and sample pretreatment conditions. A variety of trends were observed in this serious of experiments, the most important of which these can be summarized as follows. The reactivity of (111) oriented Pd films on ZnO(0001) for dehydrogenation of CH_3OH to CO and H_2 is greatly diminished compared to that of Pd(111) suggesting that interactions between the Pd and ZnO affect the reactivity of the Pd even prior to formation of the PdZn alloy. Incorporation of Zn into the Pd film decreases in the interaction energy of CO with the metal as indicated by a decrease in the CO desorption temperature and causes a significant decrease in the methanol dehydrogenation activity of the metal film. There is exchange of oxygen between the supported metal particles and the ZnO lattice suggesting that in Pd/ZnO catalysts Zn may act as a redox site that provides oxygen for reaction with CO or other intermediates adsorbed on the metal to produce CO_2. These Zn sites could be located either at the Pd/ZnO interface or on the surface of the PdZn alloy.

Zn/Pd(111)

CH_3OH TPD studies as function Zn coverage for Zn/Pd(111) samples showed that complete dehydrogenation of methanol to CO and H occurs below 300 K on Pd(111). The addition of small amounts of Zn (<0.1 ML) causes a significant decrease in the dehydrogenation activity and, consistent with the Pd/ZnO(0001) studies, decreases the interaction energy of CO with the ZnO surface. Based on thermodynamic grounds a pathway that goes through CO as an intermediate can be ruled out as the operable pathway for MSR on Pd/ZnO since the observed high selectivities to CO_2 are not consistent with the equilibrium conversion of the water gas shift reaction (WGS). Thus, while the alteration of the methanol dehydrogenation activity by the Zn must play a role in MSR on Pd/ZnO, by itself, this does not explain the mechanism of MSR on these catalysts. If the reaction proceeds via aldehyde and carboxylate intermediates, as proposed in the literature, then the Zn is likely to play a role in the formation and/or stabilization of these intermediates. In order to understand the possible effects of Zn on these intermediates we have used HREELS to characterize the bonding and orientation of methanol- and formaldehyde-derived intermediates on Zn/Pd(111). The most important observation in this work to date is that on Pd(111) the CH_2O binds in an η^2-configuration in which both the C and O atoms in the carbonyl group interact with the surface while on Zn/Pd(111) surfaces CH_2O binds in an η^1 in which only the oxygen end of the molecule is bound to the surface.

Future Work

The results of our studies of model catalysts already provide considerable insight into how Zn and the ZnO substrate affect the reactivity of Pd/ZnO catalysts towards methanol. Electronic interactions between Pd and Zn are clearly important and have the following effects (1) decrease the heat of adsorption of CO on the Pd surface, (2) significantly decrease the methanol dehydrogenation activity, and (3) alter the bonding configuration of aldehyde intermediates from an η^2 to an η^1 configuration which is likely to stabilize them from further dehydrogenation. Our data also indicates that reaction at sites at the PdZn-ZnO interface and exchange of oxygen across this interface may be important. The former observation is consistent with the results obtained from the supported catalysts. Our results also leave many questions unanswered. For example, the TPD data for as grown Pd films on the Zn-terminated ZnO(0001) surface show that alloy formation is not required to suppress methanol dehydrogenation activity, suggesting that interactions between Pd and Zn cations on the surface of the support have a similar effect. To test this hypothesis it would be useful to study Pd films supported on the O-terminated ZnO$(000\bar{1})$ surface where direct interaction between the Pd and Zn^{2+} cations in the support could be minimized. It would also be useful to know the evolution of the structure of the Pd and PdZn particles on the ZnO(0001) substrate as a function of annealing conditions in order to assess how interactions at the Pd-ZnO interface affect reactivity. It should also be noted that to date our studies have focused on only one aspect of the MSR reaction mechanism, namely the adsorption and dehydrogenation of methanol and formaldehyde on Pd/ZnO. Obviously, to elucidate the overall mechanism for this reaction we also need to understand the adsorption and reaction of water on Pd/ZnO and how water derived intermediates (i.e. O and OH) react with adsorbed methanol and methanol-derived intermediates such as formaldehyde. Future work will also include in-situ IR studies under reaction conditions. In-situ EXAFS will be used to improve our understanding of the small Pd and PdZn particles formed on these catalysts. All of these issues will be addressed in our proposed work over the next year.

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DE FG02-05ER15729 **Perla B. Balbuena and Jorge M. Seminario**

Theory-Guided Design of Nanoscale Multi-Metallic Catalysts for Fuel Cells

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Goals

Determine trends for catalytic activity towards the oxygen reduction reaction and stability against dissolution of Pt-based alloy nanocatalysts exposed to acid medium. Reactivity and stability trends are sought as a function of surface composition and atomic distribution in the first 2-3 surface layers. Investigate possible mechanisms for metal dissolution.

Recent Progress

Catalytic activity. Binding energies of oxygen reduction intermediates: OOH radical, O, and OH radical are used to evaluate catalytic activity in clusters and extended bimetallic surfaces, using a thermodynamic analysis proposed by us. In small Pt_xPd_y clusters of various compositions, we investigated the effect of the atomic distribution (mixed vs. ordered structures) on reactivity. Polarization effects such as charge transfer from the Pd atoms both to Pt atoms and to adsorbates, and the different orbital electronic population in an “average” atom clearly allows us to differentiate the activity behavior of mixed vs. ordered clusters. We have also done a similar analysis in extended surfaces focusing on the differences of reactivity due to geometric effects between clusters and extended surfaces of identical overall compositions. Other bimetallic systems (Pt_3Co and Pd_3Co) were also investigated on extended surfaces, where reactivity trends were found to follow the d-band model predictions. Since the surface atomic distribution in nanocatalysts could be very different than that expected in bulk alloys, we studied the effect of nanoparticle size of Pt-Pd alloys of several overall compositions. We have investigated the adsorption and dissociation characteristics of hydrogen peroxide, an undesired intermediate of the oxygen reduction reaction which can generate radical species that cause degradation of the polymer electrolyte membrane in fuel cells.

Solvent effects at the catalytic interface were incorporated to investigate water behavior near sulfonic sites in the vicinity of the nanocatalysts. We found three different structural and dynamical regimes as a function of the water/sulfur ratio, and further studies were oriented to determine the electronic characteristics of the water/sulfonic groups in contact with a few catalytic sites. Significant effort was also invested by our team on developing new computational approaches to characterize the catalytic interface. In addition, we have performed systematic studies of testing and developing corrections to DFT functionals for a large number of molecules. The new results have chemical accuracy, which is essential for achieving computationally-guided designs.

Most recently we have also investigated similarities between the bimetallic ionic sites found in metalloenzymes and those of bimetallic nanocatalysts and we have analyzed the interactions of charged species with the intermediates and products of the oxygen reduction reaction. These studies (as well as the polarization effects found in small clusters) suggest that metal ions may be less expensive and more efficient active sites than metal atoms. Along the same lines we are characterizing ionic complexation in dendrimers and dendrimer fragments, and we are now testing those sites as catalytic centers.

Stability of nanocatalysts against dissolution in acid medium. Metal nanoparticles in acid medium can become unstable and dissolution of metallic atoms has been detected experimentally. We have developed a systematic thermodynamic analysis based on density functional theory calculations, which allows us to determine the stability against dissolution of platinum and other elements in mono- or multimetallic ensembles. This technique can be utilized as a screening tool to determine the potential characteristics of a Pt-based alloy regarding catalytic stability. However, we are also interested on unraveling the molecular mechanisms by which such dissolution process takes place.

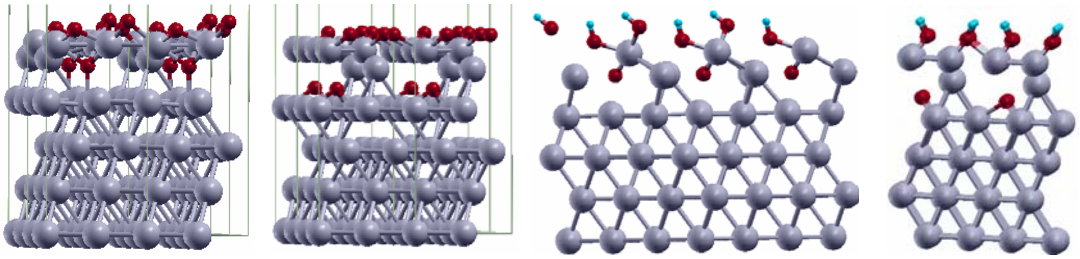

Figure 1. From left: Adsorption of oxygen on fcc surface site and absorption in tetrahedral subsurface site (first image), and in octahedral subsurface site (second image). Adsorption of OH on top site and absorption in tetrahedral subsurface site (third image), and in octahedral subsurface site (fourth image)

We have just finished a complete study of the effect of the presence of subsurface oxygen on the structure of the platinum lattice, including the determination of barriers for diffusion of oxygen from the surface to the subsurface, as a function of coverage and exposed crystallographic face. Our current work includes the analysis of the effect that other adsorbates (especially OH and H_2O) have on the interplay between subsurface and surface oxygen and on the distortion of the metal structure and the investigation of the possible mechanism for separation of the metal cation from the metal structure.

DOE interest

Hydrogen-air polymer electrolyte membrane fuel cells are promising candidate power sources for several applications. One of the remaining challenges for the successful commercialization of low-temperature fuel cells is the development of more efficient, less expensive, and more durable Pt-alloy nano-electrocatalysts. Enhanced catalytic activity of certain alloy combinations have already been demonstrated both theoretically and experimentally and the current goal adds the objective of achieving extended catalytic life. First principles computational analyses are fundamental for developing an improved understanding of catalysis and corrosion mechanisms and using such knowledge for guiding the catalytic design.

Future Plans

We intend to determine the effect of the electrolyte phase in first approximation by considering the effect that the acid medium (acidic water) and the presence of certain ions –present in the electrolyte to facilitate proton transport- may have, for instead altering the change of oxidation state of the platinum atoms and facilitating its dissolution, under the oxidized conditions established from our current studies. Once we have a better understanding of the dissolution process for platinum, we plan to extend the characterization of the mechanism of the metal dissolution process, clarifying the role that certain elements (as we have shown for iridium) may have to increase the durability of platinum. Thus, we will expand our current studies of the effects of subsurface and surface oxygen to multimetallic surfaces. In addition, we will investigate the effect of the nature of the exposed surface by examining different crystallographic faces and calculating their surface energies. Regarding alternative catalysts, we plan to continue our investigations of biomimetic systems, and the characterization of host-guest structures with ions as active sites. Our new developed computational approaches to characterize the interfacial region will be further tested including potential dependence for the analysis of reactivity of multimetallic catalysts.

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DE-FG02-00ER15104 **Jingguang G. Chen**

Structure-Property Relationship in Metal Carbides and Bimetallic Alloys

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Research Goals:

It is well known that the electronic, catalytic and electrocatalytic properties of transition metals can be modified by alloying with carbon or with another metal. The resulting metal carbide or bimetallic alloy often demonstrates properties that are distinctively different from those of the pure parent metal. The objective of the project is to use selected carbides and bimetallic alloys as model systems to unravel the relationship between the electronic/geometric structures and the chemical/catalytic properties for applications in heterogeneous catalysis and in fuel cells.

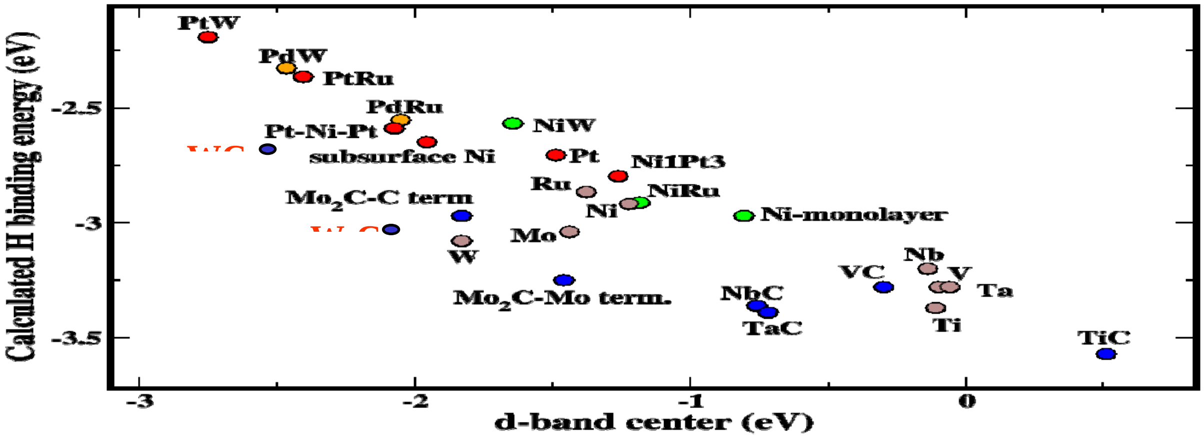
Research Approaches:

The current research project involves three parallel approaches: (1) Fundamental surface science investigations of the reaction mechanisms of several carefully-chosen probe reactions on carbide and bimetallic surfaces. (2) Correlation of chemical activities of these surfaces with their electronic properties using a combination of experimental measurements and DFT modeling. (3) Reactor or electrochemical evaluation of relevant carbide and bimetallic powders/thin films to bridge the "materials gap" and "pressure gap" between model surface science studies and heterogeneous catalysis/electrocatalysis.

Recent Progress:

A. Correlating Electronic and Catalytic Properties on Carbides and Bimetallic Surfaces

We have made significant progress in correlating the structure-property relationship by modifying transition metals either with carbon atoms to make carbides, or with metal adlayers to make monolayer bimetallic surfaces (see attached publication list). As shown in the Figure, our



DFT modeling results have demonstrated that the d-band center is significantly modified by the formation of carbides and bimetallic alloys. The DFT results also revealed a near linear correlation between the d-band center and hydrogen binding energy over a wide range of carbide and bimetallic surfaces. We have confirmed the DFT predictions on several carbide and bimetallic systems, including TiC/Ti(0001), Mo_2C/Mo(110), WC/W(110), Pd/Mo(110), Pt/W(110), and a wide range of 3d/Pt(111) and 3d/Pt(100) surfaces using experimental techniques such as TPD and HREELS. The combined DFT modeling and experimental measurements clearly indicated that the d-band center can be used as a useful parameter to predict the chemical properties of carbide and bimetallic surfaces. In addition, we have correlated the surface d-band center with the hydrogenation activities of the C=C bond in olefins, and the C=O bond in acrolein (CH_2=CH-CH=O).

B. Extending Model Surfaces to Polycrystalline Films and Supported Catalysts

One of the main objectives in the past year is to perform surface science and catalytic studies on polycrystalline films and supported catalysts, whose chemical compositions were identified from the corresponding single crystal carbide and bimetallic surfaces. For example, we have performed extensive investigation of the synthesis and characterization of polycrystalline, phase-pure WC (tungsten monocarbide) thin films using Physical vapor Deposition. The surface chemistry of the polycrystalline WC film was investigated using surface science techniques, such as TPD and HREELS. The comparative studies showed strong similarities between polycrystalline WC with WC/W(110) using several probe molecules. Another example is the synthesis and catalytic evaluation of supported Ni-Pt and Co-Pt catalysts, which showed the unique low-temperature hydrogenation pathway that was initially identified on the Ni/Pt(111) and Co/Pt(111) surfaces.

Future Plans:

In the next year we will use several probe reactions to further investigate the activity, selectivity and stability of carbides and bimetallic alloys in heterogeneous catalysis: (1) We will investigate the hydrogenation mechanisms of acrolein on several carbide and bimetallic surfaces, including WC/W(110), WC/W(111), and 3d/Pt(111) surfaces, to further unravel the correlation between the selective hydrogenation activity with the d-band center of these surfaces. (2) We will continue studies of of Pt-based bimetallic catalysts as cathode electrocatalysts for the reduction of oxygen; our main focus in these studies will be to determine the stability of the Pt-3d bimetallic structures under *in-situ* fuel cell conditions and to identify ways to improve their electrochemical stability using a combination of UHV surface science, DFT modeling, and *in-situ* electrochemical measurements.

DOE Interest:

The overall goal of the current research is to demonstrate the possibility to predict and design materials with desirable catalytic properties. We believe that carbides and bimetallic alloys are excellent model systems to directly correlate the relationship between electronic/geometric structures and chemical/catalytic properties. Such structure-property relationship, to be determined using a combination of surface science experiments, DFT modeling, and catalytic studies, should help in predicting and controlling the catalytic and electrocatalytic properties of transition metals in general and carbide/bimetallic catalysts in particular.

Publications Sponsored by Current DOE Grant (2005-2007):

H.H. Hwu, J.G. Chen, “Surface Chemistry of Transition Metal Carbides”, *Chemical Reviews*, 105 (2005) 185-212.

M.B. Zellner and J.G. Chen, “Surface Science and Electrochemical Studies of WC and W_2C PVD Films as Electrocatalysts”, *Catalysis Today*, 99 (2005) 299-307.

H.H. Hwu, M.B. Zellner, and J.G. Chen, “Effect of Oxygen Modification on Electronic and Chemical Properties of C/Mo(110)”, *Journal of Catalysis*, 229 (2005) 35-49.

J.R. Kitchin, J.K. Norskov, M.A. Barteau and J.G. Chen, “Trend in the Chemical Properties of Early Transition Metal Carbide Surfaces: A Density Functional Study”, *Catalysis Today*, 105 (2005) 66-73.

M.B. Zellner and J.G. Chen, “Potential Application of Tungsten Carbides as Electrocatalysts: Synergistic Effect of Pt-Modification on the Reactions of Methanol, Water, and CO on C/W(110)”, *Journal of Electrochemical Society*, 152 (2006) A1483-A1494.

M.B. Zellner, A.M. Goda, O. Skoplyak, M.A. Barteau and J.G. Chen, “Novel Chemistry of Hydrogen and Ethylene on Monolayer Metal Films: A Combined DFT and Experimental Study”, *Surface Science*, 583 (2005) 281-296.

L.E. Murillo, N.A. Khan and J.G. Chen, “The Effect of Hydrocarbon Structure and Chain Length on the Low-Temperature Hydrogenation Activity on Ni/Pt(111) Bimetallic Surfaces”, *Surface Science*, 594 (2005) 27-42.

M.B. Zellner and J.G. Chen, “Supporting Monolayer Pt on W(110) and C/W(110): Modification Effects on the Reaction Pathways of Cyclohexene”, *Journal of Catalysis*, 235 (2005) 393-402.

M.B. Zellner, H.H. Hwu and J.G. Chen, “Comparative Studies of Methanol Decomposition on Carbide-Modified V(110) and Ti(0001)”, *Surface Science*, 598 (2005) 185-199.

N.A. Khan, L.E. Murillo, Y. Shu, J.G. Chen, “Correlating Low-Temperature Hydrogenation Activity of Co/Pt(111) Bimetallic Surfaces to Supported Co/Pt/γ-Al_2O_3 Catalysts”, *Catalysis Letters*, 105 (2006) 233-238.

C.A. Menning, H.H. Hwu, and J.G. Chen, “An Experimental and Theoretical Investigation of the Stability of Pt-3d-Pt Bimetallic Surfaces under Oxygen Environment”, Journal of Physical Chemistry B, 110 (2006) 15471-15477.

E.C. Weigert, M.B. Zellner, A.L. Stottlemyer and J.G. Chen, “A Combined Surface Science and Electrochemical Study of Tungsten Carbides as Anode Electrocatalysts”, Current Topics in Catalysis, accepted.

L.E. Murillo, A.M. Goda and J.G. Chen, “Selective Hydrogenation of C=O Bond in Acrolein through Architecture of Bimetallic Surface Structures”, Journal of American Chemical Society, accepted.

C.A. Menning, M.B. Zellner and J.G. Chen, “An Experimental and DFT Study of the Reaction of Methanol on Pt/W(110) Bimetallic Surfaces”, Surface Science, submitted.

M.P. Humbert, L.E. Murillo, and J.G. Chen, “General Trends in Hydrogen Binding Energy and Hydrogenation Activity on Pt-3d Bimetallic Surfaces”, Journal of Catalysis, submitted.

E.C. Weigert, M.P. Humbert and J.G. Chen, “PVD Synthesis of Phase-Pure WC Films on Different Carbon Substrates”, Carbon, submitted.

Catalytic conversion of alkanes by bifunctional catalysis

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Direct activation and catalytic transformation of light alkanes by Brønsted acidic catalysts requires high temperatures and very high acid strength. However, in many cases, thermodynamic boundary conditions of the subsequent reactions require that the reaction temperatures for hydrocarbon transformation reactions are low.

In order to be able to convert alkanes at low temperatures hydride transfer reactions from carbenium ions (formed by an additional stoichiometric process) have to be utilized. The best know and most discussed case is the isomerization of alkanes by sulfated zirconia. In this case, sulfated zirconia generates the olefins from alkanes during the reaction in extremely small quantities by a stoichiometric redox process converting chemisorbed SO_3 into chemisorbed SO_2 and water. The olefins generated isomerize to iso-olefins and are being removed from the surface *via* hydride transfer. For every olefin created approximately 500 hydride transfer cycles occur. The overall true energy of activation for this process is around 115 kJ/mol. This hydride transfer is also the dominating route of transition metals are used as integral part of the catalysts.

Generation of the olefins, however, is not mandatory to be catalyzed by redox active oxides or metals. The polarization by large multiply charged cations (such as La^{3+}) is so much stronger than the interaction with the Brønsted acidic hydroxyl groups that this interaction induces direct dehydrogenation of the sorbed alkanes. The strong polarization causes the heat of adsorption of the alkanes increased by approximately 10 kJ/mol. The interaction involves polarizing C-H groups at secondary and tertiary carbon atoms, while the C-H groups of primary carbon atoms are even strengthened. At temperatures as low as 340 K evolution of molecular hydrogen and cracking of adsorbed molecules has been observed. DFT calculations indicate that the true energy of activation is approximately the same as observed for butane isomerization with sulfated zirconia.

Finally, a new potential route to activate the primary carbon atom is opened *via* the oxidative chlorination of methane using $LaCl_3$ as catalysts and HCl and O_2 as co-reactants. The role of the oxidation process appears to be to generate positively charged surface chlorine atoms, which can be exchanged in an electrophilic substitution for a hydrogen in methane. The process is selective with very little total oxidation and a small extent of generating carbon oxides.

Overall, it will be shown that multifunctional catalysts and closely coupled reaction steps are needed to activate alkanes at mild temperatures. Only the subtle control of the functions and actions lead to active and stable catalysts. New catalytic materials and new potential process routes can be developed using the rigorous understanding of the elementary steps as guiding principle.

DE-FG02-03ER15467 **PIs: Susannah Scott**
Brad Chmelka

CATALYSIS SCIENCE INITIATIVE: Hierarchical Design of Supported Organometallic Catalysts for Hydrocarbon Transformations

Collaborator: Juergen Eckert
Grad students currently supported: Anthony Moses, Ramzy Shayib, Miyako Hisamoto
Postdoctoral fellows currently supported: Ryan Nelson

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Goals

We aim to understand, control and synthetically modify the active site architecture in heterogeneous catalysts based on oxide-supported and generally isolated transition metal centers. Our general approach is to use molecular precursors to create materials with highly uniform active sites. We also aim to understand and control local support compositions and structures that exert important influences on activity and active site accessibility (e.g., transport, adsorption).

Recent Progress

Characterization of active sites in Re-based olefin metathesis catalysts. The grafted organometallic catalyst $CH_3ReO_3/SiO_2\text{-}Al_2O_3$ performs metathesis of functionalized and unfunctionalized olefins. We have identified two spectroscopically distinct sites, Figure 1, that form by interaction of the organometallic with Lewis and Brønsted acid sites, for which DFT calculations predict ^{13}C NMR chemical shifts of 30 and 16 ppm, respectively. Only the Lewis acid-activated sites are associated with olefin metathesis activity, although they are in the minority when silica-alumina (13 wt% Al_2O_3) adsorbs up to 10 wt% Re. The formation of the inactive sites can efficiently blocked by hexamethyldisilazane (HMDS) capping of the Brønsted acid sites, Figure 2. We have also shown that HMDS treatment *promotes* the olefin metathesis activity of conventional perrhenate/silica-alumina catalysts, Figure 3. This unexpected effect appears to be related

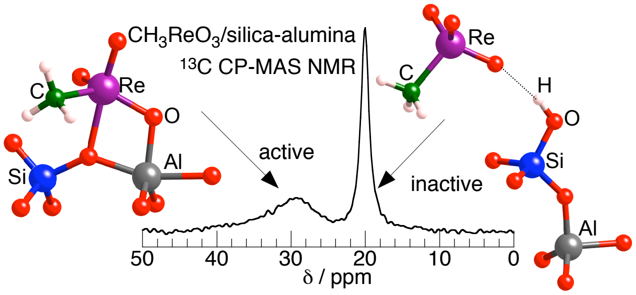

Figure 1. NMR spectrum and DFT-calculated structures for CH_3ReO_3 interacting with the Lewis (left) and Brønsted (right) acid sites of dehydrated silica-alumina.

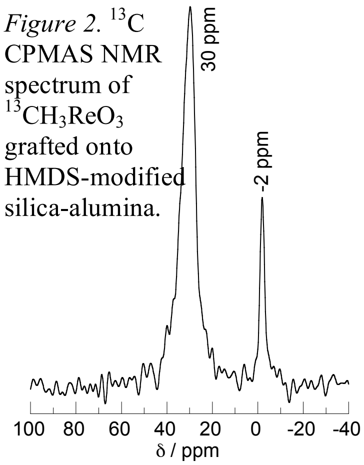

Figure 2. ^{13}C CPMAS NMR spectrum of $^{13}CH_3ReO_3$ grafted onto HMDS-modified silica-alumina.

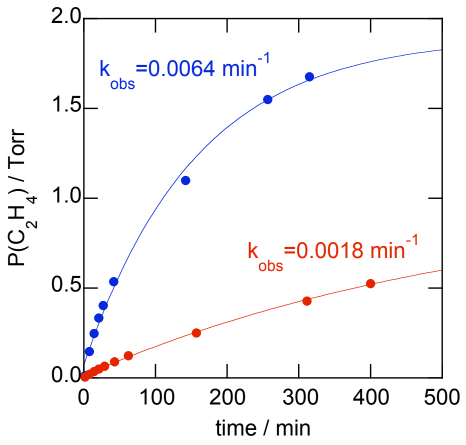

Figure 3. Gas phase kinetics of propylene homometathesis. over a Re/SiO_2-Al_2O_3 catalyst, with (blue) and without (red) HMDS treatment.

to the role of the Brønsted acid sites in catalyst deactivation by 1,1-disubstituted olefins, which is also effectively prevented by HMDS capping.

Very High Field Solid-State ^{27}Al NMR. The Lewis acid sites that promote olefin metathesis activity are five-coordinate ^{27}Al species, whose study by NMR has been hindered by poor spectral resolution and dramatic post-steaming or post-calcination reductions in ^{27}Al (I=5/2) signal intensity. Such difficulties arise generally for quadrupolar nuclei, and at surface sites, with their inherently large disruptions in local coordination. Inhomogeneous broadening due to second-order quadrupolar interactions is particularly problematic at conventional magnetic field strengths, up to and including at least 12 Tesla (500 MHz for ^{1}H). The use of very high magnetic fields, however, significantly improves both the resolution and sensitivity of solid-state ^{27}Al magic-angle-spinning (MAS) NMR spectra of amorphous silica-aluminas. We have conducted ^{27}Al MAS measurements at very-high-field (19 Tesla), and under ultrafast (40 kHz) MAS conditions, of amorphous silica-aluminas after different catalyst processing treatments. By comparing integrated ^{27}Al signal areas and corresponding elemental analyses before and after catalyst treatments, we have established that a majority (~50-60%) of the ^{27}Al species remain NMR-visible after calcination at 19 T, compared to less than 5% detectable at 12 T. In particular, we have elucidated changes in molecular composition and structure as functions of Al content, high-temperature steaming, and functional-group grafting, notably and crucially with respect to the populations of four-, five-, and six-coordinate ^{27}Al species.

On the local order present in amorphous silica. We have studied the reactions of $Ga(CH_3)_3$ and $TiCl_4$ with silica. Both form uniform, bimetallic sites interacting with pairs of surface hydroxyls. These results imply a non-random distribution of these hydroxyls, which influences and may even preclude the possibility of 'isolating' individual metal sites by grafting. The dimeric nature of the sites also has implications for subsequent surface-induced transformations, such as the evolution of $[Cl_3Ti(\mu\text{-}OSi\equiv)]_2$ to $Cl_2Ti(OSi\equiv)_2$ via liberation of $TiCl_4$. In other cases, a single metal complex may interact directly with a pair of surface hydroxyls, as in the grafting of $(CH_3)_2$Au(acac) onto silica. Its structure, investigated by EXAFS and DFT, involves the

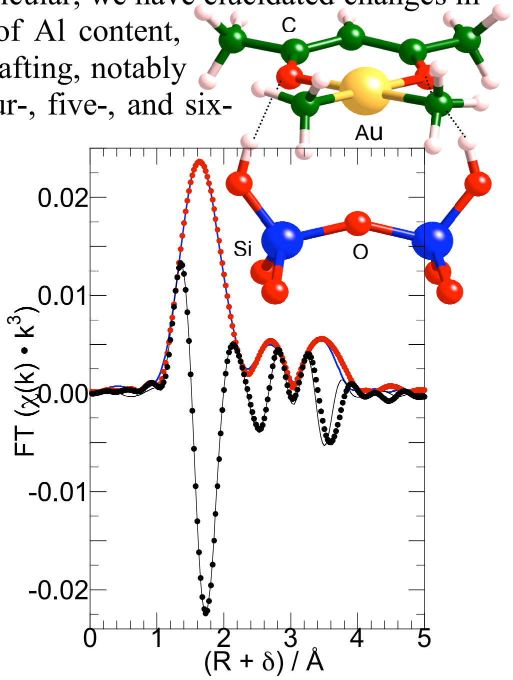

Figure 4. EXAFS of $(CH_3)_2$Au(acac) on silica, showing curvefit to DFT-predicted model structure with two H-bonds to adjacent surface hydroxyls.

formation of two hydrogen-bonds to the donor oxygen atoms, Figure 4.

DOE Interest

Oxide-supported metal catalysts are particularly useful in hydrocarbon transformations, where their stability and regenerability are valued in making more valuable chemicals and fuels from less valuable crude oil or seed oil feedstocks. Manipulating the relationships that control active site formation and deactivation requires a detailed, atomic-level understanding of structure and reactivity, which these studies aim to provide.

Future Plans

We plan to pursue, in parallel, our spectroscopic and computational investigations of oxide supports and grafted organometallic complexes in order to determine the origin of self-activation in supported metal catalysts for hydrocarbon transformations such as olefin oxidation and metathesis.

Publications acknowledging this grant (2005-2007)

Leifeste, H. D. “Kinetic Studies of Metathesis Reactions Catalyzed by Supported Methyltrioxorhenium”, M.Sc. Thesis, University of California, Santa Barbara, **2005**.

Deguns, E. W.; Taha, Z.; Meitzner, G. D.; Scott, S. L. “An X-ray Absorption Study of Two $VOCl_3$-Modified Silicas: Evidence for Chloride-Silica Interactions”, *J. Phys. Chem. B*, **2005**, *109*, 5005-5011.

Moses, A. W.; Ramsahye, N. A.; Raab, C.; Leifeste, H. D.; Chattopadhyay, S.; Chmelka, B. F.; Eckert, J.; Scott, S. L. “Methyltrioxorhenium Interactions with Lewis Acid Sites of an Amorphous Silica-Alumina”, *Organometallics* **2006**, 25, 2157-2165.

Taha, Z. A.; Deguns, E. W.; Chattopadhyay, S.; Scott, S. L. “Formation of Digallium Sites in the Reaction of Trimethylgallium with Silica”, *Organometallics* **2006**, *25*, 1891-1899.

Deguns, E. W. “Reactions of Titanium, Vanadium, Aluminum and Gallium Complexes with Silica”, Ph.D. Thesis, University of California, Santa Barbara, **2006**.

Scott, S. L.; Eckert, J.; Chmelka, B. F.; Moses, A. W.; Leifeste, H. D.; Ramsahye, N. A.; Chattopadhyay, S; Raab, C. “Supported Re Catalysts for Metathesis of Functionalized Olefins”, *Catal. Org. React.*, **2007**, *115*, 13-22.

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Moses, A. W.; Raab, C.; Nelson, R. C.; Leifeste, H. D.; Ramsahye, N. A.; Chattopadhyay, S.; Eckert, J.; Chmelka, B. F.; Scott, S. L. “Spectroscopically Distinct Sites Present in Methyltrioxorhenium Grafted onto Silica-Alumina, and Their Abilities to Initiate Olefin Metathesis”, submitted.

Deguns, E. W.; White, R. E..; Scott, S. L. “Ring-forming reactions in the deposition of $TiCl_4$ on silica”, submitted.

DE-FG02-05ER15702 **Ulrike Diebold and Annabella Selloni**

Towards a Molecular Scale Understanding of Photocatalysis on Metal Oxides: Surface Science Experiments and First Principles Theory

Students and Postdocs: Xue-Qing Gong, Erie Morales, Matthias Batzill
Collaborators: C. Di Valentin (University of Milano-Bicocca), G. Pacchioni (University of Milano-Bicocca), Ted Madey (Rutgers University)
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Goal

Titanium dioxide, TiO_2, is a highly-promising, yet inefficient, photocatalyst. This joint experimental and theoretical project will provide direct atomic-scale observations with the overall goal to obtain new insights into processes important for photo-oxidation reactions. The project focuses on a few selected, important features: (i) identification of surface trapping sites for photo-excited holes and electrons; (ii) the role of the electronic and geometric structure: how it affects adsorption, photo-excitation, and trapping events; (iii) the influence of replacing oxygen with dopants (sulfur, nitrogen) on the surface and/or subsurface region.

Recent Progress

Electronic and geometric structure of step edges and their influence on reactivity. Step edges at the anatase (101) surface were studied by Scanning Tunneling Microscopy (STM) and comprehensive Density Functional Theory (DFT) calculations of step structures and formation energies were performed. A pronounced change of STM image contrast at the step edges agrees well with the theoretical results. Calculations for the adsorption of water, methanol and formic acid show that the reactivity of step edges is very similar to that of the surfaces which are exposed at the step facets.

Nitrogen doping The influence of nitrogen doping on anatase (101) and rutile (110) has been investigated with STM. The main result was that introduction of nitrogen in the near-surface region renders the samples more prone to loss of oxygen, which, in the case of rutile (110), results in a 1 × 2 reconstruction. DFT calculations for nitrogen incorporation in anatase (101) show that, under oxygen-rich conditions, N bound to a surface O is preferred, whereas, under oxygen-poor conditions, subsurface substitutional N together with oxygen vacancies is favored. The computed cost of formation of a surface oxygen vacancy is almost cancelled in the presence of N impurities in sub-surface layers. The calculated electronic structure shows the presence of N-induced localized states in the band-gap, consistent with the experimentally observed absorption of N-doped anatase samples in the visible region. These N impurity states are very efficient traps for the Ti^{3+} electrons deriving from surface oxygens vacancies.

Electronic structure of point defects and their role as trapping sites for photo-excited holes and electrons Oxygen vacancies on TiO_2 surfaces are experimentally found to introduce localized Ti^{3+} $3d^1$ states about 1 eV below the conduction band. These states are not removed when water is dissociatively adsorbed at the vacancy and hydroxyl groups are formed. Calculations based on pure DFT functionals have not been able to satisfactorily reproduce these findings. We show that a correct description of the localized defect states on the reduced and hydroxylated rutile $TiO_2(110)$ surface is achieved only if proper geometry relaxation is accounted for using hybrid exchange functionals. We confirm the electron trapping nature of Ti(OH) groups, but find no evidence that these defects should also act as hole traps by formation of $Ti^{4+}(OH)^{\bullet}$ radicals.

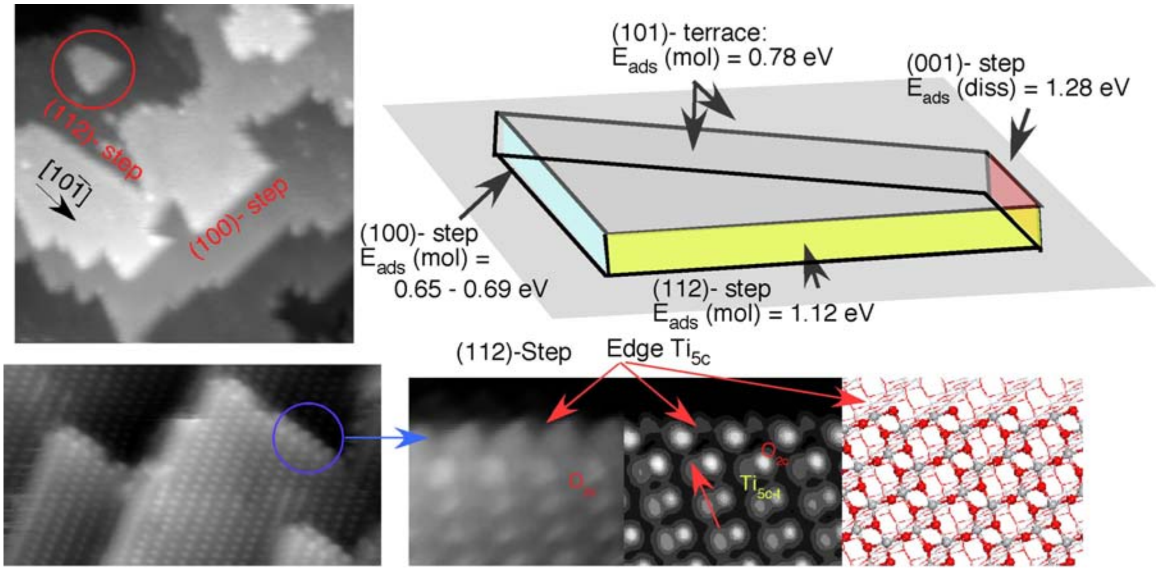

Fig. 1 (a) STM image (250 Å x 250 Å) of a TiO_2 anatase (101) surface, an island with the typical trapezoidal shape is marked with a circle. (b) Sketch of the island with step facets labeled. The adsorption energies for water, predicted from first-principles DFT calculations are included for each step edge. (c) STM image (150 Å x 180 Å) showing <010>/{100} and <111>/{112} steps with higher resolution. (d) Experimental and calculated STM image and model of a <111>/{112} predicted, showing the image contrast along step edges (b-d) adapted from ref. 3.

DOE Interest:

The project will provide an increased understanding of molecular processes and structure-activity relationships in photocatalytic systems. This can lead to guidelines on how to make TiO_2-based systems more efficient in photocatalytic reactions. As such, it directly relates to the Program's mission to develop a mechanistic understanding of chemical reactions that pertain to environmental remediation and pollution control; energy production (photoelectrochemical and production of hydrogen); and novel materials synthesis.

Future Plans:

We will continue our work on the characterization of clean and doped TiO_2 single crystalline surfaces. Our DFT calculations have shown that a rutile TiO_2(011)-2x1 with a lower energy than the previously-assumed titanyl model could exist. We are undertaking collaborative surface diffraction experiments to validate the suggested models. Our experiments show that electron-stimulated desorption results in a non-random creation of surface defects, we will investigate the mechanism that leads to this rather unusual defect configuration. The adsorption of a model molecule (catechol) will be investigated on the various TiO_2 surfaces.

Publications (2006 – 2007)

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2. E. Finazzi, C. Di Valentin, A. Selloni, G. Pacchioni, First principles study of Nitrogen doping at the anatase TiO_2(101) surface, submitted.
3. C. Di Valentin, G. Pacchioni, A. Selloni, Electronic structure of defect states in hydroxylated and reduced rutile TiO_2 (110) surfaces, *Phys. Rev. Lett.*, **2006,** *97*, 166803.
4. X. Gong, A. Selloni, M. Batzill, U. Diebold, Steps on anatase TiO_2(101), *Nature Materials*, **2006,** *5*, 665-670.
5. O. Dulub, C. Di Valentin, A. Selloni, and U. Diebold, Structure, Defects, and Impurities at the Rutile TiO_2(011)-(2 x 1) Surface: A Scanning Tunneling Microscopy Study, *Surf. Sci*. **2006,** *600***,** 4407-4417[Paper was featured in a ‘Surface Science Perspectives’ article, written by C.L. Pang and G. Thornton entitled “The many faces of rutile titania”, Surface Science 600 (2006) 4405-4406; Paper also featured in C&EN News; Oct. 16, 2006]
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In Preparation:

1. Special Issue of the Journal ‘*Chemical Physics*’ entitled ‘*Doping and functionaliztion of photo-active semiconducting oxides*’, edited by Cristiana di Valentin, Annabella Selloni, and Ulrike Diebold.

2. O. Dulub, A. Alchagirov, U. Diebold, M. Batzill, S. Solovyev, E. Loginova, and T.E. Madey “Local defect ordering in electron stimulated desorption of -oxygen from the TiO_2(011)-2x1 surface”, in preparation.

DE-AC05-76RL01830, project 47319 **Michael A. Henderson**

Fundamental Studies of Photocatalysis on TiO_2

Co-Investigators: Scott A. Chambers, Michel Dupuis, Wayne P. Hess, Alan G. Joly, Sabastien N. Kerisit, Igor V. Lyubinetsky

Postdocs: N. Aaron Deskins, Takeo Ohsawa, Robert T. Zehr

Collaborators: Prof. Hicham Idriss (Auckland, NZ), Prof. Marjorie A. Langell, (Nebr.), Prof. Hiroshi Onishi (Kobe, Jpn), Kevin M. Rosso (PNNL), Prof. J. Michael White (Texas)

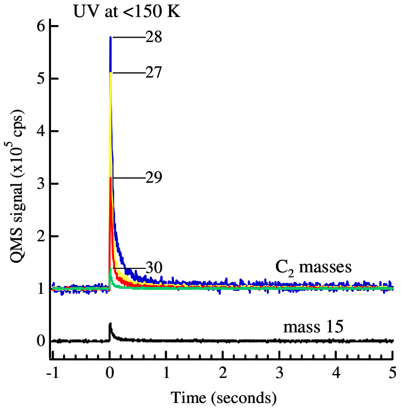
Contact: M.A. Henderson, Pacific Northwest National Laboratory, PO Box 999, MS K8-80, Richland, WA 99352; phone: (509) 376-2192; Email: ma.henderson@pnl.gov;

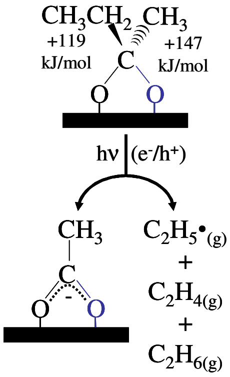
Goal

The goal of this project is to provide insights into the molecular-level properties of photocatalytic transformations on TiO_2 through combined experimental and theoretical studies of organic photooxidation reactions on model TiO_2 materials. Three key areas of heterogeneous photocatalysis on TiO_2 are examined using a variety of theoretical and experimental approaches: (1) detailed mechanistic studies of photocatalytic reaction pathways, (2) charge transfer, charge trapping and energy accommodation, and (3) surface structural and material dependences.

Recent Progress

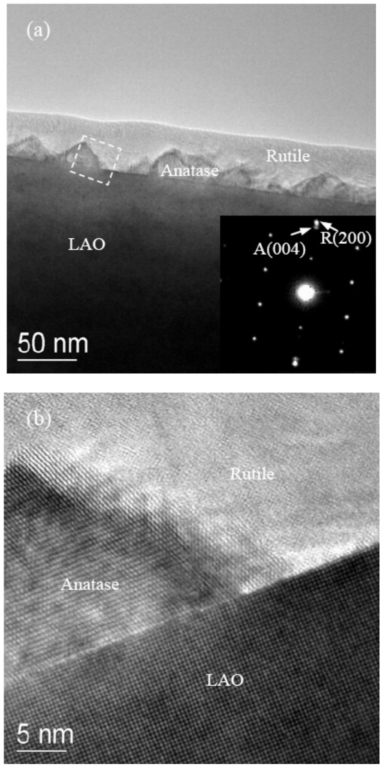
Mechanism of Ketone Photodecomposition on TiO_2: The photodecomposition of acetone and butanone were examined on the (110) surface of rutile TiO_2 using temperature programmed desorption (TPD) and photon stimulated desorption (PSD). In both cases, photoactivity required a prior thermal reaction between the adsorbed ketone and coadsorbed oxygen resulting in a ketone diolate species ($(R_1\text{-})(R_2\text{-})COO$, where R_1 is methyl and R_2 is either methyl or ethyl). The diolate photodecomposes by ejection of either R_1 or R_2 from the surface as an organic radical, leaving behind the companion fragment as a carboxylate species. In the acetone case, only methyl radical PSD was detected, and acetate was left on the surface. In the butanone case there was a possibility of either methyl or ethyl radical ejection, with propionate or acetate left behind, respectively. However, only PSD from C_2 species was detected (right above; UV exposure at time '0') and the species left on the surface was the same as in the acetone case (acetate). The main reaction processes for photodecomposition of butanone diolate are illustrated to the left. The ethyl group is ejected preferentially because of its great stability as a gas phase radical relative to methyl. At 100 K, the photodesorbing ethyl radicals sample the surface such that most of them react to form





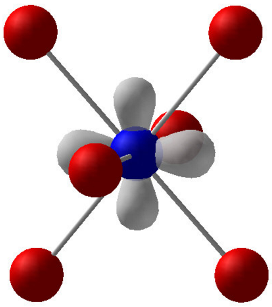
ethene and ethane, and only about ~1/8th of the escape the surface unreacted. These results suggest that the ejection of organic radicals during UV irradiation on TiO_2 surfaces may be a major mechanistic pathway in the photooxidation of organics such as ketones and aldehydes.
(From "*Ethyl Radical Ejection During Photodecomposition of Butanone on $TiO_2(110)$*," by M.A. Henderson, **Surf. Sci.**, submitted)

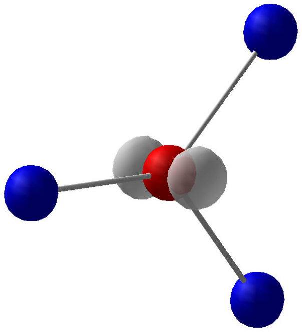
Mixed Rutile and Anatase Model TiO_2 Surfaces: The availability of well-defined anatase single crystal surfaces is an issue in studying photochemistry on this polymorph of TiO_2. We have explored the systematics of anatase nucleation on perovskite substrates during film growth by molecular beam epitaxy. The coincidental lattice match between anatase(001) and $LaAlO_3(001)$ (LAO) typically results in anatase nucleation at the interface. However, the growth conditions dictate whether or not rutile also nucleates, and the associated morphological and structural properties of the composite film. Under certain conditions, both anatase and rutile can nucleate during film growth. The microstructure of one such film is revealed by cross-sectional TEM (to the right). Anatase, rutile and substrate regions can be clearly identified both from their different contrasts in the low-resolution bright field image (above) and from the high-resolution lattice image (below). The presence of both rutile and anatase phases is also clear from the selected area diffraction patterns (SADP) in the film region (inset). The film consists of a top layer of rutile, which appears as nanoscale grains in the AFM image, and a bottom layer of anatase that serves as an interfacial layer between the substrate and rutile. Amorphous regions at the interface were not observed in any films. Four symmetry equivalent epitaxial orientations of rutile on anatase are observed when rutile nucleates as discrete particles on $LaAlO_3(001)$. Such films constitute model systems for studying the anatase/rutile interface, which is of considerable current interest in photochemistry.



(From "*Growth and Structure of MBE Grown TiO_2 Anatase Films with Rutile Nano-Crystallites*," by R. Shao, C. Wang, D.E. McCready, T.C. Droubay, S.A. Chambers, **Surf. Sci.**, in press.*)*

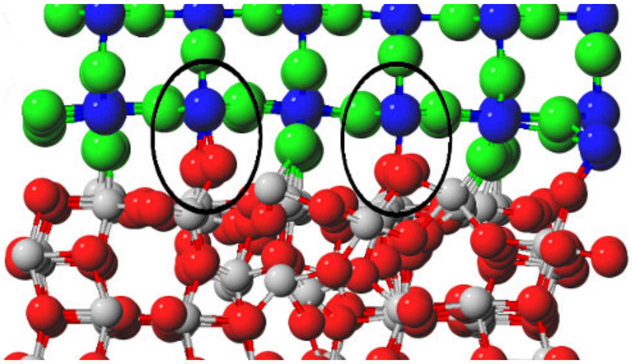
First Principles Modelling of e^-/h^+ Polaron Transport in TiO_2: This work focuses on the intrinsic e^-/h^+ transport in stoichiometric TiO_2. Electron hopping is described by a polaron model, whereby a negative charge is localized at a Ti cation center (below, left), conventionally thought of as a Ti^{3+} site. Polaron hopping (to an adjacent Ti^{4+} site) is described via Marcus theory formulated for polaronic systems and quasi-equivalent to Emin/Holstein/Austin/Mott theory. We obtain the relevant parameters in the theory (namely the activation energy ΔG^*, the reorganization energy λ, and the electronic coupling matrix elements V_{ab}) for selected crystallographic directions in rutile and anatase, using periodic DFT+U and Hartree-Fock cluster calculations. The DFT+U method was required to correct the well-known electron self-interaction error in DFT in the calculation of polaronic wavefunctions. Our results give non-adiabatic activation energies of similar magnitude in rutile and anatase, all near ~0.3 eV. The electronic coupling matrix element, V_{ab}, was determined to be largest for polaron hopping parallel to the (001) direction in rutile and indicative of adiabatic transfer (thermal hopping mechanism) with a value of 0.20 eV, while the other directions investigated in both rutile and anatase gave V_{ab} values about one order of magnitude smaller and indicative of diabatic transfer (tunneling mechanism) in anatase. We also performed similar calculations of the formation and hopping of hole polarons. Hole polarons exhibit themselves as O^- species (right; stoichiometric TiO_2 is populated by O^{2-}). Use of DFT+U led to hole localization, and activation energies, ΔG*, between 0.5 and 0.6 eV in rutile, and between 0.4 and 0.6 eV in anatase. We also were able to obtain hole localization on a (110) rutile surface. The hopping activation energy for a surface hole was found to be equivalent to the energy of a bulk hole.





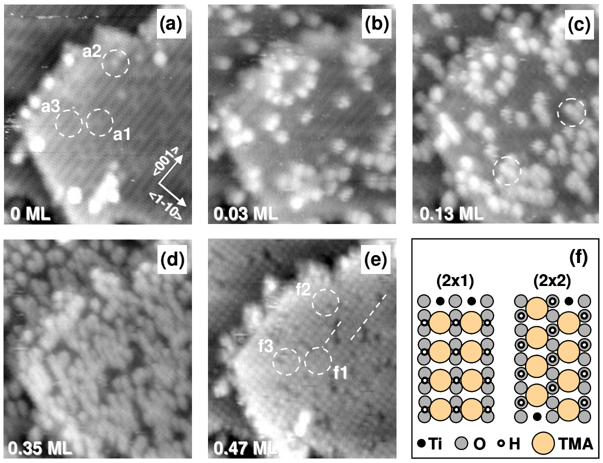
(From "*Electron Transport Via Polaron Hopping in Bulk TiO_2: First Principles Characterization*", by N. A. Deskins and M. Dupuis, **Phys. Rev. B**, submitted)

MD Simulations of Rutile/Anatase TiO_2 Interfaces: We performed molecular dynamics (MD) simulations of interfaces formed between rutile and anatase surfaces of TiO_2. These interfaces are important for understanding mixed-phase catalysts, such as the Degussa P25 catalyst. Construction of these interfaces was possible with near-coincidence-site lattice (NCSL) theory. The results show adhesion energies for the most stable interfaces typically near -2 J/m^2. The interfaces are characterized as disordered, with the disorder is limited to the interface, in agreement with TEM data. Formation of rutile octahedral structures was observed at the anatase side of the interface (see to the right). This appears to be the beginning of an anatase to rutile phase transition. These simulations show promise for interpreting the complex interfaces resulting from mixed polymorphic TiO_2 growth in model materials such as those discussed above.



(From "*Molecular Dynamics Simulation of Rutile-Anatase Interfaces*" by N. A. Deskins, S. Kerisit, K. Rosso, and M. Dupuis, **J. Phys. Chem. C**, submitted.)

Adsorbate Ordering on the $TiO_2(110)$ Surface: We have examined the coverage-dependent packing of trimethyl acetic acid (TMAA) on the $TiO_2(110)$ surface using STM. Because intermolecular interactions play an important role in surface processes, and recent work has shown these factors influence photochemical selectivities (see Henderson, et al., J. Catal. 238 (2006) 153), it is important to understand on the molecular scale how adlayers of organics are arranged. The figure below illustrates the evolution of the TMAA adsorption throughout its consecutive stages by STM image 'snapshots' of the same surface region starting from clean $TiO_2(110)$ (a) up to saturation of the monolayer (e). In the initial adsorption stages, trimethyl acetate (TMA) species are mostly isolated from each other (b-c). Beginning from ~0.1-0.15 ML coverages, pairing occurs orthogonal to the cation rows, while TMA groups tend to be separated along the cation rows. Since no significant surface diffusion of TMA has been observed in the studied temperature range, ordering orthogonal to the rows direction indicates the probable existence of a mobile precursor state, with TMAA sampling several different sites before dissociating. The tendency to occupy adjacent sites suggests an attractive interaction along this direction, most likely through the influence of the acid protons on the bridging O rows. This proton-mediated ordering of TMA is responsible for the observed (2x1) order instead of (2x2) (see f).



(From "*Direct Observation of Adsorption Evolution and Bonding Configuration of TMAA on $TiO_2(110)$*," by I. Lyubinetsky,* Z. Q. Yu, and M. A. Henderson, **J. Phys. Chem. C** 111 (2007) 4342.)

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DE-FG02-05ER15700 **Matthew Neurock**

Investigating the Reaction Pathways for Vinyl Acetate Formation on Pd(111) and Gold-Palladium Alloys

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Collaborators: W. T. Tysoe (co-P.I., Milwaukee), Dario Stacchiola (UWM), Florencia Calaza (UWM), Luke Burkholder (UWM), Zgenjun Li (UWM), Feng Gao (UWM), Yilin Wang (UWM)

Bimetallic catalysts typically present significantly improved catalytic performance over single metals for a range of different catalytic systems including the selective oxidation and functionalization of olefins. The improved activity has been ascribed to electronic (ligand) effects, geometric (ensemble) effects and/or the impedance of metal oxidation. More specifically, the alloying of an “active” group VIII metal such as Pd or Pt with a “less active” group IB metal such as Au or Ag can result in more active and selective catalytic materials for the hydrogenation of olefins, alkynes, cyclotrimerization of acetylene, the selective oxidation of ethylene and acetate and the oxidation of alcohols and acids. This has become an important area of research for the selective oxidation of biorenewable intermediates and other fine chemical intermediates. Despite the great wealth of literature on the role of bimetallic catalysts little is know about the active surface structure that forms under reaction conditions and how it controls the nature of the nanoscale environment in which the reaction proceeds. Our goal in this work is to combine detailed experimental, theoretical and simulation studies over well-controlled bimetallic surfaces to elucidate the influence of the explicit atomic arrangement of the surface and subsurface alloy on the elementary reaction steps the controlling catalytic chemistry. We are currently examining in detail the catalytic synthesis of vinyl acetate over PdAu alloy surfaces as it’s an important industrial example and in addition an ideal probe system by which we can make fundamental advances in elucidating the influence of the atomic alloy structure on surface reactivity.

The vinyl acetate monomer (VAM) is a key building block in the synthesis of various homopolymers and copolymers used in the commercial production of different adhesives, laminate films, paints and surface coatings. Vinyl acetate is currently produced via the reaction of ethylene and acetic acid in the presence of oxygen over PdAu particles supported on silica. While the reaction demonstrates fairly high selectivities (>90%), there is a considerable emphasis to improve product yield, increase throughput and extend catalyst lifetimes. Despite more than thirty years of successful commercial practice, the mechanism for vinyl acetate synthesis is still not very well understood. Various ideas concerning the controlling reaction steps have been actively debated, which include: 1) homogeneous catalysis over Pd acetate clusters that form in solution, 2) the addition of adsorbed ethylene and acetate to form an acetoxyethyl intermediate followed by the subsequent beta-hydride elimination as proposed by Samonos, and 3) the C-H activation of ethylene to form vinyl followed by the subsequent reaction with surface acetate to form VAM as suggested by Nakamura and Mosieev. Careful spectroscopic studies carried out at DuPont as well as computational efforts have shown that while homogeneous Pd catalysts do form VAM they more actively catalyze the formation of acetaldehyde (Wacker chemistry). Tysoe and Stachiolla have shown that VAM can be readily produced over well-defined Pd(111) substrates via the titration of pre-adsorbed acetate intermediates with ethylene.

VAM Synthesis over Model Pd Substrates

In order to provide a better understanding of the molecular processes that control the surface chemistry we have carried out ab initio density functional theoretical calculations to establish the lowest energy structures, binding energies, and vibrational spectra for nearly all of the proposed surface intermediates in order to compare directly with results by Tysoe. Activation barriers for all of the major pathways for various different proposed mechanisms were subsequently calculated. The calculated results have helped to aid in the resolution of the modes of ethylene, acetate, vinyl acetate over model Pd(111) and Pd(100) surfaces. Coverage effects were found to be quite important as the barrier for the ethylene/acetate coupling reaction was reduced to 73 kJ/mol while that for β-hydride elimination was increased to 61 kJ/mol as the coverage was increased to over 0.5 ML. The barriers are consistent with the experimental titration barrier of 65 kJ/mol. These activation energies were found to be almost two times lower than the key steps involved in the Moiseev path, i.e. C-H activation of ethylene and vinyl insertion into acetate. Subsequent deuterium labeling studies carried out by Tysoe demonstrated that there was a factor 6 decrease in the kinetics upon the introduction of the label. By coupling the results of theoretical calculations along with RAIRS spectroscopy we were able to show that the change in the rate was due to a hold up of the acetoxyethyl intermediate that forms on the surface. This helped to provide strong evidence for the Samanos mechanism being operative.

Influence of Alloying Pd with Au

The surface chemistry over PdAu alloys was subsequently examined by first exploring the modes and energies of adsorption for most of the critical primary and secondary reaction intermediates (including: ethylene, vinyl, acetic acid, acetate, acetoxyethyl, VAM, H, OH, H_2O and other hydrocarbons) over a range of different Au compositions between Pd(111) and Au(111) and over a different PdAu compositions between Pd(100) and Au(100). The results indicate that the binding energies for nearly all of the species examined increased in the following order: Au(100) < Au(111) < Pd(100) < Pd(111). As a result, bond making reactions such as ethylene addition to acetate become more exothermic, whereas bond breaking reactions become more endothermic. The addition of well-dispersed Au into the surface, as well as subsurface, results in a strong geometric effect whereby the addition of Au atoms significantly weakens the interaction of the all of the adsorbates bound to higher-fold coordination sites. The binding energies are lowered by some 30 kJ/mol. The presence of Au at neighboring sites in the surface leads to a weaker electronic effect which lowers the binding energies by 10 kJ/mol. The geometric effect is much stronger than the electronic effect. For systems where Pd is supported on a Au substrate (i.e. pseudomorphic overlayers), the Au lattice acts to expand the Pd atoms at the surface and this leads to stronger adsorption energies. This results in less favorable bond-making reactions and more favorable bond-breaking reactions.

While the results show the same general trends for the chemisorption energies of ethylene and acetate over PdAu surface alloys as those found experimentally, they are not quantitative. The biggest impediment to comparing theory and experiment here is the inability to establish the true PdAu atomic arrangement in UHV experiments. In the next year of this project, we will focus on carrying out combined atomic simulations along with DFT calculations to establish the lowest energy atomic arrangements of the PdAu surface and more detailed surface spectroscopy in order establish the specific atomic arrangements and positions of Pd and Au in the topmost surface layers.

VAM Synthesis over PdAu – The Influence of the Alloy

In an effort to move from the ideal UHV systems to more practical industrial conditions, we subsequently calculated the adsorption energies, reaction energies and activation barriers for all of the primary and secondary elementary steps at various different coverages and ensemble arrangements of acetate and oxygen. Under actual operating conditions, the surface is likely covered by acetate and oxygen, thus the kinetics established at low coverages may prove to be a poor model. The results indicate that higher coverages act to increase the barriers for all of the bond breaking steps (such as the β-hydride elimination from the acetoxy ethyl intermediate) since the adsorbed intermediates compete or block surface sites as already discussed. Similarly, bond making steps (such as ethylene and acetate) become more favored.

The results for surface coverage effects on the alloys were found to be the most interesting. They show that while the alloy typically acts to lower the activation barriers for bond-making processes and raise those for bond-breaking steps, this can actually reverse for various alloy arrangements since the formation of the alloy changes the local reaction environment about the active site and hence the local surface coverage. Alloys which are highly concentrated in Au will weaken the adsorbate binding energies which will lower the barriers for addition reactions such as the coupling of ethylene and acetate, while raising the barriers for bond-breaking steps. The decrease in the local coverage that results, however, will weaken the repulsive interactions between coadsorbed molecules in the adlayer. If these interactions are strong on the fully covered surface, their removal upon alloying can lead to an actual increase the barriers for bond-making steps and decrease in the barriers for bond breaking. Our initial results for VAM synthesis show that indeed the addition of Au intrinsically reduces the barrier for the coupling of ethylene and acetate. The drop in coverage at higher Au loadings ultimately makes the coupling barrier significantly higher. These changes that result in differences for bond-making and bond-breaking kinetics may ultimately result in the changes in the governing reaction mechanism. This effect has never been considered in elucidating the effects of alloys and may be quite important in various other systems as well.

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DE-FG02-84- ER13289 **Cynthia M. Friend**

Exploiting Metastable Oxygen on Gold Surfaces for the Selective Functionalization of Olefins

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Goal:

The proposed work aims to characterize the structures of nanoscale Au-based materials that are of potential importance in efficient catalytic synthesis of oxygenates and other key chemical building blocks. Our objective is to develop a fundamental understanding of how to best control the activity and selectivity for important reactions promoted by Au-based materials, with special emphasis on the use of transient, metastable states of oxygen.

Recent Progress:

1.3.1Oxidation of Au(111). Because we are interested in the oxidation reactivity of gold surfaces, we have developed methods for creating different oxygen phases on Au(111). The oxidation of alkenes by adsorbed atomic oxygen are likely to be important. We have used either ozone, electron bombardment of condensed NO_2, or reactive O_2^+ sputtering to produce atomic oxygen on the gold surface. We find that different degrees of long-range order and local bonding of the oxygen are present depending upon the

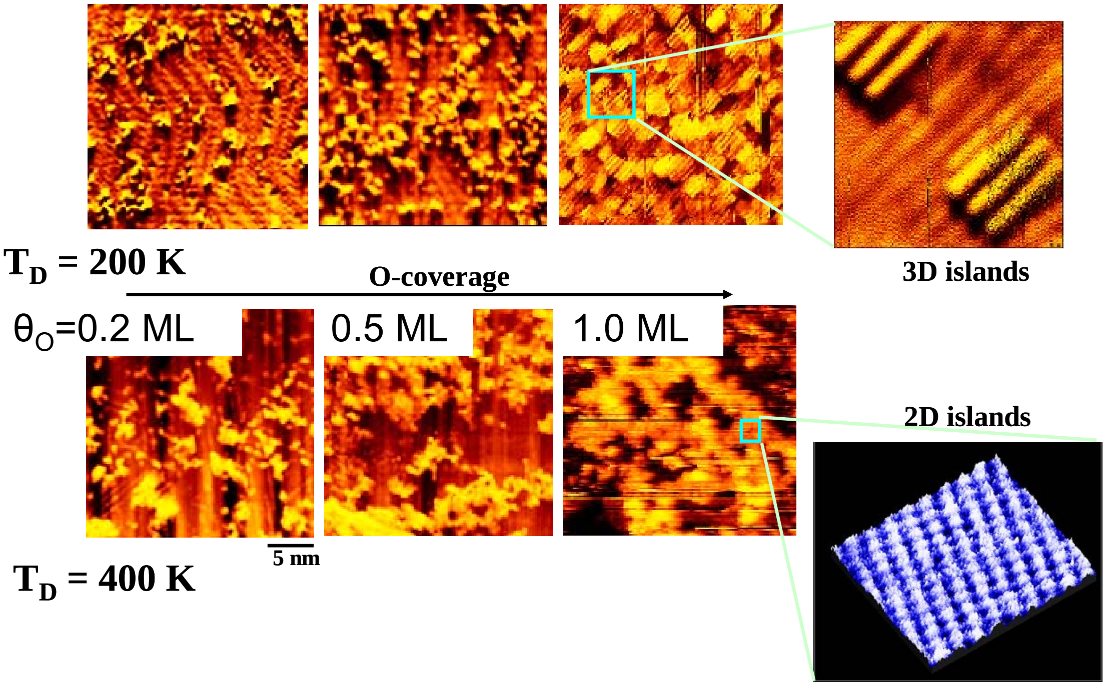

Figure 1. STM images after oxidation of Au(111) using ozone at 200 K (top) and 400 K (bottom) for three different oxygen coverages. A metastable, disordered phase forms at 200 K for coverages up to 0.5 ML, which reverts to the more ordered phase formed at 400 K upon annealing. As shown in the insets, the oxidized Au is atomically ordered at 400 K (all coverages) and at high coverage for 200 K.

conditions used for oxidation (Figure1). The temperature, the rate of oxidation, and the oxygen coverage all affect the local binding and surface structure. A reactive metastable oxygen phase is formed when Au(111) is oxidized at low temperature (≤300 K) and using high oxidation rates for oxygen coverages ≤0.5 ML. The activity and selectivity for key oxidation reactions—propene, styrene, and CO—depend on the local bonding and long-range order of oxygen on the surface.

We have observed changes in the periodicity of the structure and the roughening of Au(111) by the formation of small islands (or clusters) accompanying oxidation of the surface (Figure 1). At low oxygen coverage created using ozone decomposition at low temperature (~200 K) a low density of small clusters appear on the surface, and there is a clear decrease in the density of the "elbow" sites that create the herringbone structure. At higher oxygen coverage larger clusters ("islands") appear. The islands consist of gold-oxygen complexes. Furthermore, we have observed that the islands formed at 200 K remain following the removal of the adsorbed oxygen by reaction with CO, indicating that they also include gold in their structure, since gold is not mobile at this temperature. Importantly, we find that the ***disordered, metastable Au-O phase created at low temperature is most reactive and induces reactions with the highest selectivity.***

Our work on Au(111) clearly provides a means of studying the reactivity of adsorbed oxygen atoms for oxidation reactions. The other important issue regarding the activity of the Au nanocatalysts is the activation of O_2—the preferred oxidant in catalytic reactions—which does not dissociate with high probability on Au(111). Recent research shows that whereas dioxygen is not readily dissociated on clean Au(111), dissociation *can* be accomplished if the surface is "seeded" with a low coverage of oxygen adatoms, provided by electron induced dissociation of condensed NO_2. Following the dosing of $^{18}O_2$ onto Au(111) pre-covered with ~ 0.1 ML ^{16}O, $^{16}O^{18}O$ was observed to desorb with heating, clearly signifying activation of $^{18}O_2$ by the pre-oxidized surface. The activation of O_2 under these conditions has been attributed to the presence of undercoordinated gold in the clusters formed by the deconstruction of the herringbone structure that accompanies oxygen adsorption. In fact, several theoretical studies have suggested that undercoordinated Au present in small clusters promote the dissociation of $O_{2.}$

Hydrocarbon oxidation:

We have extensively studied oxidation reactions on oxidized Au(111) and in all cases the disordered, metastable oxygen phase formed at low temperature is most reactive and most selective. We have investigated the oxidation of CO, styrene, propene, allyl alcohol, and acrolein, to date. Although clean Au adsorbs hydrocarbons reversibly, selective oxidation is promoted on oxygen-covered Au(111). Our results clearly establish that adsorbed *atomic* oxygen promotes olefin oxidation since there are no peroxo or other O_2-species present under the conditions of our experiments.

For example, in the oxidation of styrene, styrene epoxide, benzoic acid and benzeneacetic acid are formed on Au(111) covered with 0.2 ML of oxygen atoms. The estimated selectivity for styrene epoxide formation is ~53%. Total combustion to CO_2 accounts for ~20% of the styrene reaction, with the organic acids (benzoic and benzeneacetic) comprising the remainder.

Promotion by Chlorine:

Recently, we have shown that Cl increases the selectivity for olefin epoxidation over oxidized Au(111). In the case of styrene, for example, combustion is completely suppressed. We are still actively investigating this effect; however, preliminary results show that Cl disperses the Au-O islands so as to produce a disordered, mobile phase at room temperature. We attribute the increase in selectivity to a decrease in the probability for secondary oxidation reactions.

DOE Interest:

DOE has interest in developing new materials, especially at the nanoscale for efficient chemical processes and for energy conversion. Our work provides fundamental insights into activating and improving the selectivity of nanoscale Au-based materials that are of potential importance in efficient catalytic synthesis of oxygenates and other key chemical building blocks. Our work has provide the fundamental underpinnings for controlling the activity and selectivity for important reactions promoted by Au-based materials, with special emphasis on the use of transient, metastable states of oxygen and by using promoters, such as Cl. We are also applying the concepts developed in our model studies to *in situ* experiments at higher pressure and to more complex materials, such as nanoporous Au foams.

Future Plans:

In our future work, we plan to extend our studies of oxidation over Au to higher pressure environments and to more complex materials—nanoporous Au foams and supported Au nanoparticles. We also plan to further investigate methods for improving the selectivity and activity for these important reactions by using promoters and adjustment of reaction conditions to favor more reactive phases.

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Catalysis on the Nanoscale: Preparation, Characterization and Reactivity of Metal-Based Nanostructures

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Program Goals

The purpose of this project is to explore and manipulate the size, morphology and chemical environment of metal-containing nanoparticles with the goal of optimizing their reactivity with respect to elementary reactions that are of widespread interest in heterogeneous catalysis. The materials focus is on nano-scaled molecular catalysts incorporating the early transition metals, such as Mo carbides, sulfides and nitrides, which have promising catalytic properties and may offer significant advantages over more commonly used noble metals. The main thrusts of the research program involve (1) the development new methodologies for the preparation of well-defined nanoparticles or nanoarrays; (2) reactivity studies as a function of size, morphology and chemical environment; (3) the development and application of new theoretical methods for understanding and predicting the structure and reactivity of metal-containing nanoparticles. Current methods being explored for nanoparticle preparation include reactive deposition onto metal and metal oxide substrates and deposition of size-selected clusters. Materials characterization and reactivity studies make extensive use of NSLS beam line facilities for measurements of high-resolution core-level photoemission, near-edge x-ray adsorption spectroscopy and in situ x-ray diffraction (time-resolved) under reaction conditions. This project also emphasizes theory development for describing the structure and electronic properties of molecular nanomaterials and adapting quantal methodologies for exploring elementary surface reactions.

Recent Progress

1. Deposition and Reactivity of Early Transition Metal Carbides, Oxides and Sulfides

Deposition and Reactivity of MoC_x/Au(111)

We have developed a new approach for preparing nanoparticles of transition metal compounds (TMX) that involves the deposition of a metal vapor onto a reactive layer of a compound such as ethylene or water which act as the source of carbon or oxygen atoms. The "hot" metal atoms react on contact with the cold molecular film to form metal compounds that nucleate as small nanoclusters on a Au(111) surface. This approach, *reactive layer assisted deposition* (RLAD), has the advantages of being able to perform the deposition process at low substrate temperatures which strongly influences nucleation and growth, and results in TMX particles that have nearly bulk-like compositions.

The RLAD method was first demonstrated for the production of MoC_x nanoparticles deposited on a Au(111) surface. Molybdenum carbide is known in bulk form to be a very active catalyst for a wide range of heterogeneous reactions, including methane reforming, aromatization, dehydrogenation, hydrodesulfurization (HDS), and more recently, the WGS reaction. The MoC_x

nanoparticles were formed by Mo metal deposition onto on a reactive layer of ethylene, which was physisorbed on a Au(111) substrate at low temperatures (< 100 K). The resulting clusters have an average diameter of ~1.5 nm and aggregate in fcc troughs located on either side of the elbows of the $(22 \times \sqrt{3})$-Au(111) reconstructed surface. Core level XPS shows that the electronic environment of the Mo and C atoms in the nanoparticles is similar to that found in $Mo_2C(0001)$ single crystals and carburized Mo metal surfaces. Peak intensities in XPS and AES spectra were used to estimate a Mo/C atomic ratio of 1.2 ± 0.2 for nanoparticles annealed above 500 K.

A subsequent study investigated the reactivity of cyclohexene on Au(111)-supported molybdenum carbide nanoparticles using thermal programmed reaction (TPR) and Auger electron spectroscopy (AES). The selective dehydrogenation of cyclohexene is a prototypical dehydrogenation reaction catalyzed by the noble metals and has been previously studied on bulk C/Mo(110) surfaces. Auger measurements showed that high temperature annealing (≤ 700K) of the as-deposited particles resulted in some Au atoms diffusing onto the particles surfaces ("encapsulation"). The Au atoms on MoC_x particles could be removed by light sputtering and reactivity experiments were performed for both sputtered and annealed (encapsulated) surfaces. The selectivity for partial dehydrogenation to benzene was found to be very poor (0.06) for the sputtered surfaces, whereas the Au-encapsulated MoC_x nanoparticles exhibited a selectivity for benzene formation of >0.95, with no detectable decomposition to surface carbon. The high selectivity of the Au-encapsulated MoC_x surfaces is explained by Au-atoms blocking highly reactive sites on the MoC_x clusters that are otherwise responsible for decomposition of cyclohexene.

Deposition and Reactivity of metal oxides on Au(111): TiO_2 and CeO_2

Various reactive deposition techniques were explored for the preparation of CeO_x nanoparticles on a Au(111) substrate. The latter is of interest as an "inverse" model catalyst for nanostructured Au/CeO_2 materials that have been shown to be very promising as low temperature catalysts for the water gas shift (WGS) reaction. Initial STM and XPS data on cerium growth on the Au(111) surface by simple physical vapor deposition (PVD) demonstrated that the complex bulk phase diagram of Ce-Au system has an equally intricate surface analog. Two surface intermetallic compounds were observed after deposition and annealing of Ce on Au(111). The Ce/Au alloying at the surface prevents efficient conversion to the oxide by direct exposure to oxygen, however, we were able to prepare CeO_x by using NO_2 adsorption at elevated temperatures or by vapor-deposition of Ce in elevated oxygen pressure (10^{-7} torr). Elongated ceria nanoparticles are just one layer thick, several nanometers in long and anchored mostly to steps (Fig. 1). Atomically resolved images of the ceria island taken with positively and negatively tip bias show an oxygen terminated (111) surface of CeO_2

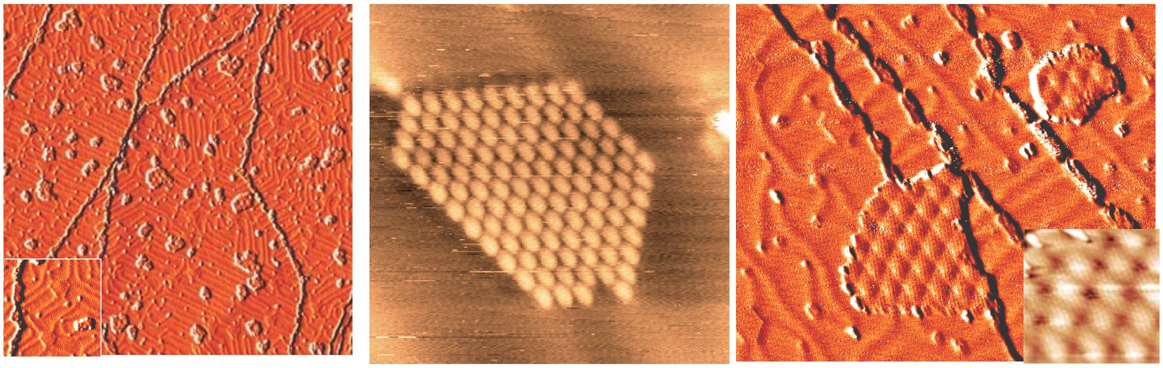

Fig. 1: STM images of Ce/Au(111) after annealing to 470K.Left panel: Image size 200 x 200 nm. Inset shows two hexagonal islands of $CeAu_3$ alloy. Central panel: Atomic resolution image of the hexagonal island. Image size Left panel: STM mage (60 nm x 50 nm) of large superlattice $CeAu_2$ alloy island. Inset size 12 x 12 nm.

with several oxygen vacancy defects (Fig. 1).

Reactivity experiments using photoemission confirm that the sub-stoichiometric ceria film on gold dissociates water molecules below room temperature while the fully oxidized stoichiometric ceria in inactive (Figure 5). This result is consistent with the postulated role of oxygen vacancies controlling the reactivity of oxide supported catalysts. Although their importance in the WGS reaction was suggested, a direct experimental evidence is not available. The water dissociation is the rate limiting step in the WGS reaction and our ability to observe reaction product under vacuum conditions and being able to link it with the structural characterization on atomic level is a great stimulus for our future work on the inverse model catalysts.

Size-selected Cluster Reactivity and Deposition

We have developed a new instrument for the preparation of small TMX clusters which can be mass-selected for size-dependent studies of reactivity in the gas-phase and deposited on surfaces. This approach is particularly effective for investigations of small nanoclusters, 1–2 nm (< 200 atoms), where rapid evolution of the atomic and electronic structure makes it essential to have precise control over cluster size. Unlike more conventional physical and chemical vapor deposition techniques, cluster deposition allows for independent control of cluster size, coverage and, in principle, can be used for any combination of cluster and substrate materials. Furthermore, mass selection makes it possible to determine the stoichiometry of TMX clusters, *e.g.*, the metal-to-carbon ratio in a carbide cluster, prior to deposition.

Initial efforts focussed on the reactivity of the $Ti_8C_{12}^+$ met-car cluster in the gas-phase (bare cluster) with a wide array of sulfur compounds (H_2S, CH_3SH, C_4H_4S, SO_2, SCO, CS_2). This study was motivated by extensive theoretical studies by Liu, Muckerman and Rodriguez on the structure and activity of titanium carbide in various forms, i.e., the Ti_8C_{12} met-car cluster, the $Ti_{14}C_{13}$ nanocrystallite and the TiC(0011) single crystal surface. Our experimental results for the interaction of the $Ti_8C_{12}^+$ met-car cluster with the triatomics, CS_2, OCS and SO_2 indicated an increase in activity for increasing oxygen to sulfur ratio (SO_2>SCO>CS_2), with the observed products corresponding to simple association, dissociation leading to adsorbed S-atoms, and break-down of the met-car cluster. Density functional theory was used to investigate cluster-adduct geometries, energy barriers and transition states leading to dissociation products. The calculated cluster-adduct stabilities and energy barriers are consistent with trends observed in the experimental product distributions and also point to unique bridge-bonding configurations on the met-car which have not been considered in previous experimental studies of the $Ti_8C_{12}^+$ cluster.

Currently, we are investigating the structure and reactivity of size-selected Mo_xS_y clusters (x/y = 3/7; 4/6; 5/7; 6/8; 7/10; 8/12) deposited on Au(111). Commercially, MoS_2 is widely used as a catalyst for hydrogenation (HYD), hydrodesulfurization (HDS), and hydrodenitrogenation (HDN), where it is dispersed as small nanoparticles (2-5 nm) on a high surface area support, typically γ-Al_2O_3. Initial studies of deposition on the Au(111) surface were motivated by recent work by Besenbacher and coworkers (Univ. Aarhus) on larger MoS_2 nano-platelets that were found to be only weakly interacting with the Au(111) substrate. Figure 2(a) shows the CO temperature programmed desorption (TPD) spectra for the Mo_4S_6 and Mo_6S_8 clusters deposited on Au(111) at the same coverage (0.25ML) and with a saturated dose of CO. Differences in the CO peak desorption temperature shift reflect differences in CO binding energy, and the larger CO yield for the Mo_6S_8 clusters is consistent with a larger number of exposed Mo-atom binding sites. For the Mo_4S_6/Au(111) system, we have also been successful in performing DFT calculations, including optimized cluster geometry, and adsorbate binding (see Figure 2(b)). Calculations of CO adsorption show that there are two distinct binding sites: the Mo top site, which bonds CO very strongly and the equatorial Mo site(s) where the adsorption energy of CO is 0.5eV weaker. The Mo_4S_6/Au(111) system represents one of the few examples where it has been possible to perform *both experimental and theoretical studies* on a model catalyst where the structure of the catalyst particle and substrate are precisely defined. Similar experimental studies are underway for the Mo_3S_7, Mo_5S_7, Mo_7S_{10} and Mo_8S_{12} clusters.

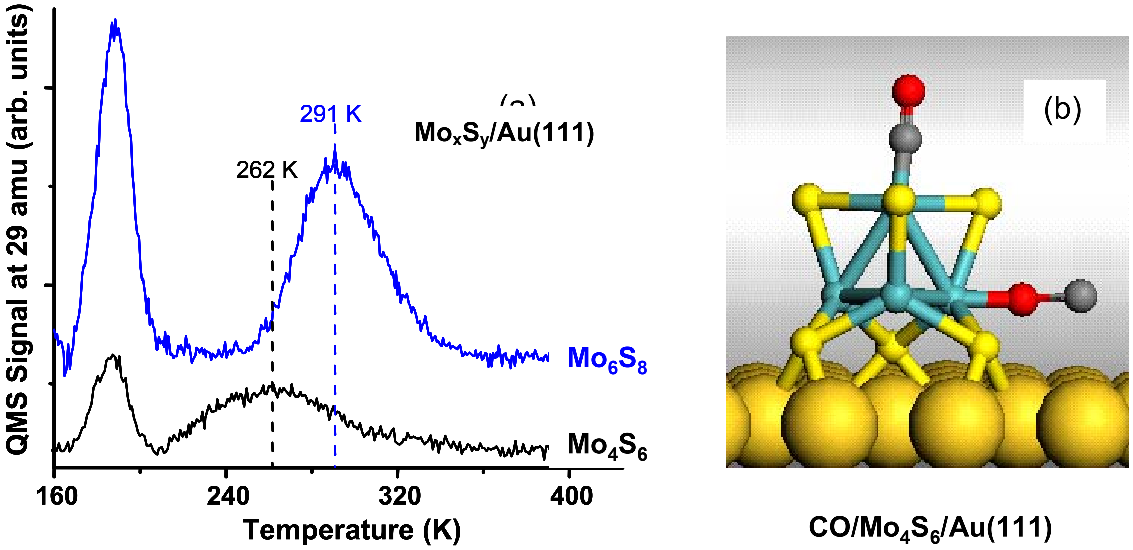

Fig. 2: (a) Thermal desorption spectra of CO from the Mo_4S_6 and Mo_6S_8 clusters deposited on Au(111) at a cluster coverage of 0.2ML. (b) DFT calculated structure of two CO molecules binding to the Mo_4S_6 cluster deposited on an ideal Au(111) surface. Note that CO binding at the atop Mo site is more strongly bound than at the equatorial Mo site(s).

2. Nanostructured catalysts for the WGS reaction: gold-ceria, copper-ceria

Chemical properties of free gold nanoparticles

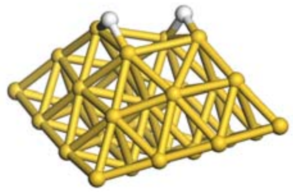

Fig. 3: Calculated structure for H_2 on Au_{29}.

Theoretical modeling is an excellent route for examining the intrinsic chemical reactivity of metal or oxide nanoparticles before deposition on a substrate. Several theoretical studies have addressed the issue of the intrinsic reactivity of unsupported or free Au clusters. Recently, we examined the interaction of H_2 with Au_{14} or Au_{29} particles and extended gold surfaces using DFT. Au_{29} nanoparticles with pyramidal shape have been seen in images of STM for model Au/CeO_2(111) catalysts. These systems exhibit interesting chemical properties. For example, the H_2 molecule did not adsorb on Au(111) or Au(100). In contrast, spontaneous dissociation occurred on Au_{29} accompanied by a large distortion of the nanoparticle structure (see Figure 3). Several factors contribute to the ability of a Au particle to interact with hydrogen: low-coordinated Au atoms, fluxionality and ensemble effects. All of these must be taken into consideration when dealing with adsorption reactions on metal particles and comparing to experimental data.

Experimental studies of the water-gas-shift reaction on gold-ceria and copper-ceria nanocatalysts

Our previous *in-situ* measurements of time-resolved XRD and XAFS indicate that the active phase in copper-ceria and gold-ceria catalysts contains pure copper or gold and partially reduced ceria. On the basis of these results, we decided to measure the reaction rates for the water-gas shift on model catalysts which contained Au and Cu. Figure 4 displays data obtained for the reaction on X/ CeO_2(111), X/ZnO($000\bar{1}$), Au(111) and Cu(100) with X= Au or Cu. The metal/oxide surfaces were generated by a simple vapor deposition of Cu or Au. $CeO_2(111)$ and $ZnO(000\bar{1})$ are oxygen terminated surfaces. Both of them did not display any catalytic activity under the reaction conditions examined in this study (P_{CO}= 20 Torr, P_{H2O}= 10 Torr, T= 300-375°C). A comparison of the catalytic activity indicates that Au/CeO_2 and Cu/CeO_2 are the best catalyst. At the present time, it is not known why these systems are so active. The shape of the curves in the right-side panel of Figure 4 points to a maximum reaction rate for a Cu coverage near 0.6 monolayers. The drop in reactivity with increasing Cu coverage is probably due to an increase in the particle size (> 2 nm) of the admetal. These results clearly show the importance of particle size for the WGS reaction.

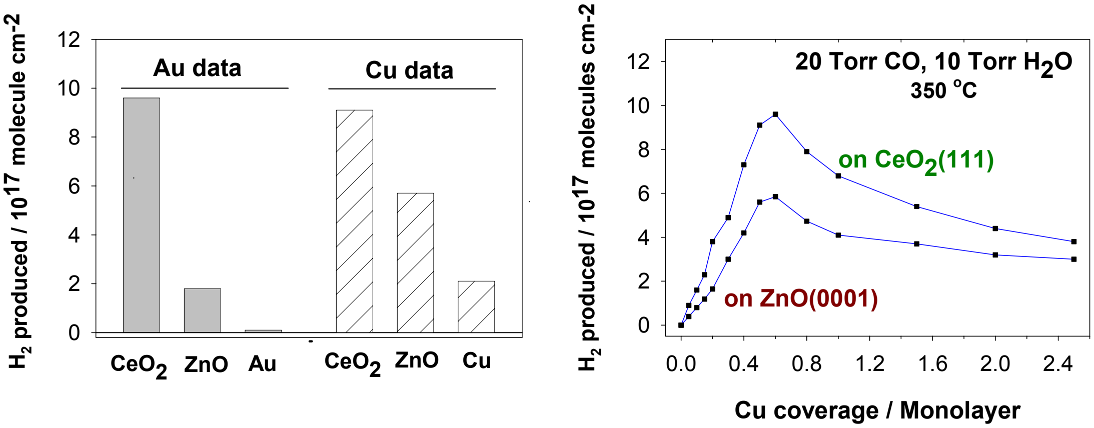

Fig. 4: Left panel: H_2 produced during the WGS on Au(111) and 0.5 monolayers of Au deposited on $CeO_2(111)$ or $ZnO(000\bar{1})$, shaded bars. The hatched bars show the corresponding results for Cu(100) and 0.5 monolayers of Cu on $CeO_2(111)$ or $ZnO(000\bar{1})$. Right panel: Effect of Cu coverage on the WGS activity of $Cu/CeO_2(111)$ and $Cu/ZnO(000\bar{1})$. Data collected in a batch reactor, 20 Torr of CO and 10 Torr of H_2O, at 350°C for 5 min.

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Early Transition Metal Oxides as Catalysts: Crossing Scales from Clusters to Single Crystals to Functioning Materials

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Goal

We are employing an integrated experimental/theoretical approach to advance our current ability to understand, design, and control the catalytic and surface chemistry of transition metal oxides, specifically for redox and acid-base chemistries. The approach combines novel solid-state inorganic synthesis, surface science, experimental and theoretical/computational chemical physics, and mechanistic organic chemistry to address this complex and important challenge.

DOE Interest

The proportion of chemical industry processes using catalysts exceeds 80%. Current commercial heterogeneous catalysts are structurally and chemically complex and data gathered from them can seldom be interpreted with atomic-level precision. We seek to reduce the complexity of TMO catalysts to levels addressable and controllable at the atomic level, while maintaining intimate linkages with practical catalysis and catalytic materials. The focus of the proposed work is to gain a fundamental understanding of chemical transformations in order to design and construct new catalysts with more precise control of specific chemical reactions. This will enable us to help DOE reach its goals of doing fundamental science to address the energy needs of the country by (1) improving energy conservation by new means of energy conversion and storage; (2) enable direct chemical conversions previously economically unfeasible and produce new routes to novel materials while at the same time minimizing by-products and environmental impact; and (3) protecting the environment

Recent Progress

Selected highlights from the results obtained in the last year are presented in this section.

Catalyst synthesis, characterization, and kinetics studies

Dispersion of catalyst particles on high surface area supports and precise control of cluster or particle sizes are critical for developing efficient catalysts and for understanding the fundamental properties of the catalysts. To date, catalysts particles are dispersed on the support using controlled infiltration or controlled surface hydrolysis. Although these methods are widely investigated, they can not be used to precisely control the particle sizes. We recently developed new approaches to achieve such control and these will be described briefly along with catalyst characterization and kinetics studies.

Dispersed vanadium oxides: Solution based atomic layer deposition (ALD) was developed to disperse transition metal oxides with controlled atomic connectivity on ordered high surface area mesoporous silica. Using a sequential ALD process, we are able to first generate a monolayer of TiO_2 which in turn works as an anchoring phase, important especially for dispersing vanadia species. TEM and EDX reveal that the titanium oxide was readily incorporated into the channels of the support with little or no condensation of bulk titania. However, a different behavior is observed after grafting of vanadia on bare MCM-41. In this case, deposits of vanadium oxide were clearly observed throughout the mesoporous silica structure. Moreover, it is easy to observe crystalline V_2O_5 particles of submicron scale segregated from the mesoporous silica particles. However, for a VO_x/TiO_2/MCM41 sample, no oxide particles on the external surface of the MCM-41 can be observed, indicating that both the supported vanadia and titania phases are very well dispersed into the internal channels of the support. In addition to TEM results, the XRD together with ^{51}V-NMR, Raman, FTIR and DRS-UV-Vis results also showed that the vanadia species are extremely well dispersed onto the surface of the mesoporous support; the dispersion being stable upon thermal treatments up to 400 °C.

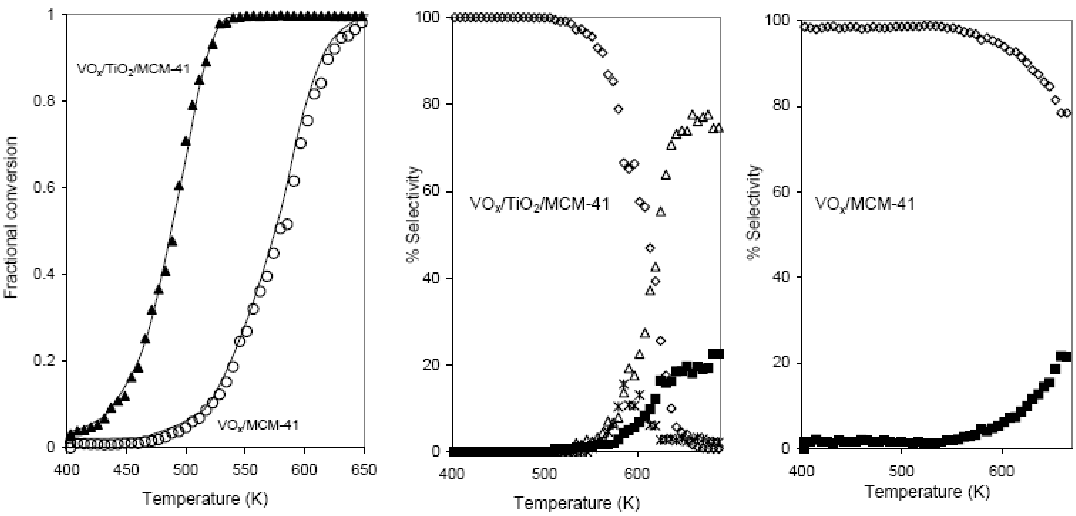


Figure 1. Left panel: conversions obtained during ethanol partial oxidation as a function of reaction temperature for (▲) VO_x/TiO_2/MCM-41 and (○) VO_x/MCM-41. Center (for VO_x/TiO_2/MCM-41) and right (for VO_x/MCM-41) panels: influence of the catalyst support on the selectivity to acetaldehyde. Symbols: (◇) acetaldehyde, (■) ethylene, (△) CO_x, and (~~x~~) acetic acid.

Studies of the catalytic activity of these materials were studied using the partial oxidation of ethanol as a model reaction. The variation of activity with reaction temperature for the catalysts used in the present study is shown in Figure 1. For both samples, the ethanol conversion increases at higher temperatures. However, the activity of the VO_x/TiO_2/MCM-41 sample was markedly superior to that of the VO_x/MCM-41 catalyst. This behavior cannot be simply rationalized in terms of surface area, since the specific surface area and vanadium loading was very similar for both samples. The higher partial oxidation activity observed for the VO_x/TiO_2/MCM-41 catalyst may be linked to the presence of vanadia species interacting with titania domains. Figure 2 also shows the distribution of the different products obtained on both catalysts. Total selectivity to acetaldehyde was observed at low reaction temperatures, while formation of other products such as ethylene, CO_x and acetic acid was also observed. However, for the case of the VO_x/TiO_2/MCM-41 catalyst, the formation of ethylene occurs only at very high conversions (~100%) while for the VO_x/MCM-41 samples, ethylene production was observed at all conversion levels. The formation of ethylene at low conversions on the VO_x/MCM-41 catalyst indicates the presence of acidic sites in this catalyst, which are very active for dehydration. We note another interesting observation from an analysis of the product distributions. Notably, acetic acid and CO_x were observed only in the case of the VO_x/TiO_2/MCM-41 catalyst, while for the case of the VO_x/MCM-41 catalyst acetic acid was not observed. This behavior of VO_x/TiO_2 systems has been previously reported and linked to a serial reaction scheme where CO_x and acetic acid arise from serial oxidation of ethanol, acetaldehyde acting as intermediate, in which very active redox centers, present on the VO_x-TiO_2 phase, play an important role. These redox centers are not present on the VO_x/MCM-41 catalyst and, as mentioned above, acetic acid and CO_x are not observed in the range of temperatures studied. This difference in the formation of acetic acid and CO_x constitutes an additional proof of the close interaction of TiO_2 and VO_x in the VO_x/TiO_2/MCM-41 catalyst.

Calculated NMR Chemical Shifts: We have predicted the ^{51}V NMR spectra of vanadium oxide clusters and vanadium-oxygen stretching frequencies in order to explain experimental measurements. ^{51}V NMR chemical shifts were calculated at the GIAO level [1] with the B3LYP functional the Wachters (for V) [2] and Ahlrichs [3] VTZ plus polarization (for all the other atoms) basis sets. Removal of protons from $V(O)(OH)_3$ to VO_4^{3-} leads to deshielding of the V nucleus. Replacing OH groups with $Si(OH)_3$ leads to the V nucleus becoming more shielded as the number of $Si(OH)_3$ groups added is increased. Our results can be used to explain the spectra observed experimentally for VO_x on silica [4]. The observed peaks were assigned as follows: the -830 ppm peak to $V(O)(OH)[OSi(OH)_3]_2$ and the -530 ppm peak to $V(O)(OH)_2OSi(OH)_3$. We calculated the shifts and predict peaks at -832 ppm and, -805 respectively. All of our calculations on molecules having just one V=O bond show peaks ranging from -714 to -881 ppm, depending on the nature of the other groups attached to the metal: OH's or $OSi(OH)_3$'s. Only species with the O_2V-O- moiety: VO_2OH (-439ppm), $VO_2OSi(OH)_3$ (-530ppm) and $O_2VOVO[OSi(OH)_3]_2$ (-480), show peaks around -500 ppm. Note that for $O_2VOVO[OSi(OH)_3]_2$ the shift for the V=O group is predicted to be -842 ppm. Experiments for ^{51}V solid state NMR (17.6T) of V cations exchanged onto ZSM-5 showed peaks at -839 ppm, which was assigned to the dimer $V_2O_4Si(OH)_2[OAl(OH)_3]_2$ and at -548 ppm, assigned to the monomer $VO_2Al^{+3}(OSi^{+4})_2$. Our calculated values are -641, -729 ppm for the dimer and -600 for the monomer structure $VO_2Al(OSiH_3)_2(OSiH_3)_2$.

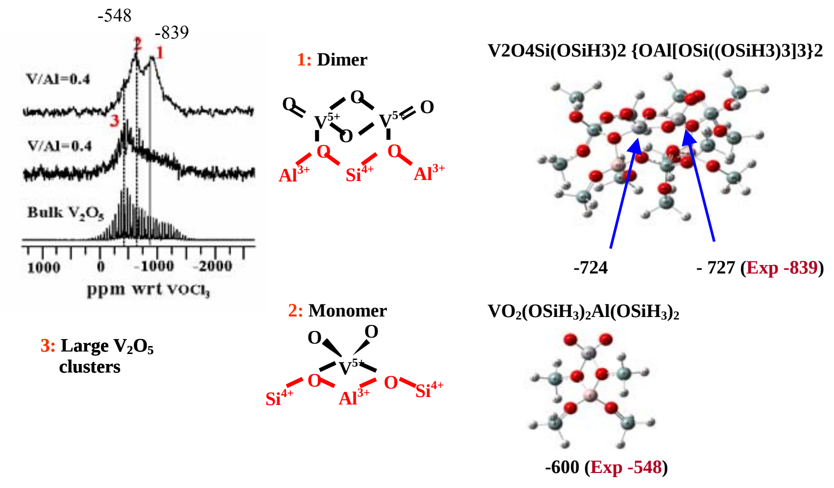


Figure 2. ^{51}V MAS NMR spectra and predictions for the tentative peak assignments.

Characterization of supported HPA species and in-situ characterization: Polyoxometalate (POM)-based clusters exhibit well-defined size and atomic connectivity, diverse chemical composition, and relatively high stability. Thus, they represent ideal structures to examine rigorously the effects of chemical composition, atomic connectivity, and cluster size on acid and redox properties, as well as the catalytic consequences of these properties in catalysis by transition metal oxides. These materials crystallize into secondary structures (structure II in Figure 3) with intracrystalline sites accessible to different extents by reactants, and with transition states of varying size and polarity. We have addressed these challenges by developing site titration protocols that allow measurements of the number of acid sites accessible during catalysis and by exploring synthetic approaches that isolate intact POM Keggin clusters on inert mesoporous supports with minimal fragmentation of Keggin clusters into smaller lacunary structures. A few very brief highlights from this work will be provided next.

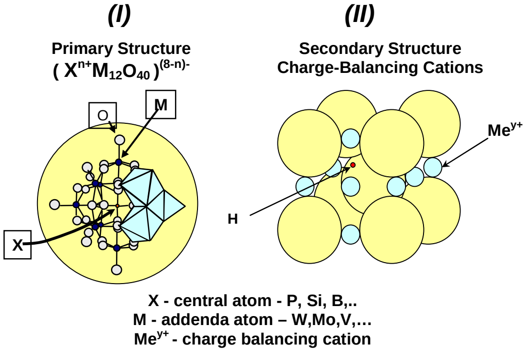


Fig. 3. Primary and secondary structures in polyoxometalates.

Dispersion of heteropolyacid. Multiple approaches have been attempted to graft tungstophosphoric acid on MCM-41 silica. The first approach, described here, uses functionalized amino groups to anchor the tungstophosphoric acid. As shown in Figure 4, the size of tungstophosphoric acid clusters are about 1nm which is close to that of primary Keggin anions, indicating that tungstophosphoric acid is highly dispersed on MCM-41 using this grafting technique. The intact of Keggin structure is confirmed using ^{31}P-NMR spectroscopy. Currently, catalytic testing of these various materials is being carried out.

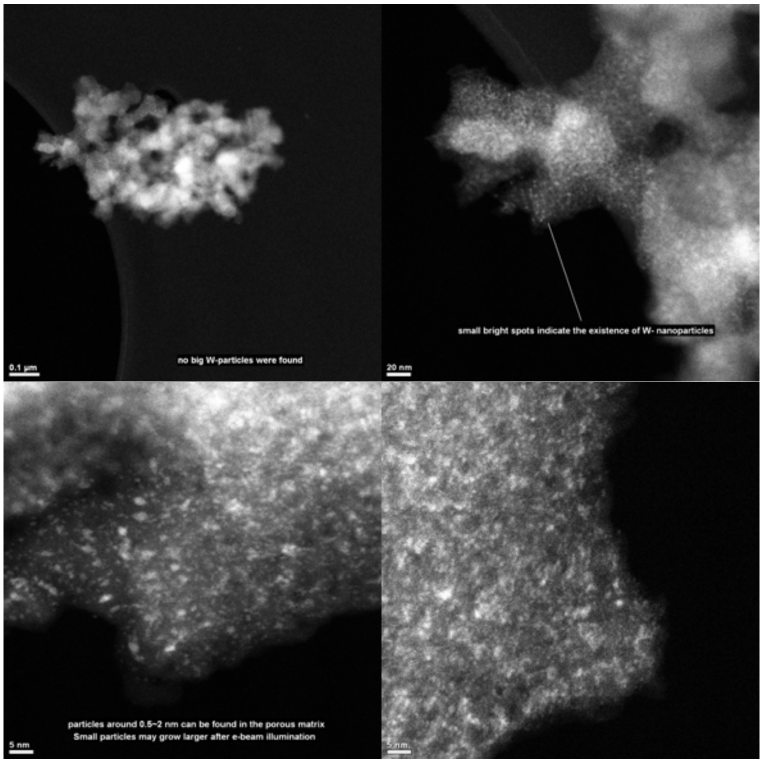


Figure 4. Grafting of tungstophosphoric acid on MCM-41 using amino functionalized groups

Acid Catalysis: Effects of Composition and Secondary Structure on the Catalytic Reactivity of Protons in POM Keggin Clusters [5,6]. The effects of central atom X (P, Si, Al, B and Co), addenda atom M (W and Mo), charge-balancing cations Me (Ag^+, Cs^+, Cu^{2+}, K^+, and Na^+) and secondary structure on the reactivity of protons in $Me^{m+}{}_{y}H_{8-n-my}X^{n+}M_{12}O_{40}$ Keggin type polyoxometalate (POM) clusters supported on SiO_2 was determined by using the dehydration of 2-butanol as a probe reaction. POM clusters with P and Si central atoms were commercially available, while those with Al, B and Co central atoms were synthesized and characterized using available protocols [7-10]. The cation exchange has been carried out using a two step impregnation procedure [11,12]. These POM clusters were supported on silica by incipient wetness impregnation methods using different solvents (H_2O, EtOH, EtOH/H_2O, DMSO) to give supported samples with surface densities ranging from 0.007-0.5 POM nm^{-2} (1-70% of the theoretical monolayer). The integrity of the P and Al containing supported POM clusters was confirmed by solid state nuclear magnetic resonance for the respective nuclei. The dispersion of the supported POM clusters depends on the surface density and was measured using 2,6-di-*tert*-butylpyridine as the titrant in the absence and presence of 2-butanol. Without 2-butanol, only external protons can be titrated by the hindered pyridine base. The presence of 2-butanol, which swells the secondary structure, makes all protons accessible to hindered pyridine. Thus, the ratio of the titrant uptakes without and with 2-butanol corresponds to the fraction of the protons accessible at external surfaces of secondary structure, which we define here as the (fractional) dispersion. All protons are accessible at external surfaces at low surface densities (0.007 and 0.04 KU nm^{-2}), consistent with the predominant presence of isolated clusters and two-dimensional secondary structures. The POM fractional dispersion decreased monotonically with increasing surface density (Figure 5). $H_3PW_{12}O_{40}/SiO_2$ with 0.5 POM nm^{-2} gave a fractional dispersion of 0.3 (Figure 5).

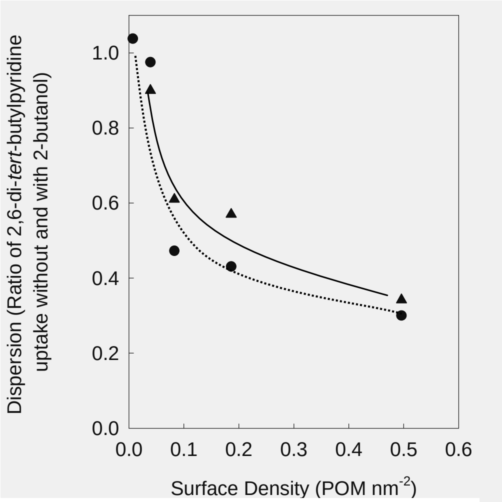
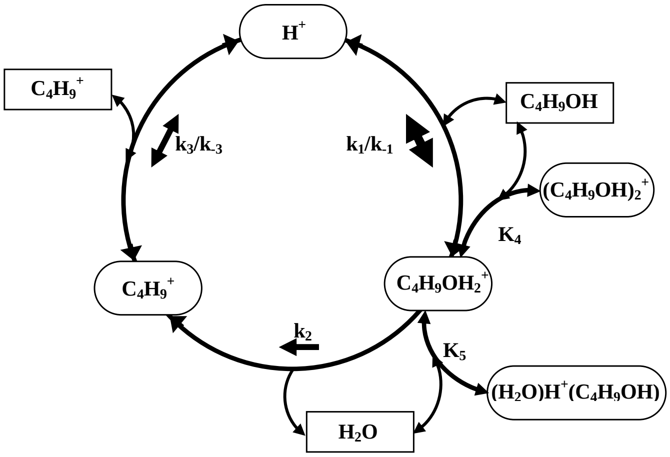


Figure 5. Ratio of the 2,6-di-*tert*-butylpyridine uptake ratio with and without 2-butanol (≈ fractional dispersion) of silica supported POM with P and Si central atoms as a function of POM surface density. ● POM with P central atom, ▲POM with Si central

Scheme. Proposed elementary steps for 2-butanol dehydration reaction on Keggin clusters.

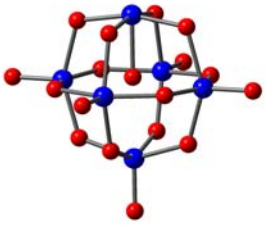


The dehydration of 2-butanol is catalyzed by Brønsted and Lewis acids. The complete inhibition by 2,6-di-tert-butylpyridine, a molecule which titrates only Brønsted acid sites because the two tert-butyl groups do not allow coordination of the N lone pair to Lewis acid sites, shows that only Brønsted acid sites are relevant for the dehydration reaction on Keggin type POM clusters. 2-Butanol dehydration reaction occurs without detectable deactivation or structural changes on POM structures at low temperatures (340-400 K). The reaction dynamics (see scheme above) obey a rate equation consistent with the reversible adsorption of 2-butanol on Brønsted acid sites (step 1), the irreversible decomposition of adsorbed 2-butanol (step 2), the reversible butene desorption (step 3), and the "deactivation" of adsorbed species by the formation of 2-butanol/water dimers (step 5) (Scheme). At low conversions, this rate equation contains only the rate constant for the kinetically-relevant decomposition step (k_2) and an equilibrium parameter that reflects the stability of 2-butanol dimers (K_4). The measurement of these kinetic and thermodynamic constants, instead of just a reaction rate at arbitrarily chosen reaction conditions, and the ability to count the number of protons accessible during reaction, which differs from those accessible in the absence of 2-butanol, allows us for the first time to assess the intrinsic reactivity and binding properties of POM clusters and the catalytic consequences of their composition and dispersion. The constant for the decomposition step (k_2), normalized by the number of accessible protons represents an intrinsic reactivity, while the equilibrium parameter (K_4) for 2-butanol dimers gives a thermodynamic indication of binding properties and, indirectly, of acid strength.

Geometric and electronic structure of oxide clusters

To provide critically needed information on the geometric and electronic structure, and stability of oxide clusters of varying size, in this program we have uniquely incorporated state-of-the-art experimental and computational studies of the native oxide clusters themselves. In the following, we provide just a couple of brief recent highlights from this work.

Calculated electronic and geometric structure of oxide clusters: We are using advanced computational chemistry techniques to advance our current ability to understand, design, and control the catalytic and surface chemistry of transition metal oxides, specifically for redox and acid-base chemistries. This work is in conjunction with the experimental efforts in the center as well as with the University of Southern California and the University of California-Davis.



We have been using electronic structure theory at the density functional theory (DFT) and molecular orbital (MO) theory (MP2 or coupled cluster (CCSD(T)) levels to predict the properties (structure, energetics, reactivity, spectroscopy) of transition metal oxide (TMO) clusters of Group VIB metals. We have predicted the properties of the TMO clusters $(MO_3)_n$, for *n* = 1 to 6 [13]. We have studied two types of structures for *n* = 3 to 6, the ring and the chain. The ring structures are more stable than the chains which have fewer μ-oxo bonds. The differences are metal dependent with the chain structures being much less stable for M = Cr and unlikely to form. For *n* = 6, a 3-D nanocluster was studied based on the polymetalloxalates (POMs) derived from the Lindqvist $M_6O_{19}^{2-}$ anion. For M = Cr, the 3-D structure is more than 100 kcal/mol less stable than the ring. For M = Mo, the 3-D structure is only 15 kcal/mol less stable than the ring structure and for M = W, the 3-D structure is 32 kcal/mol more stable than the ring structure. A structure with one of the μ-oxo groups inverted to the center was calculated for M = Mo and W as a cluster model for the surface. The inverted cage structures are 43 and 37 kcal/mol higher in energy than the normal cage structures for Mo and W, respectively.

Normalized and differential clustering energies were obtained and were shown to vary with respect to the cluster size. The results for the ring structures for M = Cr show a general increase in the normalized binding energy that levels out between *n* = 5 and 6. The cage structure for Cr for *n* = 6 clearly has a lower normalized binding energy. For the Mo and W clusters, the convergence of the normalized binding energy as a function of n for the ring structure is slower than that for Cr. The normalized binding energy for the ring clusters increases from Cr to Mo to W. For the ring structures of Cr, Mo, and W, the differential binding energy decreases as n increases. The differential binding energy increases with increasing atomic number from Cr to Mo to W. The differential binding energies are clearly not converging for Cr but do appear to be converging for Mo and W.

Proton affinities (PAs) were calculated which show that these compounds are weak Brönsted bases with most basicities falling in the range of 160 to 190 kcal/mol, between the basicities of H_2O and NH_3 [14]. The reason that these PAs are not as high as might be expected is that addition of the proton decreases the μ-oxo character in the O to which it binds, thus destabilizing this interaction. We have previously shown that the fluoride affinity (FA) is a good measure of the Lewis acidity of a site for many inorganic species [15]. The calculated FAs of the MO_3 species, are very high, 124, 137 and 147 kcal/mol, for M = Cr, Mo, and W respectively at the B3LYP level. These FAs are some of the highest ever calculated for small molecular systems and are higher than the FAs of very strong Lewis acids like SbF_5, showing the very strong Lewis acid character of an MO_3 site. The FAs decrease somewhat for the dimer but as the cluster size increases, they increase and approach the monomer values. The FAs at the center of the n = 6 cages for Mo and W are 134 and 145 kcal/mol respectively, only slightly lower than those for MoO_3 and WO_3, and show the strong Lewis acid character of the vacancy at the center of the cage, consistent with the stability of the POMs. This result suggests that one can consider the POM clusters to be nanoclusters of MO_3 with an anionic Lewis base at the center of the cluster. The strong Lewis acid nature of these TMO clusters is expected to play an important role in the catalytic functionalities of the corresponding TMO-based catalysts.

The placement of an O^{2-} at the center of a $(MO_3)_6$ cluster leads to formation of the species $M_6O_{19}^{2-}$ (see below for a discussion of the PES spectra). These molecules can bind protons to form the neutral species $M_6O_{19}H_2$ and the anion $M_6O_{19}H^-$, with the protons located on the bridging oxygens. Removal of a proton from these molecules corresponds to the acidity of these species. We have previously shown that one can calculate quite reliable acidities with the approach that we have used [16]. We predict that the acidities of $M_6O_{18}H_2$ to be quite low, 281, 273, and 267 kcal/mol at the B3LYP level for Cr, Mo, and W, respectively, making them very strong gas phase acids. Neurock and co-workers have predicted a similar low acidity of 256 kcal/mol for $PW_{12}O_{40}H_3$ [17]. For comparison, the acidity of H_2SO_4 is calculated to be 310.9 kcal/mol. It is useful to note that these high acidities almost overlap the basicities of the most basic molecules such as the imidazoles [18], suggesting that very basic neutral molecules could readily abstract a proton from these acids. The second acidities for these species (loss of a proton from $M_6O_{18}H^-$) are low for formation of a dianion, 366, 355, and 347 kcal/mol for Cr, Mo and W, respectively. These can be compared, for example, to the acidities of H_2O and H_2CO_3 which are 383.7 and 331.3 kcal/mol respectively.

The lowest energy electronic transitions for the $(WO_3)_n$ clusters have been calculated at the time-dependent DFT (TD-DFT) level with a correct form of the asymptotic exchange-correlation potential [19]. The transitions are at 1.97 eV for WO_3, 2.96 eV for W_2O_6, 4.29 eV for W_3O_9, and peak at W_4O_{12}. The transition in the 3-D W_6O_{12} cage is 3.83 eV and in the inverted cage it drops to 2.91 eV. The triplet transitions are 0.1 to 0.4 eV below the singlets. An important result is that there are often a number of orbitals close in energy to the HOMO as well as for the LUMO. For example the highest occupied orbital energies in W_3O_9 are -9.74 eV (a_2") and -9.74 eV (e") and the lowest unoccupied orbital energies are -4.04 eV (e') and -3.82 eV (a_1'). The results also show that the lowest energy transitions are dominated by transitions from the μ-oxo π bonds to virtual orbitals on the W atoms.

Experimental electronic and geometric structure of oxide clusters: A laser vaporization cluster source is used to produce metal oxide clusters with different sizes, structures, and compositions. Well-defined inorganic polyoxometalate clusters in solution are transported in the gas phase using electrospray. Two state-of-the-art photoelectron spectroscopy apparatuses are used to interrogate the oxide clusters and polyoxometalate anions in the gas phase to obtain spectroscopic and electronic structure information.

Electronic and structural properties of a series of tri-tungsten oxide clusters, $W_3O_n^-$ and W_3O_n (n = 7-10), were investigated using photoelectron spectroscopy and density functional theory (DFT) calculations. Both W 5d and O 2p detachment features were observed for n = 7-9, whereas only detachment features from O 2p type orbitals were observed for $W_3O_{10}^-$ at extremely high electron binding energies (>7 eV). A large HOMO-LUMO gap (~3.4 eV) was observed for the stoichiometric W_3O_9 cluster, which already reaches the bulk value, suggesting that W_3O_9 can be viewed as the smallest molecular model for bulk WO_3. Extensive DFT calculations were carried out to locate the most stable structures for both the anion and neutral clusters; time-dependent DFT method is used to predict the vertical detachment energies and to compare with the experimental data. It was shown that W_3O_9 possesses a D_{3h} structure, in which each W atom is tetrahedrally coordinated with two bridging O atoms and two terminal O atoms. W_3O_8 and W_3O_7 can be viewed as removing one and two terminal O atoms from W_3O_9, respectively, whereas W_3O_{10} can be viewed as replacing a terminal O in W_3O_9 by a peroxo O_2 unit. We showed that W_3O_8 contains a localized W^{4+} site (Figure 6), which can readily react with O_2 to form the W_3O_{10} clusters with a calculated O_2 adsorption energy of -78 kcal/mol. It is suggested that the W_3O_8 cluster can be viewed as a molecular model for O-deficient site in tungsten oxides.

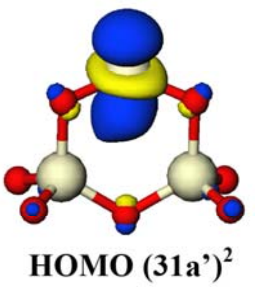


Fig. 6. The localized HOMO in W_3O_8.

TiO_2 is a wide-band gap semiconductor and it is an important material for photocatalysis. In a recent study, the electronic structure and energy gap evolution of $(TiO_2)_n$ clusters as a function of cluster size is probed using anion photoelectron spectroscopy. PES spectra of $(TiO_2)_n^-$ clusters for n = 1–10 have been obtained at 193 (6.424 eV) and 157 nm (7.866 eV). The high photon energy at 157 nm allows the band gap of the TiO_2 clusters to be clearly revealed up to n = 10 for the first time. The band gap is observed to be strongly size-dependent for $n < 7$, but it rapidly approaches the bulk limit at n = 7 and remains constant up to n = 10. All PES features are observed to be very broad, suggesting large geometry changes between the anions and the neutral clusters due to the localized nature of the extra electron in the anions. The measured electron affinities and the energy gaps are compared with available theoretical calculations. The extra electron in the $(TiO_2)_n^-$ clusters for $n > 1$ appears to be localized in a tri-coordinated Ti atom, creating a single Ti^{3+} site and making these clusters ideal molecular models for mechanistic understanding of TiO_2 surface defects and photocatalytic properties.

Aromatic molecules are usually planar species formed by main group elements, whose bonding is primarily from the s or p orbitals. We found experimental and theoretical evidence for aromaticity from d-orbitals during our investigation of tungsten oxide clusters. W_3O_9 and Mo_3O_9 were both shown to possess a D_{3h} structure with a low-lying unoccupied molecular orbital formed from the metal d orbitals. Occupation of this orbital by one or two electrons gives rise to strong three-center one-electron and three-center two-electron metal-metal bonds, respectively, significantly reducing the M-M distances in $M_3O_9^-$ and $M_3O_9^{2-}$. The totally delocalized three-center bond (Figure 7) renders aromaticity for both $M_3O_9^-$ and $M_3O_9^{2-}$, further evidenced by a large calculated resonance energy. The $M_3O_9^-$ and $M_3O_9^{2-}$ species are highly stable and represent a new class of d-orbital aromatic molecules.

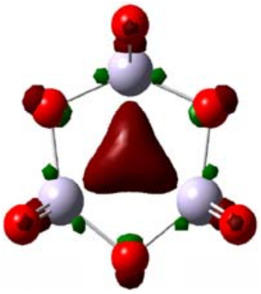


Fig. 7. The three-center bond in $W_3O_9^{2-}$.

Surface structure and chemistry of Model, Planar Supported Oxides

UHV studies of model TMO catalysts: Catalytic activity of high surface area, powdered transition metal oxides (TMO, *e.g.* vanadium, niobium, molybdenum, and tungsten) supported on Al_2O_3, SiO_2, ZrO_2 and TiO_2 have been extensively studied. In contrast, virtually no studies have been conducted for TMOs supported on well-ordered, single-crystalline oxides. This is largely due to a number of experimental difficulties related to the preparation of well-ordered oxide surfaces and to the charging problems associated with electron based probes on insulators. Furthermore, characterization at this level of detail demands control of each component (support oxides, catalytically active transition metal oxide sites, reactants, intermediates, and products) of the catalytic system. Planar model catalysts allow not only more precise control of metal oxide dispersion but also minimize structural variations, thereby enhancing the power of ensemble-averaging measurements by providing well defined, uniform structures. We have initiated studies of the partial oxidation of alcohols on planar models, both single crystals and supported oxide clusters using a combined effort involving atomically resolved imaging, and ensemble averaged techniques.

As one example from our recent work, we have focused on the preparation of well defined WO_3 clusters on $TiO_2(110)$. A traditional method for cluster deposition involves metal evaporation. In the case of oxide clusters this can be accomplished by deposition in the oxidizing environment [20,21] or by post-oxidation of deposited metallic clusters [22]. This results in a distribution of oxide clusters with various sizes. We have employed a novel deposition method using direct sublimation of WO_3 to successfully prepare monodispersed $(WO_3)_3$ clusters [23]. Previous studies have shown that the primary gas phase species formed by WO_3 evaporation is a cyclic $(WO_3)_3$ trimer [24]. The structure of various gas phase WO_3 clusters (including $(WO_3)_3$) has been studied in great detail by L.-S. Wang's group as a part of this project [25]. The empty state, atomically resolved STM image of $(WO_3)_3$ clusters on $TiO_2(110)$ is shown in Figure 8(a). The clusters appear as bright features with an inner structure resembling dark triangles pointing into the Ti^{4+} rows. Results from theoretical calculations (Figure 8(b)) for gas phase cyclic $(WO_3)_3$ show that the vacant orbitals are primarily located on the tungsten atoms. As schematically shown in Figure 8(c) this can explain the appearance of clusters in the STM image. The trimeric nature of the cluster is further supported by comparison of the cluster areal density from the STM and from the total deposited mass from Quartz crystal microbalance measurements [23].

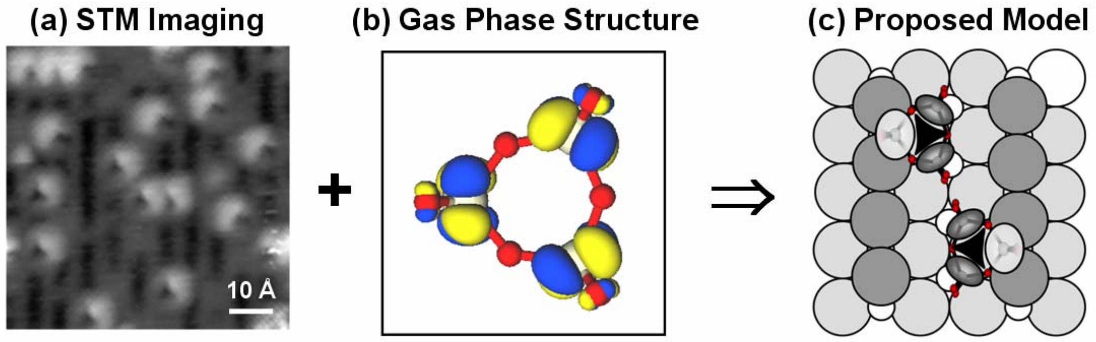


Fig. 8. (a) High-resolution STM image exhibiting strong trigonal intensity contrast within each $(WO_3)_3$ cluster. One of the corners aligns with a Ti^{4+} row and the opposite side is tilted with equal probability to the left or right away from this row. (b) The calculated gas phase $(WO_3)_3$ structure and primary location of f the empty low-lying out-of-plane molecular orbitals. (c) Schematic view of the $TiO_2(110)$ surface with two cyclic $(WO_3)_3$ clusters. The top cluster has the orientation identical with that in (b). Both clusters have the plane of the rings tilted with two tungsten atoms pointing into the Ti^{4+} row and the third tungsten tilted up and pointing towards the neighboring BBO row (one to the left and the other to the right). This tilt results in a different brightness above the three tungsten atoms of the ring, with the top one being significantly brighter than the other two.

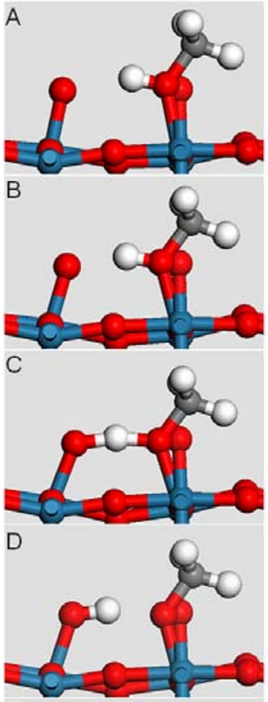
The monodispersed nature of the $(WO_3)_3/TiO_2(110)$ system allows for the investigation of cluster reactivity using ensemble averaged techniques. We have focused on adsorption/desorption measurements of CH_3OH and its potential oxidation products HCHO, CO_2, CO, H_2O. Our results show that methanol desorbs molecularly between 150 and 400 K without any appreciable dissociation. In contrast, the adsorption of HCHO leads to a polymerization reaction that is induced by the $(WO_3)_3$ clusters. The polymerization of monolayer HCHO on flat metal and metal oxide surfaces has been reported previously [26] but not for supported oxide clusters. The total amount of HCHO polymerized on $TiO_2(110)$ surfaces increases with increasing $(WO_3)_3$ coverage (data not shown). For all $(WO_3)_3$ coverages, the amount of polymerized HCHO saturates for HCHO coverages above ~ 30 monolayers (ML).

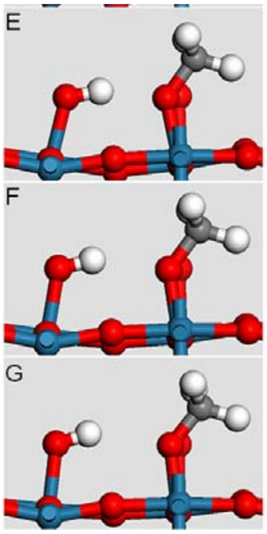
The polymerization reaction is observed only when multilayers of HCHO are present on the surface demonstrating that the polymerization occurs at temperatures that are lower than the HCHO multilayer desorption (~ 100 K). No reaction is observed on clean $TiO_2(110)$ surface.

Computations of the chemistry and physics of bulk oxides and their extended surfaces: To provide a basis for understanding the just-described chemical physics experiments, we are performing periodic density functional theory calculations of the geometric and electronic structure of bulk tungsten oxides, and their surface structure and chemistry. Similar studies of related oxides of interest to this program are also being performed. In particular, work this year has focused on the bulk and surface structures of WO_3 and ReO_3. In the course of computational studies on methanol dissociation we demonstrated that the conductive ReO_3 might be catalytically more active than the semiconductive WO_3. The calculations are using DFT-GGA theory, with structure optimization using periodic boundary conditions. These results are only very briefly described here.

There are intriguing differences between the properties of WO_3 and ReO_3. W, with an electronic configuration $5d^4 6s^2$, has 6 valence electrons and WO_3 is expected to be a semiconductor. Indeed, the measured band gap of WO_3 is 2.6 eV for the room temperature monoclinic phase [27,28]. Re, on the other hand, with an electronic configuration $5d^5 6s^2$, has 7 valence electrons and ReO_3 is expected to have one "unpaired" d electron per Re atom. This unpaired electron might contribute to the metallicity of ReO_3. Indeed, an experimental conductivity of ReO_3 approaches 10^7 $(\Omega\ cm)^{-1}$ [29]. ReO_3 has a perfect cubic structure with the metal atom being octahedrally coordinated and the neighboring octahedra being connected through their corners. WO_3, on the other hand, has a distorted ReO_3 structure, with alternating

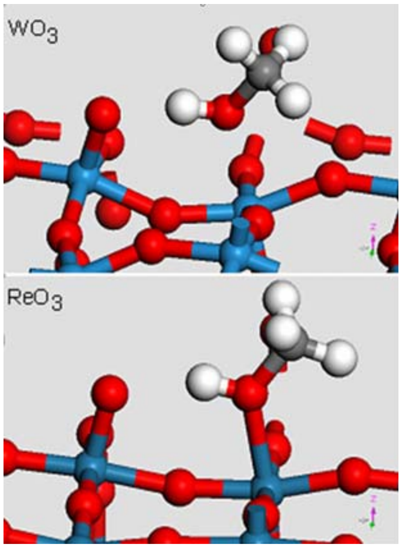
WO bond lengths and tilted octahedral [30]. Clearly, the difference of one d electron strongly affects the geometric and electronic structure of the corresponding oxides.





With the lattice constants being similar for WO_3 and ReO_3, 3.81 and 3.78 Å, respectively, new layered WO_3-ReO_3 compounds might have interesting properties. For instance, the metallic and (001) terminated ReO_3 support might serve as a metallic template for ultra-thin WO_3 epitaxial films. Here, however, we focus on catalytic properties of ReO_3 [31-33].

The catalytic activity of an oxide is frequently probed through the oxidative dehydrogenation of methanol. We have performed a density functional theory study of this reaction on the regular (001) surfaces of WO_3 and ReO_3 [34]. The transition states have been determined using the nudged elastic band method [35]. The reactivity of WO_3(001) and ReO_3(001) towards methanol was found to be markedly different. First, the adsorption energy for molecular methanol on ReO_3(001) is -103 kJ/mol while it is only -74 kJ/mol on WO_3(001) (left). Second, the dissociation of methanol to form adsorbed methoxy and H adatom is highly endothermic on WO_3 with a heat of the reaction of 108 kJ/mol. In contrast, the same reaction on ReO_3(001) is exothermic by -9 kJ/mol. An activation barrier for methanol dissociation over ReO_3(001) is ~18 kJ/mol. The A-G images (right) illustrate the minimum energy path with C being the transition state. In conclusion, ReO_3(001) is much more active than WO_3(001) for the methanol dehydrogenation reaction. Experimental studies of catalytic properties of conductive metal oxides will be a new focus point of this project in the near future, both in the High Surface Area Model Catalysts and Planar Model Catalysts branches.



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Fundamental Studies of the Adsorption and Reaction of Sulfur-Containing Compounds on Well-Defined Metal Oxide Surfaces

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Goal

The goal of this project is to provide fundamental insight into the reaction of organosulfur compounds on catalytically active metal oxide surfaces and to identify the active sites, pathways, intermediates, and energetics for the surface reactions of alkylthiols and alkylsulfides on ZnO, CeO_2, TiO_2 and supported vanadia. The motivation for this work is that thiols, disulfides, and other organosulfur compounds are present in virtually all hydrocarbon feedstock and understanding the interaction of these sulfur-containing compounds with metal oxides is important in sulfur poisoning of metal oxide catalysts, sulfur removal and remediation technologies, and the catalytic synthesis of thiols and disulfides.

Progress Report

Over the past year our work has focused on completing our studies of the reactions of thiols and disulfides on single crystal surfaces of ZnO especially the (10-10) surface. We have also continued our studies of the $VO_x/CeO_2(111)$system. To date our results for ZnO show that the reaction of thiols and alkylsulfides are highly structure sensitive with the ZnO(0001), ZnO(10-10) surfaces being active for the dissociative adsorption of thiols and alkylsulfides, while the ZnO(000-1) surface is inactive. Based on our TPD reactivity studies in conjunction with STM studies of the structure of ZnO single crystal surfaces from the literature we have been able to propose a new model of the active sites for the dissociative adsorption of Brønsted acids on ZnO. Our results indicate that both thiols and alcohols adsorb dissociatively on cation-anion site pairs that are present at step edges on both the (0001) and (10-10) surfaces rather than on (0001) terraces as previously proposed. This model helps to explain the low saturation coverages observed for thiols and alcohols on these surfaces.

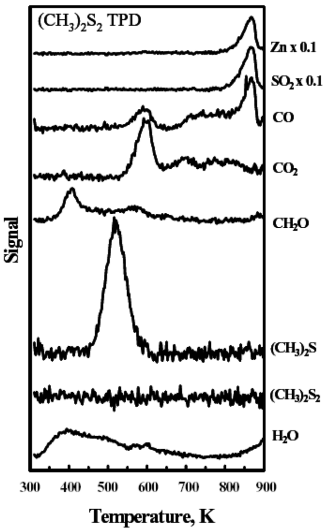

Fig. 1. TPD for the reaction of $(CH_3)_2S_2$ on ZnO(0001)

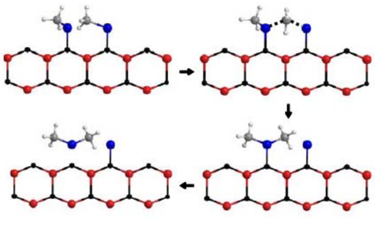

Fig. 2 Proposed mechanism for the reaction of two methylthiolates adsorbed on Zn^{2+} cations on ZnO(0001) to produce dimethylsulfide

Our TPD results for the reaction of CH_3SH and $(CH_3)_2S_2$ (see Fig. 1) on ZnO(0001) and ZnO(10-10) demonstrate that there are three separate pathways for the reaction of methylthiolate species on this surface: (1) recombinative desorption as CH_3SH, (2) coupling to produce $(CH_3)_2S$ and adsorbed sulfur, and (3) reaction to produce CH_2O. Figure 2 displays our proposed mechanism for the second pathway. The analogous reaction of two adsorbed methoxides to produce dimethylether does not occur on this surface. This difference in the reactivity of thiolates and alkoxides can be attributed to the lower energy of the C-S bond relative to the C-O bond. Two separate pathways were observed for the reaction of methylthiolate to formaldehyde on both the (0001) and (10-10) surfaces: a high-temperature pathway which produced CH_2O at 560 K, and a low-temperature pathway which produced CH_2O at 395 K. Our data indicates that the CH_2O product at 560 K results from the nucleophilic attack of surface oxygen at the carbon center in an adsorbed methoxide producing a dioxymethylene intermediate (CH_2O_2) which either desorbs as CH_2O, or is oxidized further to formate. The relatively high yield of CH_2O and formate decomposition products from CH_3SH and $(CH_3S)_2$ demonstrates that the transfer of a methyl group in a thiolate to a surface O^{2-} is relatively facile. The low-temperature pathway for CH_2O production is particularly interesting since it is a direct route for the oxydesulfurization of adsorbed methylthiolates. Our data indicates that this pathway proceeds via the reaction of methylthiolates with surface oxygen anions at step edges to produce a thio-oxymethylene ($SOCH_2$) intermediate which then decomposes to CH_2O and adsorbed sulfur. We are currently using XPS to characterize these adsorbed intermediates and hopefully this data will allow us to make a more definitive assignment of the surface species. The TPD spectra for CH_2O production on $(CH_3)_2S_s$-dosed (0001) and (10-10) surfaces are almost super-imposable suggesting that the reactions producing this product occur on similar sites on both surfaces. Previous STM studies of the (10-10) surface from the literature show that it contains steps where some of the step edges correspond to the (0001) surface. These observations are consistent with the model that the active sites on the (10-10) surface are located at these step edges.

Currently our experimental efforts are focusing primarily on the adsorption and reaction of thiols and alkyldisulfides on supported vanadia. This system is of interest because of the observation by Wachs and co-workers that vanadia is active for oxydesulfurization of thiols, dialkylsulfides, and thioesters to produce CO_2 and aldehydes or ketones. We have previously developed methods to grow monolayer and multilayer vanadia films on a variety of single crystal supports including $CeO_2(111)$. The structure and electronic properties of these films have been characterized in detail using XPS and HREELS. Preliminary data form a 0.75 ML $V_2O_5/CeO_2(111)$ sample shows that $(CH_3)_2S_2$ adsorbs dissociatively on monolayer vanadia forming methylthiolates (see Figure 3). During TPD, in addition to the parent molecule, the primary gaseous products are CH_2O and CH_3SH which desorb at 575 K. It is interesting that methoxide intermediates produced by dissociative adsorption of CH_3OH on $V_2O_5/CeO_2(111)$ also undergo dehydrogenation to CH_2O near this temperature. This suggests that the methylthiolates may react on the supported vanadia to form methoxide intermediates. This pathway is similar to what we have proposed for ZnO. On the other hand, the fact that for the $(CH_3)_2S_2$-dosed 0.75 ML $V_2O_5/CeO_2(111)$ surface both CH_2O and CH_3SH are produced at 575 K is not completely consistent with this explanation and we are sill working on identifying the reaction pathways.

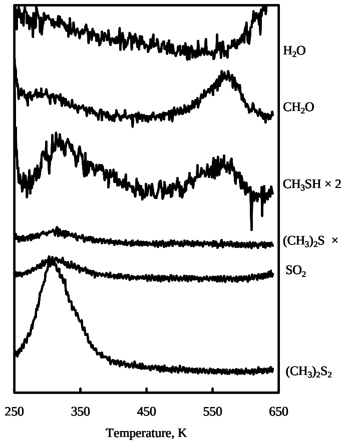

Fig. 3. TPD data from $(CH_3)_2S_2$-dosed 0.75 ML $V_2O_5/CeO_2(111)$

Another interesting observation from our studies of the $V_2O_5/CeO_2(111)$ system is that we do not observe a strong dependence of the reactivity towards thiols and disulfides on the vanadia film thickness. For alcohols we observed that only monolayer vanadia species were active for selective oxidation reactions, which is consistent with the reactivity of high surface catalysts. In contrast, TPD results obtained for $(CH_3)_2S_2$-dosed 0.5 ML and 5.0 ML vanadia films on CeO_2 were similar suggesting that bulk vanadia may be active for the oxydesulfurization reactions.

DOE Interest

Catalytic routes for the desulfurization of hydrocarbon feedstocks and the synthesis of organosulfur chemical intermediates are industrially important processes. Fundamental insight into the adsorption and reaction of thiols and organo-sulfides on catalytically active metal oxides, however, lags far behind that of other classes of oxide catalytic chemistry such as selective and complete oxidation. A detailed understanding of the mechanism and especially the active sites for the reactions of organosulfur compounds is therefore needed and will help in the development of more active and selective catalysts for these processes.

Future Plans

Our research plan for the current year is to finish our studies of the reaction of thiols and disulfides on ZnO and then concentrate our efforts on the vanadia system. Our TPD results have already provided a fairly complete picture of the reaction pathways and active sites for the reaction of these molecules on ZnO. There is still some uncertainty, however, about the identity of some of the reaction intermediates, especially whether a thio-oxymethylene intermediate is involved in the low-temperature oxydesulfurization pathway. To answer this question we are currently using XPS to characterize the adsorbed intermediates on the ZnO surfaces. For the vanadia system we plan to focus on the $VO_x/CeO_2(111)$ model system will initially finish preliminary base case studies of the reaction of thiols on the clean $CeO_2(111)$ support and then study how the oxidation state of the vanadium cations (+5, +4, or +3) affects reactivity towards thiols and compare this to our previous studies of alcohols on supported vanadia. We also plan to further explore the coverage dependence of the reactivity and determine if bulk V_2O_5 is indeed active for oxydesulfurization of thiols. Studies aimed at identifying stable surface reaction intermediates using XPS and perhaps HREELS will also be undertaken.

Publications:

1. Reactions of CH_3SH and $(CH_3)_2S_2$ on the (0001) and (000-1) Surfaces of ZnO, B. Halevi and J.M. Vohs, *J. Phys. Chem. B*, **109** (2005) 23976

2. TPD Study of the Reaction of CH_3CH_2SH and $(CH_3CH_2)_2S_2$ on ZnO(0001) and ZnO(000-1), B. Halevi and J.M. Vohs, *Catalysis Letters*, **111** (2006) 1

We are currently writing two papers describing our studies of the reaction of thiols and alkylsulfides on ZnO(10-10) (one on the C_1 reactants and the other on the C_2 reactants) which should be submitted for publication in the near future. We are also planning to write a paper that summarizes all our results for thiols on ZnO single crystals and compares these results to the data from ZnO powders. We also anticipate that there will be several papers describing our studies of the $VO_x/CeO_2(111)$ system.

DE-FG02-05ER15727 Jonah Erlebacher

Core-Shell Nanoporous Metal Membranes with Monolayer-Thick Precious Metal Catalyst Skins

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Goal

Develop new ultra-high surface area materials for electrocatalysis, using a minimum of precious metals. Our strategy use mesoporous metal membranes made by dealloying thin foils. On these high-surface area, conductive substrates, one may build designer multilayer and multicomponent catalysts with monolayer-level control of composition. In a recent discovery, we have found that by dealloying ternary alloys, one can form new core-shell mesoporous metals that have pore sizes ~2 nm in diameter and are stabilized to coarsening. By rationally correlating the performance of these materials with their microstructural characteristics, we will assess the effect of composite stresses, surface morphology and surface composition on catalytic activity, and identify the next generation of high performance catalysts.

Recent Progress

The goals of this program are to explore the use of thin nanoporous metal membranes as catalyst supports in proton exchange membrane fuel cells. We have recently been using two approaches. First, we are starting with an ultra-thin (~100 nm) porous gold membrane with pore size ca. 15 nm on which has been deposited an epitaxial catalytic layer of platinum ("Pt-plated nanoporous gold", Pt-NPG), with thickness control of order one monolayer. Second, we are dealloying ternary alloys Pt/Au/Ag alloys containing a minority fraction of Pt, which segregates to the surface during dealloying to form a core-shell material with extremely small pore size.

***Characterization of the model Pt-NPG system*:** In order to set a baseline for fuel cell activity utilizing Pt-NPG catalytic membranes, we have set up a fuel-cell testing station and developed robust Pt-NPG membrane electrode assemblies (MEAs). Pt-NPG is formed by electroless reduction of Pt on nanoporous gold membranes themselves formed by dealloying of silver/gold precursor membranes. The material formed is a highly porous form of gold with pore sizes tunably ranging from 5-30 nm which is encrusted, inside and out, with a "skin" of Pt controllable to monolayer thickness. The growth of Pt has been found to follow the Stranski-Krastanov mode in which one first observes a monolayer-thick wetting layer followed by the formation of epitaxial islands at greater thicknesses.

We have developed methods to reproducibly attach Pt-NPG membranes to Nafion membranes, and manufactured a fuel-cell testing station to characterize the performance of the material. The apparatus and testing conditions are not yet optimized, but we have

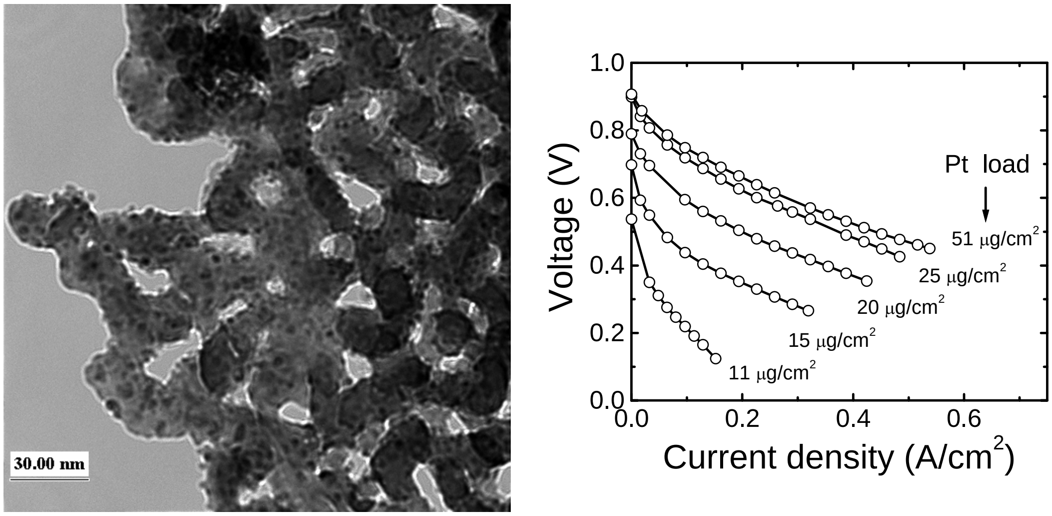

Figure 1. (left) TEM of Pt-plated nanoporous gold showing the islanded morphology we see for Pt loadings > 30 μg/cm^2. (right) Voltage-current performance of Pt-plated nanporous gold. At 30 μg/cm^2, we achieve ~5 kW/g Pt.

achieved a stable and reproducible baseline. The material works well, and we can reproducibly and stably generate 5 kW/g Pt [DOE1]. In studies of the current/voltage characteristics of cells made with Pt-NPG we have confirmed the structure/property hypothesis that the performance varies with coverage of platinum in a way related to the microstructure: with increasing (but low) Pt coverage, there is an increase in the active surface area due to the formation of Pt islands on the substrate, roughening it.

As an ancillary product of this effort, we have developed a new method to create large, single crystals of Au(111) via surface-energy driven abnormal grain growth, a metallurgical phenomena seen in highly plastically deformed rolled foils in which defect free (111) grains grow much faster than any other orientation, driven by the strain energy built up during deformation. We have examined for the first time the surface structure of such recrystallized grains, and found them to be of extremely high quality, yielding atomic resolution with minimal effort. We believe that this sample preparation method will be of significant interest to the catalyst community generally.

Ternary Pt-Ag-Au for new stable catalytic materials with ~2 nm pore sizes. NPG is very versatile, but in acidic environments tends to coarsen. Such coarsening is stabilized by the presence of a Pt overlayer, but it would be more useful to start with a stabilized structure with even smaller initial pore size (2-5 nm vs. 10-15 nm for regular NPG). To achieve this goal, we have been exploring single phase Pt-Ag-Au alloys, and have found that a 6 at. % (34/60 at. % remainder Au/Ag) alloy does precisely this. Figure 5 shows a micrograph of the material, and its very small pores. We are working to make this alloy into leaf form, so that we can make thin membranes. We expect thermal and chemical stability, and the final material should also be surface enriched in Pt, as well as low loading (0.01 mg Pt/cm^2). Incidentally, the addition of small quantities of impurities to alloys has long been known to stymie dealloying (e.g., 1% As in Cu/Zn brass); our experiments here will allow us to examine this important corrosion phenomenon in a

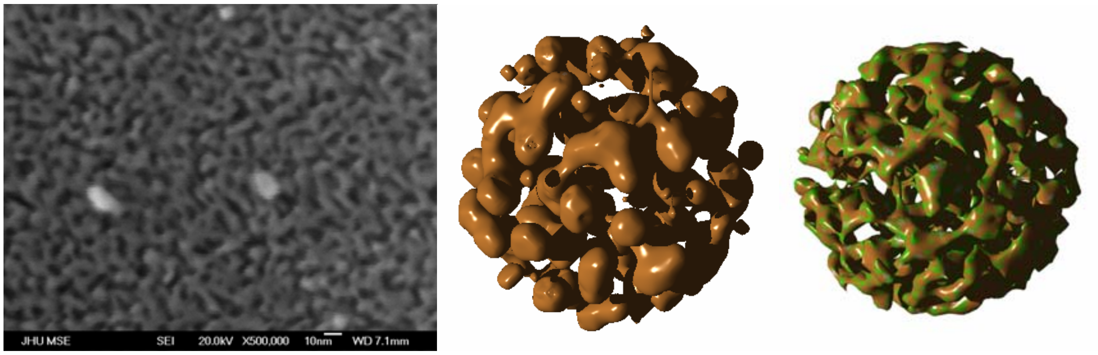

Figure 2. (left) SEM micrograph of dealloyed $Pt_6Au_{33}Ag_{61}$ *that was "coarsened" in nitric acid for 24 hours in order to make the porosity grow to an observable level (here, ~5 nm pores). This material has an initial pore size 5 nm. (center) KMC simulation of dealloyed* $Au_{35}Ag_{65}$ *(right) KMC simulation of dealloyed* $Pt_5Au_{30}Ag_{65}$ *showing surface enrichment of Pt (green) and refinement of the porosity.*

more controlled context. In addition, we are performing kinetic Monte Carlo simulations to explore the evolution of ternaries. The simulations are aiding in alloy design.

Future Work

Working mesoporous metal catalysts made by dealloying have been now made with only the simplest of morphology and composition. The degree of control over the shell structure via electroplating onto nanoporous gold membranes, in conjuction with the electroless deposition of platinum, is unexplored, and we will probe materials developmet in this direction. Core shell structures with layers of nickel followed by a monolayer of gold may mimic the much-touted Ni_3Pt system that may be particularly effective at oxygen reduction. Dealloying of ternary alloys may lead to mesoporous metals that are not based on the silver/gold system that produces NPG. In particular, we are beginning to look at Cu/Pt alloys, and hope to make core-shell mesoporous metals based on inexpensive copper.

Publications (2007)

1. R. Zeis, A. Mathur, G. Fritz, J. Lee, J. Erlebacher, "Platinum-plated nanoporous gold: An efficient, low Pt loading electrocatalyst for PEM fuel cells", J. Power Sources, **165** (2007), 65-72.
2. A. Mathur, J. Erlebacher, "Size Dependence of the Effective Young's Modulus of Nanoporous Gold ", Appl. Phys. Lett. **90** (2007), 061910.
3. T. Fujita , L. Qian, K. Inoke, J. Erlebacher, M. Chen, "Quantitative Transmission Electron Tomography of Nanoporous Gold," submitted to Phys. Rev. Lett., 2007.

DE-FG02-98ER14882 **Eric I. Altman**

Structure-Reactivity Relationships in Multi-Component Transition Metal Oxide Catalysts

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Students: Weiwei Gao (now at Harvard)

Collaborators: R.F. Klie (Brookhaven; Univ. Illinois, Chicago), C.H. Ahn (Yale), V.E. Henrich (Yale).

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Goal

It has long been known that interactions between metal cations in oxides can lead to catalysts that are vastly more reactive and selective than any of the constituent binary oxides. This effect has variously been attributed to modification of the geometry of the catalytic site around the active metal cation and to modification of the electron density around the active metal cation; however, it has not been possible to separate these two effects since compositional changes have generally been accompanied by structural changes. The goal of this project is to determine the relative importance of these two effects by characterizing the reactivity of epitaxial transition metal oxides where the electron density and geometry around the active cation can be varied independently.

Recent Progress

Over the last few years we have shown that vanadium oxides tend to grow epitaxially on transition metal oxide supports, even on the anatase polymorph of TiO_2 where no similar vanadium oxide structure is known in the bulk. This finding has several implications for supported oxide catalysts. First, transition metal oxide supports can stabilize site geometries not seen on the surfaces of the corresponding bulk oxides. Second, these new structures can alter oxidation and reduction pathways thereby changing the relative stability of different oxidation states. Finally, since oxide supports with widely varying electronic properties can be prepared in essentially identical perovskite structures, the support interaction can be varied without changing the structure.

Most of our work in the last year has focused on vanadium oxides on the rutile polymorph of TiO_2. Similar to our prior results for vanadium oxide on the anatase (001) and (101) surfaces, epitaxial VO_2 can be grown ad infinitum at temperatures above 700 K. Also similar to vanadium oxides on the anatase surfaces, we find that oxygen adsorption on the outermost VO_2 layer oxidizes the surface V to 5+. Thus, the oxidation state generally associated with catalytically active materials is produced in a structure distinct from bulk V_2O_5 which displays limited catalytic activity. We have been following the structural changes induced by oxygen adsorption on VO_2/rutile (110) with low energy electron diffraction (LEED) and scanning tunneling microscopy (STM); some of the results are illustrated below in Fig. 1. Figure 1.a shows the diffraction pattern obtained after annealing the surface in 10^{-6} torr O_2 at 875 K for 15 min, the pattern is (1x1) with some faint extra spots. Images of this surface show that most of the surface exposes the row structure typical of (110) surfaces of rutile-structured oxides, as in Fig. 1.b. Terraces, however, were also seen with large white balls (Fig. 1.c) arranged in a longer range periodicity; these features are attributed to oxygen adsorption. This assignment is strengthened based on the LEED patterns in Figs. 1.d-f. Fig. 1.d shows that after annealing at 925 K for 1 hr the faint spots in Fig. 1.a form a clear *c*(2x6) pattern; dropping the pressure to 10^{-8} torr O_2 produced a (1x1) pattern, consistent with oxygen desorbing from the surface. Meanwhile, dropping the temperature to 725 K in 10^{-6} torr O_2 resulted in the (2x2) pattern in Fig. 1.e, consistent with a higher oxygen coverage. The STM image in Fig. 1.f, suggests that the white balls associated with oxygen-induced changes move closer together as would be expected. We are currently working on more fully characterizing the surface phase transitions and looking at the reaction of the surface oxygen with methanol.

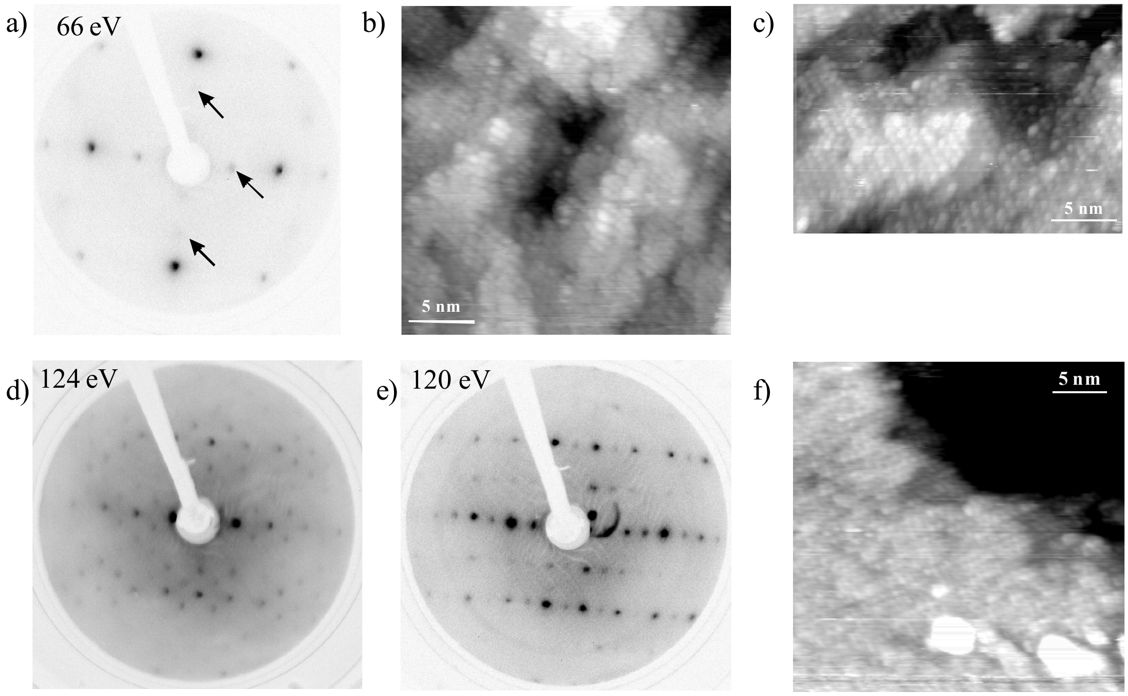

Figure 1. a) LEED pattern obtained after annealing a vanadia film on rutile (110) in 1x10^{-6} torr O_2 at 875 K. b,c) Corresponding STM images showing (1x1) terraces (b) and a higher order reconstruction in (c). After annealing the surface in a) – c) in 1x10^{-6} torr O_2 at 875 K spots in a *c*(2x6) pattern appear. e, f) Reducing the annealing temperature leads to a (2x2) structure.

DOE Interest

Oxides of the early transition metals are widely used as catalysts in the chemical and energy industries. In the chemical industry, oxides have generally been used to partially oxidize hydrocarbons to more valuable aldehydes, ketones, esters, and anhydrides. Improvements in activity and selectivity will allow more efficient use of scarce resources, transition to less expensive feedstocks, and generation of less potentially hazardous side products; all goals central to DOE's mission. In the energy sector, oxides are used to reduce the environmental impact of power generation. The fundamental research in this project aims to put design of improved catalysts for these applications on a more systematic, rational basis.

Future Plans

We have two directions we are pursuing in the immediate future: the atomic-scale mechanisms of oxidation reactions on epitaxial vanadia, and the dependence of reactivity of vanadia monolayers on the electronic properties of the oxide/oxide interface. For the former we are working on obtaining higher resolution images of the oxygen-induced reconstructions of the vanadia surface to allow us to develop a structural model of the surface. We will then use room temperature STM to identify methanol adsorption sites on the surface, and elevated temperature STM to follow the progress of the methanol oxidation/surface reduction reaction. The latter focuses on more macroscopic structural characterization via electron diffraction and reactivity via thermal desorption. We will be comparing epitaxial vanadia on WO_3 (100), $SrTiO_3$ (001), and anatase (001), all of which have the same surface structure, as well as vanadia on rutile (110) so that electronic effects can be separated from structural factors.

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Designing Metal Oxide Catalysts for Selective Gas Sensing

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Use of microelectronics fabrication methods for the creation of micro-electro-mechanical systems (MEMS) has led to the development of numerous portable sensor platforms allowing for integrated measurement capabilities with extreme accuracy. Catalytic materials contained within microchemical sensor devices can be characterized with nano-scale spatial resolution and in uniquely specified environments. Such catalytic microsystems provide a platform for new portable chemical gas detection systems with intrinsic chemical specificity created through a controlled catalytic reaction. A new catalytic sensor concept will be presented integrating a selective oxidation catalyst with microthermal transduction for selective analysis of specific analytes in multi-component gas mixtures. Key catalyst design requirements for multi-component metal oxide catalysts will be presented with applications in 1) CO detection in the presence of H_2 for fuel cell systems, and 2) ethanol analysis in gasoline mixtures. Mechanistic and kinetic requirements for highly selective reaction with only the desired analyte have been identified and used to tailor the composition and properties required of mixed metal oxide catalysts for suitable sensor performance.

DE-FG02-03ER15468

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Richard M. Crooks (U. of Texas)[2]
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CATALYSIS SCIENCE INITIATIVE: From First Principles Design to Realization of Bimetallic Catalysts for Enhanced Selectivity

Additional PIs: Douglas J. Buttrey, Jingguang G. Chen, Jochen A. Lauterbach, Raul F. Lobo, Dionisios G. Vlachos (Delaware); James A. Dumesic (Wisconsin)
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Goals:

The goal of this project is to demonstrate a new paradigm for design for catalyst selectivity. Our approach is to enhance selectivity by design via the integration of four research components: Theory and Modeling; Surface Science; Materials Synthesis, Characterization and Scale-up; and Catalyst and Reactor Dynamics and Optimization. This integrative approach is being applied to catalytic reactions where bimetallic catalysts may be advantageous.

DOE Interest:

“Catalysis by design” has been a dream for decades. To specify the composition and structure of matter to effect a desired catalytic transformation with desired and predicted rate and selectivity remains a monumental challenge, especially in heterogeneous catalysis. Our research thrusts have been chosen not only for their practical and scientific relevance, e.g. for more efficient and sustainable chemicals and fuels production, but also because they provide a foundation for developing and exploring broadly applicable principles and strategies for catalyst design.

Recent Progress:

Fundamental understanding of bimetallic surface reactivity

The focus of our efforts has been on the elucidation of trends in the chemical and catalytic properties of bimetallic surfaces for reaction of increasing complexity, and the identification of promising materials for specific selective reactions. A key result has been the development of the formalism of Near Surface Alloys (NSAs). The large variation in hydrogen binding energies that can be accessed with NSAs is illustrated in Figure 1. Some of these surfaces bind hydrogen as weakly as the noble metals (Cu, Au), and yet activate H_2 far more easily than the noble metals. The unique combination of weak binding of the dissociation products with the low bond-breaking activation energy barrier opens new possibilities for the design of highly selective low temperature hydrogen transfer catalysts. For example, in collaboration with the Besenbacher group in Denmark, we identified the Cu/Pt NSA, where Cu preferentially segregates in the 1st subsurface layer of the Pt-host, and endows the surface with promising properties for the low temperature water-gas-shift (WGS) reaction. Collaboration with the Adzic group at BNL has been aimed at identifying, synthesizing, and testing promising bimetallic and ternary NSAs which would be stable under realistic fuel cell conditions and at the same time would improve catalytic activity towards oxygen reduction reaction or possess increased CO tolerance for the anode catalyst. We have also carried out extensive Nudged Elastic Band (NEB) calculations to make quantitative predictions of the branching selectivity of competitive reactions on olefin epoxidation catalysis by different bimetallics. Even for reactions of small organics on realistic surfaces, it quickly becomes clear that exhaustive first-principles calculations demand large commitments of CPU time. To extend our limited high level calculations to a range of important problems in catalyst selectivity, we have explored various strategies to develop approximations that can provide trends and design guidance at lower computational cost. Examples include Bond-Order Conservation (BOC) methods to predict activation energies from DFT results on bimetallics, and the development of reactive force fields (ReaxFF) and neural network approximations to extend DFT calculations to make useful predictions of reaction rates on surfaces of increasing structural complexity. Theory and modeling have a crucial role to play in the understanding of catalytic processes and the design of new catalysts; the challenge is to determine the necessary level of detail to make effective use of these.

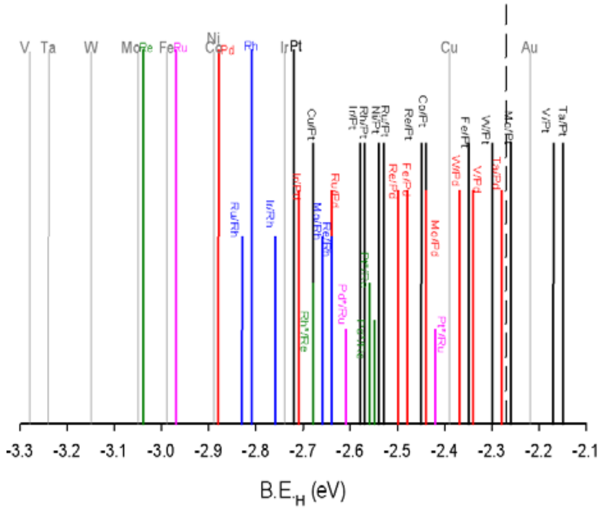


Figure 1: *Spectrum of H binding energies on NSAs*

Surface Science Experiments

The principal focus of our surface science experiments has been on the synthesis of bimetallic surfaces and the reactions of molecules such as ethylene and ethylene glycol which are the subjects of both our theoretical efforts and catalytic reaction studies. Our aim is to test predictions from theory and to provide first-principles guidance, from both theory and experiment, for catalyst formulation and design. Table 1 shows TPD results for reforming of ethylene glycol on Pt and Pt-based bimetallics.

Table 1: *Reactivity of ethylene glycol on Pt(111) and Ni/Pt(111) surfaces*

	Activity (ML)			Selectivity (%)	
Surface	Reforming	Decomposition	Total	Reforming	Decomposition
Pt(111)	0.030	0.004	0.034	88	12
Pt-Ni-Pt(111)	0.025	0	0.025	100	0
Ni-Pt-Pt(111)	0.144	0.023	0.167	86	14
Thick Ni/Pt(111)	0.122	0.016	0.138	88	12

The reactivity of ethylene glycol and ethanol can be correlated with the *d*-band centers of the corresponding surfaces. The correlation displays a fairly linear relationship, with activity increasing as the *d*-band center moves closer to the Fermi level. The *selectivity* to reforming for ethylene glycol does not display any discernable trend as a function of *d*-band center. The Ni-Pt-Pt(111) surface with the monolayer Ni residing in the top layer shows the highest reforming activity as compared to either Pt(111), thick Ni/Pt(111), or subsurface monolayer Pt-Ni-Pt(111) surfaces. Using the experimentally determined linear trend of activity vs. the surface *d*-band center, one can explore the reactivity of other Pt-3*d* bimetallic surfaces for reforming of ethylene glycol and ethanol. DFT results indicate that surface monolayer 3*d* metals on Pt(111) shift the surface *d*-band center closer to the Fermi level, therefore increasing the interactions with adsorbates. The trend predicts increased activity on surfaces with *d*-band centers closer to the Fermi level, opposite of the trend observed for hydrogenation reactions. The shift in the *d*-band of 3*d*-Pt-Pt(111) surfaces increases as the 3*d* metal moves to the left of the periodic table. Experiments on Co/Pt(111), Fe/Pt(111) and Ti/Pt(111) have been carried out to determine the trend in the reactivity and reforming selectivity to confirm the predictions from this study. These surface science results and DFT predictions are in excellent agreement with catalytic reaction studies. The Dumesic group has shown that Pt-Ni and Pt-Co are among the most active catalysts for glycol reforming. This agreement motivates further tests, both surface science and catalytic performance experiments, directed at the bimetallic combinations with d-band centers near the Fermi level.

Materials Synthesis, Characterization and Performance

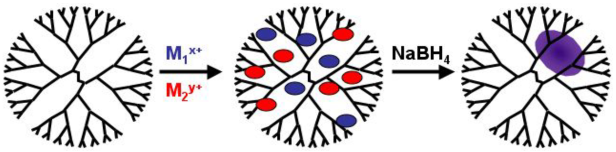
Our objective is to synthesize and characterize structurally well-defined, bimetallic catalysts, and to explore the performance of these, especially for reactions for which first-principles studies suggest that bimetallics should be advantageous. Our two main approaches involve "encapsulation" of bimetallic particles both to maintain them in the desired size range, and to take advantage of the properties of the surrounding "matrix" in catalyst synthesis and/or operation. We have focused on two principle classes of materials: dendrimer-encapsulated nanoparticles (DENs) in the Crooks group and zeolite supported nanoparticles in the Lobo and Chen groups. Together, these studies have permitted us to explore a range of catalytic reactions, to address questions of catalyst stability and selectivity, and to explore performance vs. predictions for specific cases.

Selective hydrogenation of acetylene in ethylene

The selective hydrogenation of acetylene in excess ethylene is a critical reaction in the polymerization of ethylene. Acetylene poisons the polymerization catalyst and needs to be selectively hydrogenated *without* the hydrogenation of any ethylene. Our attempts to solve this problem involves two parallel approaches: (1) selecting bimetallic catalysts that have different binding energies for acetylene and ethylene based on the computational studies described above and (2) supporting these bimetallic catalysts on zeolites to selectively enhance the adsorption of acetylene. We recently discovered that PdAg bimetallic catalysts, supported on Na^+ β-zeolite, show promising selective hydrogenation activity to acetylene in the presence of excess ethylene. These results have been confirmed both from batch reactor studies using Transmission IR and from flow reactor studies using GC. We are currently expanding our catalyst formulations to include other types of zeolite supports.

Synthesis and atomic-level characterization of PdAu dendrimer-encapsulated nanoparticles

The Crooks group has prepared palladium-gold dendrimer-encapsulated nanoparticles (DENs) using metal-ion co-complexation and reduction inside the interior void space of a generation-six, poly(amidoamine) (PAMAM) dendrimer. The ratio of the two metals was controlled by adjusting the stoichiometry during the first step of the synthesis. This resulted in particles having the composition G6-OH(PdxAu147-x), where x =118, 87, 73, 60, and 29. These materials were then analyzed using extended x-ray absorbance fine structure (EXAFS) spectroscopy. The results indicated that the particles were pure alloys regardless of the metal concentrations. The level of interaction between the nanoparticle surface and the dendrimer was below the detection limit of the EXAFS experiment, indicating that a large percentage of the surface metal atoms are freely exposed and available for catalysis. Extraction of the DENs from within the dendrimers resulted in the formation of organically soluble bimetallic monolayer-protected clusters (MPCs). EXAFS analysis of the extracted MPCs indicates that they consist of a Au core and Pd shell. Thus, we have observed an usual situation wherein the (thiol) ligands drive the conversion of the particle from an alloy to a core/shell structure. No Au-thiol interactions are observed until the number of Au atoms within the particle is sufficient to exceed the maximum number permitted in the core. For particles having lower Au number densities, only Pd-thiol interactions are observed. The dendrimer templating approach is an effective route to the synthesis of chemically and structurally well-defined bimetallic catalytic nanoparticles. We envision that these materials will provide excellent experimental models for developing the next generation of catalytic materials. Our long-term objective is to correlate the structure of these bimetallic DENs to their catalytic function. This requires extensive characterization efforts. We are presently focused on completing our study of the interesting ligand-driven structural rearrangement of the PdAu DENs and also EXAFS, XRD, and HRTEM studies of monometallic Pt and Au DENs. Next, we plan to prepare a series of PdM (M = Ni, Co, and Mo) bimetallic DENs. These materials present unique synthetic and characterization challenges, because Ni, Co, and Mo are susceptible to oxidation in solution.



Catalyst Development, Dynamics, and Optimization

In addition the bimetallic catalyst synthesis and performance studies driven by first principles theory and experiments, we have pursued two catalyst development efforts aimed at high impact processes. These have been enabled by high-throughput techniques developed in the PIs' labs. These include the development of new NO_x storage and reduction (NSR) catalysts by the Lauterbach group, and the development of new catalysts for carbohydrate reforming by the Dumesic group. The former promises to impact automotive exhaust catalysis, the latter the production of hydrogen and other fuels from biomass. These studies demonstrate the potential of high-throughput experimentation in combination with techniques and fundamental information developed by our program, to impact areas of national need.

For NO_x storage catalysts, we have extended our previous synthesis procedure via reverse micelles to the bimetallic Pt/Co system. We had found that addition of 5% Co to a 1Pt/15Ba catalyst can increase the NO_x storage by more than 100%. In order to further improve the performance of these catalysts, we have synthesized different combinations of Pt/Co based catalysts using reverse micelle synthesis procedure. The particle size and composition were analyzed using TEM After supporting the particles on a γ-Al_2O_3; the particle size remains the same after supporting them. Supported catalysts were tested for NO oxidation and storage activity. Pt/Co catalyst supported on 15%Ba-containing γ-Al_2O_3 showed comparable results to those of standard Pt/Ba catalysts. Future work will focus on the performance of Pt/Co catalysts from different preparation methods.

We also investigated the mechanism of promotion by Co using FT-IR spectroscopic imaging, temperature programmed reduction (TPR), X-ray diffraction, and electron microscopy. X-ray diffraction and temperature programmed reduction demonstrated that Co exists in a highly oxidized state (Co_3O_4). The surface oxygen can be reduced at a temperature around 300°C and can again be replenished using gas phase oxygen. The surface oxygen from Co can increase the NO to NO_2 oxidation rate and can, in turn, increase the overall NO_x storage. SEM showed that addition of Co can provide more sites for NO oxidation as well as increased surface area for NO_2 spillover to $BaNO_x$ storage sites. In situ IR studies further demonstrated that Co functions similar to Pt: increasing both the rate of nitrite to nitrate formation and the overall formation of nitrates. This increase in nitrate formation is associated with its improved oxidation capacity with the excess oxygen available from Co_3O_4 during the reaction. This was demonstrated by Co catalysts being able to oxidize NO even without the supply of gas phase oxygen at 350°C. Therefore, the increase in efficiency, after the addition of Co to Pt/Ba catalyst, can be attributed to the strong oxidizing effect of Co, providing additional nitric oxide oxidation sites and surface area for NO_2 spillover to the $BaNO_x$ storage sites

Our work on the production of liquid fuels by catalytic conversion of biomass-derived carbohydrates has followed two research directions: production of liquid alkanes (i) by the combination of dehydration and hydrogenation of compounds derived by aldol-condensation of carbonyl compounds, and (ii) by the formation of $CO:H_2$ gas mixtures derived from hydrogenolysis of polyols. During the past year we have studied the dehydration and hydrogenation of aqueous solutions of sorbitol (C_6-polyol) to produce hexane over metals and metal alloys on various solid acid catalysts. The reaction conditions for this catalyst process are significantly different from those encountered during petrochemical processing because of the presence of the aqueous solvent. In this respect, we have found that most zeolite catalysts are not stable with respect to time under our aqueous-phase reaction conditions (e.g., 250^oC, 35 atm), whereas catalysts based on niobic acid and niobium phosphate exhibit high catalytic activity and excellent stability. To probe the kinetics for this process, we have employed the dehydration of aqueous solutions of isobutanol to produce butanes. The rate of dehydration is first order with respect to isobutanol and highly negative order with respect to water. The rate data can be described by an expression that takes into account water multi-layer formation.

We have also studied the reforming of glycerol to produce synthesis gas ($CO:H_2$ gas mixtures). The rate of glycerol reforming over supported Pt catalysts is negative order with respect to the partial pressure of CO, suggesting that more active catalysts could be prepared by weakening the binding energy of CO on the surface. Our computational efforts described above have predicted that the strength of CO adsorption can be modified by the use of near-surface alloys. Several such alloys have been synthesized and characterized at Delaware, and studies of glycerol reforming over these catalysts have carried out at Wisconsin. In particular, Al_2O_3-supported 5wt % Pt, 5 wt% Ni, 6.5 wt% PtNi(1:1) and 5.5 wt% PtNi(3:1) catalysts were tested for conversion of glycerol (30 wt% in water) to CO and H_2 at 225°C. We have found that adding small amounts of Ni to Pt, increases the activity by 45% (with respect to the rates of CO and H_2 production), and significantly improves catalyst stability.

We have also carried out detailed reaction kinetics studies of the conversions of oxygenated hydrocarbons over PtRe-based catalysts, along with X-ray absorption measurements for various PtRe catalysts under different reaction conditions. X-ray absorption measurements were recorded on the Pt L_{III} and Re L_{III} absorption edges of carbon-supported Pt, Re, and bimetallic Pt-Re catalysts. The set of bimetallic catalysts consisted of freshly reduced catalysts and a PtRe catalyst that had been exposed to aqueous-phase reactions conditions, resulting in deactivation. X-ray absorption measurements were collected before, after and during reduction. Examination of the near edge regions (XANES) of both Pt and Re L_{III} edges indicated significant re-oxidation of Re and to a lesser degree Pt in all catalysts after passivation. Interpretation of the EXAFS regions showed an absence of metal-oxygen bonding in all catalysts after in-situ reduction, indicating complete reduction to the metallic phase.

Future Plans:

A variety of new bimetallic combinations – Ni/Pd for hydrogenation and dehydrogenation; Cu/Ag for olefin epoxidation; Co/Pt for NOx storage and reduction – has begun to emerge from this research. We continue to search out such synergistic combinations using fundamental surface science and computational tools, while developing synthetic methodologies to fabricate working catalysts based on these discoveries. We are exploring the design and application of bimetallic catalysts to a host of relevant processes for more efficient and cleaner fuels and chemicals production and utilization.

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DE-FG02-84ER13290 **Mark A. Barteau**

Experimental and Theoretical Studies of Surface Oxametallacycles: Connections to Heterogeneous Olefin Epoxidation

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Research Goals

This project is aimed at the rational design of catalysts for direct epoxidation of olefins. Although the epoxidation of ethylene by silver catalysts to form ethylene oxide (EO) has been practiced for decades, little progress has been made in expanding this technology to other products and processes. We have made significant advances through the combination of surface science experiments, Density Functional Theory (DFT) calculations, and catalytic reactor experiments, toward understanding the mechanism of this reaction on silver catalysts, and to the rational improvement of selectivity. The ultimate aim of this project is to extend these advances to the design of catalysts for epoxidation of more complex olefins.

Recent Progress

This research combines DFT calculations and surface science experiments as the principal tools for understanding oxametallacycle chemistry and epoxidation catalysis, as well as promoter and alloy effects at the molecular level. These results can then be integrated into microkinetic models whose predictions can be benchmarked against experimental results for heterogeneous epoxidation catalysts. Our goal is to develop a level of understanding of this process that will permit quantitative prediction of catalyst performance, including that of novel catalysts such as the bimetallics that we have advanced. The key has been our demonstration of surface oxametallacycle intermediates as the species that control reaction selectivity. This discovery permits the influence of catalyst promoters on selectivity to be probed, and new catalyst formulations to be developed.

Recently we have focused on two principal research areas: experimental and computational studies of complex oxametallacycles on silver surfaces, and development of a microkinetic model to refine predictions of promoter effects on the activity and selectivity of ethylene epoxidation catalysts. Our fundamental surface science and DFT studies of the epoxides of conjugated olefins have focused on the oxides of butadiene and styrene. For both styrene oxide (StO) and epoxybutene (EpB) on Ag(111), we have identified oxametallacycles as the reactive intermediates on the crystal surface. TPD experiments showed that both epoxides give rise to more stable oxametallacycles than does EO. In the case of StO on both Ag(111) and (110) surfaces, the oxametallacycle was observed to reform styrene oxide along with phenylacetaldehyde at ca. 485 K. These products, combined with HREELS and HRXPS results, indicate the preservation of the phenyl substituent and confirm theoretical predictions regarding the stability of these intermediates. TPD, HREELS and DFT results are all consistent with an orientation of EpB- and StO-derived oxametallacycles with their carbon frameworks roughly parallel to the surface due to stabilizing interactions of the unsaturated substituent groups with surface metal atoms.

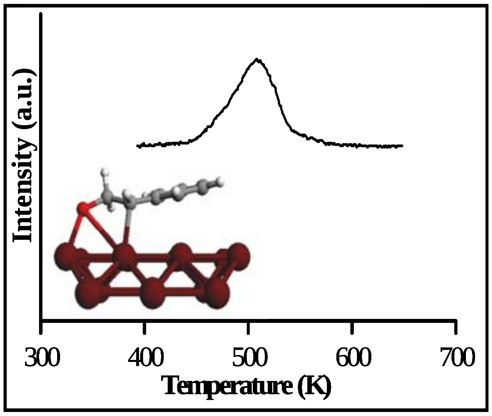

Figure 1. StO TPD on Ag(110) and DFT-predicted oxametallacycle.

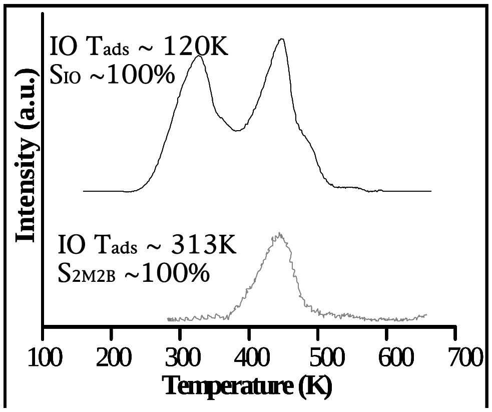

Figure 2. IO TPD on Ag(110) following adsorption at a) 120K, b) 313K.

We have extended this chemistry to isoprene oxide (IO), forming the first stable oxametallacycle containing allylic hydrogens. This is an important step toward accomplishing direct selective epoxidation of propylene with silver-based catalysts. Adsorption of IO on Ag(110) at 120K forms an intermediate that reacts *solely* to reform the epoxide in two peaks at 320 and 460K; the product distribution in these two states is identical and corresponds to the gas-phase cracking pattern of IO. Adsorption of IO on Ag(110) at higher temperatures, however, leads to complete isomerization during TPD with desorption of 2-methyl-2-butenal (2M2B) a single peak at 460K. In agreement with the absence of other isomerization or decomposition products from TPD experiments, DFT calculations predict that IO ring-opens at the carbon bound to the substituent groups to form a linear oxametallacycle; isomerization of this species via hydrogen transfer forms 2M2B.

In the area of ethylene epoxidation, we have constructed micro-kinetic models that allow us to assess the performance of multi-component catalysts based on DFT results for binding of all adsorbates, rather than focusing solely on the oxametallacycle reaction steps. These require extensive computations for input. We have explored the predicted differences in activation energies for EO and acetaldehyde formation for bimetallics including silver and its neighbors in the Periodic Table (e.g., Cu, Pd, Pt, Cd, Au, Rh, Ir, Ni, Zn, and Os). In this study we have replaced one Ag atom bonded to the oxygen of the oxametallacycle with an M atom to generate a bimetallic $Ag_{14}M_1$ cluster. $Ag_{14}Cu_1$, $Ag_{14}Pd_1$, and $Ag_{14}Pt_1$ are predicted to be more selective than pure Ag, whereas all other bimetallic catalysts are more prone to form acetaldehyde. Even though DFT results are useful in obtaining trends in EO selectivity by calculating activation energies, there are additional factors controlling the selectivity. For example, the pre-exponential factors and the magnitude of activation energies can also influence the selectivity. We have therefore incorporated the results above into a more complete microkinetic model of the catalytic process in order to predict the effect of different bimetallic combinations on both activity and selectivity.

AgCu shows higher EO selectivity than that on pure Ag, consistent with the DFT calculations. Similarly, AgCd and AgAu show lower EO selectivity than that on pure Ag, also consistent with the DFT calculations. However, AgPd and AgPt do not turn out to be better catalysts than pure Ag. It is observed that apart from the differences in activation energies, pre-exponential factors, and magnitudes of activation energies, stability of the OME is another factor controlling the selectivity. OME stability on $Ag_{14}Pd_1$ and $Ag_{14}Pt_1$ is much higher than that on other catalysts, which results in almost zero activation energy for OME formation from adsorbed EO. In comparison, the activation energy for OME formation from adsorbed acetaldehyde is more than acetaldehyde desorption, so the EO selectivity decreases significantly on these two catalysts.

Overall, AgCu is the only bimetallic catalyst showing higher EO selectivity than pure Ag, based on microkinetic analysis. In summary, the combination of DFT calculations for the selectivity-controlling steps with microkinetic models for the complete reaction have successfully identified a new bimetallic catalyst for ethylene epoxidation, while helping to eliminate "false positives" from our initial computational screening.

DOE Interest

The direct epoxidation of olefins remains one of the most challenging problems in heterogeneous catalysis. Our elucidation of the central role of the oxametallacycle in olefin epoxidation provides a platform, not only for understanding catalyst performance, but also for exploring the influence of catalyst promoters at the molecular level, and ultimately for rational design of more efficient heterogeneous catalysts.

Future Plans

Research during the next year will focus on two areas.

1. Surface science and computational studies of complex oxametallacycles, including those derived from epoxybutene, styrene oxide, and isoprene. The principal focus of this work will be on understanding the effects of surface crystallographic structure on reaction selectivity. Epoxybutene and isoprene oxide give rise to interesting isomerization reactions on the Ag(111) surface in particular, that suggest that both *cis* and *trans* oxametallacycle configurations may be feasible on this surface.
2. Surface science studies of promoter effects on oxametallacycle surface chemistry. We have made qualitative predictions from DFT calculations of the effects of Cs and Cl adsorption on the selectivity of surface oxametallacycle reactions. As we complete experimental studies of oxametallacycle chemistry on clean Ag(111) and (110) surfaces, we will introduce these promoters to test experimentally these predictions and to refine surface structures and compositions for our computational models.

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DE-FG02-03ER15464 **Ludwig Bartels**

Controlling Structural Electronic and Energy Flow Dynamics of Catalytic Processes Through Tailored Nanostructures.

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Project Goal

The overarching goal of this program is to lay the scientific foundations for a new class of heterogeneous catalysts in which materials with nanoscale structuring are utilized to control the flow of reactants to and products from optimized reaction sites and, to the extent possible, to control the flow of energy released in the surface reactions. To this end we perform experiments and accompanying theory that elucidates means of controlling adsorbates at surfaces.

Bartels focus in this project is on the investigation and characterization of (a) the dynamic behavior of adsorbates on metal surfaces as a foundation for the development of methods that enhance catalytic activity of supported nanoparticles by steering the diffusion of reactants towards active centers; (b) Substrate-mediated adsorbate excitation and adsorbate-adsorbate excitation transfer that induce/influence relevant surfaces reactions.

Research Plan and Results: Guiding Surface Motion

Hexagonal surfaces are regarded as exhibiting the highest symmetry for crystalline media. They are also among the least reactive, which renders transport across them towards sites of greater activity (e.g., step-edges, other surface irregularities, and regions of different composition) even more important.

Adsorbates generally diffuse in an isotropic fashion on metal surfaces, i.e. in all possible surface directions. Surfaces of lower symmetry are known to guide the diffusion of adsorbates along their structural features (e.g., atomic rows on (110) surfaces, step-edges on regularly stepped surfaces, etc.). STM investigations have been tremendously useful in both elucidating and quantifying the details of such processes. Our investigations have shown that similar 1-dimensional guidance can be achieved on the hexagonal fcc(111) surface despite the *absence of structural differences along the three equivalent in-plane directions.* The origin of this guidance effect is completely different from the familiar influence of the inherent surface anisotropy. It arises from the detailed molecule/surface interaction. We demonstrated this effect using a molecule, 9,10-diacetylthioanthracene (DTA), that we designed for this purpose. We found that when deposited on a Cu(111) substrate a DTA molecule diffuses exclusively along the direction in which it is initially aligned. This behavior amounts to a breaking the substrate symmetry. It converts a 2D random walk into a 1D phenomenon. The guiding principle in the design of the DTA molecule was the transfer of the concept of bipedal locomotion (i.e., walking) to the scale of individual

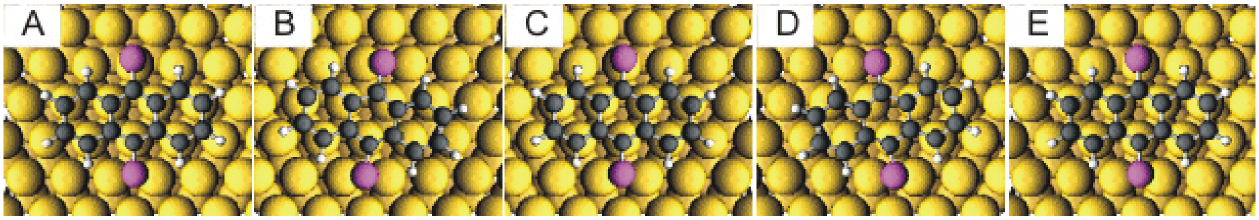

Fig. 1 Molecular configurations during the linear diffusion of DTA on a Cu(111) surface. At any instant either one of the sulfur (purple) substrate linkers is outside a favorable hollow site or the ring system as a whole is misaligned with the substrate.

molecules. In particular, we could show that if adsorbate-substrate interactions require at least one of a molecule's substrate linkers be attached to the surface at all times, guiding of the molecule's diffusive motion can be achieved (Fig. 1). The novelty of this guided diffusion process earned the findings widespread attention in the scientific community, including mentioning in C&EN news and as one of the 25 'Physics Top Stories for 2005'.

Recently we extended the concept of uniaxial surface motion of a molecule to transport of cargo molecules. To this end, we screened a number of molecules, of which we expected uniaxial motion by a similar mechanism as found for DTA as well as a range of isotropically-diffusing small species like CO, water, etc. Finally, we were successful with the combination of anthraquinone, the oxygen counterpart of dithioanthracene as a carrier and CO_2 as cargo. STM measurements show, that anthraquinone can carry up to two CO2 molecules, each of which are reversible attached to one of the carbonyl substrate linkers by means of relatively weak substrate mediated interactions. Transport of cargo slows the motion of the complex. While unencumbered anthraquinone experiences a diffusion barrier as low as 23 meV, this value rises above 50 meV upon attachment of one CO2 molecule and above 70 meV upon attachment of two CO2 molecules. For DTA the individual steps during the molecular diffusion can only be revealed by density functional theory calculations (conducted with collaborator Rahman); in contrast, the steps of the anthracquinone complex across the surface are readily resolvable by STM. This research received widespread public recognition (e.g. the Financial Times covering in an article entitled 'Molecular conveyor belt comes closer').

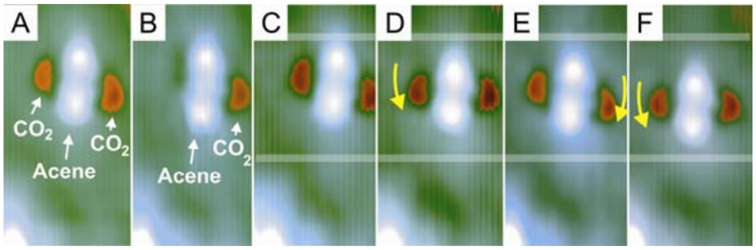

Fig. 2 A-C) detachment and reattachment of a CO2 molecule (depression, red) on the left side of an AQ (protrusion, blue/white). (C-F) diffusion of AQ with two CO2 molecules by means of individual steps of its oxygen atoms (see Fig. 3). All images V= -35 mV, I = 60 pA, T = 50K, A = 20 x 40 Å. Note the edge of a cluster of AQ molecules in the bottom left serving as a marker and the Cu(111) surface state oscillations.

We extended the study of anthracene based molecules on metal surfaces from oxygen and sulfur linkers towards carbonitrile linkers. These provide extreme structural variability in the resultant molecular films, which is currently under theoretical investigation by Rahman's group.

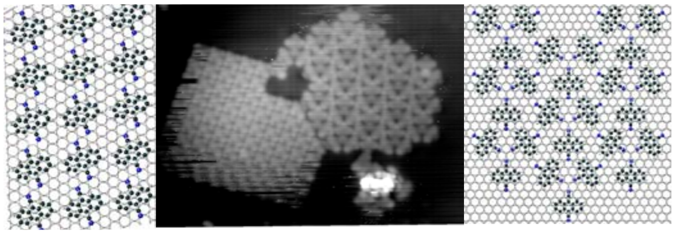

Fig. 3 9,10-dicarbonitrilieanthracene on Cu(111)

DOE Interest

Despite the great importance of catalytic reactions for a broad range of industrial and environmental processes, there is no experimental method yet for guidance of reactants through the individual steps that make up a heterogeneous catalyzed reaction. This project aims providing first steps in this direction and it is conducted in close collaborations with the T.S. Rahman (theory), T.F. Heinz (energy transfer dynamics) and S. O'Brien (synthesis of nanoparticles).

Future Plans

Development of species with extended ability to carry cargo using variations of the molecular backbone, substrate linkers and dedicated attachment groups. Measurement

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Surface studies of nitrogen-doped TiO_2

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Titanium dioxide is one of the most promising materials for photocatalytic energy conversion. Its wide band gap of 3.2 eV, however, allows absorption of light in the UV region only and thus is not very efficient in harvesting sun light. Band gap engineering by nitrogen doping has been shown to increase the photoactivity of TiO_2 in the visible spectrum [1]. In order to elucidate the influence of N-doping on the electronic structure, surface properties, and defect formation we performed scanning tunneling microscopy and photoemission studies on single-crystal rutile and anatase TiO_2 [2].

N-doped samples were prepared by low energy ion implantation and annealing in vacuum. The N-concentration was ~3 – 6 % of the anions and was low enough for the samples to retain single crystalline order. X-ray photoelectron diffraction indicates that N-dopants substitute for O in the lattice. The charge state of the dopants was identified as N^{3-} in X-ray photoemission spectroscopy. We propose that O-vacancy formation compensates for the nominal additional charge of the dopant compared to the oxygen-anion of the host material. Increased O-vacancy formation is also consistent with local 1×2 surface reconstructions that are observed on rutile TiO_2(110) upon N-doping. Ultraviolet photoemission spectroscopy of the valence band show the formation of a N-2p derived state on top of the valence band which is responsible for shifting the photoactivity of TiO_2 into the visible. This state may be described as a band gap state without any strong evidence of hybridization with the O-2p valence band of TiO_2. Thus surface studies on single crystal oxides play a crucial part in understanding fundamental mechanisms important in materials design aimed at achieving higher energy conversion rates.

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DE-AC02-05CH11231 **Alexis T. Bell**

Strategic Design of Novel Catalysts for the Selective Synthesis of Fuels and Chemicals

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Goal

The primary goals of this project are to prepare, characterize, and investigate single and multicomponent catalysts containing well-defined active sites and to relate the local composition and structure of active sites to the kinetics of elementary reactions involved in the synthesis of targeted molecules.

Recent Progress

Effects of dopants on the activity of Cu/ZrO$_2$ for methanol synthesis: Previous investigations have shown that Cu/ZrO$_2$ is an active catalyst for the hydrogenation of CO to methanol and that both components of the active play an active role in the reaction mechanism. It has also been shown that the substitution of Ce for Zr into the ZrO$_2$ lattice results in a significant enhancement in methanol synthesis activity. The present investigation was undertaken with the aim of understanding whether other substituants, such as Mn and Pr could also enhance the activity of Cu/ZrO$_2$. Zirconia and Ce, Mn, and Pr-substituted zirconia were prepared by forced hydrolysis at low pH, starting from nitrates of each metal, and Cu was then dispersed on to the surface of the calcined oxide by deposition-precipitation. All catalysts were characterized by XRD, XANES, and temperature-programmed reduction in H$_2$. H$_2$ and CO chemisorption capacities were also measured. The areas based activity of 3wt% Cu/M$_{0.3}$Zr$_{0.7}$O$_2$ decreased in the order 3wt% Cu/Ce$_{0.3}$Zr$_{0.7}$O$_2$ > 3wt% Cu/Pr$_{0.3}$Zr$_{0.7}$O$_2$ > 3wt% Cu/Mn$_{0.3}$Zr$_{0.7}$O$_2$ > 3wt% Cu/ZrO$_2$. Catalyst activity was found to correlate with H$_2$ adsorption capacity and the proportion of bridge-bonded hydroxyl groups. The importance of the latter species is ascribed to their higher Brønsted acidity, which contributes to the rapid release of methoxide groups formed on the oxide surface and the formation of methanol. Dopant cations that can participate in redox cycles (e.g., Ce and Mn) are desirable, since they can enhance the methanol synthesis activity of Cu/M$_{0.3}$Zr$_{0.7}$O$_2$ catalysts to a greater degree than cations that do not participate in redox cycles (e.g., Pr).

Supported vanadate catalysts for methanol expoxidation: The mechanism of methanol oxidation to formaldehyde catalyzed by isolated vanadate species supported on silica has been investigation by *in-situ* Raman and TPD/TPO experiments. Raman, XANES, and

EXAFS were used to characterize the V-MCM-48 sample, prepared with a loading of 0.3 V/nm^2, and it is concluded that the oxidized form of the vanadium is isolated VO_4 units. The VO_4 species consist of one V=O bond and three V-O-Si bonds in a distorted tetrahedral geometry. Methanol reacts reversibly, at a ratio of approximately 1 methanol per V, with one V-O-Si to produce both V-OCH_3/Si-OH and V-OH/Si-OCH_3 group pairs in roughly equivalent concentrations. Formaldehyde is formed exclusively by the transfer of one H atom from the methyl group of V-OCH_3 to the V=O bond of the vanadium containing the methoxide group. Formaldehyde is formed in nearly equal concentrations both in the presence and absence of gas phase oxygen. CO and H_2 are produced by the decomposition of CH_2O at higher temperature. In the absence of O_2, Si-OCH_3 groups undergo hydrogenation to form CH_4, and in the presence of O_2, these groups are oxidized to CO_x (x = 1, 2) and H_2O above 650 K. Under steady-state reaction conditions, CH_2O is produced as the dominant product of methanol oxidation at temperatures below 650 K with an apparent activation energy of 23 kcal/mol. A reaction mechanism proposed on the basis of these experimental findings is strongly supported by a first-principles theoretical analysis of the mechanism and kinetics of methanol oxidation occurring on isolated vanadate species.

Mechanistic insights into iron porphyrin-catalyzed olefin epoxidation by hydrogen peroxide: Iron porphyrins are well known for their ability to catalyze the oxidation of hydrocarbons by hydrogen peroxide and by organic peroxides in general. While many mechanistic studies have been reported, a complete description of the reaction pathway by which the olefin epoxidation occurs has emerged only recently as a result of the work reported by the authors. The aim of this review is to present a summary of the authors' research and to place it into perspective with previously published studies. What emerges is a complete mechanistic picture for the epoxidation of olefins by hydrogen peroxide catalyzed by iron porphyrins that is consistent with all experimental evidence. Rate parameters associated with elementary processes in the reaction mechanism have been determined from experimental measurements of cyclooctene epoxide formation and hydrogen peroxide consumption as a function of the composition of the solvent, axial ligand, porphyrin, and substrate. Several notable findings emerge from this effort. The first is that only iron(III) porphyrin cations are catalytically active. These species are formed by dissociation of the neutral complex, consisting of an iron (III) porphyrin cation and an anion serving as the axial ligand, into solvated cations and anions. Weakly bound axial ligands, such as triflate anions, dissociate in aprotic solvent, whereas a protic solvent is necessary to dissociate strongly bound ligands such as chloride anions. The role of solvent composition on the dissociation of iron porphyrin complex is fully described by a model of the thermodynamics of the process. The selectivity of hydrogen peroxide towards epoxidation versus decomposition is determined by two competitive processes, heterolytic and homolytic cleavage of the O-O bond of the iron(III)-coordinated hydrogen peroxide molecule. The former process leads to the production of an iron(IV) pi-radical cation which is active for olefin epoxidation, while the later process leads to an iron(IV)-hydroxo species that is active exclusively for peroxide decomposition. A competition also occurs between olefin and hydrogen peroxide for reaction with the iron(IV) pi-radical cation species. Substrate composition does not affect the individual rate parameters as long as the olefin does not interact electronically with the iron porphyrin. Solvent alcohol coordinates to the iron(III) porphyrin in the axial position, thereby modifying the electronic properties of the iron. A second effect of alcohols is to facilitate the heterolytic cleavage of the oxygen-oxygen bond of hydrogen peroxide. The quantity, position, and electronegativity of halogen substituents attached to the phenyl groups at the meso-position of the porphyrin ring also affect the activity and selectivity of the porphyrin for olefin epoxidation. All of these effects are well explained by the mechanism that we have proposed. The rate parameters associated with the proposed mechanism vary in a systematic and physically meaningful fashion with changes in the composition of the porphyrin, the axial ligand associated with the porphyrin, and the solvent in which the porphyrin is dissolved.

Selective oxidation and oxidative dehydrogenation of alkanes: Binary dispersed oxide structures prepared by sequential deposition of VO_x and MoO_x or VO_x and CrO_x on Al_2O_3 and their structure and function have been determined using Raman and UV-visible spectroscopy and propane ODH. VO_x and MoO_x were found to mix completely and that the formation of V-O-Mo bonds resulted in a lowering in the activity of such catalysts relative to one containing only V-O-V bonds. By contrast the formation of catalysts with V-O-Cr bonds led to an increase in ODH activity and selectivity relative to catalysts containing V-O-V bonds exclusively. Further investigation was undertaken to identify the effect of the order in which VO_x and CrO_x monolayers are deposited, and to characterize the distribution of V^{5+}, Cr^{6+}, and Cr^{3+} cations present at the surface of such bilayer catalysts. NO adsorbed at 153 K was found to be quite effective for the purpose of characterizing the distribution of cations present on the catalyst surface. The highest ODH activity and propene selectivity was observed for $VO_x/CrO_x/Al_2O_3$, which exhibits a surface enriched in VO_x relative to the bulk, and which has a high fraction of the Cr present as Cr^{3+}. Work has recently been initiated on the partial oxidation of ethanol to acetaldehyde on VO_x/Al_2O_3.

Water oxidation catalyzed by oxo-bridged dinuclear Mn complexes supported on silica: Absorption of a dinuclear μ-oxo bridged Mn complex onto mesoporous silica was observed when SBA15 was treated with an acetonitrile solution of $[Mn_2O_2Cl(O_2CCH_3)(H_2O)(bpy)_2](NO_3)_2$ (**1**). Cationic $[Mn_2O_2Cl(O_2CCH_3)(H_2O)(bpy)_2]^{2+}$ is surface bound by a siloxide anion with elimination of HNO_3. Weight loadings of 1% with respect to Mn were achieved. TEM imaging of the grafted material, show the mesoporous structure of SBA15. The dinuclear complex cleanly grafts onto the SBA15; particles of manganese oxide are not observed on the scale of the TEM measurement. Diffuse reflectance UV-vis, FT-IR, and magnetism measurements confirm that the dinuclear oxo bridged unit remains *intact* after grafting. Oxygen evolution is observed for Ce^{IV} oxidation of H_2O only when **1** is absorbed onto the silica support. Isotopic labeling experiments using $H_2{}^{18}O$ confirm that O_2 is produced by the oxidation of water. Homogeneous aqueous solutions of **1** treated with a Ce^{IV} oxidant do not evolve oxygen. UV-visible spectroscopy shows that in solution **1** dimerizes and becomes inactive. Thus support of **1** on silica or oxidized graphite is essential for it to be active.

DOE Interest

This program is focused on the strategic design of novel catalysts of potential interest for the production of fuels and chemicals in an energy-efficient and environmentally acceptable fashion. Of particular interest is the development of structure-reactivity relationships via the controlled synthesis of catalytically active centers, extensive characterization of catalyst structure and evolution of catalytic properties.

Future Plans

We will continue our efforts to prepare, characterize, and investigate catalysts in which the active sites are either isolated metal oxo species or oxide monolayers. Of particular interest will be the effects of monolayers of an oxide, e.g. titania, zirconia, on the adsorptive and catalytic properties of the active species. Reaction systems to be studied include the oxidation of methanol, the oxidative dehydrogenation of low molecular weight alkanes, the selective oxidation of alkanes, and the elecrocataltyic oxidation of water. Experimental studies will be complimented by studies of active site structure and activity using quantum chemical and other theoretical methods. The aim of these investigations will be to develop a molecular-level understanding of the factors controlling the activity, selectivity, and stability of catalytically active centers.

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Creation and Characterization of Nanostructure Materials Using Atomic Force Microscopy

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The nanoscale structure of materials is critical for the design of effective catalytic systems. We have been developing methods for the nanometer scale patterning on a variety of materials including gold, silicon, glass, and mica. These methods involve the use of scanning probe microscopy techniques for the pattern formation, allowing feature sizes on the order of a few nanometers. In some cases, the vertical as well as the lateral dimensions of these materials can be tuned. These methods provide opportunities for the selective attachment and spacing of reactive species on the surface.

The effect of this nanoscale structure on a variety of materials properties is also currently under investigation in our group. The nanostructured materials described above serve as well defined templates for the investigations of the effect of the nanoscale topographic and chemical variations on properties of materials. The properties under investigation include adhesion, friction, electrical conductivity, and adsorption and activity of proteins at surfaces. By using the atomic force microscope to create the nanostructured patterns, the size, shape, and spacing of the features can be varied from a few nanometers to microns. As an example, we have demonstrated the ability to discriminate chemical different regions of the material using adhesion and friction measurements.

DE-FG02-02ER15368 C. Jeffrey Brinker

Catalytic and Transport Behaviors of Model Porous and Composite Nanostructures

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Goal

The goal of our research is the design, synthesis and understanding of model self-assembled materials whose controlled nanocomposite architecture should: a) further our understanding of how nanostructuring and nanoconfinement influence catalysis and transport and b) allow investigations of the interplay between catalysis and transport in model reactive separation systems. Materials synthesis efforts exploit our expertise in multicomponent self-assembly to form model porous and composite materials integrated into platforms allowing their structural and functional characterization and providing electronic and optical addressability. Two general classes of materials, both of which embody emerging transport or catalytic phenomena, are being investigated:

- •ordered nanocrystal/oxide arrays where in the NC size and spacing is controlled by 'bottom-up' self-assembly, and the chemical and physical nature of the catalyst/support interface is controlled by 'top down' lithography and atomic layer deposition (ALD).
- •Hierarchical structures that incorporate NC catalysts within (or in series with) controlled porosity structures to create a multi-functional reactor that integrates separative and catalytic functions, provides robustness, and may avoid poisoning/fouling.

Recent Progress A) Plasma –Assisted Atomic Layer Deposition (PA-ALD)

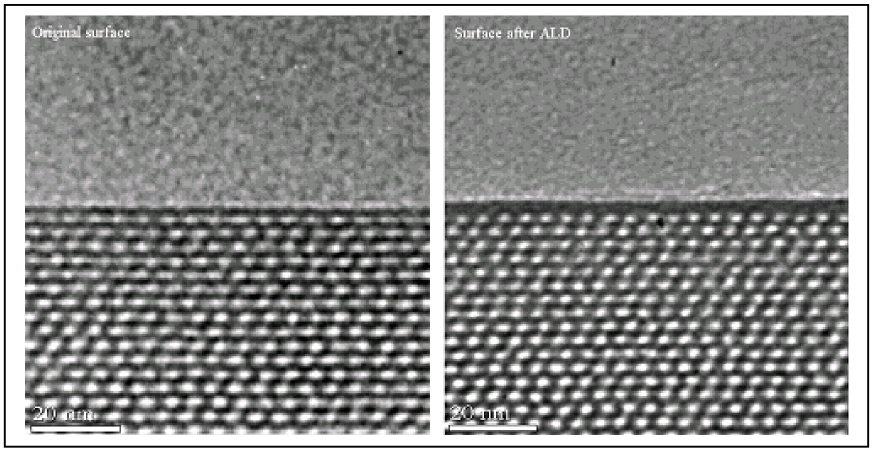

Fig. 1 - Cross-sectional TEM image of original mesoporous silica film (left) and the same film after 100 cycles of plasma-assisted ALD (right). The dark layer is a 3-nm thick film of SiO_2. PA-ALD provides a means to deposit arbitrary oxides in a layer-by-layer manner with a precision of 0.03-nm/layer!

Conventional ALD is a self-limiting conformal layer-by-layer deposition process conducted by two successive adsorption/reaction steps, e.g., $\equiv Si\text{-}OR + H_2O \rightarrow \equiv Si\text{-}OH$, $\equiv Si\text{-}OH + Si(OR)_4 \rightarrow \equiv Si\text{-}O\text{-}Si(OR)_3$. We showed previously that titania ALD performed on mesoporous silica uniformly coats the interior porosity, with a deposition rate of ~ 0.1-nm/cycle. Our newly developed plasma assisted (PA)-ALD process (*JACS*, 2006) replaces the hydrolysis activation step with an oxygen plasma step. Because the mean free path of the plasma moieties (mm) >> the pore size (nm), the creation of reactive OH sites is limited to the extreme surface (see Fig. 1) and deposition occurs exclusively there. Additionally because the plasma removes all weakly condensed species, the deposition rate is reduced to 0.03-nm/cycle but remains linear over hundreds of cycles. Conducted on a porous substrate, this new precision deposition method allows us to 'fine tune' the pore size with unprecedented control (Fig 2).

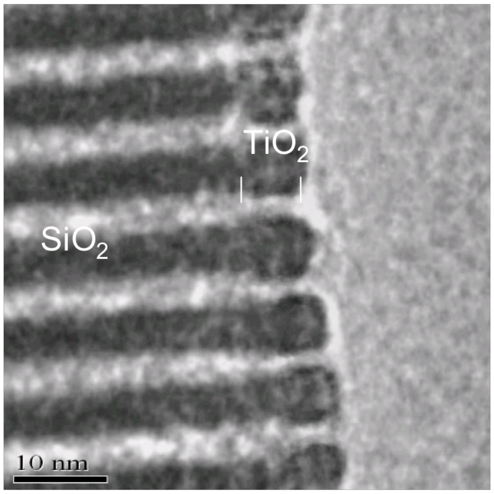

Fig. 2 - Cross-sectional TEM of hexagonally-ordered silica mesophase film after 100 cycles of TiO_2 PA-ALD. The original 5-nm diameter cylindrical nanopores (shown in cross-section - left-side) are reduced in diameter to about 2-nm in a 4-nm thick region at the surface of the film (right side). This precision sculpting of nanopores is important for control of transport and for control of catalyst/support interactions, when combined with the monolayer NC deposition technique described below.

B. Transferable Nanoparticle Monolayer Arrays –

Metallic nanoparticle (NP) arrays represent interesting model catalysts. Our prior work reported evaporation induced self-assembly of robust 3-D NP arrays embedded in silica (*Science*, 2004). However, in 3D arrays, the internal and external NPs have very different accessibilities. To create model catalyst surfaces where all NPs are equally accessible, we developed a facile route to prepare supported and unsupported NP monolayers. Our approach (Pang, CJB, unpublished) involves NP/polymer self-assembly at an immiscible interface. Resulting NP monolayers remain stable when captured on a solid or porous substrate (see Fig. 3).

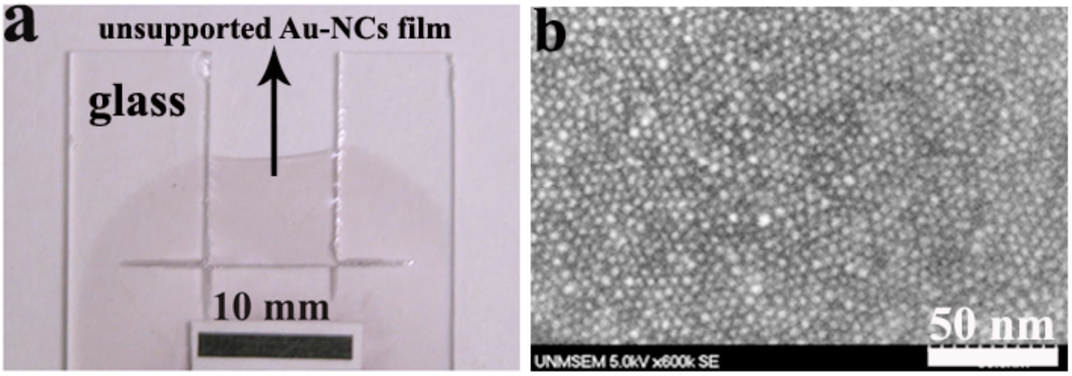

Fig. 3 a) Au NP monolayer captured on glass. **b)** HR SEM image of Au monolayer transferred to silicon wafer.

Due to their robustness, metallic NP/polymer monolayers can be transferred to arbitrary surfaces, e.g. mesoporous silica with sub-nm TiO_2, where subsequent UV/ozone or heating can de-protect the catalyst surface, and further PA-ALD steps can be used to tailor substrate interactions and potentially provide enhanced thermal stability toward ripening.

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Advanced Materials, November 4, 2005, **17**, p. 2587

FWP ERKCC50 **Gilbert M. Brown**

Nanoscale Building Blocks for Multi-Electron Electrocatalysis

Collaborators:	David R. Mullins (ORNL), Viviane Schwartz (ORNL), Peter V. Bonnesen (ORNL), Frederick V. Sloop, Jr (ORNL), Sheng Dai (ORNL), and Sharon Hammes-Schiffer (Penn. State University)
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Goal

The objective of this research project is to develop a fundamental understanding of multielectron electrochemical reactions such as the 4e$^-$ reduction of oxygen to water involving coupled electron transfer and atom transfer processes. Our approach to electrocatalysis utilizes the attachment of molecules that are selective for the reaction of interest in homogeneous solution to nanotextured conducting supports. Redox active electron donors or acceptors such as the cyclopentadienylironcarbonyl tetramer, $[(\eta^5\text{-}C_5H_5)Fe(\mu_3\text{-}CO)]_4$, that are capable of providing the multiple electron oxidizing or reducing equivalents at the required potential for near thermodynamic reversibility will mediate electron transfer between the support and the active catalyst sites such as binuclear cobalt porphyrin complexes. The kinetics and the reactivity of these supramolecular assemblies are being studied both experimentally and computationally, and we are conducting in situ XANES-electrochemistry experiments to determine the oxidation state of the electron antenna and the metal ion in the active site.

DOE Interest

The design of electrodes to efficiently carry out processes in which atom transfer accompanies electron transfer, such as the 4e- reduction of oxygen to water, is a fundamental problem in electrochemistry. This research program will provide the fundamental basis for the development of electrocatalysts with lower overpotential for oxygen reduction

Recent Progress

A molecular level understanding of multielectron electrochemical reactions that involve coupled electron transfer and atom transfer reactions will allow the design and preparation of new, efficient electrocatalysts for energy utilization and storage. The overpotential for the reduction of oxygen in fuel cells at a useful operating current density is too high because of the slow electrochemical kinetics of oxygen reduction caused by the build-up of intermediate oxidation states of oxygen. A catalyst that is active for oxygen reduction in solution will be attached to a carbon electrode with a catalyst for electron transfer. In this approach the redox active electron donor that can provide the multiple electron reducing equivalents at the required potential for near thermodynamic reversibility mediates electron transfer with the active site for oxygen reduction. Because the electron transfer catalysts will react with the conducting support with a higher exchange current density than the substrate binding site, and this catalysts will determine the electrode potential. We will use this approach to design “molecular electrodes” that are capable of carrying out multi-electron electrochemical reactions involving atom transfer in a more energy efficient manner. Fundamental theoretical and experimental scientific research is needed to understand both the reactivity of supramolecular or nanoscale assemblies that are capable of effecting selective chemical transformations driven by electrical energy and the methodology to construct these assemblies at the required density. The focus of work in this program falls within the following themes:

- preparation, characterization, and reactivity of active catalysts based on metalloporphyrin binding sites and organometallic electron exchange catalysts
- theoretical description of electron transfer coupled with atom transfer leading to the design of electrocatalysts
- in situ characterization of active electrocatalysts using X-ray spectroscopy (XANES and EXAFS)
- electrochemistry of nanostructured conducting carbon supports

Initial progress has been made in studies of monomeric cobalt porphyrins and linked cofacial biscobalt porphyrin dimers adsorbed on carbon by in situ electrochemistry-X-ray spectroscopy. EXAFS of the adsorbed catalyst gives information about the coordination site around the Co center, while the XANES band edge contains information about the oxidation state of the active site. Several new cell designs for conducting in situ electrochemistry-X-ray spectroscopy by detection of X-ray emission have been constructed and tested at the NSLS at Brookhaven National Laboratory. The XANES and EXAFS of several cobalt porphyrins that catalyze the 4e reduction of oxygen when sorbed on graphite electrodes [1] are under investigation. The XANES of a number of Fe and Co compounds were examined to determine the influence of the ligand environment as well as the oxidation state on the band edge and to determine the conditions under which changes in the band edge are a good measure of oxidation state. The band edge of iron cyclopentadienyl compounds was observed to vary little with oxidation state. The XANES of a number of Co porphyrins were examined and a combination of pre-edge features and band edge appears to be a measure of oxidation state. Figure 1 indicates that the XANES of monomeric cobalt(II) tetramethylporphyrin (CoTMP) and cobalt(II) octaethylporphyrin (CoOEP) are independent of whether the complex is adsorbed on a carbon support. A cofacial bridged cobalt porphyrin dimer (Pacman complex) [2] which was reported to catalyze the 4e-reduction of oxygen was prepared and characterized by solution electrochemistry and spectroscopy. The EXAFS of cobalt tetraphenylporphyrin (CoTPP) and CoOEP were measured and the results compared with the predictions from known crystal structures.

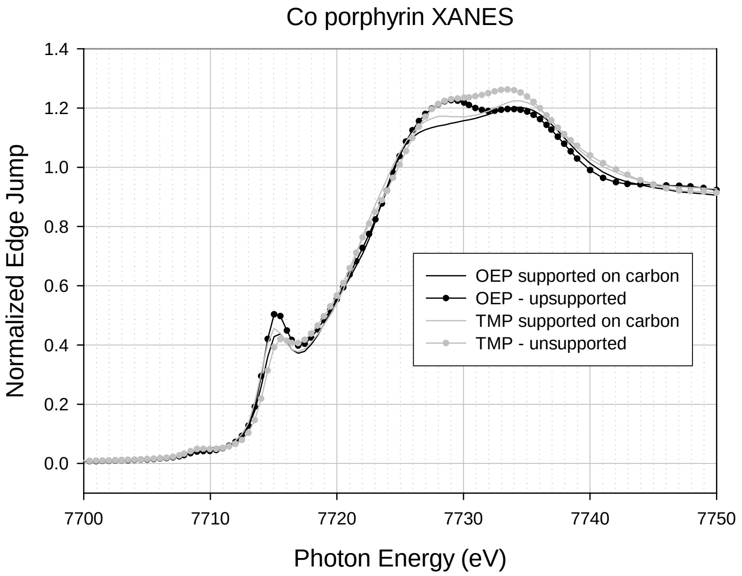
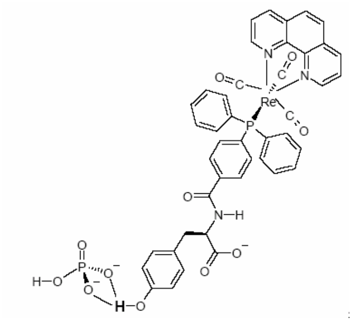


Figure 1. XANES of CoOEP and CoTMP undiluted and sorbed on carbon

The reaction chemistry of the cyclopentadienyl iron carbonyl tetramer ($[(\eta^5\text{-}C_5H_5)Fe(\mu_3\text{-}CO)]_4$) is under investigation as an electron exchange catalyst. The rate of electron exchange of the $[(\eta^5\text{-}C_5H_5)Fe(\mu_3\text{-}CO)]_4^{+/0}$ couple will be measured, and development of chemical reactions to attach the iron tetramer to the meso positions of porphyrin (either directly or with a bridging phenyl group) is in progress. The Co(II) complex of this species will be tested for catalysis of the four electron reduction of oxygen to water in comparison to an analogous ferrocene-substituted porphyrin.

The theoretical study of electrochemical reactions involving coupled electron transfer and atom transfer reactions requires an extension of our previously developed theoretical formulation for proton-coupled electron transfer (PCET) reactions. In order to assist in this extension and enhance our fundamental understanding of PCET, we have performed theoretical studies of PCET in the rhenium(I) polypyridyl system shown here. These calculations are based on the experiments of Reece and Nocera [3]. In these experiments, photoexcitation of the complex leads to a metal-to-ligand charge transfer (MLCT) excited state of the rhenium complex. This photoexcitation induces an electron transfer from the tyrosine to the MLCT excited state of the rhenium complex and a concurrent proton transfer from the tyrosine to the HPO_4^{2-} phosphate buffer or, alternatively, to a water molecule. The pH dependence of the rate for this PCET reaction has been measured experimentally. We applied our multistate continuum theory to this PCET reaction and calculated the pH dependence of the rate. Our objective was to determine if the proton is transferred to the phosphate buffer or to a water molecule. Comparison of the theoretical and experimental results indicates that the proton is transferred to the phosphate buffer. These calculations also provide insight into the detailed mechanism of this PCET reaction.



Future Plans

Experiments have been designed and theoretical studies planned to provide a molecular level understanding of multielectron electrochemical reactions that involve coupled electron transfer and atom transfer reactions. Our objective is to design and study “molecular electrodes” that are capable of carrying out multi-electron electrochemical reactions involving atom transfer in a more energy efficient manner. These supramolecular catalyst assemblies will be attached to nanotextured conducting carbon supports for demonstrating the four-electron electrochemical reduction of oxygen. A theoretical description of electron transfer coupled with atom transfer is expected to lead to the design of electrocatalysts. In situ characterization of the catalysts using XANES and EXAFS in concert with electrochemical measurements will assist in validation of models. Our anticipated research accomplishments include the following:

- Improved synthetic methods for the iron tetramer $[CpFe(\mu_3\text{-}CO)]_4$ so this species can be attached to a variety of oxygen binding sites and to the surface of carbon electrodes.
- The kinetics of the reduction of oxygen by cofacial bridged cobalt porphyrin dimers (Pacman complexes) and Co porphyrin complexes with appended proton transfer sites (Hangman complexes) with different electron acceptors will be studied by stopped-flow kinetic spectroscopy.
- Preparation of cobalt porphyrin complexes with appended electron acceptors and the kinetics of the reduction of oxygen will be measured to quantify the four-electron reduction pathway.
- Preparation of chemically modified nanostructured carbon supports and combined electrochemistry-XANES and EXAFS experiments**.**
- A theoretical understanding of the redox potential at which the four-electron reduction of oxygen proceeds at a convenient rate where oxygen and proton transfer accompany electron transfer.

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Publications

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Hydrogen Initiative: An integrated approach toward rational nanocatalyst design for hydrogen production (DE-FG02-06ER15795)

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The necessity for alternative energy solutions is motivated from increasing fuel prices, stringent emission regulations, and depleting fuel resources. The most attractive option is H_2, as it has high-energy efficiency and H_2O is the only byproduct of its combustion. Traditionally, hydrogen generation involved the use of carbonaceous substances such as methanol and methane, but the combustion of these fuels give off undesired CO_x (x = 1,2) emissions. However, one alternative is ammonia because of its high hydrogen storage capacity (17.7 %), energy density (11 MJ/kg), and the only byproduct of the decomposition is environmentally benign N_2. The decomposition reaction is endothermic ($\Delta\underline{H}$ = +46 kJ/mol) and the reaction temperature is dependent on the catalyst used [1]. Therefore, the most effective catalysts are those that maximize the decomposition efficiency at the lowest possible temperatures. To date, the best monometallic catalyst for ammonia decomposition is Ru, and this catalyst is further enhanced by the addition of alkali/alkaline earth metals [2,3]. Unfortunately, the mechanism of alkali/alkaline earth promotion is poorly understood.

Using high throughput experimentation, we have screened nearly twenty single metals and several bimetallic catalysts as a function of reaction temperature, calcination temperature, catalyst loading, inlet composition, promoter, support, and preparation solvent (~ 400 experiments). Through these experiments, we have confirmed that Ru is the best catalyst amongst all the single metal and bimetallic combinations tested. Furthermore, we have optimized the catalyst further by adding 12 wt% K to a 4 wt% Ru catalyst. This addition of K provides an additional increase of ~35% in NH_3 decomposition efficiency at 350ºC.

To better understand the enhanced decomposition efficiency, advanced characterization via FESEM and FETEM has been completed on the K-promoted Ru catalyst. Using high spatial resolution, we hope to obtain a clear microscopic picture of the catalyst that will help provide insight towards the mechanism of K promotion. Initial FESEM experiments on the pure Ru catalysts have revealed 20-100 nm particles. However, on the K-promoted catalyst, we discovered nanowhiskers that have 20-50 nm diameters and lengths ranging from a few nm to several microns. Selected-area electron diffraction shows that these whiskers have a KRu_4O_8 hollandite structure. We believe that this structure is responsible for the enhanced decomposition behavior and a necessary component of our catalyst. FESEM analysis completed before and after reaction shows that the K-promoted catalyst undergoes significant morphological changes during the reaction, but that the activity is maintained. This observation suggests that the hollandite may be a structural intermediate that aides in dispersion of K and Ru throughout the catalyst. Although the exact nature of the KRu_4O_8 hollandite is not yet known, these results appear to be the first identification of this structure in an ammonia decomposition catalyst and a first step towards understanding the role of K in Ru catalysts supported on Al_2O_3.

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DOE GRANT # DE-FG02-96ER14630 **Charles T. Campbell**

Oxide Supported Metal Nanoparticles: Catalytic Properties and Energetics

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Goals

In order to provide the energy needed for sustained industrial and economic development without causing serious environmental problems for human health, we must develop more efficient processes for a variety of chemical conversions. Catalysts consisting of metal nanoparticles supported on oxides hold great promise for many of these processes. We pursue a combined experimental and theoretical research program whose goal is to provide the basic understanding needed to develop and improve new catalysts for these important reactions. Specifically, we prepare model catalysts consisting of structurally well-defined metal nanoparticles supported on single-crystalline oxide surfaces, measured their reactivity and their sintering kinetics, and correlated these with the lateral diameter, thickness and composition of the metal nanoparticles and the structure of the oxide support surface upon which they sit. We compare these results with theoretical simulations of the growth and sintering of oxide-supported metal clusters.

Recent Progress

Earlier, we developed a unique adsorption microcalorimeter that can measure the enthalpies of the metal atoms in these nanoparticles on single-crystal oxides, or of small adsorbed molecules (or their dissociation products) on these nanoparticles, and determine how the particle size and support affect these enthalpies. We recently improved our calorimeter detection sensitivity considerably, and added other experimental capabilities (ion scattering spectroscopy and work function measurement) to our metal adsorption calorimeter. These adsorption energies provide the key thermodynamic underpinnings needed to help correlate materials' structure with catalytic function and sintering resistance.

Some of our recent findings include: (1) characterization of the nature of the defects on MgO(100) surfaces which stabilize transition metal nanoparticles in catalysis, by using Ca and Li as easy-to-model probe atoms that populate these defect sites with a very probability and high heats of adsorption; for comparison to Density Functional Theory (DFT) modelling by our collaborator, Graeme Henkelmann (UT Austin) (2) a kinetic Monte Carlo simulation of the growth and sintering of Pd clusters on MgO(100), based on DFT energetics, in collaboration with Henkelmann; (3) full derivation of a new atomistic kinetic model for catalyst sintering that is better than any model previously developed, and its application to simulate sintering of Au on $TiO_2(110)$; (4) initiation of strong collaborations for research in this area with one of the best surface science groups in Germany (H.J. Freund) and with scientists at the Institute for Interfacial Catalysis at Pacific Northwest National lab; (5) theoretical proof that a novel class of transition metal oxides must exist on the surface of transition metal catalysts that are thermodynamically stable at catalytic reaction conditions where the bulk oxide of that metal could not even exist; (6) highly accurate measurements of the activation energies and rate constants for desorption of alkanes on Pt(111) and graphite surfaces; (7) discovery of a versatile approach for generating core – shell nanoparticles with the core being silica or a polymer and the shell being a dense coating of single-crystalline Pt nanowires that extend radially in their <111> direction from the surfaces of the spherical core; and, (8) development of a new apparatus for transient kinetics / mechanistic studies on powdered catalysts at pressures up to several atmosphere. We also wrote a review article about high-throughput analysis of biomolecular binding events with SPR microscopy and microarrays, describing some of our earlier DOE-funded work.

DOE Interest

Solid catalysts improve energy efficiency during the processing of fuels and other chemicals, and reduce the corresponding production of pollutants and other undesirable side products. They also are effective at post-production cleanup of pollutants and the destruction of environmentally hazardous chemicals. Thus, solid catalysts promise to play the dominant role in future progress toward cleaner and more efficient fuels, chemicals and automotive industries. Results in our lab and others show that the catalytic activity and selectivity of transition metal particles supported on the surfaces of ceramics (oxides, carbides) can be tuned with their size below 10 nm. Thus, controlling nanoparticle size will provide an important method for improving catalyst performance if we can learn through these studies: (1) how and why metal particle size affects catalyst activity and selectivity, and (2) how to maintain catalyst particles at their optimum size for extended periods while running chemical reactions. Also, the adsorption calorimetry techniques we develop here are not available elsewhere in the world and will facilitate future basic research in this arena, as well as in all areas of surface science.

Future Plans

We have recently mounted a Pt(111) sample in our adsorption calorimeter and grown ordered $CeO_2(111)$ thin films on it. We will soon start measuring adsorption energies on this more reactive model catalyst support. One of the graduate students on this project will spend four months at the Frtiz Haber Institute in Berlin helping to develop a similar adsorptioncalorimeter there for collaborations with H. J. Freund’s group, and one of Freund’s group leaders will spend four months here learning how to repair and operate our calorimeters, for this collaboration.

Publications 2005-7

Sole funding by DOE-BES and this particular grant:

1. Growth and Sintering of Pd Clusters on α-$Al_2O_3(0001)$, by L. T. Ngo, S. L. Tait, Q. Yu, S. C. Fain, Jr., and C. T. Campbell, J. Chem. Phys. 122, art. 064712, 2005.
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4. A Kinetic Model for Sintering of Supported Metal Particles with Improved Size-dependent Energetics, and Applications to Au on TiO_2(110), S. C. Parker and C. T. Campbell, Phys. Rev. B (in press).

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5. Pyroelectric heat detector for measuring adsorption energies on thicker single crystals, S.F. Diaz, J.F. Zhu, N. Shamir, and C. T. Campbell, Sensors and Actuators, B 107, 2005, 454-460.
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DE-FG02-05ER15730 Siu-Wai Chan

Nanostructured, metal-ion modified ceria and zirconia oxidation catalysts

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Goal

The overall goal of this project is to elucidate the role of metal ions and metal clusters as catalytic sites on nanoscale oxide supports, and the role of oxide defects in stabilizing the metal species in an active state for reactions of interest to fuel reforming for hydrogen generation. Earlier the MFS's group at Tufts University found that the activity of ceria-supported gold or platinum catalysts for the water-gas shift reaction is not due to metal nanoparticles; rather, [Au_n-O-Ce] or [Pt_n-O-Ce] sites are responsible for the reaction activity. Novel synthesis (with size and facet control) and characterization methods are investigated and guide the design and development of practical catalysts for low-cost hydrogen production.

Recent Progress

Since the project start in late 2005, progress has been made on several fronts. On the catalysis side at Tufts University, a new method was identified to stabilize the activity of Au- and Pt-ceria catalysts for the water-gas shift reaction in cyclic start-stop operation, and after shutdown to ambient conditions.[2] This is achieved with the addition of a very small amount of gaseous oxygen in the fuel gas mixture that keeps the cerium oxide from forming Ce (III)hydroxycarbonate and deactivate.

At Columbia, the investigation of Ce-Zr-O phase stability as a function of nanoparticle size has come to a satisfactory conclusion. It was found that the stability range of ceria cubic solid solution extends to 90% ZrO_2 when crystallite size is small enough and when annealed in a reducing atmosphere[3, 4]. In particular, large amount of Ce3+ ions are found in these binary nano oxide particles. Further work will focus on correlating the 600cm^{-1} Raman peak, identified with oxygen vacancies, with the Ce^{3+} concentrations measured by XANES for pure ceria of different particle size and for Ce-Zr-O with different Zr content. With proper processing, pure nano ZrO_{2-y} can be maintained in cubic form. The amorphous to cubic transition was captured in a time-resolved in-situ X-ray diffraction[4]. We are interested to follow thorough with Au and Cu modified to these ZrO_{2-y} , Ce-Zr-O cubic phase nanoparticles for catalytic activities.

We have recently shown the importance of the interaction between gold or platinum and the oxygen of ceria by identifying that only the oxidized gold or platinum species strongly bound to ceria, [Au_n-O-Ce] or [Pt_n-O-Ce], are the active sites for the WGS reaction[5-7]. We have evaluated different catalyst preparation techniques to maximize the number of M-O-S sites. Firstly, among various synthesis methods (IMP, DP and UGC), the UGC method was found the best for the preparation of nano-ceria (3 nm particle size) with more oxidized Pt species strongly bound to it, as evidenced by XPS and H_2-TPR.[8] A high stability of Pt/CeO_x in realistic reformate gases was found, unlike what has been reported in the literature[9]. In the same paper, oxygen gas addition

(~1mol%) in the reformate gas mixture was shown to effectively prevent the deactivation of the $PtCeO_x$ catalysts during RT shutdown/re-start cycles.

Secondly, we found that the dry CO oxidation reaction is much more facile on Au^o than on oxidized gold clusters in $Au-CeO_2$ catalysts. In collaboration with the group of Flora Boccuzzi, U. Torino, we found by FTIR that CO binds stronger on Au^o than on the Au_n^+ clusters[10]. XANES, TPR and XPS of the fresh and used catalysts were performed to demonstrate the high stability of ionic gold in ceria up to 393 K in the reaction gas.

In the literature, most catalysts incorporating Au^o also contain cationic gold and it is very difficult to separate the function of the one from the other. In work carried out at Tufts last year[11], we were able to prepare the low-content gold catalysts with only oxidized gold species strongly bound to both supports (iron oxide and ceria). As shown in Fig.2, the activity of the leached gold-iron oxide in CO oxidation is two orders of magnitude lower than that of the parent material. Once reduced, the catalyst activity increases more than 100 times. XANES, XPS, TPR and UV-Vis analyses show that reduction is needed to activate the catalyst. On the other hand, the WGS reaction rates are similar for samples containing both Au^o/Au_n^+ or Au_n^+ clusters only.The activation energies are the same, 49±7 kJ/mol, for Au on ceria or iron oxide. Thus, activation of OH from the oxide support by the strongly bound CO on $Au^{\delta+}$ sites is a plausible mechanism for this reaction.

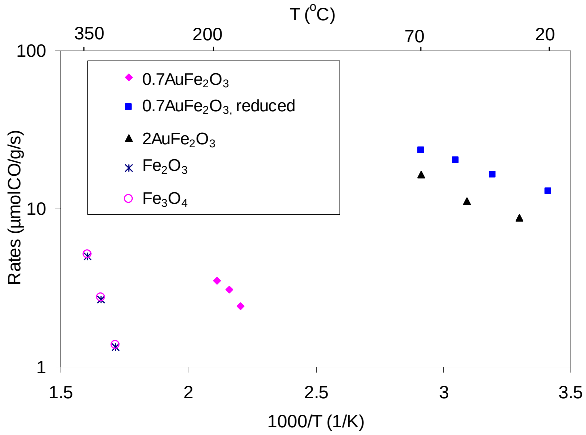
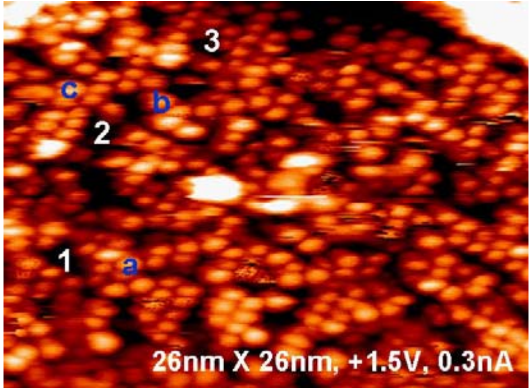


Figure 1. Steady-state CO oxidation reaction rates over gold-iron oxide catalysts measured in a gas composed of $2\%CO-1\%O_2$-balance He[11].

Raman spectra were obtained at RT in air by Ar ion excitation (488 nm). A strong peak at ~460 cm^{-1}, a weak one at ~820 cm^{-1} and another weak band at ~600 cm^{-1} are seen, assigned to bulk oxygen, surface-adsorbed peroxide and oxygen vacancies, respectively[13]. We have observed strong correlation between the intensities of the band at ~600 cm^{-1} and Ce3+ concentration by XANES in both Ce-Zr-O and Ceria nanoparticles. In situ Raman under WGS reaction conditions will identify the importance of different oxygen species.

STM/STS studies currently underway at Columbia on both CeO2 single crystals, thin films and Fe3O4 (111) crystals. The following is a STM picture of Fe3O4 (111) crystal with below 0.1 ML of Au where isolated Au adatoms were observed.

Fig. 2 (a)



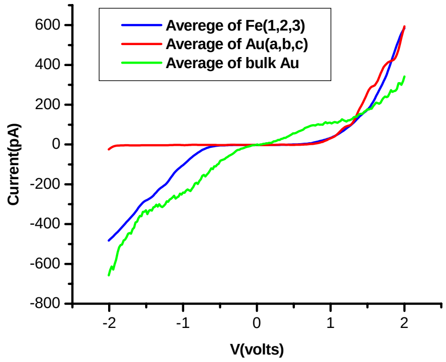


Fig. 2 (b)

Fig.2a Some isolated gold adatoms make an ordered array on the surface. These gold atoms show different electronic structure in I(V) curves as shown in Fig. 2b.
Fig. 2b I(V) curves from SPS: Red curve for single gold atoms (a, b, c), Blue curve for substrate Fe atoms (1, 2, 3), green curve for big gold nanostructure.

DOE interests

Traditional catalysts used for the water-gas shift and other fuel processing reactions in the production of clean hydrogen must be replaced in order to meet the more stringent requirements of practical fuel cell systems, including air and moisture stability, resistance to poisons, no methanation activity, and longevity required for efficient energy production. Platinum group metals are being brought into this area of catalysis to meet these requirements. Successful demonstration and development of our technology will overcome the cost associated with implementation of platinum metal catalysts on a large scale. This will be accomplished by designing catalysts with a minimum loading of gold, copper or platinum, in amounts dictated by the surface properties of the oxide support, and with potentially higher stability for the practical application than the current generation of catalysts.

Future Plans

We aim at the design and evaluation of novel oxidation catalysts based on nanoscale ceria and doped cerium oxide carrying metal ions and clusters strongly bound on the surface and subsurface layers of the oxide matrices. A well-controlled synthesis of monodispersed ceria nanoparticles[1], and zirconia-ceria nanoparticles also yielding a significant fraction of Ce^{3+} developed at Columbia University, is under investigation to produce suitable active support for the Cu, Au and

Pt ions. For pure ceria, it is a solution process at room temperature resulting in single crystals of ceria octahedra with (111) surfaces, or truncated octahedra with extra (100) surfaces. The (100) surfaces are known to have more intrinsic oxygen vacancies due to charge balance. The vacancies can stabilize the added metal ions and readily participate as sinks and sources of oxygen in catalytic redox reactions. For preparation of ceria-zirconia nanoparticles additional annealing is needed to homogenize the samples resulting in spherical nanoparticles exposing high hkl surfaces. Particles with special surface planes will be exploited in this project to answer some of the fundamental questions. A number of key analytical techniques, such as *in situ* Raman and UV-VIS (DRS), HREM, and STM/STS, are used to characterize surface metal cluster-oxygen defect complexes, to follow catalyst structural changes, and correlate them to reactivity. The reactions under study at Tufts include the water-gas shift reaction, selective CO oxidation, and steam reforming of methanol, all important reactions in hydrogen generation. Time-resolved XAS, in situ XANES and EXAFS experiments will be performed at Brookhaven National Lab under the direction of senior researchers J. Rodriguez, S. Khalid and J. Hanson. Lastly, in-situ experiments will be used to study the evolution of noble metal ions under reaction conditions.

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Publications acknowledging the grant or contract: Refs. 2, 3, 4, 7, 9, 10, 11 from the above list acknowledge the DOE-HFI grant.

DE-FG02-05ER15688

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Dedicated Beamline Facilities for Catalytic Research – Synchrotron Catalysis Consortium (SCC)

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Goals:

The mission of the Synchrotron Catalysis Consortium (SCC), which is the first of its kind in the US, is to promote the utilization of synchrotron techniques for cutting-edge catalytic research under in-situ conditions. These tasks are performed by a consortium consisting of PIs and co-PIs from academic, national, and industrial laboratories. The beamlines and supporting facilities that SCC members acquired and built are located in the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratories. The PIs and co-PIs have extensive experience in the areas of catalysis, electrocatalysis, advanced materials, and synchrotron spectroscopies. A primary goal of the SCC team is to provide assistance and to develop new sciences/techniques to the catalysis community through the following concerted efforts:

- Dedicated beamtime on two X-ray Absorption Fine Structure (XAFS) beamlines
- Dedicated facilities, including state-of-the-art *in-situ* reaction cells, gas-handling systems, and advanced detectors
- A dedicated research staff to assist the experimental set-up and data analysis
- Training courses and help sessions by the PIs and co-PIs
- Development and test of new hardware and software for catalytic and electrocatalytic research

Recent Progress:

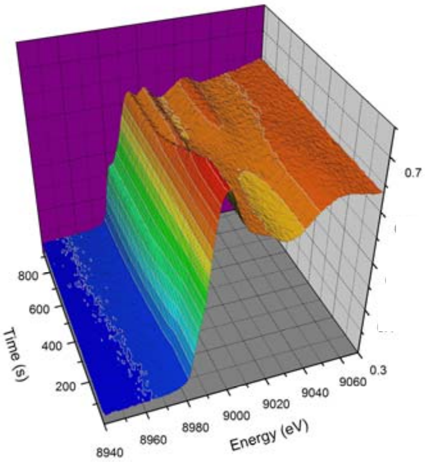
In the first year of existence the SCC has made significant progress and helped over 40 catalysis groups from academic institutions and national laboratories; the SCC has also attracted 10 new catalysis groups from US institutions: UIUC, Colorado State Univ., Univ. of Washington, Univ. Tennessee, Univ. Texas (Austin), Kent State Univ., SUNY Stony Brook, Univ. Vermont, Univ. New Mexico, and Univ. Wisconsin. During the past three cycles we have provided assistance to 128 catalysis users on the X18B and X19A beamlines, which accounted for 58% of all users on the two beamlines. The SCC beamline staff person, Dr. Ned Marinkovic, provided assistance to the catalysis GU groups in many ways, including training the students/postdoc, setting up dedicated reactors and gas-handling systems, and providing experimental assistance when needed. The SCC PIs and staff have provided training to new catalysis users. A. Frenkel gave on-site help 2-3 days a week, and consulted visiting groups on issues ranging from data analysis to planning XAFS experiments. SCC members have organized several training courses and workshops:

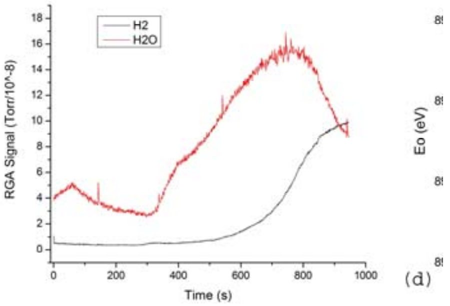
1) XAFS Analysis Course: Applications to Nanocatalysis and In Situ Chemical Transformations, NSLS, Oct. 19-21, 2006

2) Workshop on Synchrotron Catalysis Consortium: New Opportunities for in-situ Studies of Nanocatalysis, NSLS, May 16, 2006

3) EXAFS Course: Theory, Experiment, and Advanced Applications, NSLS, September 28-30, 2005

The catalysis GU groups are from academic, industry, and national laboratories. They include Argonne National Lab, BNL, Boston College, Case Western Univ., Colorado State Univ., George Washington Univ., Hunter College, Kent State Univ., Northeastern Univ., NRL, ORNL, PNNL, SUNY Stony Brook, Tufts Univ., Univ. Alberta, UC Berkeley, UC Davis, US Santa Cruz, Univ. Delaware, Univ. Illinois, Univ. Kentucky, Univ. Madrid, Univ. New Mexico, Univ. South Carolina, Univ. Tennessee, Univ. Texas, Univ. Vermont, Univ. Virginia, Univ. Washington, Univ. Waterloo, Univ. Wisconsin, UOP, Virginia Tech, and Yeshiva Univ.





New instrumentation for catalysis research: SCC team lead R&D effort on commissioning, testing and operating the new, dedicated Quick XAFS (QXAFS) facility which is one of its kind in US (see Figure). Quick scanning is enabled by an assembly containing a micro-stepping motor, a rotating cam that moves the monochromator tangent arm. Data can be collected with 1 scan per second rate or better, providing novel opportunities for catalysis research. Coupled with residual gas analysis system that we custom designed and built at the both beamlines, as well as an automated gas input and gas purification systems, QXAFS/RGA combination offers novel opportunities for *in situ* catalysis research. The Figure shows recently collected data during the reduction of Cu/ceria catalyst with 5% H_2 at 300 ^{o}C – by these PI's. Data analysis software was developed by the SCC summer research intern, N. Hould.

DOE Interest: The availability of well-maintained, user-friendly and state-of-the-art synchrotron facilities, as provided by SCC, should help a large number of catalysis and electrocatalysis groups in their efforts to perform cutting-edge beamline research. The SCC also provides a new model for operating synchrotron facilities; such odel demonstrates a closer interaction between funding agencies, beamline scientists and external researchers. The closer interaction should lead to the more efficient utilization of the synchrotron facilities, which ultimately benefits the nation as a whole by increasing the return on the investments made in our national laboratory system. As stated earlier, similar types of synchrotron consortium for catalysis currently exist in Europe and Japan. *The current consortium represents a critical first step for the catalysis community in the United States to remain competitive in catalytic and electrocatalytic research using synchrotron techniques.*

Publications Acknowledged Current DOE Grant (2005-2007): Overall there are over 40 publications. Below is a selected list of publications:

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DE-FG02-97ER14751 **David F. Cox**

Hydrocarbon Dehydrogenation and Oxidation over Model Metal Oxide Surfaces

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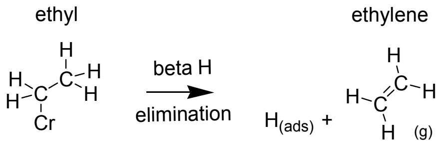
Goal

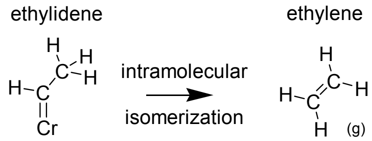
Develop an understanding of structure/function relationships in alkane oxidation and dehydrogenation chemistry over catalytic metal oxide surfaces.

Recent Progress

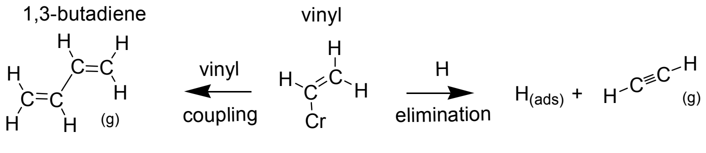
Our recent work has focused on the reactions of hydrocarbon fragments on chromium oxide surfaces in an attempt to understand the relationship between specific surface intermediates and reaction selectivity in small alkane dehydrogenation. α-Cr_2O_3 $(10\bar{1}2)$ has been used as a model chromia surface, and has been the platform for the study of a wide variety of C1 and C2 hydrocarbon fragments that are likely surface intermediates in the oxidation and dehydrogenation of methane and ethane. Alkyl and alkenyl halides have been used to generate specific hydrocarbon fragments for this study. We have shown that the formation of oxygenated products occurs in the presence of terminal chromyl oxygen (Cr=O) on the oxygen-terminated $(10\bar{1}2)$. In contrast, the stoichiometric surface is nonreducible, and the only gas phase carbon containing products produced in thermal desorption studies are hydrocarbons.

Reaction of C2 Alkyl Fragments over α-Cr_2O_3 $(10\bar{1}2)$. The reactions of ethyl and ethylidene fragments have been examined. Ethyl fragments bound at surface chromium cation sites form ethylene via a simple β hydride elimination. In thermal desorption the liberated hydrogen combines with other surface species to form ethane and H_2. Etylidene appears to form ethylene via an intramolecular isomerization process. No evidence for the release of H atoms (H_2) to the surface is observed in thermal desorption. Reactions of ethylidyne have not yet been examined.

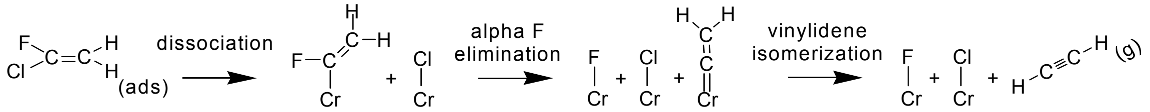




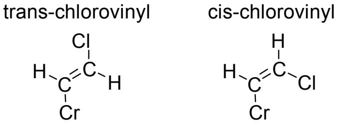
Reaction of C2 Alkenyl Fragments over α-Cr_2O_3 $(10\bar{1}2)$. The reaction of vinyl groups occurs via two parallel pathways with the selectivity dependent on surface halogen coverage. Dehydrogenation to acetylene, and coupling to 1,3-butadiene are the predominant reaction pathways.



Vinylidene can be formed via dissociative adsorption of both 1,1-dichloroethylene and 1-chloro-1-fluoroethylene. Photoemission suggests a concurrent C-Cl bond cleavage at low temperatures for the dissociation of 1,1-dichloroethylene to vinylidene, but provides evidence for some sequential C-X bond breaking with an α-fluorovinyl intermediate enroute to vinylidene from 1-chloro-1-fluoroethylene. Similar to the observations for ethylidene, the vinylidene carbene undergoes an apparent intramolecular isomerization to acetylene.



The reaction of cis- and trans-1,2-dichloroethylene was examined to determine the effect of halogen orientation on the formation of acetylene from surface vinyl species through a β-chlorine elimination route. The barrier to β-chlorine elimination is the same on the clean, stoichiometric surface, but at high surface halogen coverage a high temperature elimination channel appears for the trans-chlorovinyl intermediate. Hence, for the surface ensembles with chlorinated neighboring surface Cr atoms, the proximity of the β-Cl to the surface has a significant impact on the barrier to elimination.



DOE Interest

Process chemistries for the conversion of alkanes to alkenes and selectively oxygenated products can utilize lower-cost feedstocks and offer a more versatile usage of petrochemical resources.

Future Plans

Work is currently in progress on the characterization of the α-Cr_2O_3 (0001) surface. This surface will be used to examine surface structure effects and the impact of lower Cr^{3+} cation coordination number on the surface chemistry of C1 and C2 hydrocarbon fragments. Similar chemistry will also be examined over the isostructural α-Fe_2O_3 $(10\bar{1}2)$ surface to examine the impact of electronic differences of the cations on the observed surface chemistry.

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DE-FG02-05ER15683 **Richard M. Crooks**

Understanding Multimetallic Catalysts using Dendrimer-Encapsulated Nanoparticles

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Postdoctoral Fellows: Marc Knecht, Heechang Ye
Collaborators: Douglas Buttrey (U. Delaware), Anatoly Frenkel (Yeshiva U. and the National Synchrotron Light Source), Graeme Henkelman (UT Austin), Valeri Petkov (Central Michigan U. and the Advanced Photon Source)
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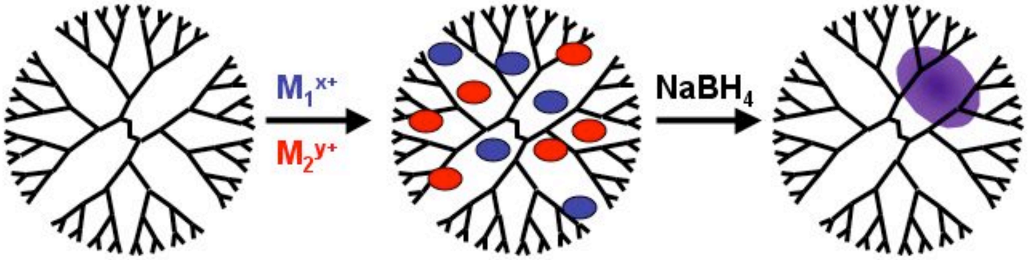
Goal

Synthesize and characterize structurally well-defined bimetallic nanoparticles using a dendrimer templating approach, and then evaluate their homogeneous catalytic properties as a function of size, composition, and structure.

Recent Progress

Atomic-level characterization of bimetallic alloy PdAu dendrimer-encapsulated nanoparticles: Palladium-gold dendrimer-encapsulated nanoparticles (DENs) having a bimetallic alloy structure were prepared using metal-ion co-complexation and reduction inside the interior void space of a generation-six, poly(amidoamine) (PAMAM) dendrimer (Scheme 1). The ratio of the two metals was controlled by adjusting the stoichiometry during the first step of the synthesis. This resulted in particles having the composition G6-OH(Pd_xAu_{147-x}), where x =118, 87, 73, 60, and 29. These materials were then analyzed using extended x-ray absorbance fine structure (EXAFS) spectroscopy. The results indicated that the particles were pure alloys regardless of the metal concentrations (Figure 1). Also, the level of interaction between the nanoparticle surface and the dendrimer was below the detection limit of the EXAFS experiment, indicating

Scheme 1



that a large percentage of the surface metal atoms are freely exposed and available for catalysis.

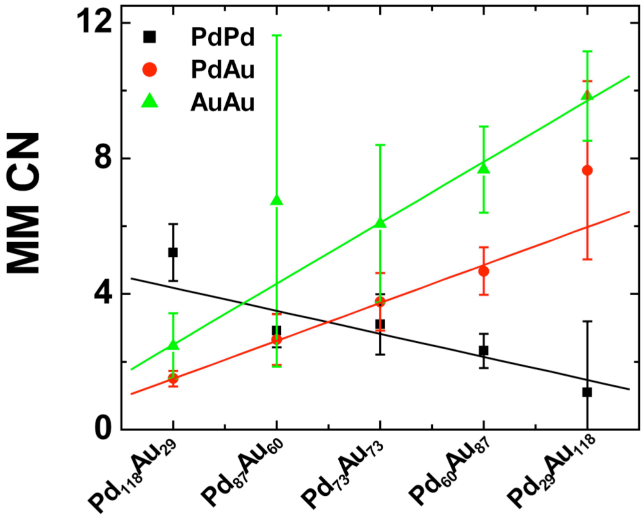


Figure 1. First nearest neighbor metal-metal coordination number (MM CN) analysis for the PdAu alloy DENs. The black plot indicates a decrease in the number of PdPd coordinations as the concentration of Pd per particle decreases while an increase in the AuAu coordinations increases with increasing Au concentrations. The number of Au atoms surrounding Pd atoms in the particle increases with the Au concentration per particle increases as expected. Such events are attributes of the random alloy structure.

Extraction of the DENs from within the dendrimers, using a microemulsion based technique, resulted in the formation of organically soluble bimetallic PdAu monolayer-protected clusters (MPCs). Dodecanethiol was used as the extractant and surface passivant in this experiment. EXAFS analysis of the extracted MPCs indicates that they consist of a Au core and Pd shell (Figure 2). Thus, we have observed an usual situation wherein the (thiol) ligands drive the conversion of the particle from an alloy to a core/shell structure. Interestingly, no Au-thiol interactions are observed until the number of Au atoms within the particle is sufficient to exceed the maximum number permitted in the core (this situation is relevant for G6-OH($Pd_{29}Au_{118}$)). For particles having lower Au number densities, only Pd-thiol interactions are observed.

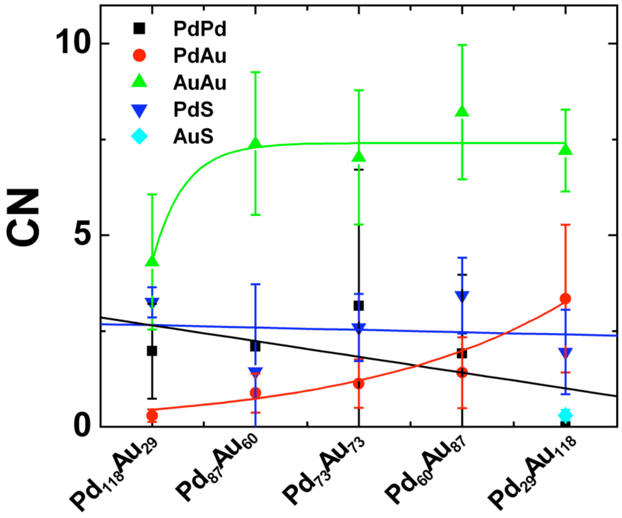


Figure 2. EXAFS analysis of the dodecanethiol stabilized PdAu MPCs. Identical data acquisition and fitting analyses were used as for the DEN templates. The results indicate that extraction results in a Au core/Pd shell particle. The surface is passivated by thiols, typically interacting with the Pd atoms on the surface. Additionally, a Pd-S complex that is free in solution is produced as is evidenced by the relatively large Pd-S coordination numbers.

DOE Interest

The dendrimer templating approach is an effective route to the synthesis of chemically and structurally well-defined bimetallic catalytic nanoparticles. We envision that these materials will provide excellent experimental models for developing the next generation of catalytic materials. The partnerships with Grame Henkelman at the University of Texas, Douglas Buttrey at the University of Delaware, Anatoly Frenkel at Yeshiva University (NSLS), and Valeri Petkov at Central Michigan University (APS) allows us to guide future development of highly selective bimetallic catalysts according to theoretical models and study their structural and catalytic properties in depth.

Future Plans

Our long-term objective is to correlate the structure of these bimetallic DENs to their catalytic function. This requires extensive characterization efforts. We are presently focused on completing our study of the interesting ligand-driven structural rearrangement of the PdAu DENs and also EXAFS, XRD, and HRTEM studies of monometallic Pt and Au DENs. Next, we plan to prepare a series of PdM (M = Ni, Co, and Mo) bimetallic DENs. These materials present unique synthetic and characterization challenges, because Ni, Co, and Mo are susceptible to oxidation in solution. However, theory suggests that bimetallics having these core metals and Pd shells should behave like Pt in some cases.

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- R. W. J. Scott; C. Sivadinarayana; O. M. Wilson; Z. Yan; D. W. Goodman; R. M. Crooks "Titania-Supported PdAu Bimetallic Catalysts Prepared from Dendrimer-Encapsulated Nanoparticle Precursors" *J. Am. Chem. Soc.* **2005**, *127*, 1380-1381.
- O. M. Wilson; R. W. J. Scott; J. C. Garcia-Martinez; R. M. Crooks "Synthesis, Characterization, and Structure-Selective Extraction of 1-3 nm-Diameter AuAg Dendrimer-Encapsulated Bimetallic Nanoparticles " *J. Am. Chem. Soc.* **2005**, *127*, 1015-1024.
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Computational Studies of Oxidative Dehydrogenation

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The selective catalytic oxidation of hydrocarbon molecules in nanoporous membranes is being studied using electronic structure methods. This work is coupled with experimental studies that use a combination of anodic aluminum oxidation and atomic layer deposition for fabricating ultra-uniform catalysts. We report on recent progress in computational simulations of the structure and properties of catalytic clusters and reaction mechanisms.

We have calculated the geometries and vibrational frequencies of a variety of monomeric, dimeric, and tetrameric VO_x structures on a TiO_2 support using B3LYP density functional theory. We find the most stable VO_x species to be the “molecular” monomer or dimer structures, which consist of VO_4H_3 or $V_2O_7H_4$ molecules that graft onto the TiO_2 surface while maintaining 2 or 4 V-O-H bridges. The vibrational frequencies of the clusters are compared to previous experimental studies to help in identifying the type and shape of the clusters. The effect of hydration by water on the vibrational frequencies is also investigated. We use the models described above for the catalytic sites to calculate possible reaction pathways for propane oxidative dehydrogenation. To better understand the catalyst-support interaction, we also calculated analogous reaction pathways for propane ODH on the VO_4H_3 and $V_2O_7H_4$ gas phase molecules. Comparisons between the results obtained using gas phase and supported molecular catalysts have helped us determine the influence of the support on the ODH reaction kinetics and find key parameters. As a part of this study we have also investigated the dependence of the results on the density functional calculational method used including plane wave methods. Significant differences for activation barriers (as much as 1 eV) have been found for some of the methods. We have resolved the differences through high level CCSD(T) calculations for some small model systems. Finally, we will present initial results for ODH on VO_x structures on a Al_2O_3 support.

DE-FG02-95ER14549 **Robert J. Davis**

Structure and Function of Supported Base Catalysts

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Students: Junhui Li (Cummins), Jianren Tai (Intel), Yuanzhou Xi, Erin Maris, William Ketchie (Maris and Ketchie are contributors, with only partial support from the project)

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Goal

Solid bases are heterogeneous catalysts that have not been broadly exploited compared to solid acids. Thus, the broad goal of the work is understand how atomic structure and composition affect the reactivity of surface oxygen atoms on supported basic compounds and transition metals.

Recent Progress

Basic Zeolites as Oxidation Catalysts

As a follow-up to our on-going studies of the basic zeolites as catalysts, we investigated the molecular processes involved in low temperature oxidation reactions inside the pores of basic zeolites. Zeolites X and Y exchanged with Group IA cations were evaluated as catalysts in the oxidation of H_2 and CO at temperatures ranging from 473 to 573 K. The CsX zeolite was the most active material of the series for both reactions whereas HX was the least active. Moreover, the selective oxidation of CO in H_2 was very selective (~80%) over the alkali-metal exchanged materials. Isotopic transient analysis of CO oxidation during steady state reaction at 573 K was used to evaluate the coverage of reactive carbon-containing intermediates that lead to product as well as the pseudo-first order rate constant of the reaction. A factor of 4 enhancement in activity achieved by exchanging Cs for Na was attributed to a higher coverage of reactive intermediates in CsX since the pseudo-first order rate constant was nearly same for the two materials (~0.7 s^{-1}). The number of reactive intermediates on both materials was orders of magnitude below the number of alkali metal cations in the zeolites, but was similar to the number of impurity Fe atoms in the samples. Since the trend in Fe impurity loading was the same as that for oxidation activity, a role of transition metal impurities in zeolite oxidation catalysis is suggested.

Aldol Condensation over Acid-Base Bifunctional Materials

A variety of catalysts consisting of MgO, SiO_2, Al_2O_3 and ZrO_2, with and without added cesium, were evaluated in the aldol condensation of propionic acid with formaldehyde to produce methacrylic acid. Stepwise TPD of pre-adsorbed NH_3 and CO_2 was used to estimate the number and strength of surface acid and base sites, respectively. Both a strong solid base such as MgO and a non-basic solid such as SiO_2 were ineffective at catalyzing the aldol condensation reaction. However, Cs-loaded silica and alumina exhibited moderate activity and high selectivity for the reaction. Results from reactivity measurements and surface characterization suggest that both acid and base sites are needed to catalyze the reaction, and the observed rates over the bifunctional ZrO_2 catalyst support this hypothesis. A reversible inhibition of the rate by added water was observed over Cs-SiO_2 and is attributed to migration and agglomeration of the cesium on the support in the presence of water.

DOE Interest

The work performed in this program elucidates fundamental principles important in the design of basic and base-promoted catalysts. Solid bases are environmentally-benign alternatives to corrosive liquid bases.

Future Plans

The project has evolved to include explorations of the base-catalyzed conversion of renewable feedstocks to fuels and chemicals. In particular, we have begun exploring the transesterification of tributyrin with methanol over calcined and rehydrated hydrotalcites (magnesium aluminum hydroxycarbonates). Tributyrin is an analog of the naturally-occurring triglycerides but contains side-chains of only 4 carbon atoms. The reaction is significantly influenced by the hydration state of the surface. Future studies will involve detailed catalyst characterization and kinetics experiments to elucidate why surface hydration plays such a key role in the base-catalyzed reaction. Moreover, additional mixed metal oxides will be explored as potential catalysts for transesterification.

We have also broadened the scope of our investigations to explore the role of hydroxyl groups on Au-catalyzed oxidation reactions and Ru,Pt-catalyzed hydrogenolysis reactions. For example, previous studies of the aqueous phase oxidation of alcohols showed Au to be comparable, if not better than, both Pt and Pd catalysts for a number of reactions, with the rate often increasing with elevated hydroxyl concentrations. A number of research groups subsequently began investigating gold's ability to catalyze selective oxidation of glycerol, a by-product from the production of biodiesel. The reaction of glycerol only occurs at high hydroxyl concentrations (high pH), but is catalyzed by both small and large Au particles (> 20 nm). These intriguing findings indicating large Au particles are active catalysts for aqueous phase oxidation led us to study the important role of hydroxyls during the oxidation of CO and glycerol over supported Au catalysts in the aqueous phase. The observed promotion of glycerol hydrogenolysis reactions with added base over Ru and Pt catalysts also suggests that hydroxyls play an important role in reducing reactions.

Publications 2005-2007

J. Li and R.J. Davis, "Raman Spectroscopy and Dioxygen Adsorption on Cs-loaded Zeolite Catalysts for Butene Isomerization," *J. Phys. Chem. B,* **109** (2005) 7141-7148.

J. Li, J. Tai and R.J. Davis, “Hydrocarbon Oxidation and Aldol Condensation over Basic Zeolite Catalysts,” *Catal. Today* **116** (2006) 226-233.

D.G. Lahr, J. Li and R.J. Davis, “Oxidation of H_2 and CO over Ion Exchanged X and Y Zeolites,” *J. Am. Chem. Soc.* published on Web 2/24/07.

W.C. Ketchie, M. Murayama and R.J. Davis, “Promotional Effect of Hydroxyl on the Aqueous Phase Oxidation of Carbon Monoxide and Glycerol over Supported Au Catalysts” *Topics in Catalysis*, in press.

J. Tai and R.J. Davis, “Synthesis of Methacrylic Acid by Aldol Condensation of Propionic Acid with Formaldehyde over Acid-Base Bifunctional Catalysts,” *Catal. Today,* in press.

W.C. Ketchie, E.P. Maris and R.J. Davis, “In-situ X-ray Absorption Spectroscopy of Supported Ru Catalysts in the Aqueous Phase,” *Chem. Mater.*, submitted.

E.P Maris and R.J. Davis, "Investigation of Carbon-Supported Ru and Pt as Catalysts for the Hydrogenolysis of Glycerol" *J. Catal.*, will be submitted in April, 2007.

W.C. Ketchie, M. Murayama and R.J. Davis, “Selective Oxidation of Glycerol over Supported Au-Pd Bimetallic Catalysts” *J. Catal.*, will be submitted in April, 2007.

DE-FG02-03ER15456 **Michael W. Deem**

Toward Rational, Nanoscale Control of Catalysis: A Fundamental Study of Zeolite Nucleation Kinetics

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Goal

Develop the theoretical and simulation technology to predict barriers to zeolite nucleation in the presence of structure directing agents and develop a database of hypothetical zeolite-like framework structures.

Recent Progress

Zeolite Structure Solution: The synthesis, structure solution, and characterization of the high-silica zeolite Stacey Zones structure 18163 was described. The framework topology and symmetry of 18163 were determined by the Monte Carlo method ZEFSAII. Rietveld refinement of the X-ray powder diffraction data is ongoing. Transmission electron microscopy confirms the unit cell parameters and the topology of the structure.

Simulation Technology: Adaptive Monte Carlo methods can be viewed as implementations of Markov chains with infinite memory. We derived a general condition for the convergence of a Monte Carlo method whose history dependence is contained within the simulated density distribution [1]. In convergent cases, our result implies that the balance condition need only be satisfied asymptotically. As an example, we showed that the adaptive integration method converges.

Hypothetical Structure Generation: We have completed a substantial amount of the work required to create a database of hypothetical structures. We developed a computational method to identify zeolite-like frameworks by sampling a zeolite figure of merit. Monte Carlo methods, including simulated annealing, are used to perform the sampling. We have begun construction of a database of hypothetical zeolite frameworks with this approach. To date, we have roughly 4 million structures in this database. This number is to be compared to the roughly 180 structures of known zeolites.

DOE Interest

Understanding zeolite nucleation is important not only scientifically for the discovery and synthesis of new materials, but also in an engineering sense for improving the performance of existing materials that are not performing as well as they could due to poor ``crystallinity." Considerations include catalysts with improved catalytic properties for improving refining economics and for reducing environmentally-unfriendly by-products, design of better, smarter, and more energy-efficient separation processes, and design of zeolites that are more effective for radioactive waste cleanup and stewardship purposes. Parallel tempering and biased Monte Carlo are general materials simulation methods now in use.

Future Plans

Monte Carlo Theory of Structure Directing Agents: Develop the open-ensemble nucleation theory to accommodate the presence of a variable number of structure directing agents.

Quantification of Templating Effects: By how much do structure directing agents lower the nucleation barrier? How do they discriminate among possible zeolite structures? Do the templates go towards the middle of the critical clusters or the surface? At what size does the cluster start to become crystalline rather than amorphous?

Hypothetical Zeolite Database Generation: Finish generation of a database of hypothetical zeolite structures. Perform geometric optimization of the structures in the database to produce a refined database.

Related Publications (2005-2007)

1) D. J. Earl and M. W. Deem, ``Markov Chains of Infinite Order and Asymptotic Satisfaction of Balance: Application to the Adaptive Integration Method,'' David Chandler Festschrift, *J. Phys. Chem. B* **109** (2005) 6701-6704 [solely BES/DOE].
2) D. J. Earl and M. W. Deem, ``Parallel Tempering: Theory, Applications, and New Perspectives," invited review, with cover, *Phys. Chem. Chem. Phys.* **7** (2005) 3910-3916.
3) D. J. Earl and M. W. Deem, ``Toward a Database of Hypothetical Zeolite Structures," Eduardo Glandt special issue, *Ind. & Eng. Chem. Res.* **45** (2006) 5449-5454 [solely BES/DOE].
4) M. Yang, J.-M. Park, and M. W. Deem, ``Evolutionary Design in Biological Physics and Materials Science," *Lect. Notes Phys.* **704** (2006) 527-548.
5) Z. Li, M. C. Johnson, M. Sun, E. T. Ryan, D. J. Earl, W. Maichen, J. I. Martin, S. Li, C. M. Lew, D. I. Medina, J. Wang, M. W. Deem, M. E. Davis, and Y. Yan, ``Mechanical and Dielectric Properties of Pure-Silica-Zeolites as Low-k Materials," *Angew. Chem. Int. Ed.* **45** (2006) 6329-6332.
6) P. A. Cheeseman, M. W. Deem, D. J. Earl, and W. I. Whitson, "Adapting an Application for Use in a Condor Based Parameter Sweep on TeraGrid," TeraGrid 2007 Conference, Madison, WI (2007).
7) E. Walkter, D. J. Earl, and M. W. Deem, "How to Run a Million Jobs in Six Months on the NSF TeraGrid," TeraGrid 2007 Conference, Madison, WI (2007).

Honors

Allan P. Colburn Award (2004)
Editorial Board Member, Protein Engineering, Design and Selection (2005)
Fellow, American Institute for Medical and Biological Engineering (2005)

Fellow, American Physical Society (2006)
Vaughan Lectureship, California Institute of Technology (2007)

DOE Grant No. DE-FG02-03ER15466 **W. Nicholas Delgass**

CATALYSIS SCIENCE INITIATIVE: Catalyst Design by Discovery Informatics

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Postdocs: G. Medvedev, C. Stanciu
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Collaborators: P. Patkar, School of Chemical Engineering; G. Bertoline, L. Arns, Purdue Envision Center for Data Perceptualization; S. Dunlop, D. McKay, M. McLennan, D. Talcott, W. Whitson, L. Zhao, Information Technology at Purdue (ITaP); S. Orcun, S. Nandi, T. Park , e-Enterprise Center

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Goal: Develop and apply an informatics-intensive, model-based approach that extracts knowledge from data for the design of catalysts, focusing on single-site aryloxide catalysts for polyolefin production, aromatics production from light olefins, and hydrogen production from the water gas shift reaction.

DOE Interest: Validation of this new design concept has the potential to change the catalysis research landscape by dramatically shortening hypothesis testing and new discovery cycles for virtually any catalyst system. A particular value of the approach is that knowledge archived in the model retains its value for new problems. Over time, overlapping knowledge bases from a variety of problems will accelerate discovery cycles even more. Though the emphasis here is on catalytic applications, the general approach has broad application to materials design and even process improvement. The informatics and data visualization tools developed in this effort also have broad application to knowledge extraction from virtually any large data set.

Research Plan: The heart of our *Discovery Informatics* approach is the *forward model,* designed to quantitatively connect chemical, structural and higher level descriptors of a catalytic material to its kinetic performance for a specified reaction. In this approach, the forward model, comprised of a catalytic chemistry component and a microkinetic model, then enables a guided stochastic *inverse search* of the descriptor space to identify trial catalyst materials predicted by the forward model to best satisfy the catalytic performance goals. Discrepancies between the predictions and high throughput evaluation of the trial catalysts can then be used to improve the model, and iteration of the cycle can continue to improve the model until it converges on a set of catalytic materials that meet the design goal. Our research objectives include building the computational, informatics, data visualization, and experimental infrastructure to support this design algorithm and to further develop the approach through application to three diverse problems. Each of these areas is strongly supported by density functional theory calculations.

- *Group IV single site catalysts for polyolefin production* - These homogeneous catalyst systems offer the significant advantage of a well-defined, single catalytic site. We began with a focus on cationic alkyls of the group 4 metals with cyclopentadienyl and substituted aryloxide ligands and are now expanding the diversity of catalyst ligands.

- *Aromatization of parafins over zeolites* - In this study, we have focused on zeolites because their crystallinity qualifies them as “molecular” heterogeneous catalysts, i.e., ones for which we can compute properties because we have a good starting point for assigning atomic positions. The reaction, conversion of propane to aromatics, has a high level of complexity and thus is a demanding test of the reaction modeling tools.
- *Hydrogen generation via the water-gas shift (WGS) reaction* - To gain robustness for fuel cell applications, the active, but fragile, Cu/ZnO catalyst must be replaced by appropriately promoted supported metal catalysts. This is a case where the reaction is stoichiometrically simple, but the combinatorial complexity of the catalyst is substantial with choices for support, metal, and multiple promoter oxides.
- *Infrastructure* – There are two additional research thrusts that support this effort. The first is *parallel mass spectroscopy* for at least semi-quantitative speciation on the timescale of seconds to minutes rather than hours. A four channel device has been designed, constructed and tested. It was reported last year and will not be included here. The second concerns *informatics*, the hardware, software, and middleware involved in data management, data analysis, model building, data visualization and the extraction of knowledge from data. This is an ongoing development area, critical to the overall success of this data-rich modeling approach.

Recent Progress:

Olefin Polymerization over Single-Site Catalysts – Using a combination of experimental measurements, kinetic modeling and DFT computations, we have developed a model for the relationship between descriptors of the catalyst chemistry and structure and the measured propagation rate constants [8]. 1-Hexene polymerization kinetics were measured by NMR at 20 °C for 18 Ti and 2 Zr based aryloxide-Cp (or Cp*) ligated catalysts with tetra- and tris-perflorophenyl counterions, e.g.$[Cp^*Zr(OC_6H(Ph)_4\text{-}2,3,5,6)(CH_3)]$ $[H_3C\text{-}B(C_6F_5)_3]$. A set of kinetic models was developed that included initiation, propagation, and catalyst deactivation. The parameter fitting procedure included a critical analysis of the error structure of the M(t) curves, where it was found that the error in M(t) is heteroscedastic, i.e. the error depends of the magnitude of the measured value. The Discovery Informatics tools were needed to keep pace with the large number of models that were analyzed for this system.

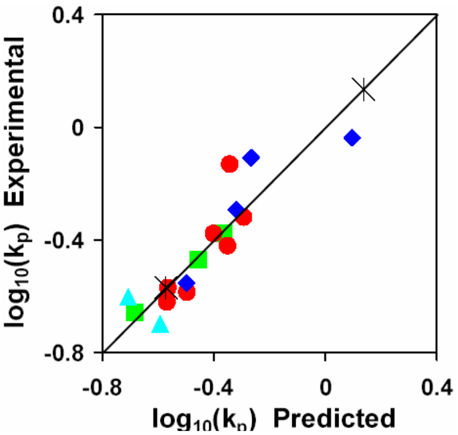


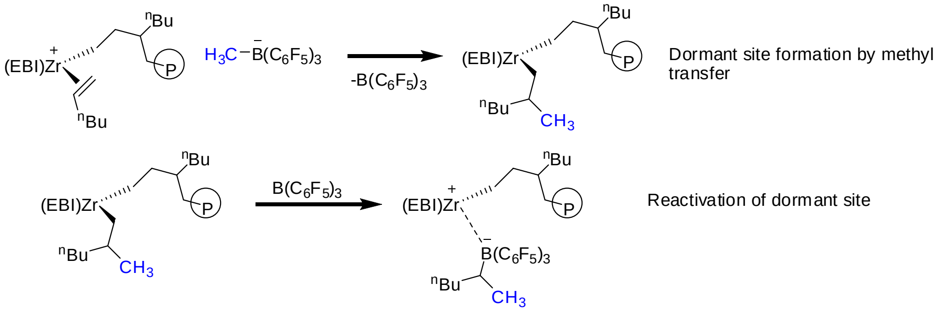
Figure 1 Prediction of propagation rate using Eqs. 1 and 2 with α = 0.300, f = 0.187, and the following values of A (M^{-1} s^{-1}) according to catalyst family: (A) 3.01x10^8 (■), (B) 5.22x10^7 (●), (C) A = 2.65x10^7 (◆), (D) 6.88x10^5 (✳), and (E) 1.77x10^7 (▲).

In order to unify the entire Ti data set with a single forward model, we included the steric effects of the ligands by evaluating the solid angle available to the monomer for docking and assigned the dominant energetic effect to the fraction of the counter ion binding energy (CIBE) that must be expended to move the anion away from the cation to allow access to the site by the monomer. The solid angles occupied by the two ligands (φ_1 and φ_2) and the CIBE were obtained via DFT calculations. The model has three fitting parameters (i) θ - the solid angle inaccessible to monomer which has not been explicitly accounted for by the ligand solid angles, including the solid angle occupied by the growing chain, (ii) α - a descriptor of the energy penalty (expressed as a fraction of CIBE) incurred when the counteranion is pushed away to enable monomer insertion ($0<\alpha<1$), and (3) A – a prefactor that scales the rate constant at the standard reaction temperature. The model predictions shown in Fig. 1 are very encouraging. The values of A, given in the figure caption, were allowed to vary from one catalyst family to another. However, A changes only slightly, with the notable exception of the catalyst family D, possessing a phenyl ring in the 2- position in the aryloxide ligand. The latter result indicates the presence of new chemistry not captured by the simple CIBE and docking space descriptor set. Notwithstanding the need for more sophisticated models to capture increased ligand bonding complexity, this is the first predictive model with physical significance that can describe how one of the polymerization rate constants depends upon the structure of the catalyst.

Recently we have been investigating 1-hexene polymerization kinetics catalyzed by $(EBI)Zr(CH_3)_2$ activated with either $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$. This catalyst system was chosen for its high activity, availability of literature data, and diversity relative to our current catalyst library.

1-Hexene (1.0 M) polymerization was followed by ^1H NMR in deutero-toluene at 0 °C using $B(C_6F_5)_3$ as the activator. Three catalyst precursor concentrations were investigated (8.0×10^{-4}, 1.6×10^{-3}, and 2.4×10^{-3} M). The kinetics of 1-hexene polymerization followed first-order dependence on 1-hexene and first-order dependence on catalyst precursor concentration. However, at $[Zr] = 8.0 \times 10^{-4}$ M the reaction reached only 40% conversion compared to 100% for the other concentrations. The incomplete conversion at the lowest catalyst loading (0.08 mol%) lead us to investigate the dependence on the activator concentration.

We followed the activation reaction by UV-vis spectroscopy. The starting reactants are colorless, while the Zwitter-ionic complex is orange with $\lambda_{max} = 420$ nm. The identity of the ionic complex formed *in situ* was found to be independent of the activator concentration even at the low precursor concentration (8.0×10^{-4}M). Concentrations of $B(C_6F_5)_3$ in excess of stoichiometric did not alter the UV-vis spectrum. However, in the catalytic reaction we found the use of 1.3:1 and 1.6:1 activator to precursor resulted in higher conversion of 1-hexene at $[(EBI)ZrMe_2] = 8.0 \times 10^{-4}$ M; 70 and 90%, respectively. Furthermore, for the higher catalyst concentrations, using 1.6-fold activator relative to catalyst precursor increases the rate of polymerization. These observations along with the GPC and kinetic analyses provide a mechanistic picture in which a significant portion of the catalyst forms dormant sites via 1-hexene dependent pathway and reactivation of dormant sites is dependent on activator concentration. The mechanism for dormant site formation is shown in Scheme 1.



Scheme 1. Dormant site formation and reactivation.

The reactivation of the proposed dormant sites is slower than the activation of the precursor $(EBI)Zr(CH_3)_2$ because the alkyl group is larger than methyl. We are in the process of testing this hypothesis by preparing $(EBI)Zr(Bz)_2$ (Bz = benzyl) from reaction of $(EBI)ZrCl_2$ and BzMgCl, and modeling the results as discussed below.

One of the main modeling objectives for this work has been the development of a robust methodology for the design of experiments and analysis to extract kinetic rate constants using batch polymerization data. This requires the development of a population balance simulator with appropriate parameter optimization to extract all of the kinetic constants with their statistical error from (i) monomer versus time profiles and (ii) the time evolution of the molecular weight distribution. Batch data is ideal because one experiment yields the rate of polymerization as a function of monomer concentration. Thus, fewer experiments need to be done to yield the same amount of information. Presently, there has been no attempt in the literature to extract kinetic rate constants by fitting molecular weight distributions obtained from batch polymerizations. This work has proceeded in the following steps (i) understanding how the various features present in the data result from different mechanisms, (ii) development of the necessary computation analysis tools and (iii) application of the understanding and tools.

In order to extract kinetic information from the batch molecular weight distribution data it is necessary to solve the ordinary differential equations determined by a population balance method in which there is an equation for each species. This means the number of differential equations is in the ten thousands. The initial code to solve the population balance model was written in Matlab, but parallel computational algorithms have now been implemented in C to allow for rapid and efficient solving of the ordinary differential equations required for model discrimination and parameter optimization of multiple rate constants.The population balance simulator has been applied to 1-hexene polymerization with $[(EBI)Zr(Me)][MeB(C_6F_5)_3]$ and it showed the need for a dormant site mechanism such as the one shown in scheme 1.

Density functional theory supports all of this work. We have experimentally and computationally explored many different combinations of metals, ligands, solvents, and counterions. Computations using different exchange-correlation functionals and basis sets have been compared to each other and to experimental data to validate the DFT methods. For the half-sandwich complexes, the E_{IPS} of a Ti-based catalyst is lower than its Zr analog. For example, $[Cp^*M(OC_6H\text{-}2,3,5,6\text{-}Ph_4)Me]^+$ $[MeB(C_6F_5)_4]^-$ has a computed E_{IPS} in toluene of 14.2 (Ti) and 22.3 (Zr) kcal/mol (OLYP/LANL2DZ). Experimentally, the Ti catalyst is active for polymerization of 1-hexene at 0 C but the Zr analog is not. However, the Zr analog can be made active by switching the solvent from toluene (dielectric constant = 2.4) to bromo-benzene (dielectric constant = 5.6) for which the computed E_{IPS} = 6.9 kcal/mol. The counterion also effects E_{IPS}: 27.5 kcal/mol $[CpTi(OC_6H_2\text{-}2,6\text{-}Me_2\text{-}4\text{-}Br]^+$ $[C_6F_5)_4]^-$ compared to 32.3 kcal/mol $[CpTi(OC_6H_2\text{-}2,6\text{-}Me_2\text{-}4\text{-}Br]^+$ $[MeB(C_6F_5)_4]^-$. Calculations for the new catalyst systems are underway and are being expanded to include initiation and chain transfer steps as well as the proposed dormant site mechanism.

Propane Aromatization over ZSM-5 Catalysts – Our focus for the propane aromatization work has been on the effects of gallium addition to HZSM-5, a method known to enhance the dehydrogenation ability of the catalyst, as well as effects of variation of the Si/Al ratio. The quantitative model using 312 elementary steps and 25 rate and equilibrium parameters to describe the aromatization of propane over HZSM-5 with Si/Al of 16 [4] serves as the base case against which to compare new results. Ga/HZSM-5 catalysts, synthesized by the incipient wetness impregnation technique and pre-treated in hydrogen at 530°C, indicated a steady decline in the strength of the 3610 cm^{-1} band with Ga content when characterized by FTIR spectroscopy at room temperature. We also observed a maximum in propane conversion and aromatics selectivity at a Ga/Al ratio of about 0.5. Our experimental observations thus point to a synergistic interaction between the proton and gallium sites. Kinetic models based on three different Ga active sites, including GaH^{2+} [3], GaH_2^+ and gallium that does not annihilate proton sites, were first used individually to describe the diverse dataset that includes conversion to 10 different products as a function of temperature, space time and Ga/Al variations. While models based on both gallium dihydride and gallium monohydride active sites resulted in good fits at low gallium loadings, only the gallium monohydride model is able to describe the data across Ga loadings (Figure 2). Modeling efforts thus support the DFT predictions of the presence of GaH^{2+} species at dual aluminum sites. We are currently attempting physical characterization of the catalyst to verify the existence of near Al species by quantifying Co UV-Vis spectra of fully exchanged Co-ZSM-5 catalysts. We are also developing a final model which combines these various functionalities in a unified description of the

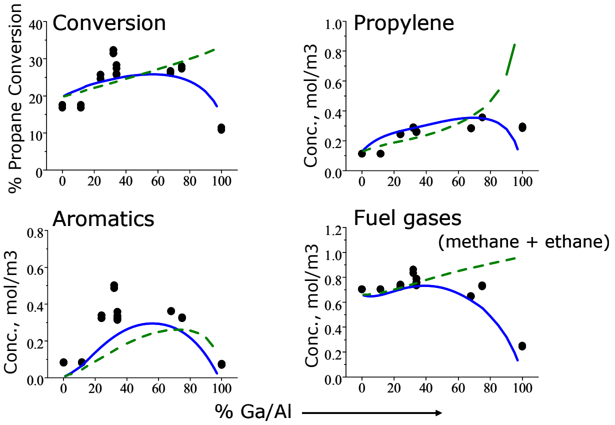


Figure 2 Comparison of the GaH^{2+} model (16 parameters) – solid line and the GaH_2^+ model (18 parameters) – dashed line: Si/Al=16, T=520°C, tau=1.514 g.cat-hr/mol

catalytic behavior to give the best fit to the data. This modeling continues to be supported by DFT computations. The current focus in that area is on C_3 to C_6 oligomerization and hydride shift reactions.

The Water Gas Shift Reaction – We have three related focal areas in the WGS reaction work:

- *Kinetics on Pt-based catalysts*. This is the most promising metal as it shows the highest rates.
- *Kinetics on Pd-based catalysts*. The Pt-based catalysts do not show measurable amounts of methanation until the temperature is too high to allow for reliable measurement of rates. Palladium however shows a high selectivity to methanation. For this reason, we are using Pd to test promoters to suppress methanation and increase WGS rates.
- *Measurement of WGS kinetics on different metals*. This is necessary for our modeling since the data are not available in the literature. The challenge is how to prepare reasonably dispersed samples in a support that will allow the metals to reduce. We have chosen titania as the support for this work.

Pt-based Catalysts - We found that residual chlorine does not affect the WGS rate. We also compared the WGS kinetics on Pt/Al_2O_3 catalysts with different dispersions and found the kinetics to be independent of the Pt particle size. The WGS turnover rate (TOR) is ~ 12 times higher on Pt/TiO_2 and ~ 50 times higher on Pt/CeO_2 catalysts than that on Pt/SiO_2 and Pt/Al_2O_3 catalysts. The significantly different CO order on Pt/CeO_2 catalysts suggest that these catalysts operate by a mechanism different from that on other catalysts.

Pd-based Catalysts: The WGS TOR exhibits the following trend for Pd catalyst supports: CeO_2 ~ ZnO ~ ZrO_2 ~ La_2O_3 > TiO_2 > Nb_2O_5 > Al_2O_3. The TOR on Pd/CeO_2 catalyst is ~ 8 times lower than that on the Pt/CeO_2 catalyst and in general the TOR on Pt is significantly larger than that on Pd. Interestingly, the support significantly affects the WGS versus methanation selectivity on Pd catalysts. The TOR(WGS)/TOR(CH_4) values on Pd/Al_2O_3, Pd/Nb_2O_5, and Pd/TiO_2 catalysts are 5, 17, and 24, respectively. No methanation was observed on other catalysts. The promotion of WGS TOR and inhibition of methanation TOR can be simultaneously achieved by adding ZnO on Pd/Al_2O_3 catalysts. Addition of 2.5% Zn is enough to stop methanation beyond detection. Moreover, the WGS TOR on Pd/Al_2O_3 catalysts with 6.2% and 9.5% Zn is roughly 5 and 7 times larger than that on Pd/Al_2O_3 catalysts without any Zn. The apparent reaction orders are somewhat changed upon Zn addition suggesting that the addition of Zn is affecting the coverage of different species.

Rh, Ru, and Ir Catalysts: The WGS TOR on TiO_2-supported catalysts exhibits the following trend: Rh >> Ru ~ Ir. The highest WGS TOR in the series of catalysts examined recently is on Rh/TiO_2 (extrapolated to 300°C: 3 s^{-1}); however, this catalyst is equally active towards methanation.

Kinetic Modeling and DRIFTS studies of WGS Reaction: Generation of kinetic models is critical in our catalyst design framework. Our modeling attempts to explain the kinetic data with Langmuir-Hinshelwood (LH) models with appropriate constraints to ensure thermodynamic consistency. The model below explains the kinetic data over Pt catalysts. The assumption that CO* is the most abundant surface intermediate (MASI) is supported by the DRIFTS studies.

<u>Mechanism:</u>

$H_2O + O^* + {}^* \rightleftarrows 2\,OH^*$ (1)
$CO + {}^* \rightleftarrows CO^*$ (2)
$OH^* + CO^* \rightleftarrows HCOO^* + {}^*$ (3)
$HCOO^* \rightleftarrows CO_2 + H^*$ RDS (4)
$OH^* + {}^* \rightleftarrows O^* + H^*$ (5)
$2H^* \rightleftarrows H_2 + 2^*$ (6)

Explains orders on Pt:

$H_2O \sim 1$ $CO_2 \sim 0$
$H_2 \sim -0.5$ $CO \geq 0$

$$Rate_{Forward} = \frac{k_4[L]K_1K_2K_3K_5K_6^{0.5}}{\{1+K_2[CO]\}}[CO][H_2O][H_2]^{-0.5}$$

$$\frac{K_2[CO]}{1+K_2[CO]} \sim K_2^n[CO]^n, 0 < n < 1, n = Order_{CO}$$

We are also working on redox and the modified redox mechanism, and the formate mechanism to model kinetics over Pt and Pd. The thermodynamically consistent models will be discriminated on the basis of (1) statistical analysis of fitted parameters, (2) a comparison of predicted surface coverages with those obtained from DRIFTS studies, and (3) isotopic transient kinetic studies. Our models account for the coverage dependence (e.g., CO) of adsorption and activation energies, will be extended over a wide range of catalysts, and will address the observed compensation relations. The objective is to identify the descriptors of the WGS and methanation activity that can then be used to develop a full forward model.

Development of Informatics Tools – An e-lab notebook, searchable archival and relational databases, computational job sequencer, chemistry compiler, statistical tools for nonlinear parameter fitting and design of experiments for nonlinear systems, and a scaleable platform for 2D and 3D visualization of data are some of the informatics infrastructure that has been developed to drive all of these projects. These information management and analysis tools in concert with an advanced data visualization environment, an environment that enables the researcher to more effectively interact with data via the eye's high-bandwidth for information transfer, will become increasingly important as our ability to generate both experimental and computational data and increasingly sophisticated models accelerates. We are now in the process of bringing up a tiled wall visualization laboratory in Forney Hall of Chemical Engineering and thus will have easy access to these tools in the near future.

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Early Transition Metal Oxides as Catalysts: Crossing Scales from Clusters to Single Crystals to Functioning Materials (C. Peden (PNNL) – PI)

Transition Metal Oxide (TMO) Clusters – Electronic Structure and Chemical Bonding

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The focus of our part of the Catalysis Center led by PNNL is to obtain a molecular level understanding of the properties of supported TMOs, and catalytic reaction mechanisms based on cluster models. Our overall approach is a coordinated experimental (photoelectron spectroscopy (PES)) and computational (density functional (DFT) and molecular orbital (MO) theories) effort to understand and predict the properties of these clusters. Gas phase clusters provide molecular systems with controlled and well-defined structures and atomic connectivity. Their spectroscopic features provide a mechanism for validating electronic structure calculations which form a central part of our program. The chemical properties of free TMO clusters are useful in addressing issues about the nature of the reactive sites of supported clusters. The dependence of chemical reactivity on cluster size and composition is well established, but, there are few spectroscopic studies on early transition metal oxide clusters and little is known about their electronic and structural properties. This work has been done in close collaboration with the other parts of our program on surface catalytic studies.

We have made significant advances in our studies of such species. The work has focused on the structures and reactivity of TMO clusters involving the Group VIB metals (Cr, Mo, W). We have studied a wide range of oxide clusters with up to 6 metal atoms. Discoveries in this time period include "d orbital aromaticity in $W_3O_9^-$ and $W_3O_9^{2-}$ and the role of low-lying electronic states in these oxides, the very high electron affinities of many of these oxide clusters, the very high Lewis acidity of the metal oxide sites, the low Brönsted basicity and high acidity of many of these types of compounds, high O-H bond energies, and novel structures. Doubly and singly charged Group VIB dimetalate species, $M_2O_7^{2-}$, $MM'O_7^{2-}$, and $M_2O_7^-$ (M, M' = Cr, Mo, W) using two different experimental techniques (electrospray for the doubly charged anions and laser vaporization for the singly charged anions) were investigated using PES and DFT calculations. Two doubly charged Lindqvist polyoxoanions, $Mo_6O_{19}^{2-}$ and $W_6O_{19}^{2-}$, were studied in the gas phase using electrospray ionization. The potential energy surface for oxidative dehydrogenation of methanol on $(MO_3)_n$ clusters have been studied as well as the geometric and electronic properties of the clusters. The electronic and structural properties of tri-tungsten oxide clusters, $W_3O_n^-$ and W_3O_n (n = 7-10), were investigated as molecular models for O-deficient sites in tungsten oxides using PES and DFT. Two O-rich tungsten oxide clusters, $W_2O_8^-$ and $W_3O_{11}^-$, were produced and studied by PES and DFT calculations. The electronic structure of the mononuclear hydroxo $MO_3(OH)^-$ and methoxo $MO_3(OCH_3)^-$ oxometalate anions (M = Cr, Mo, and W) were examined by PES and electronic structure calculations at the DFT and CCSD(T) levels of theory. In addition, we have been calculating the bond energies for MF_x, MH_x, MO_3, M_2O_6, $M(PH_3)_2$, and $MCl_2(PH_3)_2$ transition metal compounds at the CCSD(T)/complete basis set level to provide a set of benchmarks for other computational methods, especially different DFT functionals. Based on our comparison of PES and calculated results, different DFT functionals can behave quite differently.

Structure and Catalytic Activity of Model Oxide Systems

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Early transition metal oxides represent an important class of oxide catalysts. We combined atomically resolved imaging and ensemble averaged techniques to examine the adsorption, dissociation, and partial oxidation of alcohols on $TiO_2(110)$ and $(WO_3)_3/TiO_2(110)$ model catalysts. Model $(WO_3)_3/TiO_2(110)$ systems were prepared using direct sublimation of WO_3 and characterized using high resolution Scanning Tunneling Microscopy, X-ray photoelectron spectroscopy and N_2 physisorption. On clean $TiO_2(110)$ the images obtained from the same area before and after adsorption show that both alcohols and H_2O adsorb preferentially on oxygen vacancies and that alcohol dissociation occurs via O-H bond scission. The dynamics of diffusion of protons created by water and alcohol dissociation on bridge-bonded oxygen (BBO) vacancies is examined as a function of adsorbate coverage.

The detailed molecular beam dosing and temperature-programmed desorption investigations of alcohol dehydration on $TiO_2(110)$ reveal the presence of two distinct dehydration channels. We show that for the previously reported BBO vacancy-related high-temperature (500-650 K) dehydration channel, the alkene desorption temperature correlates with the induction effect of the alcohol alkyl-chain. A previously unobserved, low temperature channel (300-450 K) is attributed to a disproportion reaction between two neighboring alkoxy groups (or alkoxy and alcohol) bound on Ti^{4+} rows. Based on the above observations, we propose detailed reaction steps involved in dehydration of alcohol molecules on $TiO_2(110)$.

This work was supported by the U.S. Department of Energy Office of Basic Energy Sciences, Chemical Sciences Division and performed at W. R. Wiley Environmental Molecular Science Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research located at Pacific Northwest National Laboratory (PNNL). PNNL is operated for the U.S. DOE by Battelle Memorial Institute under Contract No. DE-AC06-76RLO 1830.

DE-FG02-99ER14998 **Raul F. Lobo**
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Catalytic Activation of Oxygen for Conversion of Hydrocarbons to Fuels and Chemicals

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Goal

To develop new materials for photocatalytic transformations of organic molecules using visible light. The focus is on a family of microporous titanosilicates, including ETS-10 and transition metal-substituted ETS-10. Using a combination of synthesis, characterization and first-principles theory, the project aims to develop an atomistic understanding of the effects of metal substitution on the optical band gap and photocatalytic activity of ETS-10, in order to identify modifications that are likely to improve the photocatalytic properties.

DOE Interest

Systematic modification of materials to improve photocatalytic efficiency in the visible range is central to developing new methods for solar production of fuels and chemicals, and environmental remediation. This work combines synthesis and characterization of such materials with computational modeling to interpret experimental observations and to guide the choice of materials for future studies. In addition, this work will establish broadly applicable principles that will be useful in designing photocatalytic materials.

Research Plan

We are investigating ETS-10 and vanadium-incorporated ETS-10 as photocatalysts. ETS-10 is a microporous titanosilicate with chains of TiO_6 octahedra embedded in a framework of SiO_4 tetrahedra. This material has similar reactivity to titania, though the band gap is even larger. However, the ETS-10 strucure allows novel modifications that can be used to alter its band gap and reactivity. The bulk of our work has concerned substitution of vanadium for titanium along the chain, producing a family of materials with varying amounts of vanadium. The amount of vanadium can be controlled over the range from 0 to 100%. Variations in the band gap, oxidation state, and reactivity have been measured as a function of vanadium concentration. First-principles computational models have been developed and their predictions have been compared to experimental observations. These models have been used to predict properties of materials with other transition metal substituents, to assess the likelihood that they will be useful as visible light photocatalysts.

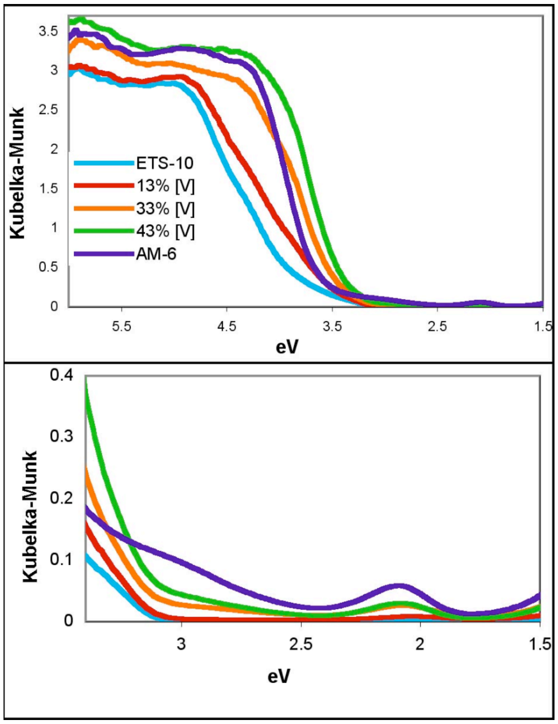
Recent Results

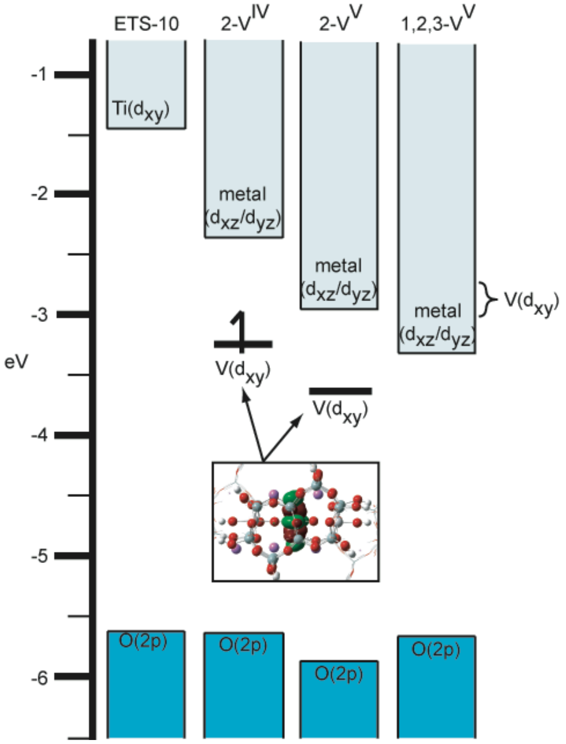
Synthesis and properties of V-substituted ETS-10. Various amounts of vanadium have been isomorphously substituted for titanium in ETS-10 creating samples with V/(V+Ti) ratios of 0.13, 0.33, 0.43 and 1.00. These have been characterized using Raman, Near Edge X-ray Absorption Fine Structure (NEXAFS), x- ray powder diffraction, N_2 adsorption, scanning electron microscopy (SEM), UV/vis spectroscopy, and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). Raman spectra reveal a disordered chain structure that contains different V-O bonds along with the presence of a V-O-Ti peak. NEXAFS results demonstrate the presence of both V^{5+} and V^{4+} in the substituted samples, with a V^{IV}/V^{V} concentration ratio of 0.2-0.4. The UV/vis spectra of the vanadium-substitued samples have two new absorption features in the visible region at 3 eV and at 2.2 eV (see Figure). The addition of vanadium lowers the band gap energy of ETS-10 from 4.32 eV to a minimum of 3.58 eV for the 0.43ETVS-10 sample. Studies of the photocatalytic polymerization of ethylene show that the 2.2 eV transition has no photocatalytic activity. The visible transition around 3 eV in the vanadium incorporated samples is photocatalytically active and the lower concentration vanadium samples have higher photocatalytic activity than AM-6, the all-vanadium analog of ETS-10.

Computational Modeling. First-principles electronic structure calculations have been done on ETS-10 and a number of transition metal-substitued analogs. The calculations use a hybrid of density functional theory and molecular mechanics (DFT/MM). Structural models have been developed that contain varying concentrations of V^{IV} and V^{V} in the O-M-O (M = Ti, V) chain. Geometry optimizations indicate that V^{V} substitution leads to larger changes in the local chain geometry than V^{IV} substitution. Energetics for V^{IV} and V^{V} substitution in different sites have been calculated to determine preferred locations of the two species, suggesting that long chains of V^{V} are not stable and demonstrating the need for both oxidation states in V-substituted materials. Wavefunctions for systems with an electron added or removed are used to identify electron and hole trapping sites associated with the V^{V} and V^{IV} doping centers respectively. An increase in photocatalytic activity is predicted at low [V] due to improved charge separation. However, photocatalytic activity is expected to decrease at high [V] due to increased carrier recombination. These results are consistent with the experimental observations.

The electronic structure of several V-substituted models shows that a $V(d_{xy})$ localized state is introduced upon V substitution (see Figure). Generally, this state is located within the mid-gap or near the bottom of the conduction band, yet the relative location of these states depends on dopant concentration for all transition metals. Additionally, the occupation of this localized state is dependent on the dopant oxidation state, leading to the addition of multiple low energy optical transitions. Consistent with the experimental observations for this system, our models predict a decrease in the optical band gap with increasing [V] due to a lowering of the conduction band at higher concentrations of V^{IV} and V^{V}. Excitation energies for the V-doped models, calculated with TDDFT methods, correlate well with experimental data, allowing for the assignment of specific optical transitions to experimental UV-vis spectra and demonstrating band gap energies in the visible range of the spectrum for ETS-10 samples with high [V].

Similar calculations have been done for materials substituted with Fe, Nb and Cr. While V is most effective at reducing the band gap, the other metals have more influence on the energy of the valence band. A simple linear regression model has been developed to predict the energy of the metal(d_{xy}) orbitals that fits all of these systems. We are currently working to extend this simple approach to rapidly predict other electronic properties of metal-substituted ETS-10.





Publications

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“Effects of Vanadium Substitution on the Structure and Photocatalytic Behavior of ETS-10,” A. M. Shough, D. J. Doren, M. Nash and R. F. Lobo, *J. Phys. Chem. C* **111**, 1776 (2007).

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Computational Photocatalysis on TiO_2: Charge Transport, Structure, and Reactivity

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This theoretical project is a part of the larger joint experiment/theory project “Fundamental Studies of Photocatalysis on TiO_2”, M.A. Henderson PI, that focuses on the chemical physics characterization of photocatalysis. We address three research areas through computational studies: i) the characterization of charge transport in bulk TiO_2 including the effect of surfaces; ii) the characterization of mixed phase titania, in particular interfaces between rutile and anatase and charge transport across the interfaces; iii) the structure of adsorbate molecules on rutile and anatase surfaces, and their charge-induced reactivity.

Acknowlegement: This work is supported by the Office of Basic Energy Sciences (BES) of the Department of Energy (DOE). Calculations are carried out in part at the Molecular Science Computing Facility (MSCF) of the Environmental Molecular Sciences Laboratory (EMSL), a national user facility funded by DOE’s Office of Biological and Environmental Research (BER) at the Pacific Northwest National Laboratory (PNNL). Battelle operates PNNL for the Department of Energy.

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Dynamics of Propane in Silica Mesopores Formed upon Propylene Hydrogenation over Pt Nanoparticles by Time-Resolved FT-IR Spectroscopy

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Propylene hydrogenation over Pt nanoparticles supported on mesoporous silica type SBA-15 was monitored by time-resolved FT-IR spectroscopy at 20 ms resolution using short propylene gas pulses joining a continuous flow of hydrogen (in nitrogen, 1 atm total pressure).[1] Experiments were conducted in the temperature range 323 – 413 K. Propane was formed within 100 milliseconds or faster depending on reaction temperature. Frequency and temporal behavior of a transient band observed at 1457 cm^{-1} is consistent with surface propyl intermediate and its hydrogenation to propane. The CH stretching region revealed distinct bands for propane molecules emerging inside the nanoscale channels of the silica support. Spectral analysis gave the distribution of the propane product between support and surrounding gas phase as function of time. Kinetic analysis showed that the escape of propane molecules from the channels occurred within hundreds of milliseconds ($3.1 \pm 0.4\ s^{-1}$ at 383 K). A steady state distribution of propane between gas phase and mesoporous support was established as the product is swept from the catalyst zone by the continuous flow of hydrogen co-reactant. This is the first direct spectroscopic observation of emerging products of heterogeneous catalysis on nanoporous supports under reaction conditions.

[1] Wasylenko, W.; Frei, H. *J. Phys. Chem. C* **111**, 000 (2007)

Advances in EXAFS analysis of monometallic and bimetallic nanoparticles

DE-FG02- 03ER15476

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The question of the fundamental interest in structural studies of nanoparticles and their applications to catalysis, is how to reconstruct their 3D geometry from experiment. We present methods of Extended X-ray Absorption Fine-Structure (EXAFS) analysis, developed in recent years, that provide three-dimensional structural characterization of metal nanoparticles, both mono- and bi-metallic. For bimetallic clusters, in addition to the size/shape determination, we are able to discriminate between random and non-random alloying of metals. For non-random alloys, we characterize short range order around each absorber in terms of the positive or negative tendency of like atoms to cluster and/or form a core/shell type nanoalloy. We also discuss the application of EXAFS to heterogeneous nanoparticle systems. We illustrate our structure refinement methods using our work with supported and unsupported Pt, Au, Pd, Pt/Ru, Pd/Au and other nanocluster systems. We emphasize that all our examples employ a self-consistent combination of complementary methods, namely, EXAFS and advanced electron microscopy techniques (HAADF-STEM).

DE-FG02-87ER13790 **Bruce C. Gates**

Dynamic Characterization of Structure and Bonding in Supported Molecular Catalysts

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Goals

Extend molecular catalysis onto surfaces by precise synthesis of supported metal complexes and metal clusters and characterization by complementary spectroscopic and microscopic methods (especially of catalyst in the functioning state).

Recent Progress

We developed syntheses using metal acetylacetonate compounds to prepare structurally simple supported catalysts, developing methods for using $Au(CH_3)_2(acac)$, $Ir(CO)_2(acac)$, and $Rh(CO)_2(acac)$ for preparations by surface-mediated synthesis. These precursor compounds have broad utility for the synthesis of essentially molecular supported metal complexes and clusters on oxides and zeolites, as they are reactive enough that when adsorbed on supports their ligands react (in part being replaced by the surface), and the products can be characterized spectroscopically and by analysis of the gas-phase products.

From $Au(CH_3)_2(acac)$ we prepared supported catalysts incorporating gold nanoclusters, which XANES data indicate to be predominantly zerovalent, although cationic gold was also present. In a family of MgO-supported gold catalysts used for CO oxidation, the catalytic activity increased with the fraction of the gold that was cationic, as determined qualitatively by XANES and TPO/TPR. We extended the work to conventionally prepared gold catalysts supported on iron oxide (made from a $HAuCl_4$), finding them to be among the most active yet reported for CO oxidation. This work involved measurements of catalytic activity and stability in flow reactor operation complemented by catalyst characterization (including in-situ characterization) to determine cationic and zerovalent gold by XANES, XPS, and Mössbauer spectroscopies; evidence of gold nanoclusters was determined by TEM and EXAFS spectroscopy. The catalytic activity increased as the fraction of the gold that was cationic increased, with some catalysts consisting almost entirely of cationic gold. The results demonstrate the role of cationic gold in catalytic sites for CO oxidation, even when the catalysts are highly active.

These demonstrations of the role of cationic gold challenged us to synthesize supported catalysts containing cationic gold in the absence of detectable zerovalent (aggregated) gold. We succeeded by using high-area (nanostructured) La_2O_3 as a support; XANES identified the gold species in the working catalyst as Au(III) complexes, shown by EXAFS spectra to be bonded to the support through Au–O bonds, with no EXAFS or XANES evidence of gold nanoclusters. This catalyst was found to have an activity for CO oxidation similar to those of the most active supported gold catalysts and to be stable in flow-reactor operation for as long as it was run (50 h). This is the first supported catalyst consisting of gold exclusively (as best we could determine) in a cationic form. We also found evidence that isolated cationic gold sites are active for ethylene hydrogenation.

These results show that nanoclusters of gold are not necessary for highly active supported gold catalysts (at least not for all of them).

Insight into the functioning of a supported gold catalyst emerged from investigations of catalysts made from $HAuCl_4$ and containing mixtures of zerovalent and cationic gold, as indicated by EXAFS, TEM, and XANES; the support was high-area (nanostructured) ceria. Raman spectra showed the presence of reactive surface oxygen species on the support (superoxide and peroxide), which were shown in transient (non-catalytic) experiments to react with CO to give CO_2; such species were not detected on conventional low-area CeO_2, which gave almost inactive catalysts, and the activity of CeO_{2-x} was very low unless the gold was present, indicating its essential role in the catalysis. These results are important in demonstrating the role of the support in the activation of O_2; it is not yet known how general these intermediates may be in oxidation by supported gold, and one of our goals in the proposed research is to learn more. Our EXAFS spectra of the CeO_{2-x}-supported gold catalysts, measured during CO oxidation, show a striking correlation between the turnover frequency for the reaction and the Au–O coordination number characterizing the Au–O contribution at a distance of approximately 3.5 Å (too long to be a bond); this result is consistent with the suggestion that CO bonded to cationic gold at the gold–support interface reacts with the reactive oxygen species such as superoxide on the support.

We also worked with rhenium, which has much less tendency than gold to be reduced and aggregated on a support. Zeolite-supported $Re(CO)_3$ complexes prepared from $HRe(CO)_5$ are precursors of catalysts for ethylene hydrogenation, and we characterized them in the functioning state by EXAFS spectroscopy, which indicates the formation of alkene ligands bonded to the rhenium, consistent with their role as reactive intermediates. The alkene ligands replaced a fraction of the CO ligands as the reactant stream of ethylene + H_2 came in contact with the catalyst. We also used EXAFS spectroscopy to characterize changes in supported Ir_6 and in (nonuniform) platinum clusters brought in contact with reactive atmospheres. The observed changes included oxidative fragmentation of the nanoclusters in O_2 and reversible cluster formation upon H_2 treatment. These results emphasize the point that noble metal nanoclusters are not always reduced and metallic during catalysis, and when they are small enough they can be oxidized fully.

We learned details of the hydrogenation reactions of alkenes on supported Rh_6, Ir_4, and Ir_6 by measuring EXAFS and IR spectra of the functioning catalysts, identifying reactive intermediates such as π-bonded alkenes and alkyls and showing that the cluster frames swelled and the clusters flexed away from the support as the concentrations of these ligands on the clusters increased. These data demonstrate how detailed structural information about the ligand sphere of supported nanoclusters can be gleaned from EXAFS and IR spectra of working catalysts, but the data set is limited and restricted to steady-state operation.

We were further motivated to synthesize and investigate the catalytic properties of a family of the smallest possible supported clusters, prepared from $Ir_2(CO)_8$, $Ir_4(CO)_{12}$, and $Ir_6(CO)_{16}$, each synthesized in high yield from $Ir(CO)_2(acac)$ in the α-cages of zeolite NaY. These clusters were decarbonylated to give supported catalysts consisting predominantly of Ir_2, Ir_4, and Ir_6, respectively, as shown by EXAFS spectra, and they were tested as catalysts for ethylene hydrogenation, a reaction occurring under such mild conditions that the cluster nuclearities were maintained. The clusters were intact, with identifiable Ir–Ir bonds, during steady-state catalysis, and the catalytic activity and the apparent activation energy for the reaction were found to depend markedly on the cluster nuclearity, but the results are not sufficient to provide a clear interpretation of the role of neighboring Ir centers, and more data are needed, including reaction kinetics and characterizations of the catalysts during changes in reaction conditions to provide information about the reactive intermediates and establish the influence of neighboring metal centers. In the work with iridium clusters in zeolite NaY, we set out to synthesize as high a loading of clusters as possible while maintaining a high degree of structural uniformity; we succeeded in preparing Ir_6 in the α-cages with a loading of 33 wt% Ir in the zeolite. This loading exceeds by an order of magnitude the highest reported loading of any well-defined metal clusters in a well-defined support; the sample consequently offered unique opportunities for characterization of clusters on supports, yielding excellent EXAFS data and the opportunity for measurement of hydride ligands on the clusters (even in the absence of H_2 in the gas phase) by ^1H NMR and inelastic neutron scattering spectroscopies, demonstrating the importance of such ligands in stabilizing the supported clusters. The high-yield synthesis of Ir_6 clusters in the zeolite was, we infer, aided by the confinement effects of the cages, hindering the synthesis of larger clusters. Building on this hypothesis, we carried out synthesis of gold clusters in this zeolite (aggregating the gold made from $Au(CH_3)_2(acac)$), finding that the resultant nanoclusters were just large enough to fit in the α-cages, although larger clusters formed readily on oxide supports under equivalent conditions. These are some of the best-defined supported gold samples and provide new opportunities for fundamental investigation of uniformly sized gold nanoclusters.

We have also compared TEM images of ensembles of 3 Os atoms on MgO with EXAFS data; the TEM and EXAFS results show a satisfying agreement in the ensemble sizes (6 Å) and a confirmation that supported clusters made from molecular precursors [$Os_3(CO)_{12}$ in this case] can be made to be nearly uniform.

DOE Interest

This work matches DOE's interests in designing, modeling, fabricating, characterizing, and using new materials and structures including metals at the nanoscale for energy-related applications and in understanding, modeling, and controlling chemical reactivity and energy transfer processes on surfaces for energy-related applications.

Future Plans

We are continuing to investigate supported metal complexes with essentially molecular structures, now emphasizing transient methods of characterization including IR, XANES, and EXAFS spectroscopies of catalysts in reactive atmospheres and in the functioning state.

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Naturally chiral surfaces: A tour of the stereographic projection

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The high Miller index surfaces of single crystal metals have chiral structure and have been shown to interact enantiospecifically with chiral adsorbates. There are many demonstrations of this phenomenon originating in several laboratories around the world. One specific example is the adsorption of R-3-methylcyclohexanone on Cu(*hkl*)$^{R\&S}$ surfaces. Several years ago we demonstrated that the adsorption of R-3-methylcyclohexanone on the Cu(643)$^{R\&S}$ surfaces was enantiospecific. The desorption energies of R-3-methylcyclohexanone adsorbed at R and S kinks differed and the orientation of the molecule at the R and S kinks differed.

Over the past two years we have completed a study of the adsorption of R-3-methylcyclohexanone on a set of surfaces spanning the entire stereographic projection as shown in the figure below. In spite of the complex variety of surface structures, we find that the adsorption sites on all surfaces can be classified as terraces, step and kink type sites and have adsorption energies for R-3-methylcyclohexanone that are quite distinct from one another. One of the important observations is that some of the nominally straight step edges such as those found on the Cu(410) surface exhibit behavior similar to that of the kinks on the Cu(643) surface. This arises because these (410) step edges are in fact quite rough. They are not formed by close packed rows of atoms.

Those surfaces that are located in the interior of the stereographic projection are all chiral and all exhibit enantiospecific adsorption of R-3-methylcyclohexanone. The important result is that enantiospecificity of the desorption energies of R-3-methylcyclohexanone differ among the surfaces in the various parts of the stereographic projection indicating complex dependence on the details of the surface structure and the types of kinks exposed by these surfaces.

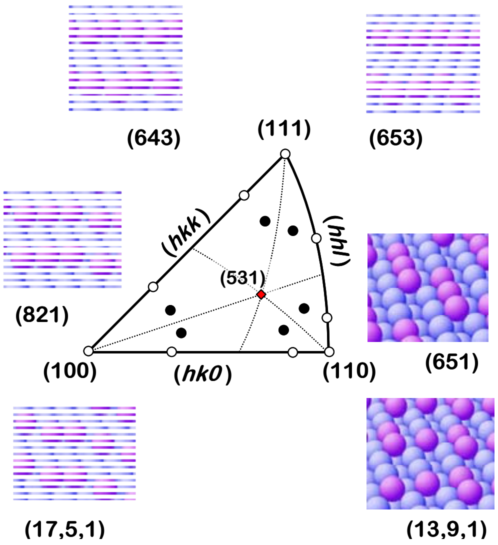

Figure 1. Stereographic projection of the fcc crystal structure. All planes in the interior of the stereographic projection are chiral. The adsorption of R-3-methylcyclohexanone ahs been studied on all 16 surfaces denoted by point on the stereographic projection. The ideal structures of the planes denoted by solid points (●) are illustrated.

DE-FG03-95ER14511 **D. Wayne Goodman**

Toward an Understanding of Catalysis by Supported Metal Nanoclusters

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Goal:

Develop an atomic-level understanding of catalysis by supported metal nanoclusters.

Recent Progress: Selected Accomplishments

Design and synthesis of highly active supported Au catalysts

The catalytic performance of supported Au nanoparticles have been attributed to structural effects, including particle thickness and shape, metal oxidation state, as well as to support effects. Recently, we have reported for the first time that Au completely wet an oxide surface forming a (1x1) mono and (1x3) bilayer structures on a TiO_x/Mo(112). This (1x3) bilayer was found to be highly active for CO catalytic oxidation. These results demonstrated that a continuous Au film on an oxide surface is an active catalyst and even more active than supported Au nanoparticles. Stimulated by this, recent work has focused on characterizing the structures of the ordered Au films on TiO_x/Mo(112).and wetting of Au on other oxide supports, as well as their catalytic performance.

Recently acquired atomic resolved STM images (see Figure 1) are consistent with the structural models of the ordered (1x1) monolayers and (1x3) bilayers proposed previously, as indicated in the insert of Figure 1. Au nanoparticles on clean and chemical modified TiO_2(110) have been imaged by STM and their stability and sinter mechanism investigated. The structures and catalytic properties of Au nanoparticles on TiO_2(110) are compared with that of the (1x3) bilayer. Ongoing parallel experiments are addressing high-surface-area TiO_2 supported Au catalysts focusing on wetting of Au on oxide surfaces and enhancement of the density of catalytically active sites.

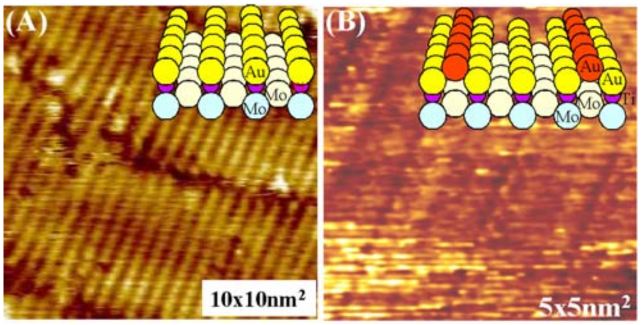

Figure 1. Atomic resolved STM images of (A) (1x1) mono- and (B) (1x3) bilayer on TiOx/Mo(112). Inserts show the structural models.

An *in situ* investigation of CO Oxidation on Pd(110) by polarization modulation infrared reflection absorption spectroscopy (PM-IRAS)

CO oxidation on various catalysts has been extensively studied for many years; however, research at the molecular level using metal single crystals is less extensive and more recent . In the latter case only a few studies have used *in situ* spectroscopy . In a recent study, polarization modulation infrared reflection adsorption spectroscopy

(PM-IRAS) has been used to monitor *in situ* CO oxidation over Pd(110) at elevated pressures (up to 90 Torr) and elevated temperatures. Various compositions of CO/O_2 mixtures show that the rate or turnover frequency (TOF) of CO oxidation reaches an unprecedented value at relatively low CO/O_2 ratios. The dramatic change in the surface composition under these high reactivity conditions is reflected in the PM-IRAS CO adsorption data that show a switch from metallic Pd sites to oxidized-Pd sites with the rapid rise in reactivity. Additional investigations by AES and PM-IRAS show that at the point of the rapid rate increase, the surface is covered by a thin oxide film rather than bulk oxide.

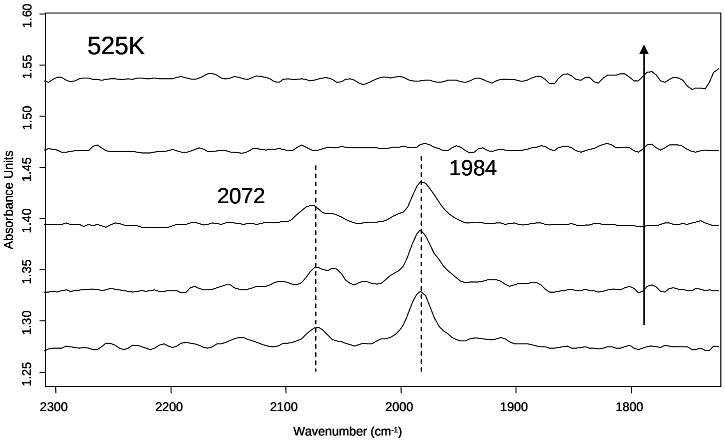

Figure 2. PM-IRAS data collected *in situ* under CO oxidation conditions at 525 K in the sequence indicated by the arrow. The collection time for each spectrum was 10 seconds. P_{CO} = 14 Torr and P_{O2} = 50 Torr at the onset of reaction.

Atomic-Scale Site Isolation in a Model PdAu Catalyst

In heterogeneous catalysis, while specific reaction ensembles are frequently discussed, to date direct atomic control of specific sites has not yet been reported. STM images have been acquired for a Pd monomer-pair catalytic site on a AuPd(100) bulk alloy surface that is highly selective for vinyl acetate synthesis from ethylene and acetic acid. These studies also demonstrate that the sample preparation method has a direct effect on the surface Pd distribution, which is far from random with a marked preference for the local c(2 × 2) configuration, i.e., a monomer-pair configuration. Moreover, this work has shown that using the unique thermodynamic properties of AuPd mixtures, it is possible to control the distribution of Pd atoms globally, and thus isolate preferred catalytic sites potentially for optimum catalytic selectivity [3].

Our findings demonstrate that known thermodynamic properties of solid mixtures can be utilized to control surface site isolation globally, on the atomic scale. This method differs from previous examples of site isolation in that it does not rely exclusively on randomness. The use of SRO—an inter-atomic property—allows for direct control over the degree of randomness. We believe that this method will impact catalysis (e. g. design of novel model catalysts) as well as other technological areas involving a “bottom up” approach to custom surfaces, e.g. self-assembly, or molecular electronics.

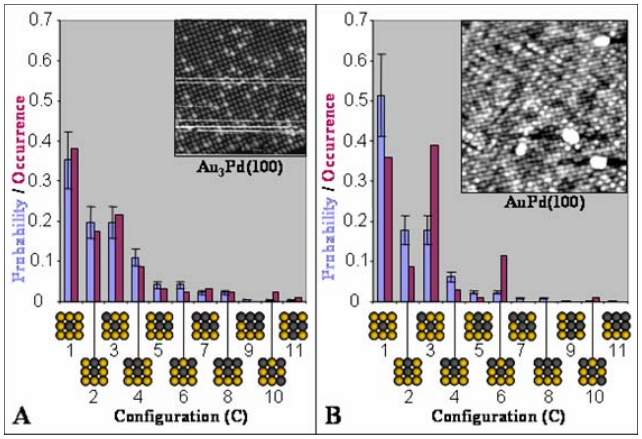

Figure 3. Comparison of Pd distributions between (A) $Au_3Pd(100)$ and (B) AuPd(100). The distribution in (A) is clearly more random than that in (B). Preferred Pd arrangements in (B) are C = 3 and 6.

DOE interest

Supported Au nanoclusters (2~3 nm) exhibit extremely high activities for a number of reactions. In particular, its high activity for the selective oxidation of CO in the presence of hydrogen at room temperature is an important application of Au catalysts in view of the current need for CO-free hydrogen for fuel cells. However, a major obstacle to the commercial utilization of Au catalysts is the rapid sintering of the nanoclusters under reaction condition. Our recent discovery of the active structure of the supported Au catalysts, together with our new strategies for synthesizing sinter-resistant supports, promise to accelerate the design of commercial gold nano-structured catalysts for a variety of selective oxidation reactions.

Future plans

Our efforts will also continue with respect to the synthesis and characterization of well-defined mixed-metal nanoclusters using our recently developed STM shadowing methodology. Our efforts to design supports for nanostructured catalysts that exhibit sinter-resistant properties at realistic reaction conditions will be extended. Finally, the identification of the key reaction intermediates in vinyl acetate synthesis will be addressed *in situ* with PM-IRAS. An understanding regarding the structure of the active centers and the key factors leading to the combustion product (carbon dioxide) will be invaluable in the design of optimum catalysts for this important technical reaction. A new thrust is underway to understand the role of surface oxides in the observed “hyperactivity” of Pd, Rh, and Pt for CO oxidation reaction. This research direction will be extended and developed over the course of the next year of this project.

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DE-FG02-85ER13350 **Raymond J. Gorte**

Studies of Redox Properties in Ceria-Based Catalysts

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Goal:

We are studying mixed oxides, with special attention towards ceria, using thermodynamic measurements of the redox properties. Specifically, we are characterizing the effect of composition, crystallite size, and surface area on the equilibrium redox properties, including the enthalpies and entropies of oxidation. As part of this work, we will be developing Coulometric titration as a relatively general method that can be applied to studying the redox properties of oxide catalysts.

Recent Progress:

Coulometric Titration: The most direct way to determine redox thermodynamics is by measuring the equilibrium stoichiometries for the oxides as a function of temperature and oxygen fugacity, ($P(O_2)$). For example, when the reaction $2V_2O_4 = 2V_2O_3 + O_2$ is in equilibrium, thermodynamic quantities can be calculated from the following equations:

$$\Delta G = RT\ln[P(O_2)] \qquad (1)$$

$$\Delta H = -R[\delta \ln P(O_2)]/\delta(1/T) \qquad (2)$$

$$\Delta S = (\Delta H - \Delta G)/T \qquad (3)$$

For most oxides at the temperatures of interest, the range of oxygen fugacities relevant for thermodynamic measurements is very low and must be established by equilibrium with a redox couple, such as a mixture of H_2 and H_2O or CO and CO_2. Coulometric titration involves placing a sample in a sealed container, separated from the atmosphere by an ion-conducting membrane, yttria-stabilized zirconia (YSZ). Electrodes on either side of the membrane are used to measure the potential across the membrane, and the potential can be related to $P(O_2)$ through the Nernst Equation:

$$V = -RT/[4F]*\ln[P(O_2)/0.21 \text{ atm}] \qquad (4)$$

Oxygen can be added to the sample by passing current through the membrane, with 1 C of charge corresponding to 5.18 μmol of O^{2-}. We have built and successfully demonstrated a working system and applied it to the study of several types of catalysts.

Comparison of Redox Properties for V_2O_5 and $Mg_3(VO_4)_2$: Coulometric titration was used to characterize the redox properties of V_2O_5 and $Mg_3(VO_4)_2$ between 823 and 973 K. As shown in Fig. 1, the redox isotherms for V_2O_5 show distinct regions corresponding to equilibrium with mixtures of V_2O_3 and V_2O_4 and of V_2O_4 and V_2O_5. From this data, the enthalpies for oxidation of V_2O_3 to V_2O_4 and for V_2O_4 to V_2O_5 are shown to be -380±10 kJ/mol O_2 and -270±20 kJ/mol O_2, respectively. Oxidation isotherms for $Mg_3(VO_4)_2$ exhibit a single step between the oxidized sample (all V^{+5}) and a completely reduced sample (all V^{+3}). The enthalpy of oxidation is found to increase with the oxidation state of the sample, from -370±30 kJ/mol O_2 at an O:V ratio of 1.5 to -460±10 kJ/mol O_2 at an O:V ratio of 2.5.

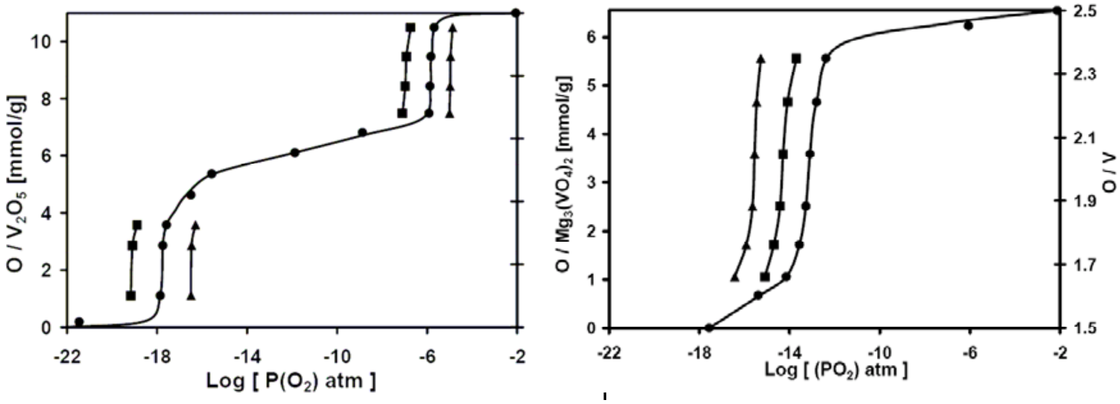

Fig. 1. On the left, oxidation isotherms for vanadia: ■ 823K, ●873K, ▲923K. The absolute amount of oxygen added to the sample from its fully reduced state is plotted on the left, relative to the weight of the fully oxidized sample. On the right, oxidation isotherms for $Mg_3(VO_4)_2$: ▲873K, ■ 923K, ●973K. The absolute amount of oxygen added to the sample from its fully reduced state is plotted on the left, relative to the weight of the fully oxidized sample. The O/V ratio was calculated without the oxygen associated with MgO.

Ceria-Zirconia Solid Solutions: It is well known from Oxygen Storage Capacitors (OSC) in automotive emissions-control catalysis and from recent work on ceria-based water-gas-shift catalysts that ceria-zirconia solid solutions are more reducible than pure ceria. We have therefore measured the redox properties for a series of solid solutions between 873 and 1073 K. While the oxidation enthalpy for pure CeO_2 was between -750 and -800 kJ/mol O_2, the oxidation enthalpies for each of the solid solutions were between -500 and -550 kJ/mol O_2 and essentially independent of the extent of reduction. The shapes of the isotherms for the solid solutions were affected by the oxidation entropies, which depended strongly on the sample composition and the extent of reduction. A model was developed which explains reduction of the solid solutions in terms of the local atomic structure, with the formation of "pyrochlore-like" clusters causing the increased reducibility of the solid solutions. Some of the changes in reducibility are associated with the number of sites from which oxygen can be removed in order to form pyrochlore-like clusters.

Surface Ceria and Rare-Earth Doping: The redox properties of surface ceria were investigated by examining ceria supported on La-modified alumina (LA). Oxidation enthalpies on ceria/LA were found to vary with the extent of reduction, ranging from -500 kJ/mol O_2 at low extents of reduction to near the bulk value of -760 kJ/mol O_2 at higher extents. To determine whether +3 dopants could affect the oxidation enthalpies for ceria, isotherms were also measured for Sm^{+3}-doped ceria (SDC) and Y^{+3}-doped ceria. These dopants were found to remove the phase transition observed in pure ceria below 973 K but appeared to have minimal effect on the oxidation enthalpies.

DOE Interest

Understanding the redox properties of mixed oxides will have a large impact on the development of many different catalyst types, ranging from partial-oxidation catalysts, like the vanadia system, to ceria-based catalysts for the water-gas-shift reaction. All of these reactions require removal of lattice oxygen from the oxide and the binding energies for this process are strongly influenced by composition and the presence of different types of cations. We are developing thermodynamic data, really for the first time, for removing oxygen from catalytically relevant materials.

Future Work

We are working to decrease the measurement temperature for using Coulometric Titration and have indications that we can obtain thermodynamic data at temperatures as low as 350ºC. This will allow us to begin studying supported oxides, learning how different supports and oxide loading affect the redox properties.

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- "Oxidation Enthalpies for Reduction of Ceria Surfaces", Gong Zhou1, P. R. Shah, T. Montini, P. Fornasiero, and R. J. Gorte, submitted for publication.
- "Probing the Effect of Local Structure on the Thermodynamic Redox Properties of V^{+5}: A Comparison of V_2O_5 and $Mg_3(VO_4)_2$", P. R. Shah, J. M. Vohs, and R. J. Gorte, submitted for publication.

Combinatorial First-Principles Screening of Alloys for Electrocatalysis

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Density Functional Theory-based techniques have the potential to efficiently screen large numbers of transition metal alloys for desirable catalytic properties at relatively low cost. However, the triple challenges of identifying suitable descriptors for reactions of interest, of finding methods to efficiently determine the values of these descriptors on different metals and alloys, and of reliably estimating the stability of promising catalytic candidates in reactive environments, have generally limited the application of computational screening techniques to electrocatalytic systems.

In this poster, I present a general methodology for electrocatalyst screening using atomic-scale simulation methods. The method employs DFT calculations to estimate important features of catalytic performance, including catalyst activity, structure, and stability, and it is applied to the analysis of hundreds of transition metal alloys for reactions of interest in electrochemistry.

DE-FG02-04ER15604 **Vadim V. Guliants**

Fundamental Studies of Propane Ammoxidation over Model Bulk and Supported V-Mo-Te-O Catalysts

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Collaborators: Drs. Hidde H. Brongersma (Technical University of Eindhoven), Alan Dozier (University of Kentucky), Soon-Jai Khang (UC)

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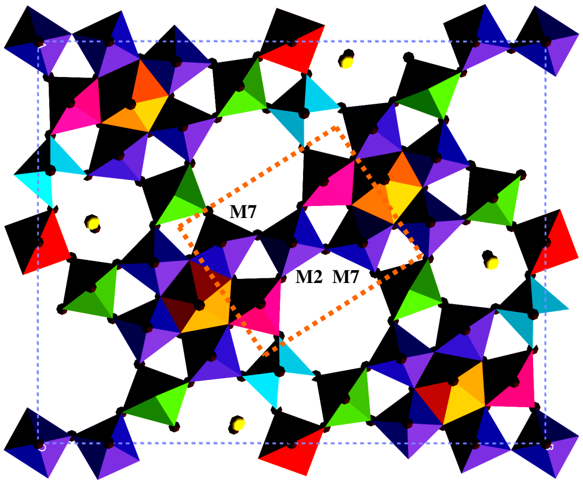
Goal

Develop synthesis methods for V-Mo-Te-O oxides. Establish the bulk and surface molecular structure-reactivity/selectivity relationships for propane ammoxidation over model V-Mo-Te-O oxides. Develop molecular models of propane ammoxidation over model V-Mo-Te-O oxides.

Recent Progress

Topmost Surface Chemistry of V-Mo-Te-O Catalysts: We investigated propane ammoxidation to acrylonitrile over hydrothermal Mo-V-Nb-Te-O catalyst containing the dominant M1 phase, recently proposed as active and selective in this selective ammoxidation reaction. The results obtained in this study were examined on the basis of two reaction networks involving propane transformation via (1) parallel routes to propylene, acrylonitrile and carbon oxides and (2) propylene as the reaction intermediate for acrylonitrile. The results obtained indicated only a slight preference for the reaction network involving the propylene intermediate, which may be explained on the basis of catalytic behavior of the M1 and M2 phases present in the hydrothermal Mo-V-Nb-Te-O catalyst. Methanol and allyl alcohol chemisorption and surface reaction in combination with low energy ion scattering (LEIS) were employed to determine the outermost surface compositions and chemical nature of active surface sites present on the orthorhombic (M1) Mo-V-O and Mo-V-Te-Nb-O phases. These orthorhombic phases exhibited vastly different behavior in propane (amm)oxidation reactions and, therefore, represented highly promising model systems for the study of the surface active sites. The LEIS data for the Mo-V-Te-Nb-O catalyst indicated surface depletion for V (-23%) and Mo (-27%), and enrichments for Nb (+55%) and Te (+165%) with respect to its bulk composition. Moreover, direct evidence was obtained that the topmost surface VO_x sites in the orthorhombic Mo-V-Te-Nb-O catalyst were preferentially covered by chemisorbed allyloxy species, whereas methanol was a significantly less discriminating probe molecule. Our findings suggested that different surface locations for V^{5+} ions in the orthorhombic Mo-V-O and Mo-V-Te-Nb-O catalysts may be primarily



The *ab* planes of the M1 phase proposed to contain the M7-M2-M7 active and selective surface sites for propane ammoxidation.

responsible for vastly different catalytic behavior exhibited by the Mo-V-O and Mo-V-Te-Nb-O phases. Although the proposed isolated V^{5+} pentagonal bipyramidal sites in the orthorhombic Mo-V-O phase may be capable of converting propane to propylene with modest selectivity, the selective 8-electron transformation of propane to acrylic acid and acrylonitrile may require the presence of several surface VO_x redox sites lining the entrances to the hexagonal and heptagonal channels of the orthorhombic Mo-V-Te-Nb-O phase. Finally, the present study strongly indicated that chemical probe chemisorption combined with low energy ion scattering (LEIS) is a novel and highly promising surface characterization technique for the investigation of the active surface sites present in the bulk mixed metal oxides.

DOE Interest

The systematic exploration of the synthesis phase diagram provided a relational database for the synthesis of model V-Mo-M-O catalysts with predictable M1/M2 phase and bulk chemical compositions. This database is expected to be of significant general utility for catalysis research, because it will guide the rational design of novel multicomponent V-Mo-M-O catalysts for selective transformation of propane to propylene and oxygenates. Secondly, the results provide a fundamental basis for the development of a new environmentally benign process of one-step propane (amm)oxidation to acrylonitrile and oxygenates over bulk mixed V-Mo-M-O catalysts.

Future Plans

We plan (1) *in situ* molecular characterization of model bulk and supported Mo-V-(Te-Nb)-O catalysts by Raman and IR spectroscopies under different environmental conditions (NH_3, O_2, propane/O_2, propane/NH_3, NH_3/O_2, H_2O/NH_3, H_2O/O_2, propane/H_2O/O_2, propylene/O_2, propylene/NH_3/O_2) in order to elucidate the states of the surface metal oxide species and reaction intermediates during propane ammoxidation; (2) transient studies of propane and propylene ammoxidation over model Mo-V-(Te-Nb)-O catalysts as a function of time, involving changes in partial pressures and isotopic labeling: $^{18}O_2$, $H_2{}^{18}O$, $CH_3CD_2CH_3$, $CH_3CH_2CD_3$, $CD_2{=}CHCH_3$, $CH_2{=}CDCH_3$, $CH_2{=}CHCD_3$, $^{15}NH_3$, ND_3 to provide fundamental kinetic and mechanistic information about the ACN formation. This work is being carried out in collaboration with a research group of Dr. Overbury at ORNL; (3) modelling studies of the mechanism of propane ammoxidation over various surface active sites present in cluster models of supported $M'O_x$ catalysts (M'= V, Mo, Sb and Te) employing the Gaussian03 B3LYP DFT methodology. This work is carried out by Dr. Anping Liu, a research associate managing the molecular modeling facility in our group. We are presently examining the olefinic pathway of propane ammoxidation over the isolated and bridged VO_x species anchored to an Nb_2O_5 cluster containing 10 Nb atoms and based on the crystal structure of the low-temperature form of Nb_2O_5.

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Engineering Nanostructured Metal Oxides for Hydrogen Storage and Catalysis

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Abstract

Novel nanomaterials for environmental and energy-related conversions are increasingly emerging from rational engineering design based on the understanding of relationships between structure at the molecular level and active nanoparticle performance. Nanostructured metal oxides have drawn wide attention because of their novel size-dependent properties and many potential applications related to them for catalysis, chemical sensing, microelectronic devices, and environmental technology. The objective of this exploratory research is to investigate ordered nanostructured metal oxides with three-dimensional connectivity and functionalized with metal nanoparticles at their surface as economically viable hydrogen storage materials and novel catalysts with unique sensitivities and selectivities. The proposed research focuses on (1) the influence of the metal oxide's nanostructure on the hydrogen storage mechanism and on the shape-selective properties in catalysis, investigated by spectroscopic characterization of the nanomaterials under working conditions; and (2) a site-specific surface functionalization of the metal oxides with size- and shape-specific metal complexes and clusters of transition metals.

DOE Interest

High prices of fossil fuels; the desire to eliminate the U.S. dependency on foreign oil; and environmental concerns due to greenhouse gases emissions have motivated the search for renewable fuels. Biofuels and hydrogen-based technologies are two proposed alternatives to the use of fossil fuels. In both research lines, development of the active materials is a crucial milestone to reach the goals. For example, hydrogen storage is a key enabling technology for the advancement of hydrogen and fuel cell power technologies. Among all the basic research areas being developed to store hydrogen, nanostructured materials offer advantages for superior hydrogen storage due to short diffusion distances, reduced heats of adsorption/desorption, faster kinetics, and better hydrogen dissociation at surfaces. The fundamental knowledge generated in this project by the use of in situ experimental techniques presents an excellent starting point in the development of many types of nanostructured metal oxide materials, with a particular interest in the filed of catalysis and hydrogen storage.

DE-FG02-01ER15183 **Gary L. Haller**

Nanopore Radius of Curvature Effect on Catalysis and Catalytic Particle Formation

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Goal

To investigate the radius of curvature effect of nanopore materials [mesoporous molecular sieves (MCM-41 and SA-15) and Single Wall Nanotubes of carbon (SWNT)] on adsorption and catalysis and to investigate improvements in catalysis afforded by high area structured supports.

Recent Progress

Synthesis and Characterization of Highly Ordered Ni-MCM-41 Mesoporous Molecular Sieves*:* Highly ordered Ni-MCM-41 samples with nearly atomically dispersed nickel ions were prepared reproducibly and characterized. Similar to the Co-MCM-41 samples, the pore diameter and porosity can be precisely controlled by changing the synthesis surfactant chain length. Nickel was incorporated by isomorphous substitution of silicon in the MCM-41 silica framework, which makes the Ni-MCM-41 a physically stable catalyst in harsh reaction conditions such as CO disproportionation to single wall carbon nanotubes (SWNT) or CO_2 methanation. X-Ray absorption spectroscopic results indicate that the overall local environment of nickel in Ni-MCM-41 was a tetrahedral or distorted tetrahedral coordination with surrounding oxygen anions. Hydrogen TPR revealed that our Ni-MCM-41 samples have high stability against reduction; however, compared to Co-MCM-41, the Ni-MCM-41 has a lower reduction temperature, and both the H_2-TPR and *in-situ* XANES TPR reveal that the reducibility of nickel is not clearly correlated with the pore radius of curvature, as is the case of Co-MCM-41.

Anchoring and Partial Occlusion of Metal Particles on the pore Walls of MCM-41*:* In order to explain the high stability of the Co- and Ni-MCM-41 catalysts, the hypotheses of anchoring effect of small metallic clusters and partial occlusion effect of the metallic clusters by amorphous silica are introduced. Carbon monoxide chemisorption on the model catalysts, and on Co-MCM-41 directly, demonstrate the metal anchoring effect on the stability of metal cluster dispersion. The partial occlusion of metallic clusters, which was monitored by CO *in-situ* FTIR and the kinetic study of CO methanation, confined the metallic clusters on the pore surface resulting in the stabilization of the catalysts against deactivation.

The Statistical Design of a Process for Methane Oxidation to Formaldehyde on V-MCM-41*:* To optimize the production of formaldehyde from partial oxidation of methane, a statistical multivariate analysis, multi-regression model analysis was used. This approach is advantageous, especially when experimental evaluation and optimization of a process is time consuming and expensive. By carrying out a finite number of experiments, statistical modeling shows reasonably good prediction ability in terms of methane conversion, formaldehyde selectivity, and space time yield.

***Multivariate Correlation for the Synthesis of Stable C10-Co-MCM-41**:* As the SWNT diameter decreases, the diversity of possible chiral conformations decreases, therefore smaller-diameter SWNT with a narrow diameter distribution is highly desirable for applications such as electronic devices and chemical sensors. Co-MCM-41 with 1.9 nm pore diameter was prepared as a catalytic template to produce SWNT with diameters as small as 0.77 nm. Both the statistical analysis of a design set of experiments and screening test experiments results based on a model from the design set show that the synthesis of Co-MCM-41 can be described by a few significant predictors and their two-factor interaction terms. Raman spectroscopy results demonstrate the success of 0.77 nm diameter SWNT synthesis with 1.9 nm diameter Co-MCM-41 catalyst with partial pre-reduction at 650°C (and reaction at 750°C) but these materials can be nearly completely reduced at 750°C and with reaction 850°C become high yield SWNT catalysts with diameters > 1nm.

DOE Interest

Metal substituted MCM-41 can be used to prepare highly dispersed and stable supported first-row transition metals, e.g., V and Co, which are good catalysts for both traditional energy related reactions, e.g., Fischer-Tropsch synthesis, hydrocarbon oxidation, etc., and emerging catalytic applications, e.g., synthesis of single walled nanotubes (SWNT) of carbon of narrow diameter distribution and use as a novel catalyst support. We are particularly interested in the development of improved catalysts for C1 reactions (CO and CO_2 methanation and methanol and methane oxidation) based on V, Co and Ni incorporated in the MCM-41 matrix and SWNT as a metal support for aqueous phase reforming.

Future Plans

Our proposed research is a continuation of the investigation of radius of curvature effects on catalyst preparation, adsorption, and catalytic activity and selectivity. The future design of improved catalysts for small diameter SWNT synthesis with a narrow diameter distribution is outlined above. We also plan to extend the range of pore sizes (relative to Figure 1) by moving to SBA-15 which has a similar hexagonal structure to that of MCM-41 but pores that are two to three times as large as our largest MCM-41. These materials can be narrowed by growing a layer by layer oxide in the SBA-15 pores, functionalized by growing a layer of anchoring cations, e.g., a layer of TiO_2 in the pores of SBA-15. This will both extend the pore size range of our study and provide new approaches to preparing anchored small metal clusters for energy related methanation, reforming and SWNT catalysts.

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In situ time-resolved X-ray diffraction (TR-XRD) and Quick EXAFS (QEXAFS) for characterizing catalysts and active sites

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At the NSLS beam line X7B, we have a facility capable of conducting *in situ*, sub-minute TR-XRD experiments under a wide variety of temperature and pressure conditions (80 K < T < 1250 K; 1 Torr <P< 150 atm)[1] Recently at X18B we have conducted 2 second in situ QEXAFS measurements in the temperature range (25-400°C)I in a plug flow reactor. Measurements include control of gas flow and measurement of gas composition of the products with mass spectrometry and gas chromatography. Thus we are able to determine molecular and electronic structures of active catalysts.

Using TR-XRD, one can obtain information about structural details, phase composition, kinetics of transformation, intermediate phases and crystal characteristics. Examples of problems studied to date with TR-XRD include: (1) Substrate binding of zeolites[2]; (2) reduction/oxidation of oxide catalysts[3]; (3) Water Gas Shift(WGS) reaction with Copper[4] and Gold [5]supported on cerium oxide; (4) Synthesis of Manganese oxide[6], Cu/MO_2 catalyst[7] and titanium oxide catalyst[8, 9]; (5) Water induced morphological changes in BaO/γAl_2O_3 NO_x storage materials[10]; (6) desorption and adsorption of H_2 on the Li-Mg-N-H hydrogen storage system[11]. Using QEXAFS we have studied Cu doped ceria under oxidization, reduction and WGS conditions. This poster will display typical results from recent experiments.

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CATALYSIS SCIENCE INITIATIVE: Supported Molecular Catalysts: Synthesis, In-Situ Characterization and Performance

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The principal goal of our ongoing DOE BES project is to synthesize supported metal complex and metal cluster catalysts that are molecular analogues, with an emphasis on those that have a high degree of structural uniformity; to characterize their structures, even in reactive atmospheres and as they function as catalysts; and to characterize catalyst performance and relate it to structure. We have a unique set of complementary capabilities based on our synthetic approaches; structural characterization capabilities with IR, NMR, and EXAFS spectroscopies; catalyst performance measurements; and computational approaches based on density functional theory.

Highlights of research accomplishments

A core hypothesis underlying our project is that well-defined supported species such as the metal complexes and metal clusters considered here play a key role in advancing the fundamental understanding of catalysis. These catalysts now include supported species that are molecular analogues; ultimately, with improved characterization techniques, we expect them to include the much more complex supported nanomaterials that are representative of typical industrial catalysts. Thus, a primary goal of this project has been to synthesize supported catalysts to be as simple and uniform as possible, thereby offering the opportunities for in-depth characterization of structure and reactivity.

Supported catalysts that are so simple and uniform in structure as to be virtually molecular in character offer the benefits of both homogeneous and heterogeneous catalysis. The catalysts in this class that we have investigated consist of single-metal-atom complexes (of Rh and of Ir) and small metal clusters (of Re and of Ir) on oxide and zeolite supports. Because of evidence indicating that supported metal complexes and clusters on oxides are often present predominantly at surface defect sties, we have also investigated $H_3Re_3(CO)_{12}$ as a probe molecule of the defect sites on an oxide support, high-area anatase. Other project goals were (a) to create solid catalysts with active sites that can function in a cooperative manner to enhance activity and selectivity, and (b) to prepare solid catalysts that can perform multiple reactions in a network that in some cases would not be possible in solution because of the incompatibilities of the various catalytic entities (for example, an acid and a base).

We prepared supported mononuclear complexes of rhodium and of iridium with olefin ligands. The essential novelty and importance of these catalysts are as follows: the reactive olefin ligands provide a facile entry into catalytic cycles with maintenance of the mononuclear metal species and their bonding to the support. Furthermore, these complexes anchored to a crystalline (zeolite) support have highly uniform structures—which implies an unprecedented uniformity of the supported catalytic sites and opportunity for the rigorous application of theory.

In the work with supported rhodium complex catalysts,[1-3] we used the precursor $Rh(C_2H_4)_2(acac)$ [acac is acetylacetonate, $CH_3COCHCOCH_3$] to prepare MgO-[1] and zeolite dealuminated Y (DAY)-[2,3]supported complexes, whereby the acac ligands react with the support and leave the ethylene ligands bonded to the rhodium. The supported complexes have been characterized by IR, ^{13}C NMR, and EXAFS spectroscopies.[4] A key to the successful synthesis on MgO was the control of the surface OH group density. A key to the successful synthesis on the zeolite was a low density of Al atoms, where the cationic rhodium complexes are bonded in isolated sites.

To move toward generalization of these results by extending the family of such catalysts to include a second metal, we prepared the iridium analogue of the rhodium precursor complex; thus, we needed to develop a new synthesis method for the precursor $Ir(C_2H_4)_2(acac)$,[5] which we have now made and characterized fully, including a determination of the crystal structure and investigation by IR, Raman, and ^{13}C NMR spectroscopies and density functional theory (DFT).[5] The compound is isostructural with $Rh(C_2H_4)_2(acac)$, differing essentially only in the strength of the metal–olefin bonding (two ethylenes are bound to Ir with a binding energy of 94 kcal/mol and to Rh with a binding energy of 70 kcal/mol); this difference carries over to the supported analogues and is important in the elucidation of their chemistry and catalysis, as stated below.

The zeolite-supported complex prepared from $Rh(C_2H_4)_2(acac)$ is a close analogue of this precursor; the bidentate acac ligand in the precursor is replaced by a bidentate zeolite ligand in the supported species (Fig. 1).[2] The structural data determined by EXAFS spectroscopy match within error those determined by DFT when an appropriate model of the zeolite is chosen. The ^{13}C NMR spectra are also well represented by the theoretical results.[4]

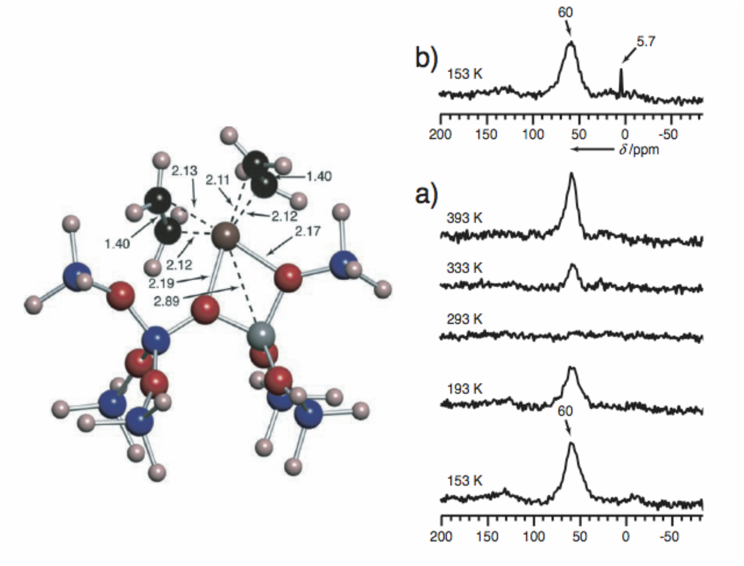

Figure 1. Optimized geometry of the DAY zeolite-supported rhodium ethylene complex with associated bond lengths and the variable temperature ^{13}C CP MAS NMR spectra of same following exchange of ligands for ^{13}C labeled ethylene. a) Temperature dependence of signal intensity. b) Spectrum taken at low temperature following heating indicative of reverse hydrogen spillover as evidenced by the presence of an ethane peak at 5.7 ppm.[2]

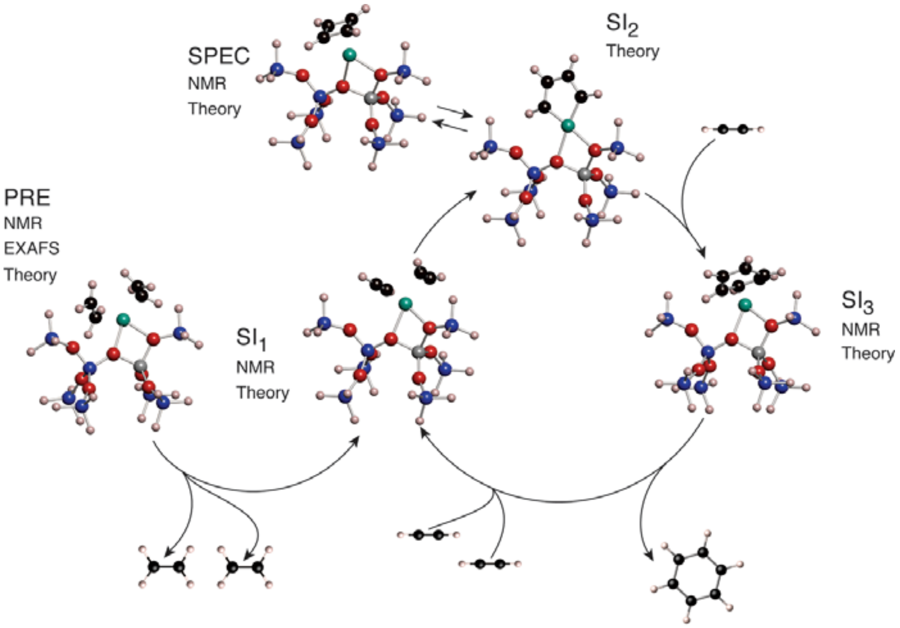

Figure 2. Catalytic cycle for cyclotrimerization of acetylene catalyzed by a single-site Rh^+ center bonded to a zeolite support by two Rh–O bonds. The reactive organic groups bonded to Rh in the as-synthesized catalyst (at left, **PRE**), two ethylenes, allow facile entry into a catalytic cycle. **PRE** has been characterized by EXAFS and ^{13}C NMR spectroscopies as well as density functional theory. (Characterization methods for all the species are shown on the figure.) When the sample is brought in contact with gas-phase acetylene, the ethylene is replaced by acetylene, to form the stable intermediate **SI$_1$**, initiating the catalytic cycle. This intermediate undergoes ring closure via transition state **TS$_{1\rightarrow2}$**, forming the metallacycle **SI$_2$**, which equilibrates with the more stable cyclobutadiene complex (**SPEC**, a spectator species). The pool consisting of **SI$_2$** and **SPEC** crosses via transition state **TS$_{2\rightarrow3}$** into the stable benzene complex **SI$_3$**. Dissociation of product benzene into the gas phase, compensated by adsorption of reactant acetylene, closes the cycle.

When the zeolite-supported rhodium complex was brought in contact with acetylene, the ethylene ligands were replaced by acetylene, and catalytic cyclotrimerization to give benzene took place. Some of the reaction intermediates were observed by ^{13}C NMR spectroscopy (Figure 2). Having a strong basis in structure of the zeolite-supported rhodium acetylene complexes determined by ^{13}C NMR and EXAFS spectroscopies, we were able to benchmark density functional theory (DFT) calculations with these results and to use DFT to predict the full cycle in a model of the catalysis, including the energetics of the transition states (Figure 2). The theory and experiments agree well. This is one of the best-understood catalytic cycles involving a supported species, and the key to the rigor of the approach is the uniformity of the supported complexes on the crystalline support.

We have extended the investigation to include the iridium analogue of the zeolite-supported rhodium ethylene complex, having characterized it by EXAFS and IR spectroscopies.[6] Again, we made the gem-dicarbonyl species by treatment of the supported ethylene complex with CO and observed very sharp ν_{CO} bands in the IR spectrum—(indirect) evidence that the structural uniformity and opportunity for rigorous application of computation compared with experiment has been extended to the supported iridium complexes. Attempts to exchange the relatively strongly bonded ethylene ligands on Ir with ^{13}C-enriched ethylene to allow an NMR experiment to test the dynamical uniformity of the sample have not yet been successful, however, because the ethylene in $Ir(C_2H_4)_2(acac)$ (and presumably its supported analogue) is more tightly bonded that the ethylene in $Rh(C_2H_4)_2(acac)$ (and presumably its supported analogue), as stated above.

The supported iridium ethylene complex has been found to be active for oligomerization of ethylene, whereas such reactivity was not observed for the rhodium analogue, although both were found to be active for ethylene hydrogenation; this preliminary observation provides a starting point into the proposed research, whereby we plan to use DFT to contrast the catalytic properties of the supported complexes for various olefin reactions, including oligomerization, hydrogenation, and isomerization.

We have also prepared and characterized supported catalysts synthesized from metal cluster precursors, including $H_3Re_3(CO)_{12}$. Because the sites for binding of metal complexes and clusters on oxides have often been postulated to be defect sites and because the evidence for this postulate is essentially all indirect, we sought to test it with $H_3Re_3(CO)_{12}$ as a probe.[7] The oxide we used was TiO_2 (anatase), in part because there is a rich known surface chemistry of TiO_2 (its relatively high conductivity allows many UHV surface-science experiments) and in part because there are well-known treatments to prepare surface Ti^{3+} defect sites.

The IR spectra of surface OH groups associated with the Ti^{3+} defect sites show that they formed (a) as bridging OH groups disappeared during high-temperature evacuation and (b) as surface defect sites and oxygen radical species simultaneously formed (as demonstrated by EPR spectra). These results appear to be the first demonstrating that the formation of the defect sites and oxygen radicals is accompanied by the disappearance of bridging OH groups and the formation of OH groups associated with the defect sites.[7]

$H_3Re_3(CO)_{12}$ clusters were adsorbed in various amounts on the surfaces of anatase that had been treated (in O_2 or under vacuum) to produce various densities of Ti^{3+} defect sites, which were characterized by EPR spectroscopy.[7] The adsorbed rhenium carbonyls at low and high surface concentrations were characterized by IR and EXAFS spectroscopies. The data show that (a) the rhenium carbonyls at a low surface coverage were bonded to the anatase defect sites; (b) these sites were quenched (saturated) at higher coverages; (c) the adsorption took place with the trirhenium frames intact; (d) the strong cluster–TiO_2 interaction affects the Re–Re, Re–C, and Re–O distances (in contrast to those in the less strongly bonded clusters not at defect sites); and (e) adsorption of the clusters involved OH groups of the TiO_2 surface. The data underlie a model of the surface chemistry for the predominant anatase (101) surface, whereby surface defect sites (Ti^{3+}) in the evacuated anatase result from the removal of bridging lattice oxygen atoms and react selectively with $H_3Re_3(CO)_{12}$, which the results thus show to be a useful probe of oxide surface defect sites. We propose that smaller metal carbonyls such as $HRe(CO)_5$ might be even more sensitive probes of these sites and plan to investigate them in the proposed research. Because of the importance of the methods used in this work to what we propose, details are given in Appendix 2.

Samples prepared from $H_3Re_3(CO)_{12}$ were also investigated as catalysts for high-temperature hydrocarbon conversion, with the catalyst testing done at UOP in collaboration with Simon Bare and Mike McCall.[8] Clusters formed by adsorption of $H_3Re_3(CO)_{12}$ on porous γ-Al_2O_3 were decarbonylated at 773 K in flowing H_2 and characterized by XAS. The EXAFS results show that the average distance between Re atoms in the decarbonylated sample (2.67 Å) is shorter than that in metallic rhenium (2.73 Å). This result, combined with the average Re–Re coordination number of approximately 2, indicates that the rhenium was present as small supported clusters, with the nuclearity of 3 essentially matching that of the precursor $H_3Re_3(CO)_{12}$. The rhenium framework was evidently maintained during the decarbonylation process. The rhenium edge position in the X-ray absorption spectrum provided only an imprecise characterization of the rhenium oxidation state, in the range between +3 and +7, but the literature of rhenium clusters allows us to narrow this range: for rhenium to have sufficient electrons to form Re–Re bonds (which may be multiple bonds), it is necessary for the rhenium to be in an intermediate oxidation state, typically, for a three-metal-atom cluster, +4 or less. Thus, on the basis of rhenium chemistry, we infer that the oxidation state of rhenium in the supported clusters was in the range of 3–4.

The performance data measured at UOP show that the catalyst consisting of trirhenium clusters on γ-Al_2O_3 is active for the conversion of methylcyclohexane.[8] The main reaction is dehydrogenation to give toluene, and the other products demonstrate that other classes of reaction also took place. The presence of ethylcyclohexane in the products, combined with the absence of any other (substituted) cyclopentane products, indicates selective ring isomerization reactions. The presence of *n*-heptane and 3,3-dimethylpentane shows that ring-opening reactions also took place (and the selectivities were relatively high). The presence of methane and propane indicates hydrocracking. Because there were numerous unidentified compounds, we emphasize that reactions of other classes may also have occurred; we are now doing more thorough product analysis to characterize the reactions more completely.

Most important, the supported clusters were stable at high temperatures and the product distribution differs from that observed with conventional supported rhenium catalysts, indicating new opportunities in hydrocarbon conversion catalysis offered by small supported cationic clusters of metals to the left of group-8 metals in the periodic table. The activity of the catalyst decreased during operation in the flow reactor, but, because the EXAFS data demonstrate that the rhenium clusters remained trinuclear, we infer that phenomena other than sintering of the clusters caused the deactivation. The product distribution also changed as the experiment proceeded, but we lack sufficient information to explain the complicated patterns of the selectivity changes. The shortening of the Re–Re bond as a result of exposure of the catalyst to reaction conditions suggests stronger Re–Re bonding in the used than in the fresh catalyst.

The near-edge regions of the X-ray absorption spectra of the decarbonylated sample and the sample that had been used as a catalyst show that there was a significant increase in the white line intensity during catalysis. This comparison indicates that the supported rhenium clusters remained as cationic species, consistent with the EXAFS results, which indicate a short Re–O contribution. The change in intensity of the white line, combined with the disappearance of the shoulder at approximately 10,555 eV, suggests that the environment surrounding the trirhenium clusters changed during operation of the catalyst. This inference agrees with the structural changes demonstrated by the EXAFS data.

The EXAFS data show that treatment of the sample in H_2 at temperatures as high as 773 K (as well as operation as a catalyst) did not alter the nuclearity of the clusters initially adsorbed on the support. Thus, the trirhenium cluster frame is inferred to be extremely stable, much more so than those of clusters of group-8 metals on oxide supports under similar conditions. This stability is attributed to the oxophilic nature of rhenium and the fact that rhenium is known to form stable clusters with oxygen-containing ligands, such as those offered by the support in our samples. Thus, these samples appear to open the door to a new class of highly stable supported early transition metal clusters that, are cationic.

Bimetallic MgO-supported catalysts were prepared by adsorption of $Pt_3Ru_6(CO)_{21}(\mu_3\text{-}H)(\mu\text{-}H)_3$ on porous MgO.[10] Characterization of the supported clusters by IR spectroscopy showed that the adsorbed species were still in the form of metal carbonyls. The supported clusters were decarbonylated by treatment in flowing helium at 300 °C, as shown by IR and EXAFS data, and the resulting supported PtRu clusters were shown by EXAFS spectroscopy to have metal frames that retained Pt–Ru bonds but were slightly restructured relative to those of the precursor; the average cluster size was almost unchanged as a result of the decarbonylation. These are among the smallest reported bimetallic clusters of group-8 metals. The decarbonylated sample catalyzed ethylene hydrogenation with an activity similar to that reported previously for γ-Al_2O_3-supported clusters prepared in nearly the same way and having nearly the same structure. Both samples were also active for *n*-butane hydrogenolysis, with the MgO-supported catalyst being more active than the γ-Al_2O_3-supported catalyst.[9]

The key structural parameters characterizing the bimetallic clusters (determined by EXAFS spectroscopy) show the following: (a) for both supports, the following metal–metal contributions became smaller relative to the precursor: Pt–Pt, Pt–Ru, and Ru–Pt; on the other hand, the Ru–Ru contributions became larger (although perhaps not significantly for the γ-Al_2O_3-supported sample; (b) the coordination numbers characterizing the Pt–Ru contributions in the two supported catalysts are about the same; the same is true for the Ru–Pt contributions; (c) the monometallic contributions in the two supported catalysts appear to be significantly different from each other, and the changes with respect the precursor are greater for the MgO-supported sample than for the γ-Al_2O_3-supported sample. These data at best provide a preliminary basis for suggesting structural models of the average supported bimetallic clusters, but we can infer that in each sample, the metal clusters were bonded rather strongly to the support, as indicated by the significant metal–oxygen coordination numbers characterized by bonding distances near 2.0 Å. On MgO, the clusters appear to be enriched in platinum at the edges, as indicated by the result showing a Pt–O than Ru–O coordination number.

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DE-FG02-03ER15463 **Tony F. Heinz, Stephen P. O'Brien (Columbia U.)**

Controlling Structural, Electronic, and Energy Flow Dynamics of Catalytic Processes through Tailored Nanostructures

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Collaborators:	Ludwig Bartels (UC Riverside), Talat Rahman (U. Central Florida), Radoslav R. Adzic (Brookhaven), Christopher Murray (U. Penn), Daniel Resasco (U. Oklahoma), Stanislaus S. Wong (Brookhaven); and Columbia U. collaborators: Louis E. Brus, George W. Flynn, Jim Hone, Philip Kim, Gertrude Neumark, Colin Nuckolls, Richard M. Osgood, Nicholas Turro
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Goal

The overall goal of this project, which is being carried out jointly with co-PIs Ludwig Bartels (UC Riverside) and Talat Rahman (U. Central Florida), is to pursue the development of new catalysts that produce specific surface reactions by applying steric and entropic control using appropriate nanostructures. The research program involves three principal thrust areas: (1) The synthesis of nanostructured materials suitable for novel catalysts; (2) experimental investigations of non-equilibrium surface processes, particularly on nanostructured materials; (3) and theoretical investigations to understand the electronic properties and reactivity of the corresponding systems. Within the experimental surface-science component, research involves the traditional tools of surface science, but also places special emphasis on scanning tunneling microscopy to understand the nature of behavior on heterogeneous surfaces and laser sources to induce and probe non-equilibrium processes. Elementary surface processes and model reactions with nanoscale materials will be examined to pursue these ambitious goals.

Recent Progress

Copper Oxide Nanocrystals for CO Oxidation Reactions**:** The efficient removal of CO by oxidation to CO_2 is not only a model problem in catalysis, but one of great practical importance. The Cu-Cu_2O-CuO system is known to facilitate oxidation reactions in the bulk, suggesting its potential as a cost-effective substitute for existing catalysts. We have demonstrated the advantages of using Cu_2O particles of controlled, nanometer dimensions for this reaction. Over sustained periods of time, as shown in Fig. 1, conversion of 99.5% of CO to CO_2 is observed. The performance of the nanoparticle catalyst is superior to that of equivalent quantities of conventional powered copper oxides.

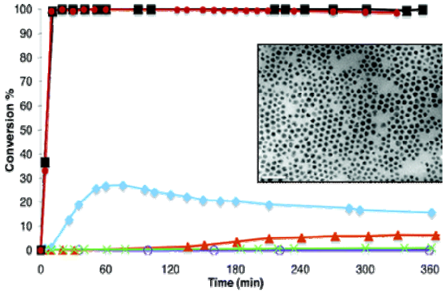

Fig. 1: Conversion rates of CO to CO_2 for various types of copper and copper oxides run at 240 °C in 93% N_2, 3% O_2, and 4% CO: (■) 24 nm Cu_2O nanoparticles, (●) 11 nm Cu_2O nanoparticles, (▲) Cu_2O powder; (♦) CuO powder; (×) silica gel. Inset: TEM image of 6 nm Cu_2O nanoparticles.

To gain insight into reaction mechanisms, a collaboration with co-PI Talat Rahman (U. Central Florida) has been pursued to understand the energetics and dynamics of the process. Using density-functional theory, the pathways for CO adsorption, diffusion, and reaction on the $Cu_2O(100)$ surface have been examined. The calculations indicate the reaction proceeds by a Langmuir-Hinshelwood mechanism and that lattice oxygen, not gas-phase oxygen, plays a critical role in the CO oxidation process.

Multi-component Nanoparticle Superlattices for the Design of Novel Catalytic Nanostructures: The vision for a new class of catalysts calls for the development of functional catalytic materials that take advantage of techniques emerging in nanotechnology, such as self-assembly. One such approach is based on arrays of multi-component nanoparticles. Nanocrystals of different size and functionality (e.g., noble metals, oxides, and semiconductors) can be made to self-assemble into ordered binary superlattices

(BNSLs). The ability to tune particle size and separation and to build arrays from a variety of constituents lends itself to the rational design of complex catalytic nanostructures. In the current funding period, we have built a variety of novel binary BNSLs from monodisperse PbS, PbSe, $CoPt_3$, Fe_2O_3, Au, Ag and Pd nanocrystals, mixing and matching these building blocks to yield multifunctional nanocomposites (Fig. 2). These materials provide new opportunities for optimized catalysts through control not only of chemical reactivity, but also of photoexcitation.

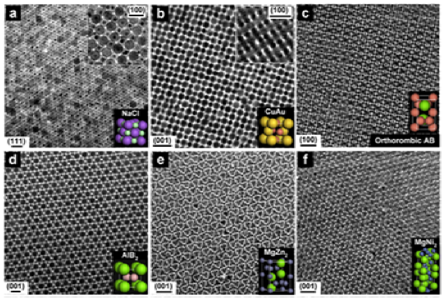

Fig. 2: TEM images of binary superlattices, as self-assembled from different nanoparticles.

Catalytic Growth and Properties of Carbon Nanotubes**:** The preferred method of producing long, well-defined single-walled carbon nanotubes (SWNTs) is through chemical vapor deposition (CVD) growth with carbon-containing feedstock gas and a suitable nanostructured catalyst. Our research has made progress in both the catalytic growth and characterization of the resulting nanostructures. This work is motivated by two interrelated goals. The first goal is optimization of catalytic growth, including growth starting at a given location and proceeding in a given direction, as well as development of selectivity towards particular nanotube chiral structures. Such highly controlled catalytic growth is needed for many advanced applications of nanotubes. The second goal is understanding of energy storage and transport in photoexcited carbon nanotubes for their use in novel photocatalytic systems. Progress has been made along both of these lines. Research has yielded new optical probing techniques capable of providing the structure of individual SWNTs. This has permitted detailed study of the structure and crystallinity of individual nanotubes for characterization of the catalytic growth process. Complementary investigations have also elucidated the nature of the optically excited states in nanotubes.

With respect to new catalytic growth processes, we have developed a simple and efficient CVD process that produces high-purity, long SWNTs with control over the orientation and length. We use ethanol feedstock in conjunction with Co nanoparticles, formed spontaneously by heating ultrathin (0.5-2 nm) metal films, as the catalyst. Representative results are shown in Fig. 3.

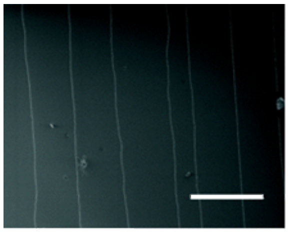

Fig. 3: SEM images of SWNTs grown by ethanol CVD with Co a nanoparticle catalyst. The nanotubes grow parallel to one another over distances of mm's. Optical analysis shows that the nanotubes have diameters of ~1.8 nm.and maintain their chiral structure. Scale bar: 1 mm.

DOE Interest

Catalytic reactions have great importance for a broad range of industrial and environmental processes. It is the aim of this project to explore new approaches that rely on recent developments in nanostructured materials and on advances in our fundamental understanding of molecule/surface interactions to produce catalysts with higher efficiency and greater selectivity, with the potential for impact on a diverse and significant set of chemical processes. Current investigations at Columbia University relate to improved CO oxidation processes, carbon nanotube synthesis, and photo-driven processes using nanostructured materials. While these problems were chosen largely for their scientific interest, they also represent reactions with implications for diverse applications.

Future Plans

Planned work on CO oxidation will examine possible improvements afforded by the introduction of CeO2 nanoparticles as co-catalyst to control the availability of catalytically active oxygen. This study will serve as model for catalysis involving two distinct nanostructured components. With respect to the binary superlattices, our next step will be their optical characterization and identification of opportunities for photocatalysis with inter-particle energy transfer. Efforts to improve carbon nanotube selectivity in the CVD growth process will be undertaken, including exploration of possible catalytic growth from synthesized end-cap structures. Efforts will be pursued to demonstrate the possibility of using carbon nanotubes to transport photogenerated excitation from a region where optical absorption occurs to a reaction site where this energy can activate a chemical reaction.

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Growth and Reactivity of Ce and CeOx on Au(111)

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Poster Abstract

Various reactive deposition techniques were explored for the preparation of CeO_x nanoparticles on a Au(111) substrate. This system is of interest as an “inverse” model catalyst for nanostructured Au/CeO_2 materials that have been shown to be very promising as low temperature catalysts for the WGS. Initial STM and XPS data on cerium growth on the Au(111) surface by simple physical vapor deposition (PVD) and temperature annealing revealed the presence two surface intermetallic compounds (see Figure, top right image). The Ce/Au alloying at the surface prevents efficient conversion to the oxide by direct exposure to oxygen, however, we were able to prepare CeO_x by vapor-deposition of Ce in elevated oxygen pressure (10^{-7} torr). Elongated ceria

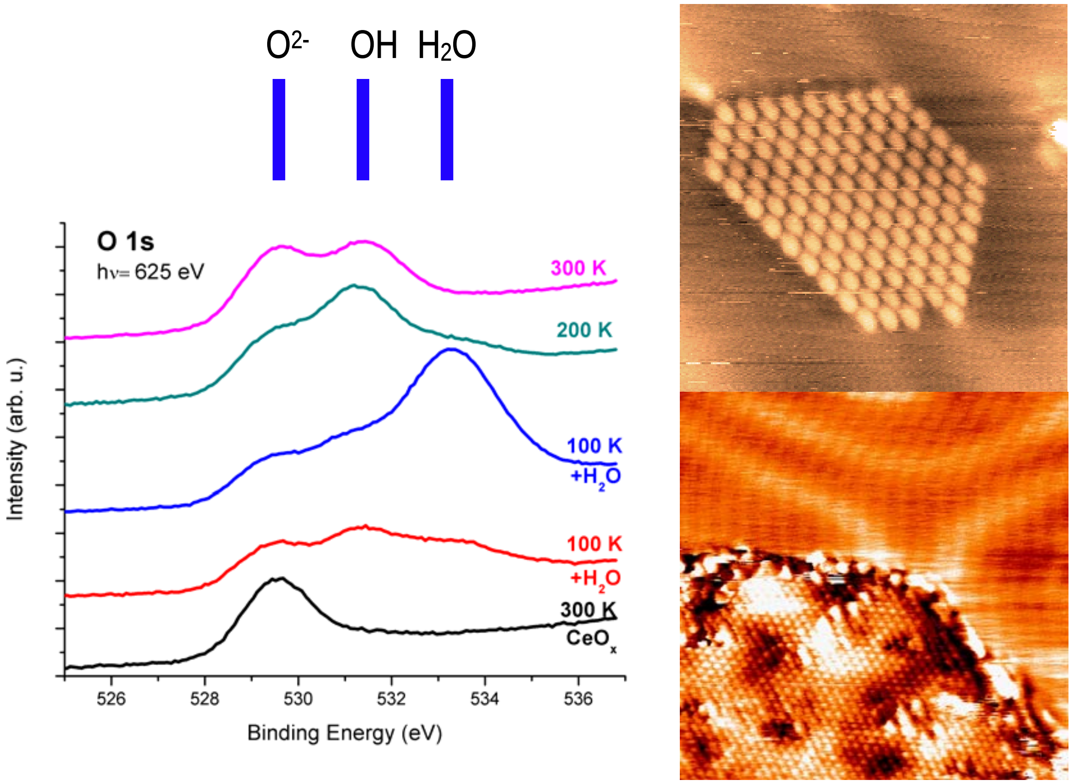

Figure: Left: O 1s core level spectra acquired at indicated temperature with a photon energy of 625 eV. The CeOx/Au(111) surface was covered by ice in two steps at 100 K and then annealed to higher temperatures. Water dissociates forming OH on sub-stoichiometric ceria even at 100 K. Right top: STM image of hexagonal islands of $CeAu_3$ alloy (10 nm x 10 nm); Bottom right: STM image of the CeO_2(111) island with a positively (+806 mV) biased tip (15 nm x 15 nm).

nanoparticles are just one layer thick, several nanometers in long and anchored mostly to steps. Atomically resolved images of the ceria island show a cerium terminated CeO_2 (111) surface with several defects (see Figure, lower right image).

The oxide support is not a simple spectator and plays an essential role in the WGS process. The dissociation of water can take place on the oxide and the stability of key intermediates (carbonate, formate) depends on the nature and state of the oxide itself. Au(111) is an inert surface for the WGS reaction and it can be used as a template for the growth of oxide nanoparticles. In the CeOx system we are able to control the concentration of oxygen vacancies, opening the possibility for variations in reactivity when changing the Ce/O stoichiometry. Our initial photoemission data indicate that sub-stoichiometric ceria nanoparticles supported on gold surface dissociate water molecules below room temperature while the fully oxidized stoichiometric ceria is inactive (see Figure, left panel). As the water dissociation could be the rate limiting step in the WGS reaction, our ability to observe reaction products under vacuum conditions and link them with the structural characterization at the atomic level is a great stimulus for our future work on these inverse model catalysts. In addition our recent measurement of significant catalytic activity in WGS reaction at relevant conditions (i.e. higher pressure and temperature) makes the inverse CeO_2/Au(111) catalysts a valuable model for understanding reaction mechanism on a molecular level.

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CATALYSIS: REACTIVITY AND STRUCTURE (FWP CO-009)

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Goals:

The goal of this program is to provide an improved understanding of chemical catalysis by elucidating details of the fundamental properties of molecules, surfaces, and their reactions that are critical to catalysis and energy conversion. Reactivity-structure correlations explored and unraveled by utilization of synchrotron radiation are a key aspect of these studies. Complexities stemming from the inherent multi-component aspects of heterogeneous catalysis are explored using both ultra-high-vacuum surface science investigations of well-defined model systems, and powder diffraction and x-ray absorption studies of "real-world" systems. In the former, emphasis is placed on understanding of basic principles of surface reactivity and its control by surface modification, on identification of active sites and full characterization of their electronic and structural properties. X-ray photoemission and absorption spectroscopies at the U7A beamline at the National Synchrotron Light Source (NSLS) are essential to this work. In the latter systems, in-situ time-resolved studies of the formation and transformations of supported metal clusters and metal oxides and carbides under catalytic reaction conditions are carried out using our x-ray diffraction facility at beamline X7B. Quantum-chemical calculations based on density-functional theory are performed to help in interpretation of experimental results and to study basic aspects of catalytic reactions.

DOE Interest:

The objective of this program is to provide new insights into the nature of matter and energy and (i) to provide improved understanding of catalysis for energy conversion and (ii) to increase fundamental understanding of surface chemical reactivity and its modification and (iii) to operate NSLS beam lines U7A and X7B as a state-of-the-art resources in support of the “Fuel of the Future”, “Protect our Living Planet” and “Provide Extraordinary Tools for Extraordinary Science” themes of the Office of Science as outlined in the Science and Technology Statement of the DOE Strategic Planning document.

Recent progress and future plans:

Over the last three years, this program has been focused on investigating the behavior of catalysts used for the cleaning of fossil-derived fuels (desulfurization processes) and for the processing of non-conventional fuels (H_2 generation through the water-gas-shift reaction). Experimental and theoretical studies have been performed exploring correlations between the structure and reactivity of typical metal catalysts or catalysts that contain compounds of metals with light elements (C, N, O, P, S). Due to the nature of our research, we develop and optimize synchrotron-based techniques for in-situ characterization (XRD, XAFS, photoemission).

In the last three years, major research achievements within this program have been:

- Establishment for the first time of the role played by carbon and phosphorus sites in hydrodesulfurization processes occurring on metal-carbide or metal-phosphide catalysts.
- Identification of the importance of O vacancies for the destruction of SO_2 and other chemical reactions on gold/oxide surfaces.
- Systematic studies for the oxidation mechanism of metal carbides. Large differences in the reactivity of the metal and carbon sites depending on the electronic properties of the carbide and the filling of its valence band.
- In-situ characterization of the active phase in gold-ceria and copper-ceria catalysts for the water-gas shift (WGS) reaction. Relative activity of Cu(100) and Au(111) with respect to Cu/CeO_2 and Au/CeO_2 surfaces.
- Discovery of Cu/MoO_2 and Ni/MoO_2 as efficient non-expensive WGS catalysts.
- Demonstration of the utility of time-resolved X-ray diffraction for studying the structural properties of powder catalysts in-situ.
- Participation in the design and implementation of instrumentation to carry out in-situ quick-XAFS studies at the NSLS. Active members in the Synchrotron Catalysis Consortium.

Desulfurization processes

The search for better desulfurization catalysts is a major issue nowadays. It has been established that β-Mo_2C and other metal carbides are very active for the cleavage of C-S bonds, but their HDS activity decreases quickly with time. The degradation of β-Mo_2C has been ascribed to the formation of a chemisorbed layer of sulfur or MoS_xC_y compounds on the surface of the catalyst. In recent studies, transition metal phosphides have shown a tremendous potential as highly active HDS catalysts. Among all the phosphides, Ni_2P has demonstrated the highest HDS activity and does not deactivate with time as β-Mo_2C does.

We used XPS and first-principles DFT calculations to study the interaction of thiophene, H_2S and S_2 with $Ni_2P(001)$, α-$Mo_2C(001)$ and MoC(001). It is usually assumed that the non-metal atoms in the surface (P or C) are simple spectators and do not participate directly in HDS reactions. In general, the reactivity of the surfaces increases following the sequence: MoC(001) < $Ni_2P(001)$ < α-$Mo_2C(001)$. At 300 K, thiophene does not adsorb on MoC. In contrast, $Ni_2P(001)$ and α-$Mo_2C(001)$ can dissociate the molecule easily. The key to establish a catalytic cycle for desulfurization is in the removal of the decomposition products of thiophene (C_xH_y fragments and S) from these surfaces. Indeed, our experimental and theoretical studies indicate that the rate determining step in a HDS process is the transformation of adsorbed sulfur into gaseous H_2S.

Ni_2P is a better catalyst for HDS than Mo_2C or MoC. The P sites in the phosphide play a complex and important role. First, the formation of Ni-P bonds produces a weak “ligand effect” that allows a high activity for the dissociation of thiophene and H_2. Second, the number of active Ni sites present in the surface decrease due to an “ensemble effect” of P, which prevents the system from the deactivation induced by high coverages of strongly bound S. Third, the P sites are not simple spectators and provide moderate bonding to the products of the decomposition of thiophene and the H adatoms necessary for hydrogenation. These insights will be developed further in the future work.

Chemical properties and oxidation of metal and metal-carbide surfaces

The carbides of the early-transition metals have a low cost and are able to catalyze desulfurization processes, the WGS reaction, the reforming of ethanol or other hydrocarbons and the conversion of methane to synthesis gas. Usually, the formation of metal-carbon bonds modifies the electronic properties of the metal, producing a decrease in its density of states near the Fermi level and a metal→carbon charge transfer. In these materials, the chemical bonding exhibits a mixed character.

The interaction of oxygen with surfaces of metal carbides is an important issue. The catalytic properties of metal-carbides can be drastically modified by adsorption of oxygen from the air or by reaction with O centers of oxide supports. Our group has performed systematic studies of the oxidation of metal-carbide surfaces using high-resolution photoemission and DFT. A key point is the relative importance of the O↔metal and O↔C interactions. Usually, it is assumed that the C sites of a metal carbide surface play a secondary or minor role in the chemical properties of the system. C 1s core-level spectra taken after adsorbing O_2 on ZrC(001) surface exhibit a distinctive line shape with two strong peaks at 283.4 and 281.9 eV. The peak at 283.4 eV points to a strong interaction between O and C atoms (oxygen could be adsorbed directly on top of C sites) or a O↔C exchange could take place in the surface. For clean VC(001), the C(1s) peak shows up at 282.0 eV. Thus, it appears that the O↔C interactions are negligible in O/VC(001). The C(1s) spectra point to a big difference in the mechanisms for the oxidation of ZrC(001) and VC(001). Our DFT calculations corroborate this and highlight the importance of the electronic properties of each carbide. These results will serve as a background for futures studies in which the behavior of oxocarbides as catalysts for the WGS reaction or the processing of ethanol will be examined.

Fundamental studies related to the water-gas shift reaction

The high activity of ceria-based catalysts (Cu-CeO_2, Au-CeO_2 and Pt-CeO_2) for the water-gas shift reaction is well documented in the literature. However, there is no generally accepted picture for the role of the oxide and the metal in the WGS reaction. The existence and role of reduced vs. cationic metal centers (e.g., $Cu^{\delta+}$) is debated. The Catalysis Group at BNL has CuO/CeO_2, $Ce_{1-x}Cu_xO_2$ and AuO_x/CeO_2. In Figure 1 the results of in-situ time-resolved XRD show diffraction lines for CuO and CeO_2 in a freshly prepared copper-ceria nanocatalyst. Once the catalyst is exposed to the reactants of the WGS at temperatures above 200°C, the diffraction lines for CuO disappear and new lines appear for metallic Cu. Significant catalytic activity is only observed at temperatures higher than 200°C when Cu and partially reduced CeO_2 are present. XAFS data indicate that AuO_x also does not survive under WGS reaction conditions. Our in-situ measurements show that the active phases of these catalysts consist of Cu/CeO_{2-x} or Au/CeO_{2-x}, and when these active phases are exposed to oxygen from the atmosphere, they undergo reoxidation making unreliable any ex-situ characterization. These results are a major step forward in the understanding of the nature of these promising new catalysts, and lay the foundation for a substantial new effort to develop a clearer understanding of the role of the oxide and the reduced metal we propose to explore in future. Our studies point also to the importance of in-situ characterization.

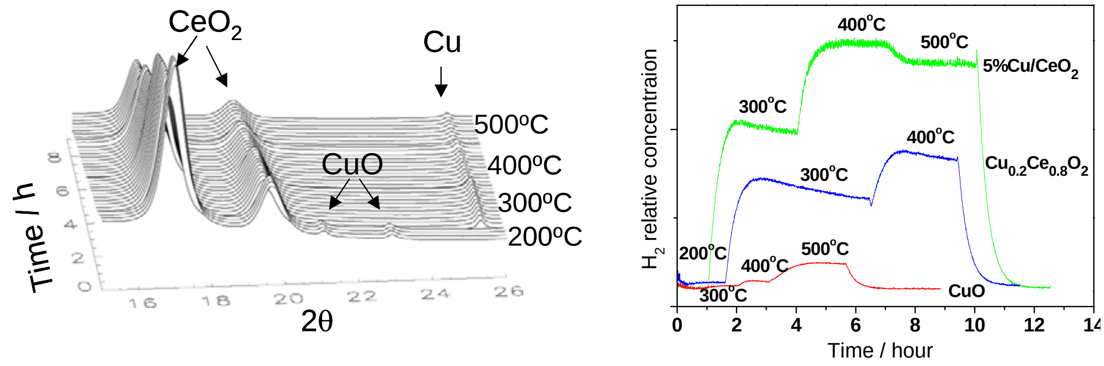

Fig. 1: *In-situ* time-resolved XRD patterns for a 5%CuO/CeO_2 catalyst during the WGS reaction. The right-side panel shows the amount of H_2 produced at several temperatures for three different catalysts containing Cu.

The DFT-calculated energy profiles for the WGS on Au(100) and Cu(100), including kinetic barriers show that on Cu(100), the highest energy-consuming step, or rate-limiting step, is water dissociation. In contrast, dissociation of adsorbed OH and formation of CO_2 are more facile. All the adsorbates bond more weakly on Au(100) than on Cu(100). Consequently, the dissociation of H_2O on Au(100) is even more endothermic and the corresponding barrier is also higher. These DFT results are in good agreement with our measurements, which show that Cu is a good WGS catalyst while Au is an extremely poor one. In gold-ceria catalysts, ceria probably helps during the cleavage of the first O-H bond of water. Once this step is overcome, the WGS becomes a downhill process on gold surfaces. In the case of copper-ceria systems, the role of ceria is not essential, although it does help during the WGS catalysis.

Another type of catalysts that we have investigated contains Cu or Ni on a molybdena (MoO_2) support. The high WGS activity of these catalysts have been discovered at BNL within the last year. They are more active than the commercial Cu/ZnO catalyst and the combinations Ni/MoO_x and Cu/MoO_x involve non-expensive metal elements. Some precursors for these catalysts are the mixed-metal oxides $NiMoO_4$ and $CuMoO_4$, which are partially reduced in an atmosphere of hydrogen before reaction.

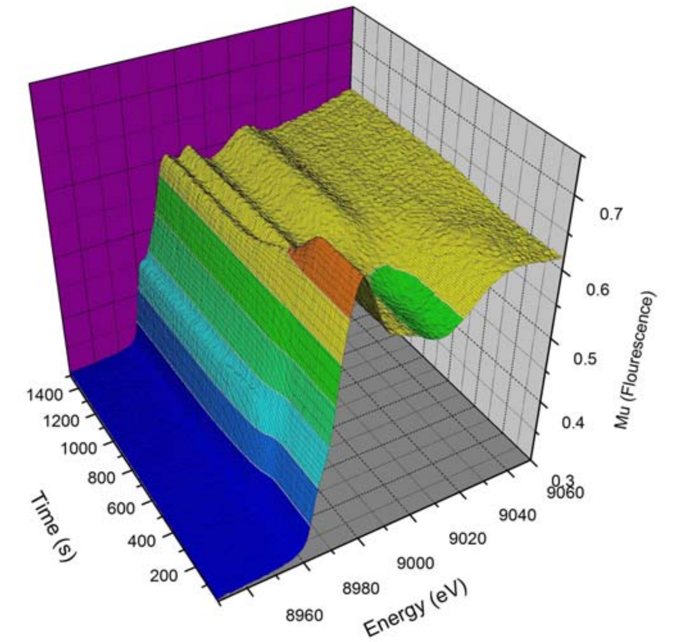

Fig. 2: *In-situ* time-resolved Cu K-edge XANES for a $Ce_{1-x}Cu_xO_2 \rightarrow Cu + CeO_2$ chemical transformation at 300°C under 5mol% H_2 gas in helium. (15 s/spectrum)

In-situ time-resolved X-ray diffraction and the characterization of powder catalysts

The development of techniques for characterizing the structural properties of catalysts under the high-pressure conditions of industrial processes is widely recognized as a top priority in the area of heterogeneous catalysis. Under reaction conditions a catalyst can undergo chemical transformations that drastically modified its composition with respect to that obtained during the synthesis of the material. To optimize the performance of the catalyst, it is desirable to know what its active phase is. Investigations at BNL have established the feasibility of conducting sub-minute, time-resolved in-situ x-ray diffraction (XRD) experiments under a wide variety of temperature and pressure conditions ($80\ K < T < 1200\ K$; $P < 50$ atm). This important advance results from combining the high intensity of synchrotron radiation with new parallel data-collection devices. Using time-resolved XRD, one can get information about phase identification and composition of catalysts under reaction conditions, kinetics of crystallization of bulk solids and nanoparticles, crystallite size as a function of time/temperature, and structure changes during the processes.

In the near future, we plan to acquire detectors that will reduce the acquisition time of the diffraction data by a factor of 10^2, and we will combine the technique with XAFS and IR measurements to obtain simultaneous information about the structural, electronic and chemical properties of powder catalysts.

In-situ quick-XAFS and the characterization of powder catalysts

XRD is effective when dealing with crystalline materials, while XAFS provides short range order structural features in less ordered or amorphous catalysts. In addition, XAFS also provides information about the electronic properties of the catalysts. Our group has recently tested a new fast XAFS instrument at beamline X18B of the NSLS, see Figure 2. The in-situ data point to the chemical transformation of copper oxide to zero valence copper under reducing conditions. In our instrumentation proposal to DOE we propose to combine fast XAFS and fast XRD measurements. This capability will be very important in the planned work on WGS and other in-situ catalysis problems.

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Processing of Biomass-derived Feedstocks in a Petroleum Refinery: Catalytic Cracking of Biomass-Derived Feedstocks

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Production of biofuels from sustainable-domestically available biomass resources is a near term solution to alleviate problems caused by our dependence on fossil fuels. One option for making biofuels a practical reality, is to use petroleum refinery technologies (i.e. catalytic cracking and hydrotreating) for biofuels production. Petroleum refineries are already built and using this existing infrastructure for biofuels production would require little capital cost investment[1, 2]. Fluid catalytic cracking (FCC) is the most widely used process for the conversion of the heavy fraction of crude oil into gasoline and other hydrocarbons in the oil refinery[3]. It would be desirable to use the FCC process for biomass-conversion. In this poster we discuss the feasibility of utilizing of the FCC process for biofuel and biochemical production.

We have studied the reaction pathways for conversion of glycerol and sorbitol (representative biomass-derived feedstocks) over six different catalysts including: a fresh FCC catalyst (FCC1), an equilibrium FCC catalyst with metal impurities (ECat), a mesoporous Al_2O_3, a USY zeolite (Y), a ZSM5-based FCC additive (ZSM5) and an inert silicon carbide (SiC)[4]. In this process, oxygen is removed from the feed as H_2O, CO or CO_2. Repeated dehydration and hydrogen transfer allows the production of olefins, paraffins, and coke. Aromatics (in yields up to 20 molar carbon %) are formed by Diels-alder and condensation reactions of olefins and dehydrated species. Sorbitol and glycerol have similar product distributions with the primary difference being that sorbitol produces more CO than glycerol.

Glycerol can also be converted by FCC when co-fed with petroleum-derived products (i.e. vacuum gas-oil) without significantly altering the product selectivity. This suggests that biomass-derived products could be co-fed with petroleum-derived streams in an industrial FCC reactor. When glycerol is fed together with a vacuum gasoil, interactions between the hydrocarbon components and the glycerol reaction intermediates occur that results in final selectivities that are better than those calculated by considering a simple additive effect.

A modified FCC process can also be used to make valuable oxygenated intermediates from biomass-derived feedstocks. For example, we have also used this process to produce acrolein in yields up to 56 molar % from glycerol based feedstocks[5].

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Developing the Science of Immobilized Molecular Catalysts

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Goal

Immobilized organometallic catalysts, in principle, can give high rates and selectivities like homogeneous catalysts with the ease of separation enjoyed by heterogeneous catalysts. However, the science of immobilized organometallics has not been developed, in part because the field lies at the interface between the homogeneous and heterogeneous catalysis communities. By assembling an interdisciplinary research team that can probe all aspects of immobilized organometallic catalyst design, the entire reacting system can be considered. The transition metal complex, the complex-support interface and the properties of the support can be considered simultaneously from both experimental and theoretical perspectives. Researchers at Georgia Tech and the University of Virginia are studying palladium complexes as catalysts for basic feedstock and building block reactions (e.g. carbon-carbon bond formations,) and metal salen complexes (as catalysts for enantioselective reactions) immobilized on polymeric, silica and nanoparticle supports. Using these model systems, the fundamental principles needed to understand and design future classes of immobilized organometallic catalysts are being elucidated.

DOE Interest

The work performed in this program elucidates fundamental principles important in the design of immobilized catalysts. These catalysts have the potential of being very active and selective while being easy to separate for the reaction medium. All of these aspects provide a substantial energy advantage in chemical processing.

Recent Progress (2006-present)

Over the last twelve months, efforts have focused on developing immobilized, asymmetric salen complexes on a number of supports. The salen ligand was chosen as a target for immobilization due to the myriad different asymmetric reactions it can promote when complexing a wide variety of metals. A key aspect of our program is to elucidateing how metal salen complexes should be immobilized to obtain optimal catalytic properties. In particular, we hypothesize that different immobilization strategies will be required for the two broad classes of reactions that metal salen complexes catalyze – (i) reactions that involve a single metal center vs. (ii) reactions that are bimolecular in metal complex. In parallel, studies stemming from the first phase of this program on supported palladium catalysts are being completed. Key foci over the last twelve months were:

(a) Systematic studies of DFT functionals for applicability to various metal salen complexes[11,25];
(b) Development of molecular models of supports: (i) SBA-15 mesoporous silicate supports,[20] and (ii) ROMP poly(norbornene) [21];
(c) Synthesis and assessment of different catalyst supports and complex-support linkers applied to Co-Salen hydrolytic kinetic resolution (HKR) catalysts[6-8,17];
(d) Assessment of deactivation mechanisms in Co-Salen catalyzed HKR reactions[24];
(e) Design and synthesis of supported Al-Salen catalysts;
(f) Synthesis and assessment of superparamagnetic nanoparticle supported acid catalysts[10,13,22];
(g) Establishing the role of leaching in "stable" supported Pd precatalysts in Heck and Suzuki reactions[1-2,4,9,12,15,19,23];
(h) Evaluation of Au nanoparticles as catalysts supports;

M-Salen Complex Catalysts

Despite a large number of literature reports on attempts to immobilize Jacobsen's salen catalysts, highly active and selective, *recyclable* salen systems have not been fully realized to date for many reactions. M-

Salen catalysts generally follow two distinct types of reaction mechanisms: a) a single M-Salen complex works alone and b) two metal salen complexes are required that work collaboratively. In some cases such as Mn catalyzed asymmetric epoxidation, a monometallic reaction path is used and supported catalysts with perfect site isolation are expected to be ideal. In contrast, the HKR of epoxides uses a cooperative bimetallic pathway, with one cobalt activating the epoxide while a second metal site activates the nucleophile (water). In this case, a system allowing an easy interaction of the two metal centers is desired, whereas a system with site-isolated catalytic centers should be less selective. Because of the very different mechanistic paths of AE and HKR, we proposed that, once design principles for the synthesis and activity of supported catalysts for these two reactions have been worked out, the development of supported salen catalysts for myriad other reactions should be straightforward, as the reactions will fall into one of the two classes of salen reactions discussed above.

The supported salen complexes that have been investigated during the last 12 months are active catalysts for the HKR terminal epoxides (Co-Salen) and the asymmetric 1,4-addition reactions to α,β-unsaturated ketones and imides (Al-Salen). In both cases, the reactions are reported to require two M-Salens in the catalytic transition state. Only the Co-Salen results are described here.

One hurdle we had to overcome early in our studies was the large-scale synthesis of *monofunctionalized* salen catalysts. Whereas the vast majority of preparative and catalytic studies on this family of compounds have been dedicated to salen ligands with C2-symmetry, recent studies have demonstrated that unsymmetrical salen ligands, where the term unsymmetrical describes two distinct substituents on the two aromatic rings, hold important advantages. However, at the start of our studies, the synthesis of unsymmetrical salens was difficult and low yielding. We developed a practical one-pot synthesis of enantiopure unsymmetrical salen ligands and demonstrated the utility of this one-pot approach by synthesizing a variety of monofunctionalized salen ligands containing different linkers ranging from rigid phenylene ethynylenes to alkyl chains and ethylene glycol-based linkers. In all cases, the new synthetic protocol can readily be performed in good yields (60–85%) on the multigram scale with good tolerance toward various functional groups.[7]

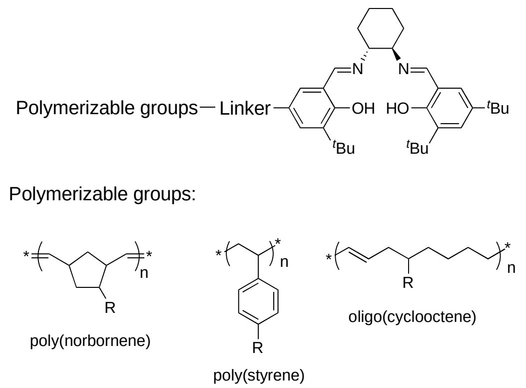

Figure 1: Polymer/oligomer supported salen-based materials studied.

Next, three different polymer/oligomer supports were utilized with tethered Co-Salen complexes for the HKR of epoxides (norbornene, styrene, and cyclooctene-based monomers – Figure 1). The poly(norbornene) supported cobalt catalyst gave similar reaction rates and enantioselectivities compared to the homogeneous salen complex. While it was anticipated that supported catalysts based on polymeric materials would enhance the bimetallic interaction of the metal centers and higher rates should be observed, this was not the case here. We hypothesized this to be due to the fairly rigid polymer backbone.[8] Next, we turned to styryl-salen functionalized monomers. The poly(styrene)-supported catalysts were slightly more active and similarly enantioselective as the poly(norbornene) supported system in the HKR of epichlorohydrin.[6] Copolymer-based supported catalysts showed the most desired catalytic performances. In this case, the best supported catalysts were more active and equally selective compared to the original Jacobsen catalyst (99% ee at 55% conversion). The soluble poly(styrene)-supported catalysts were recovered by precipitation after the catalytic reactions and were recycled three times to afford almost identical enantiomeric excesses as the first run, with slightly reduced reaction rates.

To further enhance the polymer backbone flexibility, we synthesized oligo(cyclooctene)-based supported Co complexes that were expected to be highly flexible and to have a random coil conformation in solution.[17] Interestingly, the ruthenium-based olefin metathesis resulted in the formation of larger ring cycles rather than linear polymers. MALDI-TOF and NMR spectroscopies provided unambiguous insights into the structures of these oligomers at a molecular level (Figure 2). These data, when coupled with GPC analysis of the polymers/oligomers formed under different experimental conditions, also led to a consistent mechanistic picture. The oligo(cyclooctene)-supported Co- Salen complexes were examined for their catalytic efficiency in the HKR of terminal epoxides. For most epoxides, an exceptionally low catalyst loading of 0.01 mol% was employed. In all cases, enantiomeric excesses above 99% were observed within several hours and isolated yields (crude conversions measured by GC or HPLC were usually approximately 5% higher) of 43-48% were obtained. At the same catalyst loading, the unsupported Co-Salen catalyst developed by Jacobsen showed no catalytic activity, demonstrating the superiority of our cyclic catalyst. Compared to the poly(styrene) system under identical conditions, our cyclic oligomeric system derived from cyclooctene metathesis is 40-50x more active and equally selective. We attributed this high activity to the close proximity of two Co-centers in our cyclic oligomers, *i.e.* an increase in local molarity of the cobalt centers that enhanced the formation of a bimetallic transition state, in contrast to the high dilution of the small molecule Jacobsen system catalyst. The effect of concentration of the new polymeric catalyst on the rate of the reaction was also studied. As the catalyst concentration was doubled, the conversion of epichlorohydrin at short reaction times also doubled. Thus, the rate was directly proportional to catalyst loading, unlike the reaction with Jacobsen's catalyst. *It is noteworthy that the oligo(cyclooctene)-supported Co-Salen complexes are the most active and selective unsymmetrically functionalized catalysts developed to date. Catalyst loadings as low as 0.01 mol% can be used with complete conversions within several hours for a variety of epoxides.*[17]

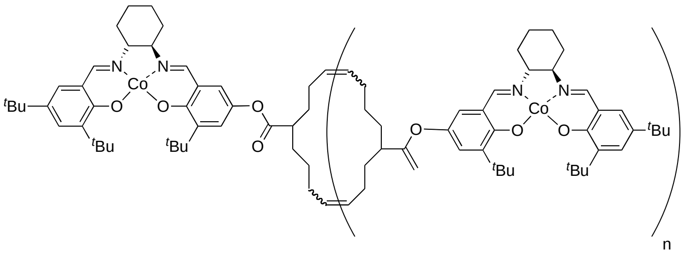

Figure 2. Cyclic Co-Salen oligomers.

After establishing the activities and selectivities of these novel catalysts, we carried out preliminary recycling studies on the homogeneous Jacobsen's Co-Salen catalyst without intermediate regeneration with acetic acid. The catalyst was recycled up to four times by evaporating the reaction products from the previous run under vacuum. However, the reaction rate decreased significantly with each cycle. This was hypothesized to be due to the reduction of Co(III) to Co(II) during the HKR reaction. Therefore we studied the state of the metal using UV-Vis and XANES spectroscopy. Using UV-vis spectra of the Jacobsen Co(II)salen catalyst (inactive) and Jacobsen Co(III)salen catalyst (active) before and after the catalytic reaction, we established that the mechanism of catalyst deactivation is not due to cobalt reduction. Ongoing studies continue into the mechanism of the deactivation process[24].

Most recently, we synthesized a series of styryl-substituted salen monomers with oligo(ethylene glycol) spacers of different chain lengths to afford the polymer-supported Co(II)(salen) precatalysts **Co-HP-*m*** (*m* = 0-3, Figure 3). The catalytic properties of **Co-HP-*m*** as well as **Co-HP-phenylene** were investigated in the hydrolytic kinetic resolution (HKR) of racemic epichlorohydrin with a cobalt loading of 0.01 mol %. Catalyst **Co-HP-1** (with one oxyethylene unit) showed the best catalytic performance with an *ee* of >98% achieved in 10 hours. Decreasing the spacer length to *m* = 0 or using the more rigid phenylene linker lowers the reactivity as well as the enantioselectivity dramatically. From these data, we suggest a) the length of the linker plays a key role in designing a desirable catalyst for a reaction involving a bimetallic cooperative mechanism, b) the best length of the linker for poly(styrene)-supported HKR catalysts should be about 6 carbon/oxygen atoms (e.g. $CH_2OCH_2CH_2OCH_2$), and c) by choosing a proper linker, the catalytic performance of supported catalysts in HKR can be significantly enhanced.

Co-Salen catalysts are also widely used in epoxide-CO_2 coupling reactions to produce cyclic carbonates. As this Co-catalyzed reaction is suggested to be monometallic in nature, it represented a nice compliment to the bimetallic HKR reactions described above. Early in our studies, we discovered that under typical conditions reported by others in the literature, the cyclic carbonate synthesis could be promoted in the absence of the M-Salen complex while in the presence of the "co-catalyst," N,N-dimethyl-4-aminopyridine (DMAP). This observation was pursued further and we prepared a recoverable, metal-free DMAP-silica hybrid catalyst capable of promoting the reaction. In addition, we proposed a metal-free mechanism for the observed coupling reaction[16].

In parallel with this experimental study, a theoretical characterization of the Mn-Salen was also carried out. Despite a large number of theoretical studies, extracting definitive conclusions from theory has proven challenging; indeed, the two most commonly used theoretical approaches for transition metal catalysts, B3LYP and BP86, yield qualitatively different pictures for the reactivity of oxo-Mn-Salen.

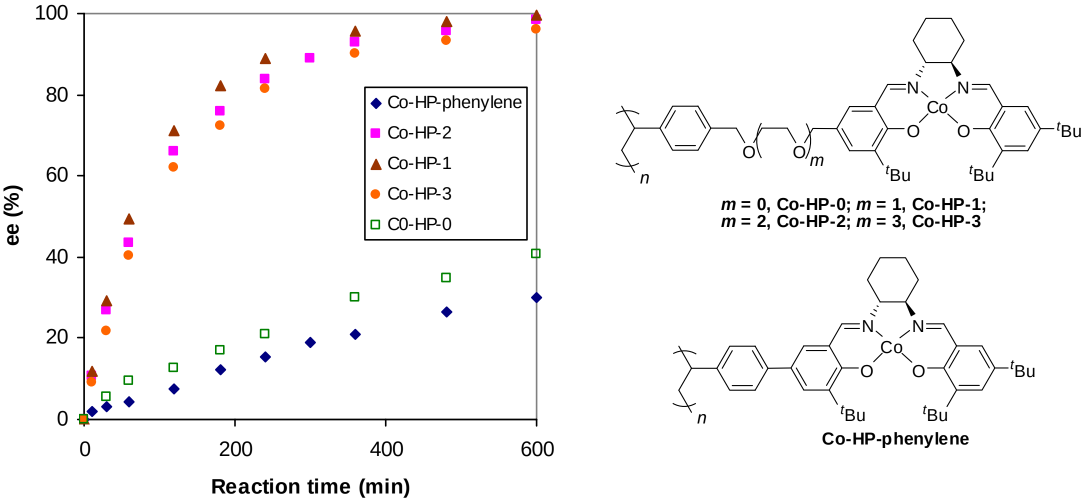

Figure 3. HKR of epichlorohydrin with **Co-HP-*m*** and **Co-HP-phenylene** catalysts.

Using robust multi-configurational wavefunctions (e.g., state-averaged complete active space self-consistent field, SA-CASSCF), we have examined many of the low-lying electronic states of oxo-Mn-Salen, several of which have not been explored previously. Our highest-quality results, including corrections for finite basis and relativistic effects, indicated the ground spin state to be a closed-shell singlet, followed by a pair of low-lying triplet states at slightly more than 3 kcal mol^{-1}. A pair of nearly degenerate open-shell singlet states, 2 ^{1}A and 3 ^{1}A, lie around 35 kcal mol^{-1} followed by the high-spin 1 ^{5}A state a little more than 40 kcal mol^{-1} above the ground state. The presence of a second, low-lying triplet state nearly isoelectronic with the singlet and the other triplet has not been discussed previously. The proximity of so many states may result in highly complex potential energy surfaces involving conical intersections and avoided crossing effects, which may complicate reaction mechanisms for Mn-Salen catalysis. Our results suggest that much care should be taken in theoretical studies of Mn-Salen systems when applying more "black box" computational methods like density functional theory or single-reference wavefunction methods[11].

Based on these findings, we have undertaken a more systematic study of the electronic structure of numerous metal-Salen systems, comparing DFT to high-level single- and multi-reference results. To date, most theoretical studies of metal-Salen complexes has focused on the Mn-Salen systems, and to our knowledge, the only multi-reference studies are those performed by us or Ivanic for just four systems. Our approach is to systematically examine metals with different formal charges and to examine state splittings using CASSCF, CASPT2, and CCSD(T) methods, as appropriate; results are analyzed qualitatively in terms of how the d orbital energies behave as a function of the metal formal charge. We are focusing initially on d0 and d2 Salen complexes[25]. Our current results indicate that d0 systems, perhaps not surprisingly, are amenable to treatment by standard single-reference methods; additionally, as the formal charge on the metal increases, the metal d orbitals mix with the ligand pi orbitals, leading to greater stabilization of high-spin states. For the d2 systems, electronic near-degeneracies become more important, but it appears that DFT performs reasonably well given our CASSCF data so far. Fortunately, our data suggest that only "minimal" active spaces suffice in multi-reference computations on the d2 systems.

Catalyst Supports

Two novel catalyst supports are being developed in parallel with the studies on mesoporous silica and soluble polymers – superparamagnetic nanoparticles and gold nanoparticles. Nanosized spinel ferrite nanoparticles were functionalized with amino-organosilanes and used as solid base catalysts in one pot multi-step catalytic reactions[10]. By using the magnetic catalysts in tandem with traditional catalysts that are recovered via settling or filtration, we were able to effect one-pot multi-step catalytic reactions with catalyst recovery in pure form for the first time. Weakly basic amine-functionalized nanoparticles were used in tandem with Pt/alumina as a hydrogenation catalyst or with acidic Merrifield resins as acid catalysts. Subsequently, we evaluated the use of amine-functionalized magnetic nanoparticles as intrinsically (internal) transport limitation-free non-porous catalysts in Knoevenagel condensations[13].

When comparing the magnetic catalysts to benchmark ordered mesoporous silica catalysts with the same organic groups, it was apparent that the activities were comparable if large pore SBA-15 materials (60-100 Å pores) were used. However, the non-porous catalysts were more active than the smaller pore mesoporous silicate, MCM-48, with ~22Å pores. This study effectively cast the activity of the new magnetic catalysts against benchmark catalysts commonly used for this reaction and showed that they could be comparably active, with the added benefit of facile separation by application of a magnetic field.

We have also introduced a new synthetic method for the functionalization of gold nanoparticles. This new method allows for the introduction of a wide variety of functional groups by using "click" chemistry to add the desired functions onto azide functionalized gold nanoparticles. The synthetic protocol consists of using 5-40 mol% of $CuSO_4$ and 10-40 mol% of sodium ascorbate along with a terminal alkyne and an alkyl azide coated nanoparticle. Using microwave-assisted synthesis, 80-100% conversions were obtained for every functional group studied. Using this newly developed nanoparticle functionalization method, we introduced catalytic moieties onto gold nanoparticles. These included N-heterocyclic carbene (NHC)-based palladium complexes that were useful in Suzuki couplings.

Molecular modeling was used to investigate the behavior of ROMP-poly(norbornene) polymer supports. The initial hypothesis to be tested was that this polymer would form a helix, displaying catalytic side chains effectively in solution as accessible catalytic sites. This hypothesis was based on the similarity of ROMP-poly(norbornene) to other polymers such as non-ROMP-poly(norbornene), and substituted poly(acetylenes). The structure of ROMP poly(norbornene) differs from these polymers in the presence of a cyclopentyl group in the polymer backbone. To insure that the effect of the dynamics of this cyclopentyl group was accurately assessed on the polymer conformation, a study of the effect of simulation parameters on the dynamics was made. Contrary to previous studies, it was found that the force-field that more accurately reproduced the equilibrium structure, not the high-energy planar conformation was best at reproducing the dynamics of the cyclopentyl ring. While the dynamics of the cyclopentyl group was sensitive to the coupling parameter for the constant-temperature thermostat in the Berendsen (LFB) algorithm, it was not sensitive in the Nosé-Poincaré (NP) algorithm. Molecular dynamics simulations, using the NP algorithm have now demonstrated that ROMP poly(norbornene) does not form an extended helix, regardless of the backbone configuration, because this cyclopentyl group is simply too flexible[21]. The non-helical conformation of these poly(norbornene) polymer is now being studied to determine the sensitivity of catalyst site accessibility as a function of polymer and side-chain structure.

Palladium Studies

Previously, extensive investigations of polymer and silica tethered Pd(II) SCS and PCP pincer complexes in Heck coupling reactions showed that these complexes decompose under reaction conditions, liberating soluble ligand-free palladium that are the sole active species in the coupling reactions. Subsequently a detailed critical review[9] of the existing literature on Heck and Suzuki coupling catalysts was compiled, and a relatively complete and consistent picture was developed concerning the nature of the true catalytic species in these important coupling reactions. This detailed review highlighted a few systems in the literature where the purported active form of palladium was unclear, or where the suggestion went against conventional wisdom (as defined by the review). This motivated us to apply a series of kinetic and poisoning studies to the elucidation of the active species when using the popular, commercially available and purportedly "leach-proof" Pd-EnCat. The range of techniques applied in our studies of palladium pincers, when used on Pd-EnCat, showed that these catalysts also leach active palladium and only the leached species were participated in the reaction[12]. This study was fully consistent with the broader picture of Heck couplings developed in our review paper, whereby only leached species are active using any solid catalyst under high temperature Heck coupling conditions (T > 120 ºC)[19].

We also investigated the synthesis of a new class of polymer-supported *N*-heterocyclic carbene ligands, their metallation, before and after polymerization, and their use as supported catalysts for a variety of carbon-carbon bond formations. For all transformations studied, our catalysts show high activities that are comparable to their small molecule analogues. We have shown by using poisoning studies that the stability of our palladium-based polymeric catalysts depends on the ligands around the palladium center in the Suzuki, Sonogashira and Heck couplings. For the ring-closing metathesis we demonstrated the ability to remove the polymeric catalysts from the reaction mixture, thereby ensuring the removal of any undesirable metal species from the product obviating extensive purification steps.[15] A comprehensive review on supported NHC complexes in catalysis also stemmed from this work.[18]

Summary

Supported M-Salen complex catalysts are being evaluated in two classes of reactions – those that require a single metal center in the transition state of the rate-limiting step and those that require two metals. Several different polymer/oligomer supports, and complex-support linkages have been evaluated in the bimolecular HKR of epoxides. In parallel, the electronic structure of various M-Salens and polymer and oxide support structural conformations are being probed computationally. New uses for nanoparticle supports are being developed, and future studies will focus on solid-supported M-Salen complexes.

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DE-FG02-05ER15696 **Alexander Katz**

Understanding the Role of Surface Defect Sites in Ti-Catalyzed Olefin Epoxidation

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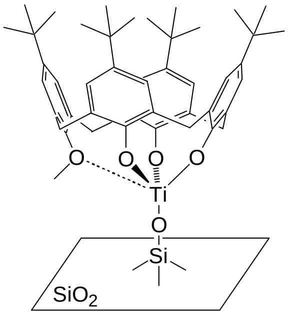
Goal

Goal is to understand the role of outer-sphere environment, as defined by an inorganic oxide surface, in controlling Ti(IV)-catalyzed olefin epoxidation using organic hydroperoxides. This requires deconvoluting inner-sphere effects of coordination and active site Lewis acidity, characterized here using Ti K-edge XANES, on the intrinsic rate of epoxidation catalysis. The knowledge gained suggests a mechanism in which defect sites on the inorganic oxide surface actively participate in a bifunctional Lewis acid-Brönsted acid mechanism for catalyzing olefin epoxidation, and how tuning the outer sphere, namely defect site acidity, provides sensitive control over catalyst activity.

Recent Progress

Inner-Sphere Ligand Effects:

We investigate the use of grafted calixarenes on silica as persistent surface organometallic ligands, to study the effect of isolated Ti(IV) Lewis acidity on heterogeneous epoxidation catalysis. This is accomplished by systematically varying the metal coordination environment and characterizing d-electron occupancy at the metal center using Ti K-edge XANES. Use of a *tert*-butyl-calix[4]arene as ligand leads to catalyst **1**, whereas use of a *tert*-butyl-homooxacalix[3]arene leads to catalyst **2**.



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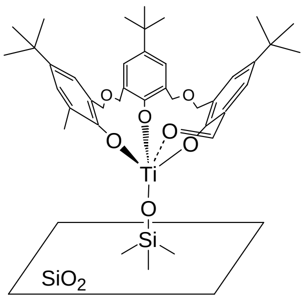

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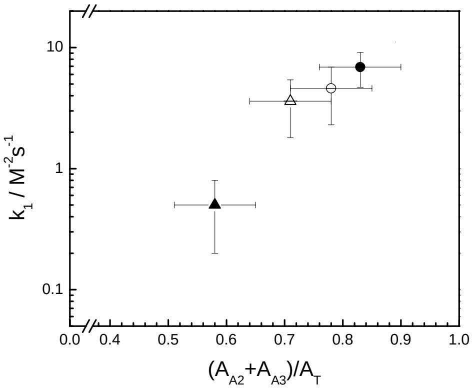
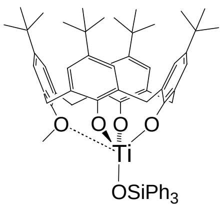


Figure 1: Epoxidation rate constants per Ti as a function of the relative area of peaks A2 and A3 for Ti-containing materials **1** (•), calcined **1** (Θ), **2** (▲), and calcined **2** (A).

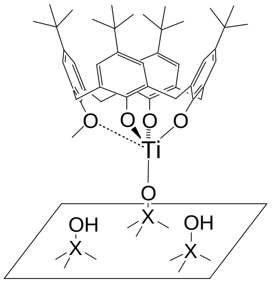
Catalyst **2** exhibits significantly weaker and broader pre-edge features, which are located at higher energies (4968.7 eV), relative to features in **1** (4969.3 eV), suggesting a higher degree of coordinative unsaturation in **1**. This increased breadth can be quantified by the relative intensities of the A2 and A3 transitions, which are measured to be 0.89 for **1** and 0.58 for **2**, when dehydrated at 120 ^{o}C; both catalysts show a relative intensity of ~0.75 in the preedge features upon calcination in oxygen at 450 ^{o}C, indicating that it is intrasite connectivity to the calixarene rather than any intersite connectivity between Ti center sites that is responsible for these results. We have found that the logarithm of the epoxidation rate constant, proportional to activation energy, is directly related to the relative intensity of the A2 and A3 transitions in XANES, demonstrating use of the latter as a direct measure of d-orbital occupancy. This correlation is shown in the semilog plot in Figure 1 above for all materials.

Outer-Sphere Ligand Effects:

The inner-sphere study above enables rigorous comparison of catalysts with similar Ti coordination environments and d-orbital occupancy but having differing outer-sphere environments due to changes in support as outer-sphere ligand. We investigated **3** as a relevant homogeneous model of **1**, and in addition, grafted titanocalixarenes on alumina and anatase. While Ti K-edge XANES demonstrates similar coordination environments for **1**, **3**, and **4** in terms of relative peak ratios for A2 and A3 preedge features, epoxidation rate activities for **1** were at least 17-fold greater than for the other catalysts. In addition, by comparing catalytic rates for calixarenes with varying upper-rim substituents (calixarenes and data not shown), a more comprehensive understanding of heterogeneous Ti-catalyzed epoxidation in grafted calixarene systems has emerged. The only possible explanation for all of these results is an active role of support defect sites within the mechanism for activating bound hydroperoxide: too strong a defect site acidity disfavors peroxide binding while too weak a defect site is unable to activate bound peroxide for epoxidation.



3



4-Al_2O_3, X = Al
5-TiO_2, X = Ti

Future Plans

We are applying the above-mentioned concepts towards the discovery of new V(III)- and V(V)-based oxidation catalysts. We are also synthesizing Ti(IV) catalysts within hydrophobic environments that can be used in conjunction with aqueous hydrogen peroxide instead of organic hydroperoxides requiring the use of organic solvents. Finally, we are investigating the use of **1** for catalyzing sulfoxidation reactions with high levels of selectivity.

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Configuration dependent oxygen adsorption energies on Pd(111) and Ag(111)

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We have investigated the coverage dependence of the adsorption energy of oxygen on Pd(111) and Ag(111) using density functional theory to examine the oxygen adsorbate phase diagram on those surfaces. We found that the adsorption energy is not a simple function of coverage, but rather is highly configuration dependent for a given coverage. We utilized a cluster expansion method and direct enumeration scheme to ensure that all possible ground state structures were examined in the construction of the phase diagrams. Although the oxygen adsorbate phase diagrams of Ag(111) and Pd(111) differ from each other, we found significant correlations in the configurational dependence of the adsorption energies on these two surfaces, suggesting that the adsorbate interactions are similar on the two surfaces. We believe these correlations will also exist for other close-packed (111) surfaces.

Hydrogenation of 1,3-butadiene on Sn/Pt(111) surface alloys

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Bimetallic catalysts involving Sn and Pt have important applications in hydrocarbon conversion catalysis, but little fundamental information is known about the chemistry and catalysis that occurs at distinct Pt-Sn alloy phases, how this chemistry varies with composition and structure, whether various phases are optimal or detrimental to catalyst performance, and whether novel nanostructures have special chemical properties. The need for improved selectivity of catalysts, and improvements in catalyst performance overall, drive our studies. We have carried out a wide range of investigations probing chemisorption and reaction kinetics on well-defined, bimetallic Pt-Sn surfaces in order to improve basic understanding of the chemistry of hydrocarbon molecules and reactive intermediates on such surfaces. Recently, adsorption and reaction of 1,3-butadiene (C_4H_6) on H-precovered surfaces of Pt(111) and the (2×2) and (√3×√3)R30° Sn/Pt(111) surface alloys was studied by using TPD mass spectroscopy and AES. Alloyed Sn opens a new hydrogenation reaction pathway, compared to Pt(111). Butadiene hydrogenation by coadsorbed H occurs with 100% selectivity to liberate butene (C_4H_8) in reaction rate-limited peaks in TPD and no deeper hydrogenation product (butane) was observed. The activation energy barrier for hydrogenation of strongly bound 1,3-butadiene is estimated to be 91 and 72 kJ/mol on the (2×2) and √3 alloys, respectively. Butadiene conversion was highest on the (2×2) alloy, reaching 100 % at high H precoverages. Strong site-blocking effects of preadsorbed H adatoms were observed for 1,3-butadiene chemisorption on both alloys under these conditions; butadiene chemisorption was eliminated by $\theta_H = 0.49$ ML on the (2×2) alloy and $\theta_H = 0.34$ ML on the √3 alloy. These studies addressing the influence of alloyed Sn on the reaction barrier to 1,3-butadiene hydrogenation and the effect of surface Sn concentration on hydrogenation activity provide observations of several novel phenomena and may aid in the development of heterogeneous catalysts to selectively remove dienes in alkene streams.

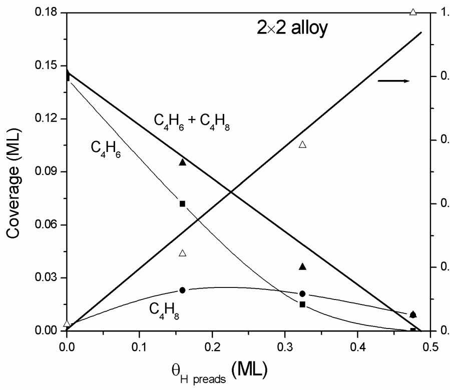

Fig. 1. Influence of H-adatom precoverage on the amount of 1,3-buta-diene adsorption, desorption, and hydrogenation on the (2×2)Sn/Pt(111) alloy.

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DE- FG02-01ER15184 **Harold H. Kung**

Synthesis Strategy for Novel Oxide Catalytic Materials

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Goal

An ultimate goal in heterogeneous catalysis is the ability to design catalysts with the desired activity and selectivity, which can be achieved if one can control the nature and location of the active sites and their environment. The objective of this research is to develop novel synthetic strategies and techniques to truly accomplish catalyst by design.

Recent Progress

Molecular-size nanocages offer many opportunities to custom-design catalytic active centers with control of their environment, as well as the ability to control the access to these active sites by varying the pore size of the cage wall. Unlike the examples reported in the literature where the cages are defined by multilayer-thick shells and there is limited control over their other properties, ideal nanocages for catalysis should have uniform but adjustable cage sizes, possess single atom-layer thick shell with tunable pore sizes, and have provisions to incorporate various functionalities in the structure. We have successfully synthesized a 2 nm-diameter siloxane nanocage (Fig. 1) by using a micelle as a template, and cross-linking (by condensation reaction) of the head groups of the surfactant molecules to form the shell. A cage is formed when the carbamate groups of the surfactant molecules are cleaved. These nanocages exhibit molecular size-selectivity, as well as confinement effect in the activity and selectivity in the decarboxylation of acetylacetone catalyzed by amine groups tethered to the interior surface of the cage wall. These amine groups are five times more active than a corresponding amine group in solution, and produce much more acetals and hemiacetals as the initial products than amines in free solution.

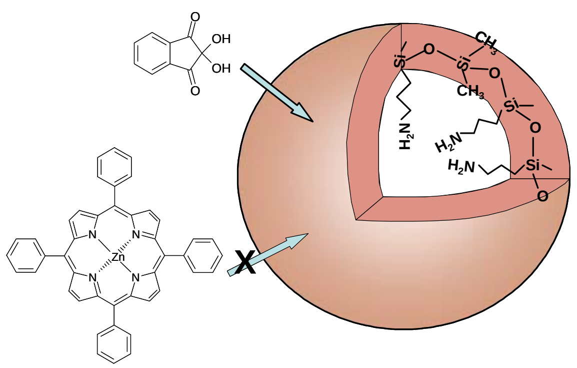

Fig. 1. Schematic drawing of a 2 nm diameter, size-selective siloxane nanocage containing amine groups tethered to the interior surface of the cage wall.

In order to obtain a higher level of control of the size of the nanocage and the ability to incorporate different functional groups in the structure, an improved synthetic method was developed, utilizing dendrimers as structure-directing agents. These dendrimers also contain immolative bonds that can be cleaved later in the formation of cages. Fig. 2 shows the two different classes of dendrimers being investigated.

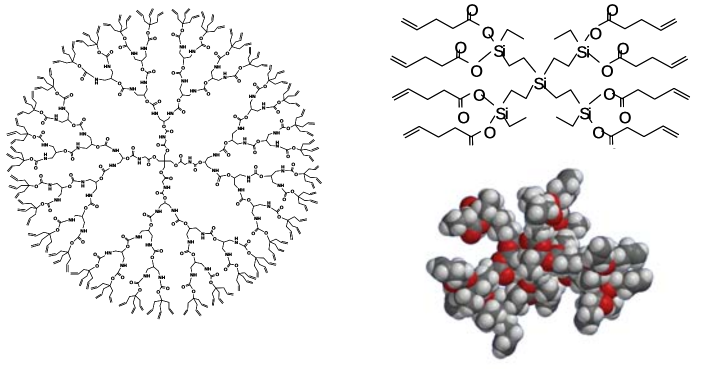

Fig. 2. Two dendrimers being used as structure-directing agents to form nanocages with encapsulated cores. The dendrimer on the left contains immolative carbamte bonds, and the one on the right contains immolative acyloxysilyl bonds.

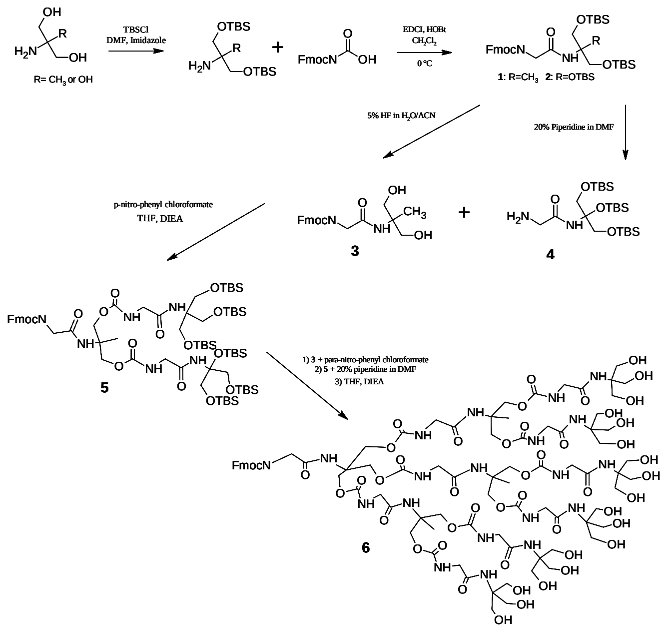

Fig. 3. One synthetic route for a carbamate-containing dendrimer

The unique features with using these dendrimers to form nanocages include: ability to control the hydrophobicity/hydrophilicity of the cage walls; ability to encapsulate a functionalized core structure in the cage; and ability to incorporate at least two different types of functional groups in the structure.

The third generation dendrimer possessing carbamate bonds, and a first generation dendrimer possessing acyloxysilyl bonds are shown in Fig. 2. The third and fourth generation of these dendrimers have been synthesized, and reaction of the one on the left with shell cross-linking agents have also been carried out successfully. Fig. 3 shows one synthetic route of the dendrimer on the left.

In the course of exploring different synthetic routes to these dendrimers, various new silane and siloxane molecules have to be synthesized. As part of the supporting activities for these syntheses, we have also developed a new solid-state method to synthesize siloxane molecules, some of which are structural building units of dendrimers. The method we developed employs either an alkoxysilane or an acyloxysilane linker protocol. The unique feature is the recognition that the reactivity of the linker molecule depends on the ligand of the Si atom, which allowed us to find an appropriate ligand that is sufficiently robust to permit growth of a siloxane molecule, but fragile enough to permit cleavage of the final molecule from the support. This synthetic method can be used to prepare many novel siloxane molecules.

DOE Interest

Catalysts that exhibit high selectivity can lower the energy requirements in many chemical transformation processes commonly found in the petroleum refining and chemicals production industries, by lowering the energy for separation and purification of the desired products. Whereas catalysts in nature (enzymes) make use of a variety of molecular properties and long-range interactions for high selectivity, these interactions have not been fully utilized in traditional heterogeneous catalysis due to the lack of synthetic techniques to control the environment of an active site. The research pursued in this project could significantly broaden the know-how in catalyst synthesis, and, in particular, permit control of the functionalities and environment of active sites and reaction selectivities. Successful completion of this project would result in a family of chemical catalysts that exhibit the high selectivity of enzymes but are much more robust to the processing environment.

Future Plan

We plan to complete the synthesis of a number of nanocage material using the dendrimer-directed approach. The two types of dendrimers of different immolative bonds will be used to generate nanocages of different shell wall properties, and to encapsulate core molecules with different functional groups. With these nanocages, for example, we will be able to study the effect of hydrophobicity of cage wall on catalysis and on chemistry that take place inside the cage. We will determine selectivity based on molecular size by varying the porosity of the cage walls. We will examine the cooperative effect of different functional groups in the proximity of each other.

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Principal Investigator: Suljo Linic DE-FG02-05ER15686

Investigations of Alkali Promotion in Heterogeneous Catalysis: first principles DFT and ab-initio thermodynamics studies of Cs promotion in oxidation reactions over Ag

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Goals

Although the impact of alkali promoters in heterogeneous catalysis has been recognized for decades it is sticking how little is understood about molecular level mechanisms underlying this phenomenon. This project aims to investigate molecular mechanisms of alkali promotion in heterogeneous catalysis on transition metals. The focus is on developing a predictive theory of alkali promotion to aid in the rational design of new catalysts and the improvement of existing catalytic processes.

DOE Interest

Understanding molecular level mechanisms of promotion is an important component in accomplishing a long-term goal of “catalysis by design”.

Research Plan

Alkali promoters (Li, Na, K, Rb, Cs) enhance activity and/or selectivity of various catalytic processes. These promoters are utilized in Fisher-Tropsch and alcohol synthesis, water-gas shift reactions, ammonia synthesis, olefin epoxidation, automotive three way converters. Although the impact of alkalis in heterogeneous catalysis has been recognized for decades, not much is known about the underlying physical mechanisms that govern the alkali promotion. This project attempts to identify the mechanisms of alkali promotion in chemical reactions on metal surfaces.

The issue is addressed in a case study of the role of Cs promoters in oxidation reactions on Ag. We focus on the Cs/Ag system since it is well established that alkali promoters enhance selectivity and activity in olefin epoxidation reactions over Ag. It is also likely that the fundamental insights obtained in the studies of the Cs/Ag system are transferable to any other system where electropositive alkali elements interact with electronegative adsorbates.

Our ultimate objective is to obtain a knowledge-base that will be utilized to formulate a predictive theory of alkali promotion in heterogeneous catalysis by transition and noble metals. We have identified a few important objectives that will be addressed:

a. We will study the impact of alkali promoters on various physical characteristics of metal surfaces. The focus will be on the Cs-induced modifications of Ag(111) surface.
b. We will investigate the mechanisms that govern the interactions of alkali adsorbates with co-adsorbates on metal surfaces. We will attempt to unearth the underlying

physical factors impacting the alkali-induced modification of the chemical reactivity of metal substrates.

c. We will study how a working state of an alkali promoter changes as a function of external conditions, i.e., the pressure and temperature of reactants. We will examine possible formation of Cs-oxide complexes as a function of gas-phase O_2 chemical potential (pressure and temperature). We are interested in whether and how the extent of promotion depends on the nature of the alkali complex.
d. We will study the effect of alkali promoters on the working state of a promoted catalyst. Here, we will investigate possible Cs-induced formation of Ag-oxide structures at elevated O_2 pressures and temperatures.

In our studies we utilize Density Functional Theory (DFT) calculations along with ab initio thermodynamic and kinetic simulations.

Recent Progress

1. Cs-induced modification of Ag(111) surface

We have investigated the effect of Cs adsorbates on the physical characteristics of Ag(111) substrate. The main conclusions of these studies are:

- We find that Cs decreases the electronic work function of Ag(111) surface. The decrease in the work function is a consequence of the Cs-induced dipole moment which opposes the clean substrate charge spill-over dipole.
- We observe that Cs induces a substantial electrostatic potential above the Ag substrate, i.e., along the z-direction. The induced electrostatic potential is significant even over those surface sites that are relatively far, a few Å, from the Cs adsorption sites. The gradient in the electrostatic potential along the z-direction leads to a significant electric field along the same direction.
- The adsorption of Cs on Ag(111) modifies the electronic structures of the Ag atoms that are directly bonded to Cs. These changes are localized and the Ag atoms that are further away from the Cs adsorption site do not experience any shifts in their electronic structure, i.e., their electronic structure is unchanged as compared to the pure Ag.

We have also demonstrated in the investigations of Na/Ru, Cs/Pd, and Na/Pd systems that the observed effect of Cs on Ag(111) is universal for alkali adsorbates on metal surfaces.

2. The effect of Cs on the activation of O_2 on Ag(111): Mechanism of promotion[1]

Based on the results presented in the previous section, we have hypothesized that Cs adsorbates affect the adsorption energy and the chemical behavior of co-adsorbates on metal surfaces via long-range electrostatic interactions. To test this hypothesis we have utilized DFT calculations to study the dissociation of O_2 on the Cs-promoted and on unprompted Ag(111). These studies have demonstrated that Cs affects dramatically the dissociation of O_2, and that the activation barrier associated with the activation process is significantly lower in the presence of Cs.

To probe the origin of the observed Cs promotions, we have developed a very general formalism that allows us to describe the interaction energy is terms of additive contributions combining: (i) charge transfer among the adsorbates, (ii) electrostatic interaction among the adsorbates, and (iii) the electronic polarization between the adsorbates. These different additive contributions can be computed based on DFT calculations

Our analysis has demonstrated that the origin of the Cs-induced lowering in the activation barriers is the long-range electrostatic communication between the transition state for the O_2 dissociation and the Cs adsorbates. This electrostatic interaction can be described adequately by capturing the interactions between the Cs-induced electrostatic field and the dipole moment associated with the transition state.

3. Investigations of the formation of alkali complexes: Case study: Formation of Cs-oxide complexes ender elevated temperatures and O_2 pressures.[2]

Another objective of our effort is to identify whether and how the working form of an alkali promoter is affected by external conditions. For example, in an oxidation reaction, the working form of Cs promoter might be a Cs_xO_y complex. The stoichiometric formula of the complex is a function of temperature and the O_2 pressure. To address this issue we have utilized ab initio thermodynamics approach to investigate the pressure- and temperature-dependant structure of Cs_xO_y complexes on Ag(111). To effectively probe the complex configurational space we have utilized lattice gas Hamiltonian methodology to obtain relevant energies and Monte Carlo simulations to probe the phase space. The results of these studies suggest that the stoichiometry of the equilibrium Cs_xO_y complex on Ag(111) is a function of external temperature and O_2 pressure. We are currently investigating whether the mechanism of alkali promotion depends significantly on the exact nature of the Cs_xO_y complexes.

4. Cs-induced oxidation of the Ag(111) substrate

Another important factor that affects the surface chemistry of metals is its oxidation state. For example, it has been suggested that subsurface oxygen plays an important role in promoting the selectivity of Ag toward epoxides in epoxidation reactions. We are currently analyzing whether the Cs promoters affect the extent of the oxidation of Ag. Preliminary results are showing that the Cs-induced oxidation of Ag is another mechanism by which the Cs promoter can affect the chemical activity of Ag substrates.

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Surface chemistry of carbon on Ni and Ni-alloys: promotion of the long-term stability of reforming Ni catalysts by surface alloying

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Reforming of hydrocarbon fuels is one of the most important heterogeneous catalytic processes. Current reforming catalysts such as Ni, however, suffer from two major problems: (i) carbon-induced deactivation and (ii) sulfur poisoning of the catalyst.

We have utilized Density Functional Theory (DFT) calculations to study the surface chemistry of carbon atoms and carbon fragments on various Ni facets.[1] These studies demonstrated that there is a strong thermodynamic driving force to form extended carbon networks which diminish the long-term activity of Ni. We have further utilized DFT to identify Ni-containing alloys that are more carbon-tolerant than monometallic Ni, i.e., that have a lower propensity to form the carbon networks. Subsequent steady-state reactor studies validated the predictions of the DFT calculations. Aside from the steady-state reactor tests, the catalysts were characterized with multiple spectroscopic and microscopic tools.

We will provide a very general and physically intuitive model that can explain the enhanced performance of the Ni alloys.

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[1] E.Nikolla, A. Holewinski, J. Schwank, S. Linic; “Controlling Carbon Surface Chemistry by Alloying: Carbon Tolerant Reforming Catalyst”, **Journal of the American Chemical Society, 2006**; *128*(35); 11354-11355**.**

DE-FG02-06ER15837 Meilin Liu

Understanding the Interfacial Structures – Chemistry Relationships in Solid Oxide Fuel Cells (SOFCs)

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Goal

The objective of the proposed study is to gain a profound understanding of the reaction processes at the two-phase boundaries (2PBs) and three-phase boundaries (3PBs) in solid oxide fuel cells (SOFCs) using quantum-chemical and continuum modeling together with experimental measurements. We hope to correlate the phenomenological behavior of electrode materials, as predicted from continuum modeling and validated by electrochemical measurements, with the surface/interface structures/properties, as predicted using quantum-chemical calculations and probed using vibrational spectroscopy.

Recent Progress

Oxygen reduction on cathode materials is predicted using quantum-chemical calculations to gain insight into the mechanism of molecular scale interfacial processes as well as the surface and interfacial structure and properties. The most widely used cathode material in SOFCs, $La_xSr_{1-x}MnO_{3\pm\delta}$ (LSM), were examined in detail. To identify the most plausible surface adsorption sites, an O_2 molecule was placed at various surface sites near La, Mn, or O ions. Schematically shown in Figure 1 represents a stepwise reaction mechanism: adsorption of a superoxo- or peroxo-like species, isomerization of superoxo- to peroxo-like species, dissociation, incorporation into an oxygen vacancy (**V**), and diffusion to a more stable site on the surface. In addition, the atomic charge analysis clearly suggests that charge transfers from the surface to the adsorbed species. The non-existence of any reaction barrier for oxygen adsorption, reduction, and dissociation signifies fast O_2 reduction kinetics on LSM-based cathode materials. Further, quantum molecular dynamics (MD) calculations at 1073 K reveal that

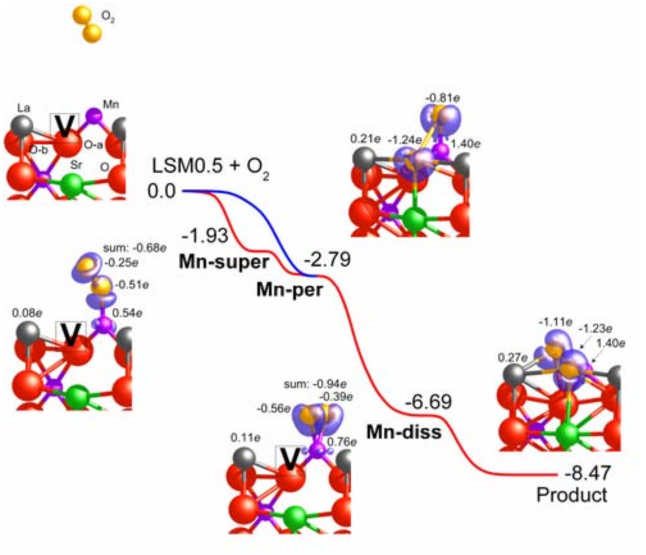

Figure 1. Potential energy profiles for the interactions of O_2 and LSM0.5.

the time it takes from oxygen adsorption to dissociation is ~530 fs on $La_{0.5}Sr_{0.5}MnO_{2.75}$ (LSM0.5)and ~ 650 fs on $LaMnO_3$(LM), implying that the presence of oxygen vacancies accelerates the kinetics of oxygen dissociation.

Ionic transport through ABO_3-type cathode materials is also examined using DFT calculations. As shown in Figure 2, the ionic conduction through LSM0.5 lattice follows a curved trajectory with a 0.76 eV reaction barrier. The predicted activation energy is in line with the activation energy for oxygen diffusion in the same material measured using secondary ion mass spectrometry (SIMS), 3.71 ± 0.33 eV after adding the reaction barrier to an O-vacancy formation energy of 3.25 eV (Ref. R. A. De Souza and J. A. Kilner, *Solid State Ionics*, **1998**, Vol. 106, p. 175).

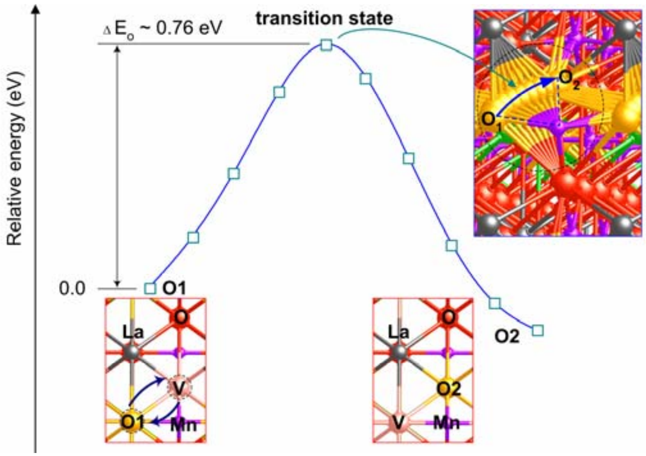

Figure 2. Schematic of oxygen ion transport through LSM0.5.

We have developed models for the electrochemical response in thin and patterned mixed conducting films, along with a process for quantitatively coupling model and experiment. Thin and patterned films are good experimental vehicles for the study of electrochemical reactions, since the close control of geometry available leads to better insight into the various processes comprising the reaction. However, at these extreme aspect ratio geometries, electronic resistance in the thin mixed conducting films becomes an important issue. Development of a model that treats sheet resistance is an important step toward using thin and patterned films to study surface reactions and transport in mixed conductors (see Figure 3).

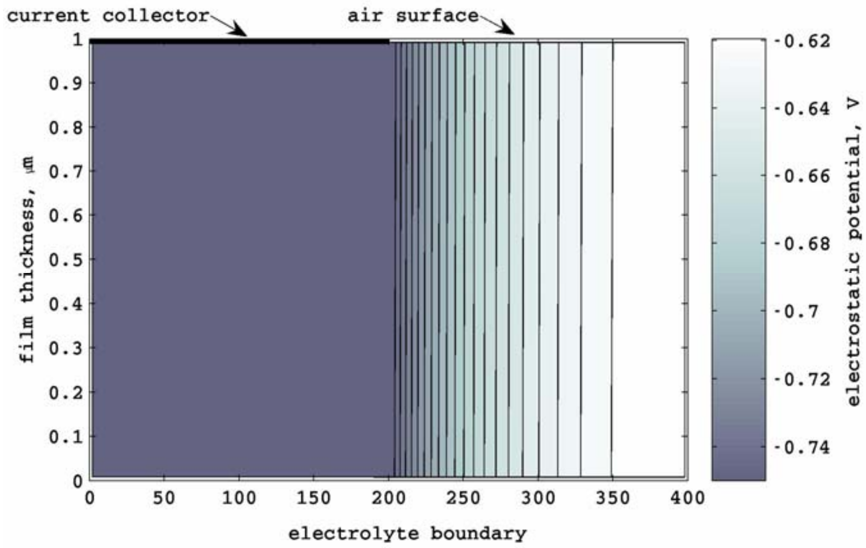

Figure 3. Simulated electrical potential distribution in a mixed conducting thin film.

We have also developed computational methods for comparing experimental results with models in a mathematically rigorous manner. We have implemented the particle swarm optimizer as our optimization algorithm, and have instituted methods for assessing the uniqueness and distinguishability of optimized solutions. These techniques will enable an estimation of unknown parameters such as surface reaction rate constants, which may then be compared with results from first principles modeling or direct measurement. We have compared models for the bulk defect structure in $La_xSr_{1-x}MnO_{3\pm\delta}$ with nonstoichiometry data taken from the literature.

DOE Interest

One of the grand challenges facing the hydrogen fuel initiative is the creation of novel materials and nanostructures that not only promote fast transport of ionic/electronic defects, but also facilitate rapid surface electrochemical reactions. It is well known that the performance of fuel cells are often determined by *interfacial losses*, especially those based on thin-film electrolytes/membranes operated at low temperatures. Our approach is to explore electrode reactions as well as relevant ionic and electronic transport processes at or near two-phase and three-phase boundaries using *quantum-chemical and* continuum *modeling* coupled with direct experimental measurements.

Future Plans

Based on the computational framework we have developed, we plan to investigate into the mechanism and kinetics of oxygen reduction on surfaces as well as ionic and electronic transport along surfaces, across interfaces, and through lattice of ABO_3-type electrode materials as the A and B cations are systematically substituted. The B-site will be substituted by transition metal ions such as Mn, Co, Fe, V, Ti where as the A-site will be substituted by La, Sr, Ba, and other ions. We hope to predict thermodynamic and kinetic parameters relevant to surface reactions and transport processes that can be directly incorporated into continuum modeling. We also plan to further advance a series of carefully designed experiments for the purpose of gathering both qualitative and quantitative information about material behavior. Ultimately, we hope to identify the critical design factors for achieving intelligent design of better materials.

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DE-FG02-93ER14331 **Theodore E. Madey**

Nanoscale Phenomena in Surface Chemistry: Structure, Reactivity and Electronic Properties

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Collaborators: F. Cosandey (Rutgers), U. Diebold (Tulane), H. Idriss (Auckland, New Zealand), T. Jacob, M. Scheffler (FHI, Berlin), S. Kelty (Seton Hall), M. Kiskinova (Elletra Synchrotron), J. Rowe (UNC)
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Goal

To identify the causes of faceting and other nanometer-scale growth phenomena on adsorbate-covered metallic (and bimetallic) surfaces, and to correlate surface structure, surface reactivity and surface electronic properties of surfaces with nanometer-scale features.

Recent Progress

Faceting of metals: Many planar metal surfaces that are rough on the atomic scale, such as fcc Ir(210), hcp Re($12\bar{3}1$) and Re($11\bar{2}1$), and the bimetallic alloy NiAl(111), are morphologically unstable when covered by monolayer films of oxygen, nitrogen, or of certain metals: they become "nanotextured" when heated to elevated temperatures. Faceting occurs when an initially planar surface converts to a "hill and valley" structure, exposing new crystal faces of nanometer scale dimensions. Faceting is driven by surface thermodynamics (anisotropy of surface free energy), but controlled by kinetics (diffusion, nucleation).

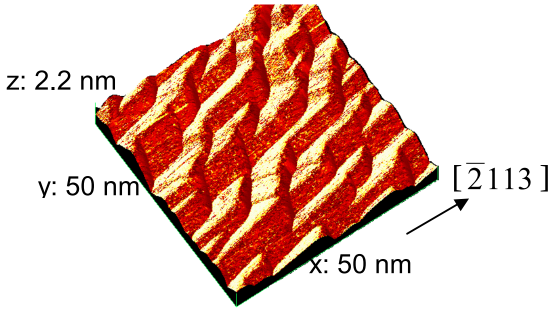

Figure 1. A typical 3D STM image of the faceted Re($12\bar{3}1$) surface prepared by adsorbing ~1 monolayer of oxygen at 300K and annealing at 900K.

In the past two years, we have observed exciting new phenomena on all of the above-mentioned surfaces, including an unusual adsorbate-dependence for O-induced and N-induced faceting of Re($11\bar{2}1$), a complex sequence of coverage-dependent faceting of Re surfaces (e.g. Fig. 1), eruption of nanoscale spinel features from the oxidized NiAl(111) surface (see Fig. 2), nanometer scale size effects in NH_3 decomposition over faceted Ir(210)

(Fig. 3), and structure sensitivity in CO oxidation over planar and faceted Ir (210). We have characterized the relations between structure, reactivity and electronic properties. Measurements include scanning tunneling microscopy (STM), atomic force microscopy (AFM), LEED, temperature programmed desorption (TPD), low energy electron microscopy (LEEM) and soft x-ray photoemission (SXPS) using synchrotron radiation at NSLS. The faceted surfaces are excellent models for studies of structural sensitivity in catalysis, and are potential nanotemplates for growth of metal nanostructures.

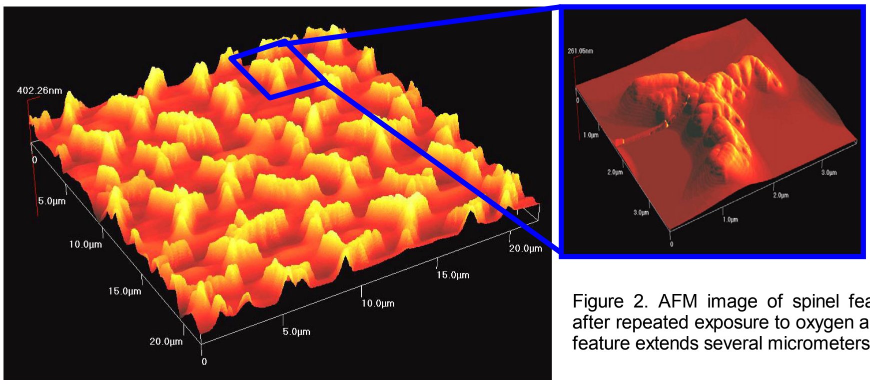

Figure 2. AFM image of spinel features formed on NiAl(111) after repeated exposure to oxygen and annealing. In-plane, each feature extends several micrometers, and is 250-400nm high.

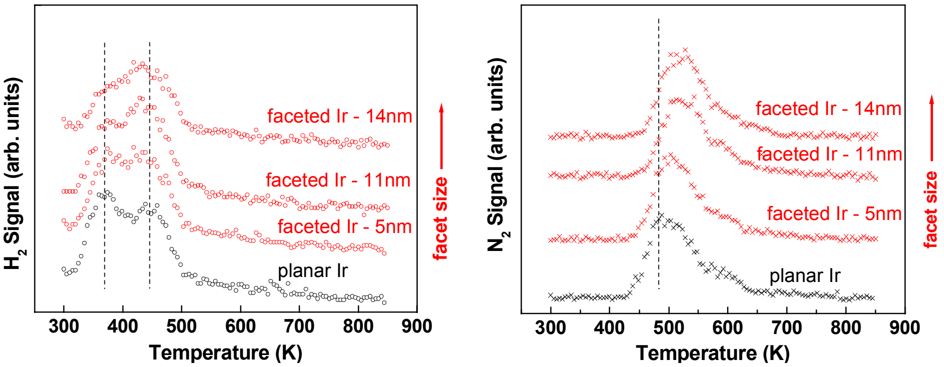

Figure 3. TPD spectra of H_2 and N_2 from adsorption of 5L NH_3 on clean planar Ir(210) and clean faceted Ir(210) with tunable average facet sizes from 5nm to 14nm, showing structure sensitivity and size effects in ammonia decomposition on Ir.

Theoretical collaborations: We have an active collaboration with Dr. Timo Jacob and Prof. Matthias Scheffler at the Fritz Haber Institute in Berlin. They are doing DFT calculations of the stability of various O/Ir, O/Re and N/Re surfaces, in an attempt to understand details of our faceting data. They are also addressing the structure sensitivity of CO oxidation over planar and faceted Ir.

DOE Interest

The factor that distinguishes this work from other studies of model metal and oxide catalysts is our emphasis on atomically rough, high-surface-energy surfaces that can be morphologically unstable during reaction conditions. We believe that these results may be important for energy-related catalysis, in understanding dynamic structural rearrangements at the surfaces of high area catalysts, and in clarifying the role of nanometer-scale size effects in surface reactions under operating conditions.

Future Plans

We will characterize the oxygen-induced growth of facets and the possibility of generating clean faceted surfaces by removal of O at low T, to ì freeze inî the faceted structures; this works for faceted Ir(210), and will attempt it for Rh(210). We will characterize structure sensitivity and nanoscale size effects in reactions (NH_3 decomposition, NO reduction, CO oxidation) over planar and faceted surfaces of Ir, Rh, and Re. We will assess the utility of faceted surfaces as nanotemplates for nucleation and growth of metallic nanostructures (clusters, nanowires, etc) on faceted O/Re and faceted Al_2O_3/NiAl(111). A search for nanoscale spinel formation in other catalytically-active Ni/metal alloy surfaces (e.g., Fe/Ni) will be initiated.

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DE-FG02-89ER14048 **Eric McFarland**

Investigations of Electronic Promotion of C-x Bond Transformations on Supported Transition Metal Clusters

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Graduate Students: Wei Tang, Burcin Temel
Post Docs: Michael Sushchikh, Jung-Nam Park, Ju Chou
Collaborators: H. Metiu (UCSB), Raj Pala (UCSB), K.S. Choi (Purdue), V.V. Styrov (Mariupol, Ukraine)
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Goal

A major challenge in the use of hydrocarbon resources for fuels and chemicals is to understand and control the reactivity of chemical bonds with carbon atoms on solid catalyst surfaces. Our research addresses this central problem by investigating the influence of the electronic interactions between transition metal and metal oxide nanoclusters and their support on C-x bond transformations. Whereas the organic ligands of homogeneous catalysts can systematically alter the electronic structure of the coordinated metal, we are interested in defining how the surrounding solid matrix supporting a mono or mixed metal or metal oxide nanocluster similarly controls the electronic structure of the reactive supported metal atom(s), i.e., “electronic promotion.” Our recent goals included design and implementation of catalytic activity testing systems which are capable of providing accurate comparison of per site catalytic activity of different catalysts including testing stations (reactors), consistent methods of the catalyst preparation and the establishing of suitable testing and analysis protocols.

Recent Progress

System development: We have designed and built two different batch microreactors for obtaining accurate and comparable reaction rates of otherwise similar but morphologically different samples. A variable volume (1.2 mL to 85 mL) batch reactor used for studying small quantities of powder supported catalysts, and a 5 uL microreactor used for studying wafer-supported catalysts were designed and constructed. The main features of the reactors are: micro-probing capability using principle of variable leak valves (minimal altering of the amount of gases in the reactor volume); direct probing of the gases into ultra-high vacuum (UHV) mass-spectrometer volume (high sensitivity); enclosure of the reactor volume in larger tank (leak-proof by design). Both reactors are made of UHV-compatible components. The 5 uL microreactor is ready to be attached to an UHV chamber equipped with linear stage sample transfer. These reactors will complement our existing Packed Bed Reactor (PBR) and UHV systems such that we now have a set of testing equipment covering a wide range of catalyst samples and pressure ranges.

C-x activation: We have started to study new class of catalysts, the doped oxides. Our theory collaborators predict that the ability of the dopant atoms and of the host oxygen atoms to activate C-x bonds may be fine-tuned by appropriate choice of the dopant and of the host. We have studied alumina-doped zinc oxide and alumina-doped zirconia as catalysts for reforming of methanol. In both cases addition of small (~1%) amounts of aluminum led to an activation of otherwise completely inactive catalysts. Zirconia-based catalysts produced dimethyl ether whereas zinc oxide based catalysts produced CO and CO_2. Apparently, aluminum dopant facilitated the initial reaction step of the methanol adsorption; the selectivity is due to the host material. Remarkably, Al-doped ZnO has performed in the CO oxidation reaction at the temperatures where neither ZnO nor alumina oxidizes CO.

Electronic Interactions: We have utilized non-destructive luminescence methods for *in situ* characterization of the electronic properties of catalysts. In particular, the correlation between temperature quenching of the photoluminescence and the catalytic activity has been demonstrated for gold nanoclusters supported on titania. Charge transfer from the support to the active metal clusters was suggested to be a non-radiative pathway for electron-hole pair recombination. By comparing different polar ZnO surfaces we have shown how the mechanism of surface reactions can be deduced from the chemiluminescence accompanying exothermic reaction steps.

DOE Interest

Our work leads to an improved understanding of fundamental steps of chemical reactions involving carbon-contained molecules. Not only are such molecules primary energy sources for the American economy, but they are considered to be key intermediates in the future “hydrogen” economy. In addition, as a university-based research program, a principal objective is education. To date, the project has helped to fund the education of several outstanding young students (including undergraduates) and postdocs.

Future Plans

In the coming 12 months we plan to continue studies of nanocluster metals and doped metal oxides as catalysts for C-x bonds activation. We will combine data obtained in the plug-flow and batch reactor systems in order to better understand the kinetics and to compare pelleted and idealized catalyst configurations. The trends predicted in the titania-doped ZnO system by DFT calculations will be tested for partial oxidation of hydrocarbons. Optical methods including luminescence will be used in parallel to characterize the electronic configurations of the host-dopant system. We will combine the electronic spectroscopy (luminescence) with vibrational spectroscopy (IR) to identify the reaction mechanisms and identify exothermic reaction steps by monitoring chemiluminescence. New systems we are exploring include catalysts based on Pd nanoclusters to extend our previous observations of C_2 coupling on Pd supported on TiO_2, to Cu-Pd/TiO_2 systems which are thought to facilitate peroxide formation for C-H bond activation in methane.

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Methane Oxidation Activity of Mixed -Conducting Perovskite Oxides under Solid Oxide Fuel Cell Conditions

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Introduction

Solid Oxide Fuel Cells (SOFCs) are considered one of the leading technologies for efficient future power generation. Like all fuel cells, SOFCs consist of three main components: a cathode (air electrode), an anode (fuel electrode), and an electrolyte. Under operation, molecular oxygen is reduced to oxygen anions at the cathode, using electrons supplied from an external circuit. The generated anions then migrate to the anode through a dense ceramic electrolyte. Fuel oxidation occurs at the anode and the liberated electrons flow through an external circuit to the cathode, completing the process. Since the transported ionic species is an oxygen anion, SOFC can theoretically operate directly on a range of hydrocarbons from methane to gasoline [1]. The primary challenge in achieving this goal is the choice of SOFC anode materials. The anode must conduct oxygen anions and electrons and be catalytically active for fuel combustion. The perovskite structured oxide $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ [2,3], has recently been proposed as a potential anode material that can meet all of these requirements. δ is the oxygen non-stoichiometry material and is a function of cation reducibility, temperature and pO_2.

The SOFC anode environment is highly reducing with no gas-phase oxidant; the oxygen for fuel combustion is supplied via solid-state ionic diffusion through the anode material. In order to investigate the catalytic properties of SOFC materials, it is necessary to reproduce these conditions. In this study, we utilize a pulse reactor system to probe the activity of $La_{0.75}Sr_{0.25}Cr_xMn_{1-x}O_{3-\delta}$ towards CH_4 oxidation under SOFC anode conditions. The oxygen for combustion is supplied from the perovskite lattice, leading to a reduction of δ throughout the experiment.

Materials and Methods

Powder samples of the materials $La_{0.75}Sr_{0.25}Cr_xMn_{1-x}O_{3-\delta}$ (x=0,0.25,0.5,0.75,1) were prepared from nitrate salts via a combined EDTA/citric acid complexometric route. The product powders were calcined at 1273K for 4 hours to produce the perovskite structure, as confirmed by XRD. 0.3g of powder, particle size 100-200 µm, was loaded into a quartz reactor tube and heated in flowing Ar, $pO_2=10^{-5}$ atm. Upon equilibration, 6 second pulses of 20% CH_4 in Ar interrupted by 120s periods of Ar were repeatedly applied to the sample. The reactor exit composition was analyzed via an online mass-spectrometer (Omnistar, Pfeiffer Vacuum, Nashua, NH).

Results and Discussion

Figure 1 shows the instantaneous CO_2 and CO selectivity of for $La_{0.75}Sr_{0.25}Cr_xMn_{1-x}O_{3-\delta}$ at 1173K as a function of oxygen stoichiometry, with x as a parameter. The initial oxygen stoichiometry in flowing Ar, $pO_2 = O(10^{-5})$ atm, is close to 3.0 for all compositions. Each pulse of CH_4 consumes a small fraction of the lattice oxygen forming CO_2 and/or CO. The non-stoichiometry decreases until it reaches an equilibrium value, at which point reaction ceases. As shown in Figure 1, at high oxygen stoichiometry all of the materials show a high selectivity towards total oxidation of methane. As the oxygen stoichiometry decreases, the CO2 selectivity decreases as CO production increases. At stoichiometry close to the equilibrium value, all materials form predominantly CO. Increasing Mn concentration decreases the final equilibrium oxygen stoichiometry (as Mn is more easily reduced than Cr) and increases the total oxidation window

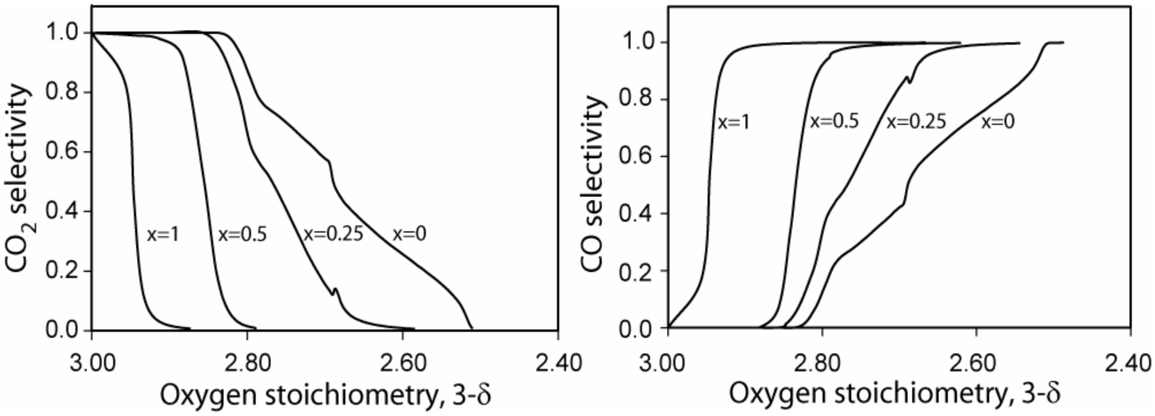

Figure 1: Instantaneous selectivity towards a) CO_2 and b) CO production as a function of bulk oxygen stoichiometry for $La_{0.75}Sr_{0.25}Cr_xMn_{1-x}O_{3-\delta}$ at 1173K for x=, x=0.5, x=0.25 ad x=0. Each pulse of CH_4 yields a change in stoichiometry between 0.05 and 0.01. Symbols indicating each pulse are omitted for clarity.

In order to realize the maximum efficiency in a fuel cell system, it is necessary to maximize the CO_2 selectivity from the catalyst. Within the SOFC anode, the lattice oxygen stoichiometry is a function of both the intrinsic surface reaction rate, which consumes surface oxygen, and the bulk oxygen anion conductivity, which replenishes the depleted surface sites. As such, it is desirable to utilize a catalyst that exhibits high selectivity towards total oxidation over a wide range of oxygen stoichiometry. The driving force for the oxidation reaction under SOFC conditions may be considered as the difference in oxygen stoichiometry (the oxygen chemical potential) between the measurement condition and the equilibrium value. Based on this, it is understandable that at high oxygen stoichiometry, all samples show high selectivity towards total oxidation - there is a greater driving force for the oxidation reaction; however, the nature of the catalytic sites also dictates the nature of the reaction. In this case, higher Mn content provides greater CO_2 selectivity over a wider range of driving force.

Further studies are currently underway to decouple the influence of stoichiometry and cation composition and relate these purely catalytic measurements to fuel cell performance.

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Density Functional Theory Study of Pt and Pd-based Pseudomorphic Monolayer Alloy Catalysts for NO_x Storage Reduction Applications

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One of the great challenges of our time is the efficient and equitable consumption of fossil fuels. One of the consequences of our need to conserve our finite petroleum resources is a transition to more efficient diesel engines and lean burning gasoline engines. Associated with the switch to these lean burning engines is an increased difficulty of NO_x abatement due to the highly oxidizing conditions which results in a need to improve conventional three-way exhaust catalysts. The NO_x storage reduction (NSR) catalysts have emerged as the most successful approach to combat this problem. These systems are required to operate under two distinct regimes: a lean condition in which NO is oxidized over a noble metal component (usually Pt) to form NO_2 which can subsequently adsorb on the storage agent (usually barium oxide) and a reducing atmosphere during which a reducing agent (e.g. H_2, CO, C_3H_6) reacts with NO_x released by the catalyst reacts to produce N_2.

Surface science studies of epitaxially grown metal layers on top of a different metal single crystal have revealed that these pseudomorphic monolayers have novel adsorption properties and therefore could potentially serve as a whole new class of catalysts. Specifically, we propose the use of pseudomorphic monolayers of Pt over other transition metals has been examined for their ability to perform in demanding task of operating both reducing and oxidizing environments in the NSR system. From these calculations, it is hoped that suitable candidates are identified for replacement of monometallic Pt catalysts thereby simultaneously improving performance and reducing cost. As a starting point, the oxidation of NO to NO_2 was examined for a variety of potential candidate catalysts. It is important to recognize that the stable surfaces in the oxidizing environment may in fact be surface oxides. Furthermore, core-shell systems like Pt/Cu may be reversed in the presence of oxygen such that a surface oxide of copper forms above a Pt core depending upon the temperature and partial pressure of oxygen. Density functional theory based calculations were performed using the program VASP with plane wave basis set and ultrasoft pseudopotentials with periodic supercells. Transition state calculations for the evaluation of kinetics will use the climbing nudged elastic band method as described by Jonsson and coworkers.

FWP ERKCC43 **David R. Mullins**

Surface Chemistry Related to Heterogeneous Catalysis

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Goal

The long-range goal of this program is to develop a detailed understanding of how the interactions between a reducible oxide support and supported metals control the mechanisms of reactions they catalyze. The focus is on well-characterized model surfaces and on particular redox reactions (e.g. CO, ethylene or ammonia reacting with O_2, NO or NO_2,) which are likely to involve oxygen exchange with the oxide support. Detailed reaction mechanisms are determined by spectroscopy of surface species and mass spectral analysis of products.

Recent Progress

We have conducted several parallel areas of investigation during this period. We have studied the interaction of related molecules with cerium oxide surfaces to understand how different molecular functionalities react with the reducible oxide and how their reactivity is modified by the presence of metallic nanoparticles. Scanning Tunneling Microscopy experiments have been initiated to better understand the structure – function relationships of the cerium oxide surfaces. First principles calculations are being conducted to provide a fundamental understanding of the molecular reactions observed on the ceria and to help interpret the STM images. Finally, preliminary experiments have been conducted to study catalytic reactions using an effusive molecular beam source under UHV conditions.

Interactions of Oxygenates with Cerium Oxide and Rh / CeO_X: The adsorption and reaction of CH_3OH, CH_2O and HCOOH on oxidized and reduced cerium oxide films were studied by temperature programmed desorption (TPD), soft x-ray photoelectron spectroscopy (SXPS) and near-edge x-ray absorption fine structure (NEXAFS). CH_3OH was one of the first molecules we have studied that strongly adsorbs on fully oxidized CeO_2 forming a methoxy that is stable to above 500 K. Methanol is a very effective reductant producing H_2O and CH_2O. Although the methoxy is the stable intermediate on both oxidized and reduced ceria, its fate changes as a function of the ceria oxidation state. The methoxy desorbs as formaldehyde on oxidized ceria and decomposes to CO and H_2 on reduced ceria.

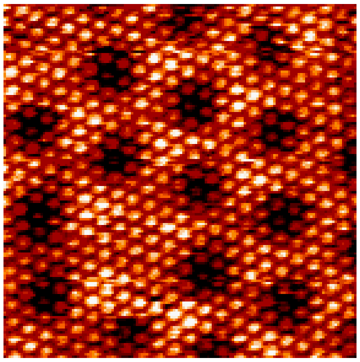
The addition of Rh to the substrate surface alters the reaction pathway. Formaldehyde formation is completely suppressed and total decomposition to CO and H_2 is shifted to lower temperatures. The methoxy adsorbed directly on the ceria diffuses to the Rh particles and reacts.

Formaldehyde also strongly chemisorbs on oxidized ceria but it doesn't reduce the substrate and desorbs as formaldehyde between 220 K and 320 K. The chemisorbed species interacts with both the Ce^{4+} and O^{2-} on the surface forming bridge-bonded dioxymethylene (CH_2O_2). On a reduced surface, the dioxymethylene disproportionates to form formate and methoxy that subsequently decompose into CO and H_2. The use of labeled $Ce^{18}O_X$ demonstrates substantial incorporation of substrate oxygen into the reaction products.

Our most recent work has focused on the reactions of formic acid with ceria. Formic acid can act as either a reductant or an oxidant depending on the initial oxidation state of the ceria. Formic acid removes oxygen from CeO_2 producing H_2O and CO_2. Alternatively, it can add oxygen to CeO_X forming H_2 and CO. The steady state condition appears to be ca. 80% Ce^{4+} and 20% Ce^{3+}. Spectroscopic characterization is underway to determine the reaction mechanisms and intermediates.

Structural Characterization of Ceria Films and Metals on Ceria: Highly oriented $CeO_X(111)$ films are grown on single crystal Ru(0001) by evaporating Ce metal in a low pressure oxygen environment. We have recently succeeded in obtaining atomically resolved STM images of these films. Monolayer ceria displays the hexagonal structure expected from $CeO_2(111)$. However a higher order superstructure is evident that results from the lattice mismatch between $CeO_2(111)$ and Ru(0001). The origin of this Moiré structure is currently under investigation.

We have also examined Pd and Rh deposited on ceria. Pd forms larger particles than Rh when deposited at 300 K and demonstrates much more sintering when annealed to 800 K. We are currently trying to correlate the structure of these two metals on ceria with the reaction of CO on the metal covered surfaces.



Monolayer $CeO_2(111)$ grown on Ru(0001). The scale is 9 nm x 9 nm.

First Principles Calculations: Calculations have been performed on the adsorption of methanol on CeO_2. These calculations support a model whereby methoxy displaces O on the ceria surface through the desorption of water. Current calculations are examining the change in reaction products from formaldehyde on CeO_2 to CO and H_2 on reduced CeO_X. Computer modeling is also being used to simulate the STM images obtained from ceria on Ru(0001) to help explain the origin of the Moiré structure.

Catalytic Reactions on Model Surfaces: An effusive molecular beam source is being used to study the reaction of CO + NO to form $CO_2 + N_2$. Reaction products and rates are monitored by mass spectrometry and surface intermediates are determined by soft x-ray photoelectron spectroscopy (sXPS). Preliminary experiments have investigated the reaction on a single crystal Rh(111) surface. Experiments are underway to compare these results to Rh supported on a cerium oxide surface.

DOE Interest

A detailed understanding of the interactions between adsorbates, supported metals and oxide supports is related to many catalytic processes relevant to energy utilization including emission control, lean burn catalysis, and catalysts for fuel cells and hydrogen utilization. This project also funds the U12a soft x-ray beamline at the National Synchrotron Light Source. This facility is used for high-resolution, high-sensitivity sXPS and soft x-ray absorption (NEXAFS). We have collaborated with a number of DOE supported investigators and support an over subscribed General User program.

Future Plans

We will expand our study of the fundamental interactions between molecules and oxide surfaces to other catalytically important molecular species. These will include N-containing molecules that have been proposed as reductants in selective catalytic reduction applications and S-containing molecules that are present in petroleum fuels and may poison the oxide catalysts.

We have previously observed that the activity of Rh varies depending on whether the ceria support is oxidized or reduced. We are using STM to determine whether there is a structural origin for this change in activity.

Theory will be utilized to model the activity of metals supported on ceria. The primary areas of investigation will be the variation of metal activity as a function of ceria oxidation state and variations between different supported metals such as Pd, Rh and Pt.

Finally, the effusive molecular beam experiments will be applied to supported metal systems and compared to the single crystal metal results. We will determine whether metal-support interactions alter reaction rates or products and study the origin of these changes if they occur.

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Three-dimensional Structures of Supported Metal Nanoparticles Determined by Coordinated X-ray Absorption Spectroscopy, Electron Microscopy and Theoretical Simulations Efforts

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Goal: This project involves the characterization of metal nanoparticles with the goal of achieving a fundamental understanding of their dynamical and structural properties and the correlations these have with behavior seen in catalytic chemistry. Nanomaterials prepared via controlled chemical syntheses are characterized using a variety of analytical techniques, highlighted by the complementary use of X-ray absorption spectroscopy and advanced electron microscopy. Theoretical calculations further augment an understanding of structures that are characteristic of the nanometer dimensions of catalyst materials or of the local environment of the catalyst (support, ligands, and reactant molecules).

Recent Progress

**** Develop EXAFS data analysis methods:*** EXAFS measurements of coordination numbers in nanoclusters contain size- and shape-specific information. For bare metal clusters, a number of different minimum-energy, regular polyhedral geometries have been proposed as structural motives. We have developed a suite of computer programs for cluster geometry generation for most regular polyhedra, as well as a data analysis package to process cluster coordinates and obtain radial distribution function information that can be directly compared with experiment. For bimetallic alloys, our methods of multiple-edge, constrained fits can discriminate between quasi-random and core-shell structures.

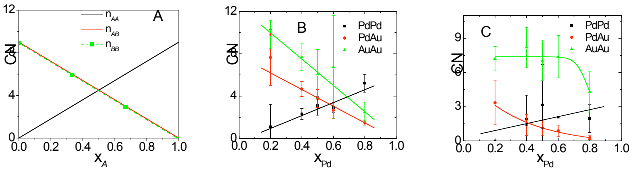

Fig. 1. Coordination numbers in nanoalloys: model of a random alloy (A), quasi-random dendrimer-stabilized Pd/Au alloys (B), and core-shell alloys (C). Samples: **R. M. Crooks**

**** DFT modeling of ligand-stabilized Au_{13} nanoclusters:*** We simulated thiol/phosphine-stabilized Au_{13} nanoclusters via DFT, and compared structure/ligand placement patterns with recent EXAFS/TEM measurements of these clusters. The nanoclusters are stabilized in a distorted icosahedral structure by on-top phosphine ligands and a combination of on-top and bridging thiol ligands. The ligand-induced bond-length disorder is predominantly tangential, not affecting radial Au-Au distances.

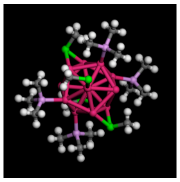

Fig. 2. Optimized Au_{13} structure.

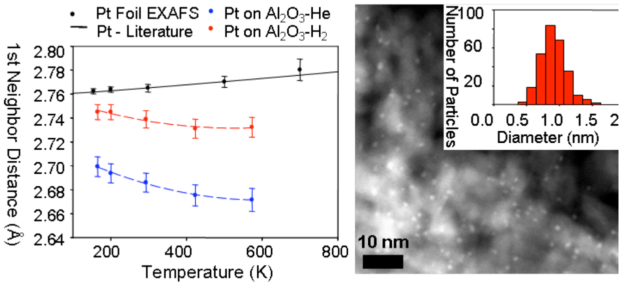

Fig. 3 Pt-Pt first nearest neighbor distances measured by EXAFS and STEM analysis of 1 wt % Pt on Al_2O_3.

**** Negative Thermal Expansion:*** We recently made a discovery that appears to hold significant implications for understandings of heterogeneous catalysis**.** Particles under both H_2 and He show contraction with increasing temperature, with the effect greater for the bare Pt particles. Passivation with hydrogen relaxes this contraction (to ~1% at 293 K) (Fig. 3).

**** Reduced sintering of Au_{13} nanoclusters using reactive oxygen post-treatments:*** We explored the effects of post-treatments in reactive oxygen to thermal annealing on ligand-removal and sintering of ligand-protected Au_{13} clusters deposited onto anatase TiO_2. Both the EXAFS and TEM results revealed apparent nanoparticle growth as a result of ozone or oxygen treatment. However, average particle size for the ozone treated sample is smaller with a narrower range of sizes (1.2±0.5 nm, 40±49 atoms) as compared to calcination (2.7±0.6 nm, 324±264 atoms). The atomic oxygen exposed gold clusters also showed smaller average cluster sized than calcination, but larger and wider distribution of sizes and shapes (Fig. 4) as compared to ozone exposure (2.1±0.7 nm, 72±98 atoms).

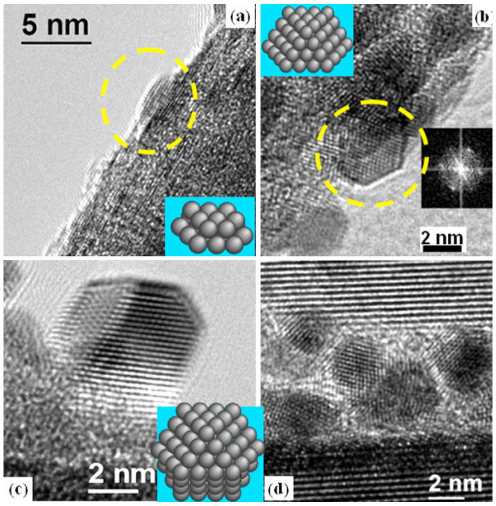

Fig. 4. HRTEM of atomic oxygen treated Au particles with various sizes and shapes.

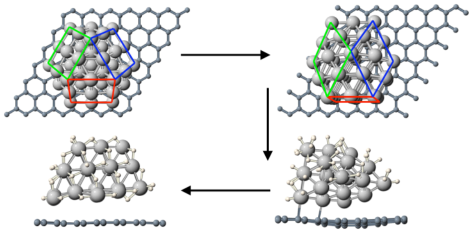

Fig. 5. Structure of truncated cuboctahedral Pt_{37}/C. (top) Without H, (100)-facets shear into pseudo-(111) facets. (bottom) With H (max. 46 H), there is no barrier to recover the observed truncated cuboctahedral structure.

**** Shear-instabilities in metallic nanoparticles: H-stabilized structure of Pt_{37}/C:*** Via DFT-based molecular dynamics we have studied the morphology of a Pt_{37} on carbon with(out) hydrogen (H) passivation that arises with post-processing of nanoparticles before characterization. We find that without H (e.g., in He atmosphere or evacuation at high T) the morphology change of a truncated cuboctahedral Pt_{37} is driven by shearing of (100) to (111) facets to lower surface energy. With H passivation, the sheared structure reverts to the observed truncated cuboctahedral structure and the average nearest-neighbor Pt-Pt bond length increases by 3%, now in excellent agreement with EXAFS (see Fig. 5). This shear instability may be a general trend for end of transition-metal row elements. The stabilization of the truncated cuboctahedral structure is due to adsorption energetics of H on Pt(100) and (111) facets, specifically, the preference for H adsorption at bridge sites on (100) facets, which should be considered in a realistic model for H adsorption on Pt nanoparticles. Critical to EXAFS analysis, we find that <u>dramatic morphological change</u> of a nanoparticle can occur even with <u>small changes</u> to first-shell Pt-Pt coordination number.

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FWP ERKCC47 **Steven H. Overbury**

Nanocatalysts: Synthesis, Properties, and Mechanisms

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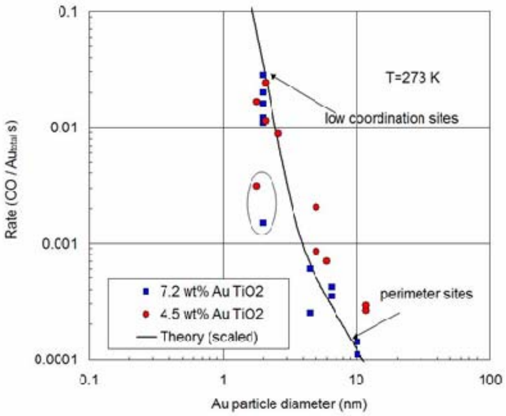
Goals

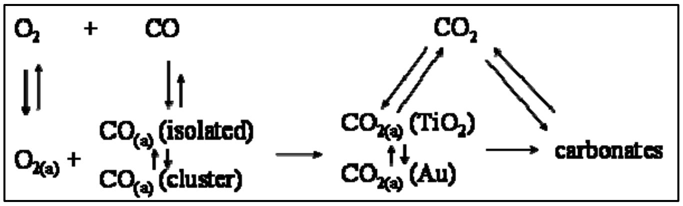
This program has focused on improved understanding of how catalytic reactions occur on Au nanoparticles and the role of nanostructure and support upon the activity and stability of the Au catalysts. To this end we have addressed size dependence both experimentally and computationally, probed reaction pathways by operando techniques, and explored new synthesis routes to Au catalysts and factors that control stability and activity of supported Au particles.

Recent Progress

Various theoretical explanations for size sensitivity in Au catalysis have been proposed and their validation is often based on comparison with limited data. In addition, Au catalysts are sensitive to many factors relating to type of support and their synthesis and so the size sensitivity is difficult to extract from comparison of many different types of catalysts. To clarify the size dependence we have used EXAFS in conjunction with a flow reactor to measure size dependence for catalysts on a single support (TiO_2) in which the Au particle size is systematically varied by sequential anneals. Temperature dependent activities were obtained following anneals which yielded mean Au particles sizes, d, from 2 to 10 nm. Activities, in terms of CO converted per total amount of Au per second, were parameterized by power law dependence. The activity varies as d^{-x} where x varies from 2-3, for two catalysts with different loading, suggesting activity a specific types of surface sites. DFT calculations were applied to simulate and interpret this data. Fully relaxed Au clusters containing from 5 to 35 Au atoms particles were simulated on single crystal slabs of TiO_2 with a rutile or anatase structure. Adsorption energetics of O_2 and CO were calculated for different bonding configurations and sites. CO adsorption was generally stable and weaker molecular O_2 adsorption occurred with energy dependent upon the coordination of the Au atoms. Nudged elastic band algorithm was used to determine reaction barriers for CO oxidation. Low coordinate bonding of Au provides both an increase in O_2 adsorption energy and structural flexibility which lowers the reaction barrier. Both factors increase reaction rates on low coordinate Au sites. Statistical evaluation of the coordination on the relaxed Au particles permits determination of the reaction rate vs mean Au particle size which can be directly compared with experiment (see Fig.). Low coordinate Au sites dominate reactivity for smallest sized <2nm while perimeter sites become important more important for larger size particles.



Gas transient methods have been used to probe reaction pathways in catalytic CO oxidation under *operando* conditions. A low dead volume reactor was designed which permits monitoring of surface reaction species by repetitive FTIR and gas phase reaction products and conversion by QMS during rapid (~1s) transient gas switching. FTIR signals characteristic of adsorbed CO, CO_2 and carbonates are observed and used to follow surface processes under reaction. CO desorption rates are measured from an active Au/TiO_2 catalyst under He and CO_2 and are consistent with literature values for CO desorption from Au single crystals and Au films on TiO_2. The rate of the reactive removal of adsorbed surface $CO_{(a)}$ was used to determine a turnover frequency of about 0.043 s^{-1} for CO oxidation on the Au particles, comparable to the rate obtained in a steady state flow reactor. Gas switching is used to investigate the storage of oxygen on the catalyst. It is found that following O_2 exposure, the amount of adsorbed active oxygen is either undetectably small, less than 3.1 μmoles of O/g catal, or it desorbs very rapidly at 298 K. Although storage of oxygen is very ineffective on this catalyst, CO_2 is stored by its dynamic interaction with the support to form carbonates or bicarbonates causing slow removal of product CO_2 from the reactor bed. These results are summarized by the Scheme describing the pathways for CO oxidation.



Although Au catalysts can be readily prepared on titania via the deposition-precipitation (DP) method using $HAuCl_4$ the preparation of silica-supported Au catalysts by this approach results in diminished success. We have explored an alternative method based upon gold cationic complex precursor $[Au(en)_2]^{3+}$. The cationic gold precursor was immobilized on negatively charged surfaces of mesoporous and nanoparticle silica making use of the deprotonation reaction of ethylenediamine ligands. The pH value of the gold precursor solution plays a key role in the deposition through the regulation of $[Au(en)_2]^{3+}$ deprotonation reaction and the surface interaction of silica with the gold precursor. For deposition at pH 10, the mesoporous catalyst has been demonstrated to be highly active for CO oxidation and resistant to sintering, in part because of the stabilization of Au nanoparticle inside mesopores. Other routes to stabilization of Au particles have been explored based upon modification of the support surfaces. We have functionalized SiO_2 with single layers of TiO_2 or Al_2O_3 using a surface sol-gel approach which leads to enhanced activity, due primarily to the stabilization of small Au particles on these surfaces. We have explored the use of surface phosphate as a means of stabilization of Au particles on TiO_2 supports. Phosphate adsorbed on the support either prior or subsequent to Au precursor deposition inhibits sintering of Au particles on TiO_2 leading to a catalyst which can be calcined to 500°C without the deactivation typically observed for the untreated Au/TiO_2 Many metal oxides (including main group, transition metals, rare earth and silica) can have this stabilization effect. These can be deposited onto TiO_2 supports by simple impregnation.

DOE interest

New catalysts are needed to achieve incremental or revolutionary improvements in technologies related to emission control, fuel cells and hydrogen utilization. This work provides a research basis for preparing, testing and understanding catalysts with potential application in these technologies.

Future Plans

The mechanisms by which surface modifiers stabilize Au particles will be examined using structural characterization techniques such as high resolution microscopy and PDF spectroscopy using neutrons and x-rays to probe the interfaces between Au particles and the support. The role of the surface modifiers upon the reaction pathways will be further explored using transient and operando techniques. The roles of carbonates and water in the reaction pathways for CO oxidation will be explored. Other catalytic reactions besides CO oxidation will be examined also including other oxidations and trans-esterification. Incorporation and interactions of Au with carbon supports and the use of these catalysts for anode reactions in fuel cell reaction conditions will be examined.

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DE-FG02-96ER14669 S. Ted Oyama (Virginia Tech)

Molecular Level Studies of Advanced Hydrotreating Catalysts

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Goals:

This project deals with the study of a novel class of hydroprocessing catalysts that differ fundamentally from existing sulfide-based catalysts. The new materials are the phosphides of transition metals, a class of robust metallic substances with ideal properties for catalysis. The goals of this project are to explore different bimetallic compounds and compositions containing noble meals. Studies of mechanism will be carried out for both hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) by using reactant molecules such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) and piperidine as *in situ* probes. These will be supplemented by determinations of the structure of adsorbed intermediates by infrared spectroscopy measurements and ab initio calculations. The sites of interaction of the reactant with the catalyst surface will be determined by in situ extended x-ray absorption fine structure (EXAFS) measurements.

DOE Interest:

Recently enacted regulations limiting the emissions of pollutants and the continuing decline in the quality of petroleum feedstocks have made sulfur and nitrogen removal one of the paramount problems in the refining industry. It has been recognized that current hydrotreating catalysts are not adequate to meet the regulated levels, and this has given rise to widespread research efforts to develop a new generation of replacement materials.

Research Plan:

Work so far in our laboratory has focused on supported MoP, WP, FeP, CoP, and Ni_2P, and it has been found that Ni_2P is the most active catalyst. Because of the known high activity of sulfides containing group 6 and group 8 elements, bimetallic alloys like $NiMoP_x$ and $CoWP_x$ have also been tried, but surprisingly, have been found to have poor activity. In this project we present a molecular interpretation that accounts for the contrasting results on $NiMoP_x$ and $CoWP_x$, and which indicates that CrNiP, FeNiP, and CoNiP are interesting candidates for study. We also suggest Pd and Pt phosphide phases for investigation as new materials.

The characterization of the new compositions will be carried out with EXAFS before and after reaction, and by Fourier transform infrared spectroscopy of adsorbed CO. The reactivity measurements will be carried out at realistic conditions in an existing trickle-bed reactor at high pressure (20-30 bar) and temperature (280-350 ^{o}C). The main subjects for these measurements and the mechanistic studies to be described below will be 4,6-DMDBT and piperidine, two refractory S- and N-compounds representative of the difficult components in real feeds.

Aside from the study of new compositions, our research has concentrated on the kinetics and mechanism of the HDS and HDN reactions, and we plan to continue this work with emphasis on molecular level understanding of the reactions. This will be carried out by a combination of in situ kinetic, isotopic, and spectroscopic studies. The kinetic studies will be conducted with a new reactor system that has recently been set up that permits short contact time measurements to determine pathways in reaction networks such as those involving 4,6-DMDBT and piperidine. These studies will be complemented by isotopic substitution experiments to obtain quantitative measurements of rates in the networks. In addition, in situ infrared and EXAFS measurements will be carried out to determine the nature of adsorbed intermediates and the identification of adsorption sites. Together, this information will be used to build a detailed picture of the surface processes occurring during reactions.

Recent progress:

EXAFS analysis of catalysts showed a slightly disordered Ni_2P phase, which was likely due to the formation of a phosphosulfide layer on top of the Ni_2P phase during reaction. There were two types of sites Ni(I) sites with four-fold coordination and Ni(II) sites with five-fold coordination. The Ni(II) sites were more numerous on the more active and more highly dispersed samples, indicating that they were the active sites in the nickel phosphide phase. The poor activity of $NiMoP_x$ and $CoWP_x$ is explained by substitution of Ni and Co for the active Ni(II) sites.

DE-FG02-03ER15465 **Talat S. Rahman**
DE-FG02-07ER15842

Controlling Structural Electronic and Energy Flow Dynamics of Catalytic Processes Through Tailored Nanostructures.

Collaborators: T.F. Heinz and S. O'Brien (Columbia University), L. Bartels (University of California, Riverside); R. Adzic (Brookhaven National Laboratory)
Postdocs: Sergey Stolbov and Sampyo Hong
Students: Faisal Mehmood, Sampyo Hong, Duy Tran Le, R. Perry (co-advised with L. Bartels)
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Project Goal

The overarching goal of this program is to lay the scientific foundations for a new class of heterogeneous catalysts in which materials with nanoscale structuring are utilized to control the flow of reactants and products to and from optimized reaction sites, and of the energy released in the reaction. To this end we perform experiments and theoretical calculations which elucidate factors that control reaction pathways of adsorbates at surfaces.

Rahman's focus is on theoretical and computational investigations of (a) factors that control diffusion and reactivity of simple adsorbates on nanostructured metallic and oxide surfaces; (b) the dynamics of more complex molecules on metal surfaces, as foundations for the development of methods that enhance catalytic activity of supported nanoparticles by steering the diffusion of reactants towards active centers.

Research Plan and Results: Brief synopsis of three projects is presented below.

Understanding CO Tolerance of Pt Islets on Ru(0001) (with R. Adzic)

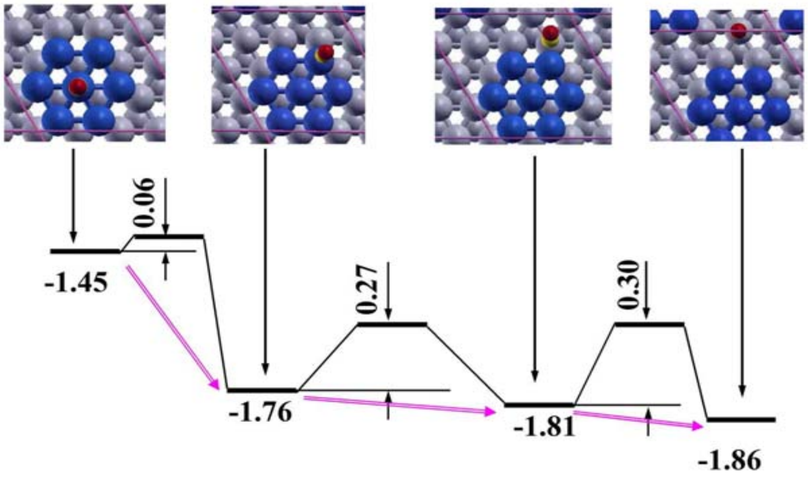
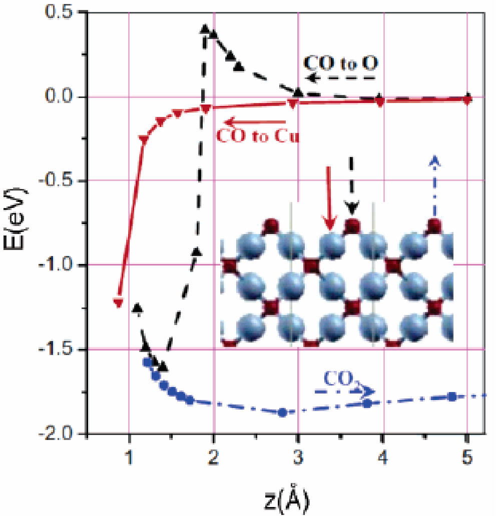


Fig. 1. Energetics for CO diffusion on Pt islets on Ru(0001)

Proton exchange fuel cells are promising tools for hydrogen economy. However, CO traces, inevitably present in hydrogen, block active Pt sites of anode and hence poison its reactivity. However, Ru nanoparticles with submonolayer Pt coverage are found [1] to be much more tolerant to CO than commercial catalysts. To understand, we have performed density functional theory based calculations of the energetics of adsorption and diffusion of CO on Pt islets on Ru(0001). We find that the total energy of the system gradually decreases as the CO molecule moves from the center of the islets to its edge and further onto substrate. As shown in Fig. 1, diffusion barriers for CO are found to be low: 0.06 eV to move from the center of the island to its edge, 0.27 eV to "jump" from the Pt island edge to a neighboring substrate site, and 0.3 eV to move further along the Ru surface. Assuming the pre-factor of CO diffusion to be 10^{12} sec^{-1}, the diffusion rate at the operating temperature 350K is estimated to be around 10^{7} sec^{-1}. These results suggest that this catalyst is CO tolerant because of the propensity of CO to move from active Pt island site to the Ru substrate. We trace this effect to the features of the local densities of electronic states around the Fermi-level.

Understanding the role of the substrate in CO oxidation on $Cu_2O(100)$ (with S. O'Brien)

Recent experimental results indicate that cuprous oxide surfaces [2] and nanoparticle facets [3] are quite reactive for CO oxidation, leading to questions about the role of surface atoms and their vacancies in the reactions. First, by applying the *ab initio* thermodynamics approach to the surface in contact with gaseous O_2, we find that the O-termination of $Cu_2O(100)$ is preferred for all reasonable range of temperature and O_2 pressure. We show that a CO molecule landing on surface O associates with it to form CO_2 without any activation barrier. On the other hand, if CO lands on a surface Cu atom, it also slides towards the neighboring O atom to form CO_2 (as in the figure). Since the reaction leaves oxygen vacancies in the surface, the issue of restoration of the Cu_2O surface becomes critical. Our DFT calculations of the geometry and energetics of O_2 dissociative adsorption on the surface with O vacancies show the barrier to be 0.3eV and that one O atom fills the vacancy while the other occupies the hollow site next to the vacancy, thereby restoring the surface. Calculated plots of the electronic structure reveal their environment dependencies.



Controlling the rate of CO oxidation on Pd Surfaces

We have applied DFT calculations to examine the effect of the well-known catalytic promoter K [4] on the energetic of CO oxidation on the Pd(111) surface. First we find that K and CO on co-adsorption with atomic O on Pt(111) spontaneously move to form an ordered structure with K aligned with O and CO located between K-O rows (see Fig. 2). With this ordered configuration as the initial state, we have calculated the CO + O =>CO_2 reaction barrier which is summarized in Fig. 3. Clearly, the oxidation energy barrier is reduced upon K co-adsorption, in agreement with experimental observation that K works as a promoter for CO oxidation.

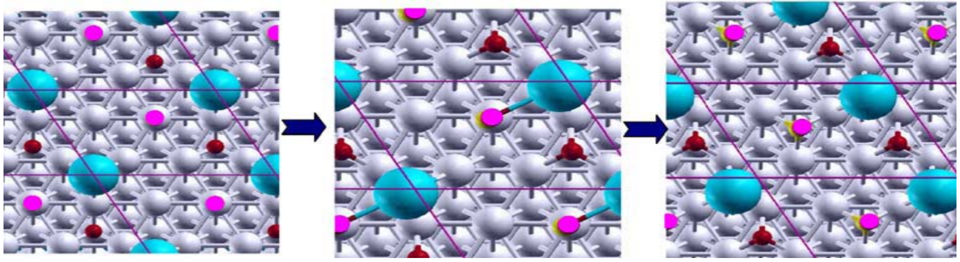


Fig. 2. Spontaneous reorganization of K, O, and CO co-adsorbed on Pd(111). Blue balls denote K, pink and yellow – CO, red – atomic O.

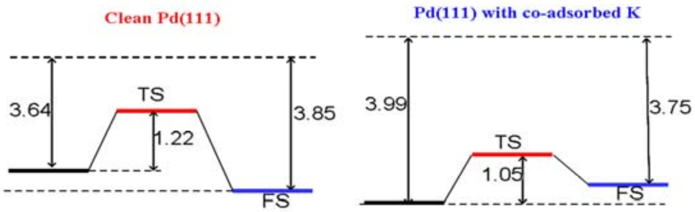


Fig. 3. Energetics for CO oxidation on clean Pd(111) and that with pre-adsorbed K.

Guiding Surface Motion (with L. Bartels)

Our DFT calculations of the diffusion characteristics of "walking" and "cargo" molecules on Cu(111) supplement and provide insights into the experimental findings of Bartels et al.

DOE Interest

Despite the great importance of catalytic reactions for a broad range of industrial and environmental processes, there is no experimental method yet for guidance of reactants through the individual steps that make up a heterogeneous catalyzed reaction. This project aims providing first steps in this direction and it is conducted in close collaborations with the L. Bartels (guided molecular motion), T.F. Heinz (energy transfer dynamics) and S. O'Brien (synthesis of nanoparticles).

Future Plans

We will engage in further development of theoretical calculations and computational techniques that incorporate temperature and pressure dependencies and kinetic effects in chemical reactions and surface diffusion, to be get a more complete picture of the role of competing processes under realistic conditions. These will be done by coupling our DFT calculations and ab initio thermodynamics with the kinetic Monte Carlo method. We are also interested in extending our calculations to include excited states of systems for which the standard DFT is not a solution. Another future project is the examination of the physical significance of diffusion pre-exponential factors, the role of vibrational entropy and conditions under which anomalous values may be obtained. Of course, all of the above will be done in connection with experimental directions taken by collaborators, Bartels, Heinz, O'Brien, and Adzic.

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Polarization Effects on the Surface Chemistry of PbTiO3-Supported Pt Films

Authors: Alexie M. Kolpak, Ilya Grinberg, and Andrew M. Rappe
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Chemistry, University of Pennsylvania

To demonstrate a new paradigm of dynamical control of surface structure and reactivity, we perform density functional theory calculations of the adsorption of several molecules and atoms to the surface of ultrathin Pt(100) films supported on ferroelectric $PbTiO_3$. We show that reorienting the polarization direction of the substrate can dramatically change the chemisorption energies of CO, O, C, and N and alter the reaction pathways for dissociation of CO, O_2, N_2, and NO. We discuss the structural and electronic effects of a polarized substrate on the metal surface, and we suggest potential applications in tunable catalysis.

DE-FG03-02ER15345 **Daniel E. Resasco**

Understanding the Mechanism of Nanotube Synthesis for Controlled Production of Specific (n,m) Structures

Students: L. Zhang, S. Cosma, F. Scodelaro, Y. Tan, G. Lolli
Collaborators: L. Balzano (SWeNT), P. Balbuena (TAMU), Warren Ford (OSU), Tobias Hertel (Vanderbilt), Esko Kauppinen (VTT, Finland), Antonio Monzon (U. Saragosa, Spain)
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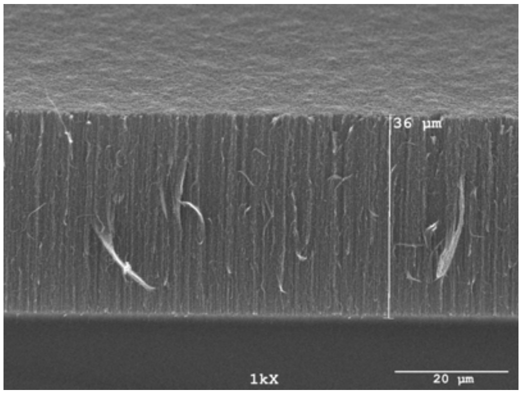
Goal

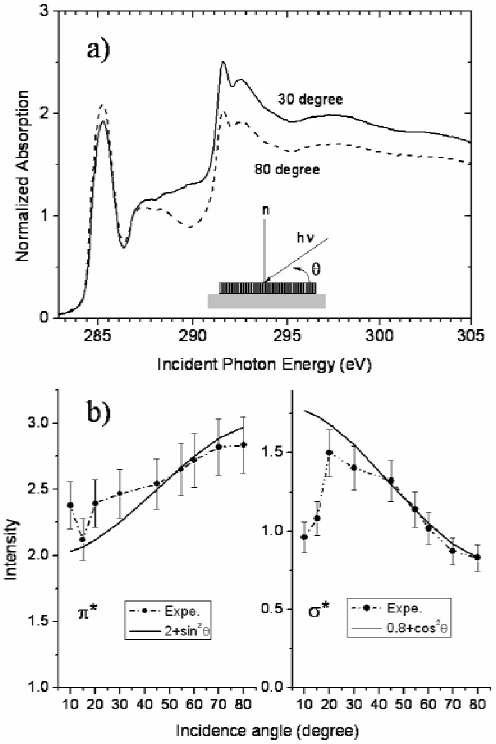
Advance the knowledge of the mechanisms responsible for the formation of single-walled carbon nanotubes to get control over their structural parameters.

Recent Progress

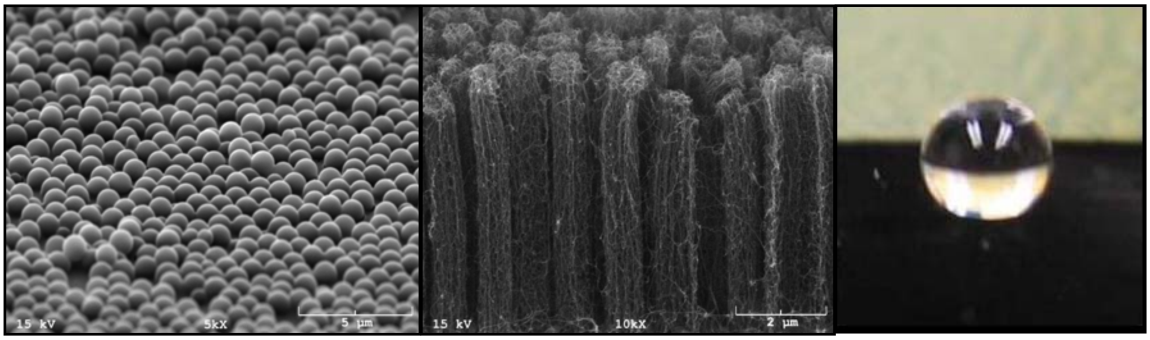
Vertically oriented forests of SWNT. CO disproportionation on Co-Mo bimetallic catalysts has been used in the synthesis of vertically oriented forests of SWNT (see SEM image of forest). This is the first time that these forests are obtained by a CVD method at atmospheric pressure. Resonant Raman and transmission electron microscope (TEM) were employed to characterize the as-produced SWNT, which display a high purity and very low concentration of other carbon forms. Combination of AFM and SEM gives evidence for the crucial role of the surface distribution of the bimetallic (Co/Mo) catalyst particles on the substrate during the growth of SWNT.



A detailed analysis of the structure of SWNT forests as a function of growth time reveals that a two-step process is responsible for the formation of a SWNT forest. The first step is the weaving of a <u>crust</u> of entangled SWNT which grow with different rates and with random orientation over the surface. The second step is a concerted growth of vertically aligned SWNT constrained by the uniform top crust. Several techniques were employed to examine the growth process and the results are all consistent with this mechanism. The angle-resolved x-ray absorption near edge structure results (see Figure below) show that a fraction of the tubes on top of the forest are parallel to the surface, rather than perpendicular as the majority of the tubes in the forest. Direct SEM observations agree with this morphology. Several examples are presented to demonstrate that the crust influences the morphology of the resulting forest. Catalysts which are non-uniformly distributed on the substrate produce curved crusts instead of the consistent forest with a flat top obtained when the catalyst layer is uniform.



Nanostructured SWNT towers that exhibit superhydrophobic behavior. In a recent study, we have discovered that while the contact angle for water-graphite is about 86°, that for SWNT-water greatly depend on the mesostructure of the nanotube system. That is, the same type of SWNT have very different wetting behavior depending on the nanotube arrangement. For example, the contact angle for a 2D mat of SWNT is close to that of graphite (86°); it goes up drastically to 135° for the nanotube forest, and become superhydrophobic (~180°) for a new type of SWNT arrangement that we call SWNT "towers." To achieve this SWNT array we have prepared the Co-Mo catalyst on silicon wafer employing the *nanosphere lithography method* that results in tailored distribution of catalysts and produces the distribution of SWNT shown in the image. These micro-towers of SWNT exhibit the "Lotus effect" that impart super-hydrophobicity to the surface.



DOE Interest.
SWNT exhibit exceptional chemical and physical properties. Tight control of their structural properties by tailored catalytic surfaces is opening a vast number of opportunities for research and it is also generating technological applications in diverse fields such as nanoelectronics, nanosensors, field emission, fuel cell electrodes, tailored catalyst supports, smart surfaces, etc.

Future Plans We plan to continue improving our ability to control of producing nanotubes with specific structure by manipulating catalyst composition and structure. Our next focus will be on utilizing nanoparticles catalysts of controlled size and composition.

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DE-FG02-03ER15408 **Fabio H. Ribeiro**

Fundamental Studies on the Kinetics of Oxidation Reactions

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Goal

The goal is to understand the mechanism of heterogeneous catalytic oxidation reactions on noble metals. The work in this period concentrated on Pd and Pt surfaces.

NO Oxidation Reaction Study on Pt(111)

The reaction kinetics for the NO oxidation reaction on Pt(111) were measured using a custom atmospheric pressure batch reactor system combined with an ultrahigh vacuum (UHV) system. The results show the highest activity reported in the literature. For example, at 250°C, 55ppm NO, 20ppm NO_2, 10% O_2 and N_2 balance, the TOR is 0.20 s^{-1}, approximately 200 times greater than a Pt/Al_2O_3 monolithic catalyst with an average particle size of 2.3 nm. Figure 1 shows the results from the study. The apparent activation energy (Ea) and O_2 order decreased significantly from the 2.3nm catalyst which had an Ea of 82 kJ/mol and O_2 order of 1 to 64±6 kJ/mol and 0.5±0.1, but the NO and NO_2 orders remained the same at about 1 and -1 respectively. Since the Pt(111) surface represents the dominant surface orientation of Pt under the limit of large particle size, and the rates increase with particle size, it is expected that the TOR on a Pt(111) single crystal represents the highest TOR possible on a platinum catalyst without support effects.

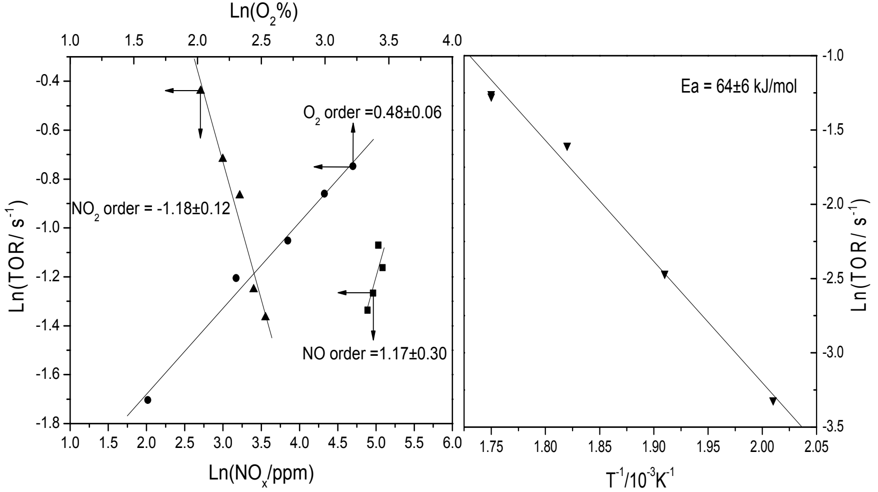


Fig. 1 Reaction orders and Activation energy for the NO oxidation reaction on Pt(111). Each point represents an average of 2-3 measurements at each condition

In-situ XPS Study on Pt(111)

In-situ XPS study was carried out at the Advanced Light Source at LBNL in order to determine coverage of surface species under simulated reaction conditions. To determine the maximum oxygen coverage under reaction conditions, the Pt(111) was exposed to 0.275 torr NO_2 at 523 K which yielded an atomic oxygen coverage of 0.7±0.1 ML. The error represents the standard deviation of five repeat measurements. No surface nitrogen species and Pt oxide formation were observed during the experiment which lasted about an hour. In comparison, 10^{-6} torr NO_2 at 523 K yielded the same oxygen coverage to within experimental error. In a separate series of experiments with O_2, Table 1, we were unable to achieve oxygen coverages above 0.5 ML. Since

NO_2 is a much more effective oxidizer than O_2, we believe that the maximum oxygen coverage on a Pt(111) single crystal is 0.75 ML even with the addition of O_2 up to 1 bar at 523 K. Figure 2 shows an example of the XP spectra and peak deconvolution.

Table 1. Atomic oxygen coverage measured by XPS as a function of oxygen pressure, PO_2, and temperature

PO_2 (Torr)	T (K)	Θ (ML)
10^{-6}	380	0.25
0.11	350	0.48
0.11	430	0.49
0.11	485	0.48
0.11	590	0.4
0.11	660	0.39

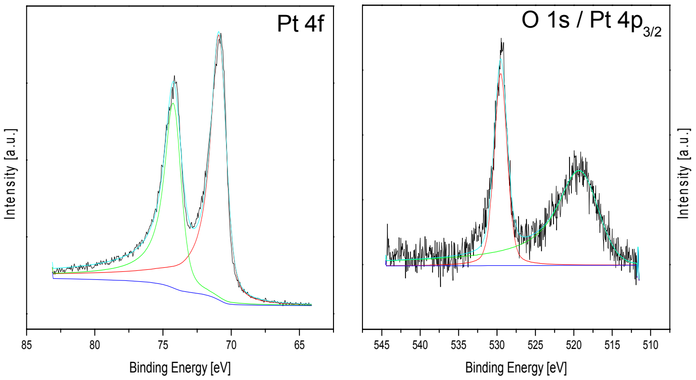


Fig 2. Pt 4f and O 1s/ Pt $4p_{3/2}$ spectra collected from the Pt(111) surface at 180°C in $1x10^{-7}$ Torr NO_2

From these results combined with other kinetic and XPS studies on supported catalyst studies in our lab, we believe that metallic Pt is the active state of Pt in the NO oxidation reaction and the Pt oxide is inactive. We believe that large platinum particles resist oxide formation due to the closed-packed structure and remain active whereas small particles which have a more open structure on average are more easily oxidized and become inactive.

NO Oxidation Reaction Study on Pt supported on SBA

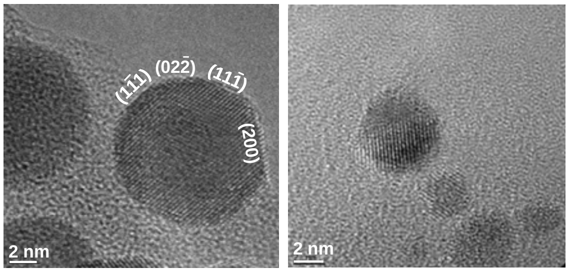
Table 2 summarizes the results of the NO oxidation kinetics measurements on the Pt catalysts with different supports and average Pt particle sizes. Over the concentration range studied, similar reaction orders (close to +1 with respect to NO and O_2, close to -1 with respect to the product NO_2) were obtained on all these catalysts, indicating that the reaction kinetics is independent of the Pt particle size and support. The turnover rate (TOR) of the reaction, however, was found to be a strong function of both, the Pt particle size and the catalyst support. The TOR increased about 50 times when Pt size increased from 2 to 9 nm on SBA-15 support; and about 20 times on alumina support (for same size range). Based on the particle size distribution obtained by transmission electron microscopy (TEM) measurements, it appears that only large Pt particles are responsible for the observed activity, with the smaller Pt particles deactivating under the oxidizing reaction conditions. From reactor and XPS measurements, this catalyst deactivation was attributed to the increase in the oxidation of the Pt particles as the reaction progresses. High resolution TEM imaging (Fig. 2) revealed the presence of single crystalline large Pt particles with <111> faces exposed on 9 nm (average) Pt/SBA-15 catalyst, which was not the case with the other two SBA-15 supported samples having smaller Pt cluster sizes. This result, combined with the high TOR seen on the 9 nm Pt/SBA-15 sample, suggests that (111) surfaces may be the active sites for NO oxidation reaction, capable of resisting oxidation and hence, deactivation, when compared to the more open surfaces. NO oxidation rate measurements on a Pt(111) single crystal, under similar conditions noted in Table 2, indeed gave a TOR of 0.2 s^{-1}, similar to the TOR seen on the 9 nm Pt/SBA-15 catalyst, and may represent the limiting rate on Pt for NO oxidation reaction. Titania was found to be a better support for this reaction, with TOR increasing about 18 and 8 times when compared to Al_2O_3 and SBA-15 supports respectively, for the same average Pt particle size (about 9 nm). This suggests that Pt particles supported on TiO_2 probably have (111) surfaces predominant, making them resistant to Pt oxidation under reaction conditions, thereby resulting in higher TOR when compared to Al_2O_3 or SBA-15 supports.

Table 2. Summary of NO Oxidation reaction kinetics on Pt catalysts

Catalyst	Pt size/ nm	Ea/ kJ mol^{-1}	NO order	O_2 order	NO_2 order	TOR*/ 10^{-3} s^{-1}
Pt/Al_2O_3	1.8	70	0.9	0.9	-0.9	3
Pt/Al_2O_3	2.1	71	0.7	0.9	-0.9	4
Pt/Al_2O_3	2.9	85	0.7	1.0	-1.0	30
Pt/Al_2O_3	9.1	100	1.1	0.9	-1.1	64
Pt/SBA-15	1.9	74	1.0	1.0	-0.8	2.9
Pt/SBA-15	3.8	76	1.1	0.7	-1.0	77
Pt/SBA-15	9.1	74	0.9	0.7	-1.1	140
Pt/TiO_2	8.3	83	0.5	1.1	-1.1	1150

*TOR at 250°C, 300 ppm NO, 170 ppm NO_2, 10% O_2, balance N_2

Figure 2. High resolution TEM images showing representative Pt clusters on (A) 9.1 nm Pt/SBA-15, (B) 3.8 nm Pt/SBA-15



DOE Interest

Oxidation reactions are critical in many technologies. Understanding of the details of these reactions, including how the surface oxidize, and the reaction mechanism is important in the development of new technologies.

Future Plans

Study the reaction kinetics on Pt(100) and Pt(110) and use *in situ* XPS to determine the oxygen coverage. We intend to study the well defined Pt clusters on SBA with *in situ* TEM to follow variations of morphology under reaction conditions. Use of *in situ* XAS at the Advanced Photon Source (Argonne) will indicate how the particles oxidize under reaction conditions.

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In-situ Studies of the Active sites for the Water-Gas shift Reaction over Cu-CeO_2 Catalysts: Complex Interaction between Cu and O Vacancies

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Abstract

New information about the active sites for the water gas shift (WGS) reaction over Cu-CeO_2 systems was obtained using *in-situ* time-resolved X-ray diffraction (TR-XRD), X-ray absorption spectroscopy (TR-XAS, Cu K- and Ce L_3-edges) and infrared spectroscopy (DRIFTS). Cu-CeO_2 nanoparticles prepared by a novel reverse microemulsion method (doped Ce_{1-x} Cu_xO_2 sample) and an impregnation method (impregnated CuO_x/CeO_2 sample) were studied. The results from all the samples indicate that metallic copper and oxygen vacancies in ceria were both involved in the generation of active sites for the WGS reaction. Evidence was found for a synergistic Cu-$O_{vacancy}$ interaction. This interaction enhances the chemical activity of Cu, and the presence of Cu facilitates the formation of O vacancies in ceria under reaction conditions. Water dissociation occurred on the $O_{vacancy}$ sites or the Cu-$O_{vacancy}$ interface. No significant amounts of formate were formed on the catalysts during the WGS reaction. The presence of strongly bound carbonates is an important factor for the deactivation of the catalysts at high temperatures. This work identifies for the first time the active sites for the WGS reaction on Cu-CeO_2 catalysts and illustrates the importance of *in-situ* structural studies for heterogeneous catalytic reactions.

DE-AC02-98CH10886 **Ping Liu**

Water Gas Shift Reaction on Metal Nanoparticles and Surfaces

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Density functional theory (DFT) was employed to investigate the water-gas-shift reaction (WGS, $CO + H_2O \rightarrow H_2 + CO_2$) on Au_{29} and Cu_{29} nanoparticles seen with scanning tunneling microscopy in model $Au/CeO_2(111)$ and $Cu/CeO_2(111)$ catalysts. Au(100) and Cu(100) surfaces were also included for comparison. According to our calculations, the WGS on these systems operate via either redox or associative carboxyl mechanism, while the rate-limiting step is same, water dissociation. The WGS activity decreases in a sequence: Cu_{29} > Cu(100) > Au_{29} > Au(100), which agrees well with the experimental observations. Both nanoparticles are more active than their parent bulk surfaces. The nano-scale promotion on the WGS activity is associated with the low-coordinated corner and the edge sites as well as the fluxionality of the particles, which makes the nanoparticles more active than the flat surfaces for breaking the O-H bond.

In-situ electronic and catalytic properties of supported size-selected gold nanoparticles synthesized by diblock copolymer encapsulation

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TiC-supported size- and shape-selected Au nanoparticles with well defined interparticle distances were synthesized by diblock copolymer encapsulation. Atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) have been used to investigate the correlation between the nanocatalyst morphological/electronic structure and its chemical reactivity.

Significant changes in the electronic local density of states (LDOS) of the nanoparticles, in particular, the onset of non-metallic behavior, were observed with decreasing particle size. The nanoparticle-support interaction was studied, and evidence for substrate-induced modifications in the LDOS of interfacial gold atoms is found.(*1*)

Using the low temperature oxidation of CO as a model reaction, our TPD results also showed an enhancement of the catalytic activity with decreasing particle size. Two desorption features were observed and assigned to kinks/steps in the gold surface and the Au-TiC interface. The role of the interparticle distance on the activity is discussed. AFM measurements showed drastic morphological changes (Ostwald ripening) on the nanoparticles after CO oxidation when the initial interparticle distance was small (~30 nm). However, no sintering was observed for Au nanoparticles more widely spaced (~80 nm) (2,3).

1. A. Naitabdi, L. K. Ono, B. Roldan Cuenya, *Appl. Phys. Lett.* **89**, 43101 (2006).
2. L. K. Ono, D. Sudfeld, B. Roldan Cuenya, *Surf. Sci.* **600**, 5041 (2006).
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Size, oxidation and substrate effects on the decomposition of methanol for H_2 production via size-selected Pt nanoparticles

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The influence of the nanoparticle size on the decomposition of methanol (MeOH) over Pt nanoparticles supported on polycrystalline (anatase)-TiO_2 powder will be discussed. Micelle encapsulation has been used to create narrowly distributed Pt catalysts with average particle sizes of ~ 4, 6, and 8 nm. A packed bed mass flow reactor and mass spectrometry were employed to quantify the catalyst's reactivity. Among the catalyst tested, the smallest nanoparticles (~4 nm) showed the best performance, including an onset reaction temperature for H_2 production of ~145 °C. At 300°C, no CO_2 signal was detected, and only about 1 % CH_4 byproduct was obtained. Further, metallic Pt catalysts displayed better MeOH conversion that partially oxidized clusters.

Finally, the influence of the cluster support on activity and selectivity will be discussed by comparing reducible (TiO_2 and CeO_2) to non-reducible oxides (SiO_2, Al_2O_3, etc).

DE-FG02-06ER15839 **William F. Schneider**

Towards Realistic Models of Heterogeneous Catalysis: Simulations of Redox Catalysis from First Principles

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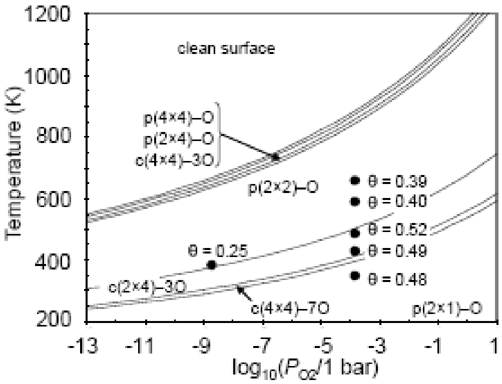
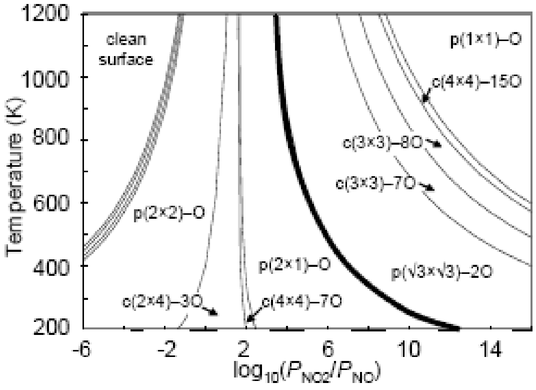
Goal

Use density functional theory (DFT) simulation to develop a systematic understanding of the dependence of heterogeneous catalytic activity on metal particle size, particle-support interaction, and catalytic reaction environment. Do so by contrasting catalytic oxidation reactivity on discrete metal particles, supported metal particles on alumina surfaces, and extended surfaces of Pt, Pd, Au, and Ru and their oxides. Use these insights to guide design of catalyst-support combinations with desirable reactivity.

Recent Progress

Environmental effects in NO oxidation on Pt(111): Catalytic oxidation of NO to NO_2 is both a technologically important reaction and a sensitive probe of the general mechanisms of catalytic oxidation. Recent experimental results from the Ribeiro group at Purdue indicate that NO oxidation occurs preferentially on large particles and (111) terraces of Pt and is associated with high (~0.7 ML) coverages of oxygen on the catalyst surface. We have used DFT and first-principles thermodynamics to examine the probable structures of surface-chemisorbed oxygen on Pt(111) under the conditions representative of the catalytic reaction.

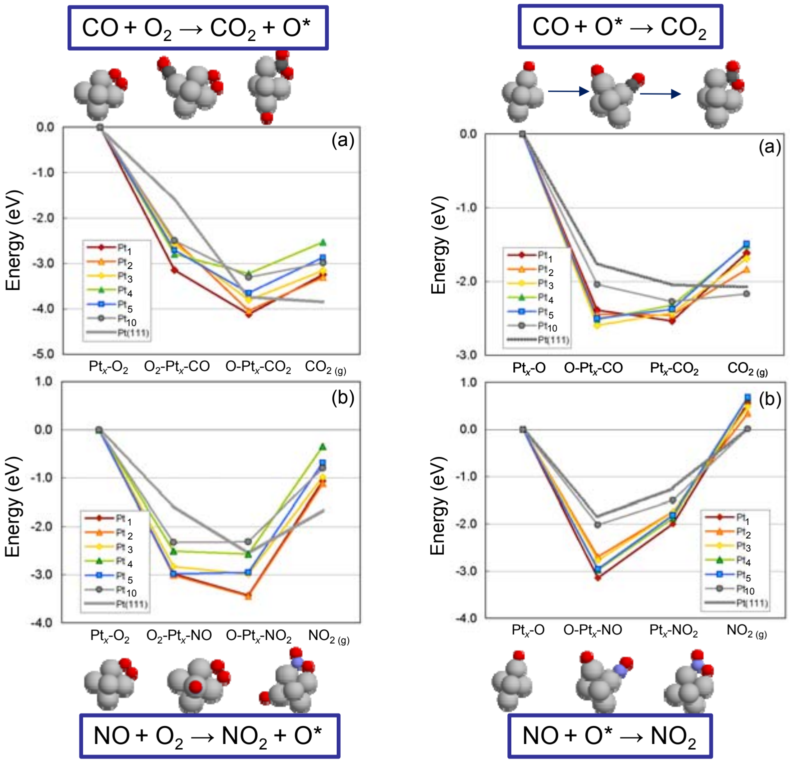




The figure on the left above shows the calculated equilibrium ordered phases of chemisorbed oxygen on Pt(111) at various exposures (T and P) to O_2 (g). The simulations capture the experimentally observed ¼ ML coverage at low P_{O2} dosing and the ½ ML coverage at near-ambient P_{O2} dosing. Notably, however, coverages greater than ½ ML are predicted to be thermodynamically inaccessible at any practically relevant conditions. The figure on the right shows the predicted coverages if surface oxygen is supplied by NO_2—the product of catalytic oxidation—rather than O_2. Such a condition is possible if the NO_2 surface reaction is much faster than the O_2. Because of the stronger oxidizing power of NO_2 than O_2, much higher oxygen coverages become accessible (those to the right of the bold line), including coverages consistent with the experimentally observed 0.7 ML. These results strongly implicate this high O covered surface induced by NO_2 as the relevant state of a functioning NO oxidation catalyst

Particle-size effects in reactivity of Pt clusters:

The results above show the importance of coverage-dependent O surface binding to NO oxidation on Pt(111). We have begun to address similar questions on finite, unsupported Pt_x clusters. Previous work has considered the equilibrium oxygen content of Pt particles Pt_xO_y as a function of O_2 exposure. We have begun to contrast the energetic of oxidation reactions of Pt_x particles and a Pt surface with CO and NO as a function of particle size. The results, shown in the figure above, demonstrate the very different energetics of reaction at small particle sizes, and in fact indicate that these small particles by themselves bind oxygen too strongly to be effective catalysts.



Equilibrium states of oxygen on $RuO_2(110)$:

The surface metal oxides of some transition metals are suspected to be the active surfaces for some catalytic oxidation reactions. The $RuO_2(110)$ surface is a prominent example of an ordered surface that is a good model for Ru catalysts in oxidizing environments. We have begun simulations to contrast surface oxygen reactivity of RuO_2 with that of Pt above. Recent results show Thus, we are approaching catalytic oxidations from three complementary perspectives: from extended metal surfaces, finite supported metal particles, and extended metal oxide surfaces. We intend to illuminate the common and contrasting features of these three representations to catalytic oxidation activity.

DOE Interest

Advancement of heterogeneous catalysis science is one of the key needs for ensuring US energy security. In particular, the catalytic activation of O_2 is central to the effective use of hydrogen and biofuels, e.g. in fuel cells. The research performed here and in collaboration with experimental colleagues contributes to the general understanding of this catalysis and thus to the general goal of predictive, rational design of heterogeneous catalysts.

Future Plans

Future work will explore the kinetics of catalytic oxidations on Pt at high oxygen coverages, in particular to examine the potential role of molecularly bound O_2 as a surface intermediate, as suggested by experiments. Collaborations with Purdue will continue on this effort. We intend to extend the studies of metal particles in two directions: first, to establish trends in reactivity of particles as a function of size and oxygen content simultaneously; and second, to explicitly interrogate the metal particle-support interface, to understand both the nature of binding and its impact on reactivity. Lastly, we will further pursue development of RuO_2 models for oxidation catalysis at extended oxide surface.

Publications Sept. 2006-2007:

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DE-FG02-06ER15834 **Udo D. Schwarz**

Atomic Resolution Imaging and Quantification of Chemical Functionality of Surfaces

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Goal

The goal of this project is to demonstrate new capabilities in atomic-scale *imaging* combined with local interaction strength *quantification* by atom-specific local spectroscopy (3D force spectroscopy) using a unique low temperature (5 K), ultrahigh vacuum combined non-contact atomic force microscope/scanning tunneling microscope (NC-AFM/STM) in combination with chemically sensitive tips. In particular, we aim at investigating the specifics of the atomic interactions that give rise to chemical sensitivity in NC-AFM as well as the factors that govern stability, resolution, and the ability to quantify the strength of chemical interactions in NC-AFM measurements made with chemically modified tips.

DOE Interest

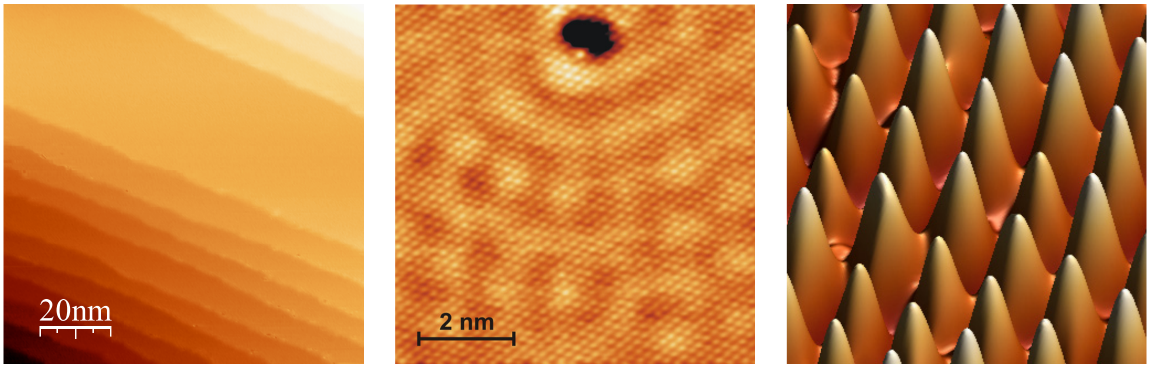
Full understanding of chemical reactions at surfaces requires the availability of a tool that allows to not only *identify* the chemical nature of specific atoms at surfaces, but also to *quantify* the interaction strengths of these surface atoms with adsorbed atoms and molecules. With our approach, which ultimately should result in complete 3D force maps of a surface with atomic resolution, we hope to achieve significant progress in this direction. In addition, the ability to chemically modify the tips and to compare the resulting changes with pre-modified data will allow new insights into local chemical interactions, enabling the precise identification of catalytically active centers.

Research Plan

Our research plan comprises two different approaches. One part of the project is directed towards manipulating the sensitivity of a metallic tip to anions and cations on a transition metal oxide surface by oxygen adsorption. We chose Fe_3O_4 (110)-type surfaces because the iron and oxygen atoms are co-planar but arranged in entirely different sublattices, making changes in sensitivity to the different atoms obvious. The results will be compared with theoretical predictions of the effect of oxygen atoms at the end of the tip, allowing the sensitivity to the different surface atoms to be associated with specific chemical changes to the tip.

In the other part of the project, functionalizing tips through molecular assembly is investigated in order to probe more complex chemical interactions that require the ability to modify tips using different functional groups. Initially, Au tips are functionalized through thiol self-assembly to create acidic, basic, and neutral tips. These tips will be tested by probing their interactions with individual acidic, basic, and neutral molecules anchored to a TiO_2 surface. By comparing the strengths of the tip–sample interactions measured through force–distance curves with the expected values for these simple interactions, the ability to quantify the strength of individual functional groups on a surface will be determined. To increase the stability of chemically sensitive tips, rutile tips functionalized through carboxylic acid adsorption will be also explored. Once robust, controllable chemically sensitive imaging is achieved, the atomic scale variations in the reactivity of a bare rutile (110) surface will be mapped out as a technologically relevant test case.

As an ultimate goal, we will try to establish procedures that allow us to pick up different functional molecules with the tip so that the reactivity of the same surface feature to different chemical functionalities can be sequentially probed.



Results obtained with our experimental setup during the optimization process. *Left:* Monoatomic steps revealed on Cu(001) in NC-AFM mode. *Middle:* Charge waves superimposed on the atomic lattice on Cu(111). Corrugation of the charge waves is 10 pm, the atomic corrugation is 2 pm. *Right:* Atoms on Cu(111) displayed in 3D representation. Corrugation is 8 pm from peak to valley.

Recent Progress

Optimizing the new Yale low-temperature NC-AFM/STM for low noise and high stability: One of the most important single pre-requisites for a successful local 3D force spectroscopy with atomic resolution and specificity is the availability of a high-resolution, high-stability instrument that not only enables force detection with excellent signal-to-noise ratio, but also allows for the long-term data acquisition necessary for 3D force spectroscopy without significant thermal drifts. In the first three months of the course of the project, we thus concentrated on achieving such conditions by testing and further improving our measurement setup where necessary. As we were focusing on electrical noise and mechanical stability at this stage, experiments were mainly performed in STM mode, as this allows faster experimenting, even though some NC-AFM measurements were performed in parallel. For most experiments, we used copper single crystals due to their easy of preparation and their excellent conductivity. In addition, the low atomic corrugations usually observed set a good benchmark for the performance of the instrument.

Exemplary results are presented in the figure above. At the end of our optimization process, we were able to achieve conditions where atomic corrugations of below 1 pm could still be safely resolved.

Test measurements on oxides: Some initial test measurements were also performed on oxide materials. We mainly focused on TiO_2, which is one of the important substrates for the investigations to be performed later in this project. The main goal of these early experiments was to establish adequate sample preparation procedures.

Tip testing: For the next three months (we are now six months into the project), we worked intensively on testing different tip materials and tip preparation procedures. As our NC-AFM works using tuning forks, we are flexible in the choice of tip materials, which is an invaluable advantage for chemical imaging. However, as tuning forks can only heated to very modest temperatures in-situ due to depolarization and decomposition of the glue used to mount it, tip preparation becomes an issue. In addition, tips suitable for high-resolution NC-AFM imaging are much more delicate to produce compared with STM tips as long-range force effects may greatly affect the imaging process. Therefore, the exact shape of the foremost several tens or even hundreds of nanometers of the tip becomes important, as opposed to STM, where only "the first atom wins". Currently, we are experimenting with a number of different tip materials (W and Pt/Ir, later to be added by gold, iron, etc.), tip etching procedures (electronic control, double lamella technique, etc.), tip wire diameters, and in-situ and ex-situ tip cleaning procedures.

Publications

As the project is only running since six months, no publications are to be reported yet.

Laser Spectroscopy/Imaging at the Nanoscale (ERKCA01)

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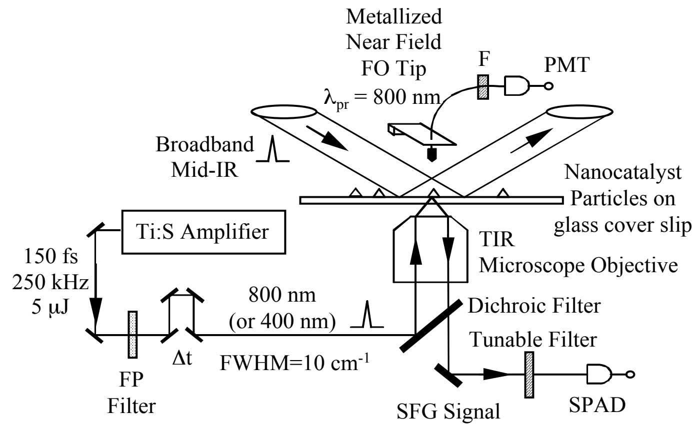
DOE/BES/Chemical Sciences/Separations and Analysis

The objective of this program is to advance the state of the art of high sensitivity and high specificity laser-based chemical measurements to further our understanding of chemical systems at the molecular level, particularly for catalysis investigations. Nanoscience offers the promise of revolutionary change in the chemical and materials sciences, but that promise will not be realized until we understand chemical structures and reactions at the nanometer length scale. Our approach is to use linear and nonlinear optical spectroscopy as a means to probe structures, bonding, and reactions of molecules at chemically important surfaces and interfaces. We are integrating second harmonic (SHG) and sum frequency generation (SFG) measurements with spatial resolution for creation of images and with picosecond and femtosecond time-resolved measurements for dynamics. This combination of imaging capability and ultrafast dynamics is the unique feature of our effort and will provide new insights into chemistry at interfaces. To achieve our goals we will undertake three specific aims: (a) investigation and improvement of the detection sensitivity that can be achieved for surface species *via* surface SHG and SFG; (b) addition of lateral spatial resolution to SFG vibrational spectroscopy to probe individual nanoparticles that exhibit different adsorbate bonding geometrics; and (c) extension of imaging spectroscopy to include dynamics experiments by use of delayed pulse sequences.

Signal enhancements will be sought *via* three mechanisms: (a) total internal reflection excitation for the 800 nm input beam, (b) a carefully designed and fabricated scanning metal probe tip with plasmon resonances at 800 and 650 nm, and (c) close coupled collection of the SFG light to relax phase matching requirements. Fifty to one hundred nanometer spatial resolution will accrue from this configuration as well. The Figure shows our proposed experiment.



Proposed experimental arrangement for sensitive surface SFG with spatial resolution.

An additional program objective is to implement efficient computational methodologies that accurately describe laser-matter interactions to aid in the interpretation as well as prediction of experimental results. Spectroscopic measurements of individual particles, as opposed to ensembles, will create enhanced understanding of surface chemical reactions. New fundamental chemical understanding will lead to significant strides in many important DOE mission areas, including nanocatalysis.

Nanochemistry. The Synthesis, Characterization and Catalytic Reaction Studies of Platinum, Rhodium and Bimetallic (1-10 nm) Monodispersed Nanoparticles

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Monodispersed platinum, rhodium and bimetallic nanoparticles with controlled shapes are grown in colloid solutions in the 1-10 nm size range, capped with polymers or inorganic shells that inhibit their aggregation. These are characterized by TEM, XRD and SAXS. Thin films of these nanoparticles are deposited using the Langmuir-Blodgett technique on oxide surfaces, or the particles are encapsulated in high surface area mesoporous silica. Catalytic reaction studies show that the product distributions change with particle size and surface structure. Hot electrons are generated in platinum thin films in the 5 nm range during exothermic reactions, and the current flow can be detected continuously in a Pt/TiO_2 or Pt/GaN Schottky barrier configuration. High-pressure STM, SFG and XPS techniques are being developed for *in-situ* characterization of the metal nanoparticles on the atomic and molecular scale under reaction conditions.

DE-AC02-05CH11231 **Gabor A. Somorjai (LBNL)**

CATALYSIS SCIENCE INITIATIVE: Nanoscience & Nanoparticles for 100% Selective Catalytic Reactions

Additional PIs:	Heinz Frei, Miquel Salmeron and T. Don Tilley (Lawrence Berkeley National Laboratory)
Collaborators:	Peidong Yang and Paul Alivisatos (Lawrence Berkeley National Laboratory)
Post-docs:	Drs. Yawen Zhang, Steven Humphrey, Joan Vignolle, H. Han, Xingyi Deng and Tirma Herranz
Students:	Michael Grass, Kaitlin Bratley
Contact:	Gabor A. Somorjai, Chemical and Materials Sciences Divisions, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., Berkeley, CA 94720

Goals:

Most heterogeneous catalysts are highly dispersed metal nanoparticles supported on porous oxides. Recent breakthroughs in synthesis in nanosciences have achieved control of nanoparticles in the 1-10 nm range that are relevant for catalyst design. The phenomena associated with reduced dimensions, such as reaction intermediates variation with metal nanoparticle size and shape, chemical interaction at oxide-metal boundary sites are fundamental questions in catalysis. The purpose of this research is to study the structure, composition and dynamic properties of monodispersed metal catalysts to achieve 100% selectivity in multipath surface catalyzed reactions. The project has three main areas of emphasis.

1. to fabricate monodispersed 2-dimensional and 3-dimensional catalyst systems with control of catalyst nanoparticle location, structure, thermal and chemical stability;
2. to characterize these nanoscale systems by a combination of techniques that identifies their size, location, structure and composition during and after fabrication and under reaction conditions;
3. to carry out multipath chemical reactions and correlate reaction selectivity with variables of nanoparticle catalyst fabrication.

DOE Interest:

Although enzyme catalysts often exhibit 100% selectivity, heterogeneous catalysts that are used in energy conversion and the chemical technologies do not. To produce the desired product without byproducts or chemical waste is often called “green chemistry” and implies 100% selectivity in chemical conversions. To do this catalysis science will have to undergo major developments in order to achieve atomic level control of parameters such as type of surface active sites, catalyst particle size, promoters, surface structure and distance between active sites and oxide-metal boundary sites. In this project we are using nanotechnology approaches to study the nanoscience of catalyst selectivity and to design and synthesize new metal nanoparticle catalyst systems based on this knowledge.

Research Plan:

Monodispersed platinum and rhodium nanoclusters and other transition metal catalysts (Pd, Ni, Fe, Co) are synthesized in solution and capped with a polymer film to prevent their aggregation. Shell-core nanoparticles in which the metal catalyst particles are capped with an inorganic shell (such as cobalt or iron oxides) will also be synthesized in the 1-12 nm particle size range. The synthesis is carried out in collaboration with PIs participating in this program (Somorjai, Tilley), and the Molecular Foundry at LBNL (Peidong Yang and Paul Alivisatos).

For producing 2-dimensional films nanoparticles are deposited on an oxide support using the Langmuir-Blodgett technique which controls the packing density. For 3-dimensional systems, monodispersed metal nanoclusters are incorporated inside oxide supports such as microporous SBA-15. Nanoparticle systems are characterized by a combination of electron microscopy, small angle X-ray scattering and X-ray diffractions and chemisorption. New characterization techniques are developed by collaborating PIs (Frei, Salmeron and Somorjai) including time resolved FTIR, and surface enhanced Raman spectroscopy, high pressure XPS, STM and SFG.

The reaction selectivity is probed by studies using multipath catalytic reactions that include cyclohexene hydrogenation/dehydrogenation, benzene hydrogenation, crotonaldehyde hydrogenation and ethane hydrogenolysis (Somorjai Group).

Recent Progress:

The product distribution changes with platinum nanoparticle size in the 1-7 nm range for cyclohexane hydrogenation/dehydrogenation, ethane hydrogenolysis and crotonaldehyde hydrogenation due to changes in activation energies. Two-dimensional films of platinum nanoparticles capped with polymer were successfully utilized to carry out benzene hydrogenation and CO oxidation at high rates. 2 nm platinum nanoparticles used as seeds to grow palladium and rhodium nanoparticles. High pressure STM, SFG and XPS techniques are being developed for in-situ characterization of metal nanoparticles on the atomic and molecular scales under reaction conditions.

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KC-03-04-01 **Peter C. Stair (Argonne National Lab)**
DE-FG02-03ER15457 **Peter C. Stair (Northwestern University)**

INSTITUTE FOR CATALYSIS IN ENERGY PROCESSES (ICEP): Catalytic and Photocatalytic Chemical Transformations

Additonal PIs:
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NU: L. Broadbelt, V. Dravid, F. Geiger, K. Gray, J. Hupp, H. Kung, M. Kung, T. Marks, S. Nguyen, W. Sachtler, R. Snurr, E. Weitz

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Goals :
The overall goals of this subtask are to achieve a fundamental understanding of factors that influence elementary catalytic and photocatalytic reaction steps and to advance the development of highly effective catalytic and photocatalytic systems. Previously the catalytic and photocatalytic chemistry focused on NOx abatement, CO oxidation and oxidative degradation chlorinated hydrocarbons. Currently the effort is evolving toward developing selective catalysts and photocatalysts for oxidation, hydrogen production and CO_2 utilization. The components of this subtask include:

- Novel synthesis of catalytic and photocatalytic phases.
- Catalyst and photocatalyst testing and reaction studies.
- In-situ characterization of elementary reactions.
- Theory and modeling.

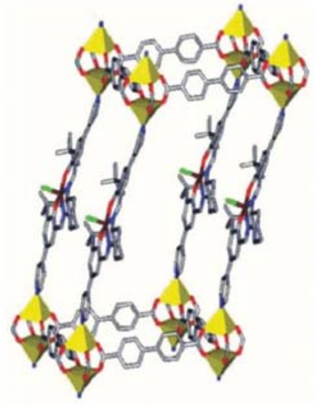
DOE Interest:
The understanding and control of reactions catalyzed on solid surfaces *at the molecular-level* is a “grand challenge” for 21st Century catalysis science. We expect that the fundamental results of this research will provide structure-function relationships between catalytically active sites and the chemical reactions they catalyze that are at the heart of this challenge. This project brings together a team of university and national laboratory researchers who develop methods for the design and synthesis of active catalytic sites at the atomic scale and tailored support structures at the nanometer scale, diverse spectroscopy, microscopy, and x-ray scattering techniques for detailed characterization (both ex-situ and in-situ) of catalyst structure and dynamics, elucidation of catalytic reaction mechanisms, and theory applied to catalytic processes.

Some Representative Results:

Design and Synthesis of Highly Active and Selective Catalysts
Achieving the goal of highly active and selective catalysts for energy conversion applications requires the synthesis of new catalytic materials. ICEP has three efforts on this topic whose results are summarized in this section.

Heterogenization of Homogeneous Catalysts for the Selective Oxidation of Hydrocarbons
The coordination polymerization of chiral homogenous catalysts is targeted as a strategy to obtain practically useful heterogeneous asymmetric catalysts for the oxidation of hydrocarbons. Two solid-state catalytic structures were constructed: the first is a crystalline metal-organic framework (MOF) assembled using labile coordination interactions; the second is an amorphous coordination polymer material employing stronger metal-ligand linkages.

A new microporous MOF compound featuring chiral (salen)Mn (**L**) struts was synthesized and found to be a highly effective as an asymmetric heterogeneous catalyst for olefin epoxidation. L was incorporated into a robust pillared paddlewheel structure, **1**, containing pairs of zinc ions at vertices together with biphenyldicarboxylate (bpdc) as the second ligand. Framework confinement of the manganese salen entity greatly enhances catalyst stability, imparts good substrate size discrimination, and permits readily catalyst separation and reuse. The observed enantiomeric excesses (ee) rival those of the free molecular catalyst, and they do not diminish even after the catalyst was recycled three times. However, a small loss of activity was observed between cycles due to a minor (4-7%) loss of Mn after each catalytic run. This MOF fragmentation is most likely due to the lability of the zinc-pyridine bond.



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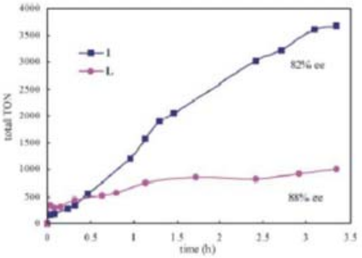

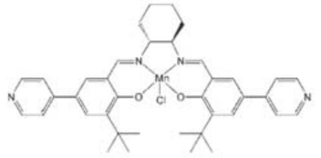

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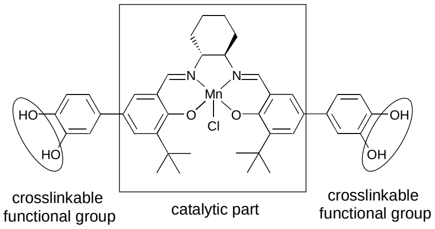

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To address the aforementioned issue, we forewent crystallinity, and opted for stronger metal-catecholate linkages which resulted in amorphous coordination polymers. A bis(catechol)-functionalized Mn(salen) ligand (**1**) was synthesized, and a series of exceptionally stable enantioselective heterogeneous epoxidation catalysts were made via the coordination polymerization of **1** with several metal ions. The resulting catalyts exhibit comparable catalytic activity to the homogeneous [bis(catechol)salen]Mn^{III} building block when used for the enantioselective epoxidation of 2,2-dimethyl-2*H*-chromene. Under practical oxidant concentrations, the copper variant was recycled up to ten times with little loss of activity and no loss of enantioselectivity.

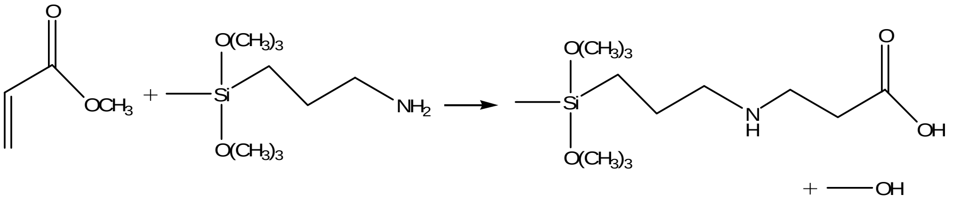
Synthesis of Uniform Supported Bimetallic Clusters

The objective of the current project is to develop methods to synthesize uniform composition, bimetallic nano-size clusters as catalysts, using the novel shell cross-linked siloxane nanocages developed in our laboratory as functionalized scaffold to deposit metal precursors. Specific objectives include improving the synthetic procedure of siloxane nanocages, determine binding of precursors of Au and other metals to these cages, and monitoring transformation of the precursors into metallic clusters.

Because of the quantity of nanocages needed for the synthesis of bimetallic clusters, an improved method to synthesize the nanocages needed to be developed. Several alternative steps were tested. In the preparation of the silyl surfactant, instead of the early purification technique of column chromatography with elusion by an aqueous acid (or base), flash chromatography using an organic solvent was found to cause less degradation and could achieve separation faster. Thus, this technique was adapted for later synthesis.

Instead of using silyl iodide to cleave the carbamate bond in order to remove the core material to generate the cage-like structure, two other reactions were tested. One is to use methyltrichlorosilane, and another NaOH solution. However, methyltricholorosilane reacted slowly with the carbamate bond, and complete cleavage could not be obtained. Use of NaOH cleaved the carbamate bond, but it also degraded the siloxane cage. We were not able to find a concentration of NaOH that could selectively cleave the carbamate bond without damaging the cage. Thus, we returned to using silyl iodide, although this reaction generates alkyliodide, which must be kept from photo-degradation to avoid the formation of HI that could damage the siloxanecage.

We have also prepared to examine a multidentate ligand for metal binding. Specifically, we examined the modification of an amine group with Michael addition of methyl acrylate to form a bidentate ligand. A model compound, shown in the equation below, was synthesized and ready for testing of metal complex binding.



Synthesis and Properties of Single-Site Heterogeneous Oxidation Catalysts

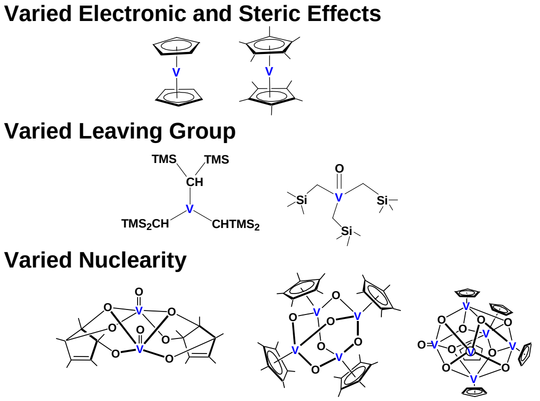


Figure 3: Molecular precursors synthesized for supported vanadium catalysts.

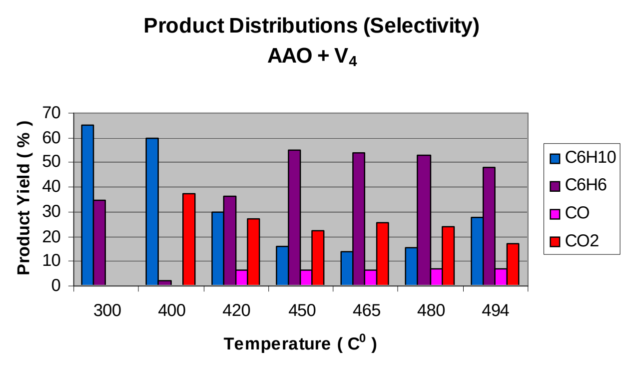


Figure 4: Temperature dependence of cyclohexane oxidation products for the V_4 cluster of Fig. 9 supported on nanostructured alumina membranes.

The overall research goal of this effort is to create and definitively characterize well-defined molecular catalysts chemisorbed on selected inorganic surfaces. We have been studying hydrocarbon oxidation reactions over catalysts prepared from well-defined organovanadium molecular precursors having sequentially varied metal ligation and nuclearity (**Figure 3**) and supported on nanostructured anodized aluminum oxide (AAO) membranes. Detailed studies of cyclohexane oxidation as a function of organovanadium catalyst precursor structure, catalyst deposition method (adsorption from hydrocarbon solution or vapor phase atomic layer deposition), catalyst loading, and reaction conditions have been carried out. We find that there are very large catalyst differences in cyclohexane to cyclohexene conversion selectivity, with the V_4 catalyst giving significantly greater selectivity in certain temperature ranges (**Figure 4**). Currently in progress are catalyst characterization studies by UV-

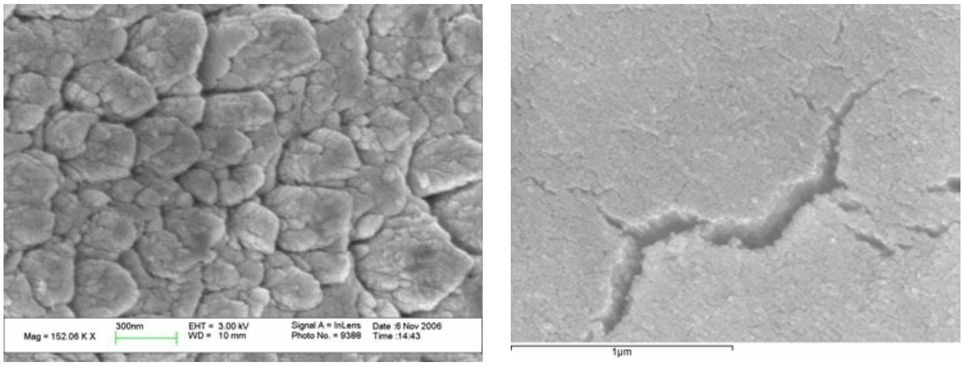


Figure 5: SEM images of typical mixed phase titania thin films prepared by reactive DC magnetron sputtering (left) and a low-temperature solvothermal method (right).

Raman, EPR, solid state NMR, and infrared spectroscopy, as well as mechanistic studies of reaction kinetics and isotopic labeling. Screening for other catalytic hydrocarbon and olefin reactions is also underway.

Photocatalysis

A primary goal of our research is to fabricate photoactive TiO_2-based nanocomposite materials for solar fuel applications and in doing so test the hypothesis that the solid-solid interface is the key to tailoring highly efficient catalysts with unique activity. Specifically, TiO_2-based nanocomposites are prepared by chemical and physical methods, characterized by spectroscopic and microscopic tools and tested to photocatalytically reduce carbon dioxide to methane and methanol, thereby producing energy-rich fuels.

We have successfully synthesized mixed-phase TiO_2 by different methods. TiO_2 thin films prepared by reactive DC magnetron sputtering have high densities of anatase-rutile interfaces. Nanostructure control of the sputtered thin films was realized by varying parameters such as deposition angles, target power, total pressure, oxygen partial pressure, and substrate bias. The sputtered mixed-phase TiO_2 thin films, composing of highly textured polycrystals with random orientations (Figure 5), have unique charge trapping characteristics and demonstrate superior photoactivity in both acetaldehyde degradation and CO_2 reduction.

We also synthesized mixed-phase materials by a low-temperature solvothermal method. The thus prepared mixed-phase TiO_2 materials were found to be far better photocatalysts than commercial mixed-phase TiO_2 (Degussa P25) or pure-phase materials for CO_2 reduction (Figure 6). The improved photoactivity of mixed-phase TiO_2 was correlated to effective charge separation between anatase and rutile, as indicated by the EPR results (Figure 6, inset). In addition, we have recently prepared copper-doped TiO_2 materials which showed excellent photoactivity for CO_2 reduction. Methane production was also enhanced on catalysts fabricated by creating Ag(I) sites (adlineation) when doping TiO_2 with Ag.

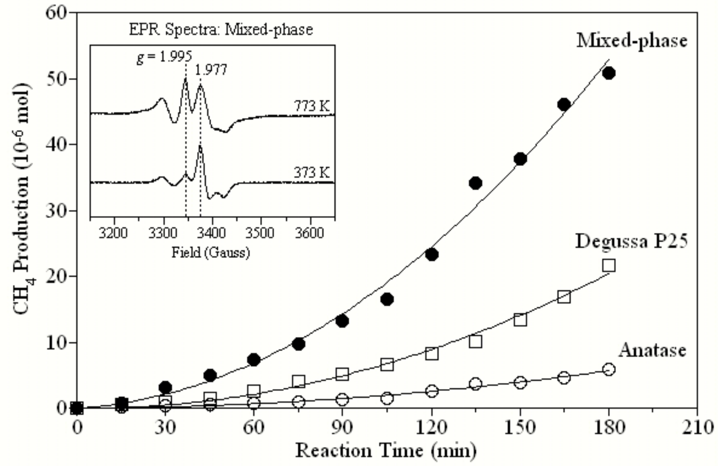


Figure 6: Methane formation by photoreduction of CO_2 in the presence of a hole scavenger. Mixed-phase TiO_2 was synthesized by the solvothermal method. Inset: EPR spectra of the synthesized mixed-phase TiO_2 after thermal treatment at 373 K and 773 K. Signals corresponding to electron trapping in anatase ($g = 1.995$) and rutile ($g = 1.977$) phases are labeled.

Legacy Research Projects Related to Environmental Catalysis

Mechanism of NOx Reduction

Previous published work on the mechanism for NOx reduction with acetaldehyde over BaNa/Y and Ag/γ-Al_2O_3 has been continued to elucidate the multi-step mechanism for the reduction of NO_x with ethanol over silver exchanged zeolite Y (Ag/Y). In brief, ethanol reacts with O_2 and/or NO_2 to form CH_3COH even at 200 ^{0}C. The acetate ions formed from CH_3COH react with NO_2 to yield nitromethane. This crucial intermediate reacts swiftly with NO_2 to form dinitromethane which decomposes to HNCO, a compound that is easily hydrolyzed to NH_3 and CO_2. The short-living dintromethane is not observed by IR; its involvement follows from our isotopic labeling data on BaNa/Y. NH_3 reacts with HONO to form ammonium nitrite (NH_4NO_2) which decomposes to N_2 and H_2O above 100 ^{0}C. We have demonstrated that this decomposition is catalyzed by HCl vapor or solid acids such as the HY; the protonated NH_4NO_2

actually decomposes at room temperature. The nitrate, NH_4NO_3, which is formed from NH_3 and HNO_3, while being thermally more stable, is easily reduced by NO to the nitrite, NH_4NO_2. This is one of the key steps in the catalytic reduction of NO_x. It has been studied in a flow reactor with FTIR monitoring.. The data show a catalytic effect of acid sites; while neat NH_4NO_3 is reduced by NO only above 170°C, this reduction takes place below 100°C on weakly acidic surfaces. The mechanism of NH_4NO_3 reduction by NO is being studied further to quantify the number of acid sites on different materials. A second factor contributing to the catalytic superiority of Ag/Y over Ag/γ-Al_2O_3 is their different oxidation activity. With both NO_2 and O_2 the oxidation of ethanol to acetate is more efficient over Ag/Y than over Ag/□-Al_2O_3 and surface acetate reacts at lower temperatures on Ag/Y. The N_2 yield over Ag/Y approaches 60% and remains constant for at least five hours, making Ag/Y a promising De-NOx catalyst.

Nitromethane (NM) very efficiently reduces NO_2 to N_2 over Ag/Y. Between 140 and 400 ^{o}C, the N_2 yield is close to 100 %. This high N_2 yield results from the ability of Ag/Y to catalyze the reaction between NM and NO_2 which is minimally affected by CN^-, NC^-, or acetate, all of which are thermally and chemically stable below ~300^{o}C. Above 400 ^{o}C, a reaction path exists yielding N_2 from NM even in the absence of NO_2, though at 400^{0} C, most N_2 molecules still originate from NM reacting with NO_2.

Barium is not widely studied using density functional theory (DFT), so the choice of basis set and functional is not obvious. To validate our choice, geometries of gas-phase barium dihalides and heats of reaction for gas-phase reactions involving barium were determined and compared to experiments from the literature. These studies show that the choice of basis set for barium is important and that SDD with B3LYP is a suitable combination of basis set and DFT functional.

To study the effect of the surrounding zeolite framework on the adsorption properties at the barium site, the size of the zeolite cluster was increased from 6T atoms to 36T and 96T using the embedded ONIOM (QM/MM) method. Adsorption energies, geometries, and frequencies were calculated for adsorbed acetaldehyde, nitromethane, and water and compared to experiment where available. Inclusion of van der Waals interactions by increasing the size of the MM part of the cluster only changed the heat of adsorption by a small amount for the adsorbates studied. The relative errors of calculated frequencies are within 3% of experimental values.

The free energy landscapes for the corresponding gas-phase reactions were also constructed. Transition-state structures between the stable intermediates were also found to provide some insight into the mechanism, and they will be used as initial structures for future calculations on the BaNaY surface.

Objectives for the Coming Year

Spurred by the success of the Mn(salen) MOF and coordination polymers as active catalytic materials, we are currently building catalytic membrane structures using both of these strategies as a way to deposit catalytic entities on porous supports.

For the project on synthesis of bimetallic clusters using the nanocage approach, the investigation of binding of metal complexes to the nanocages will be completed. Then the emphasis will shift to generating bimetallic metal particles, and characterizing their compositions and chemical properties.

The synthesis of supported single-site vanadium oxide catalysts will proceed with answering questions about the reasons for the rather remarkable alkane to olefin selectivity and the nature/number of active sites. Preliminary results indicate that it is possible to poison these organovanadium catalysts with certain silicon compounds. This offers the possibility of both counting the percentage of active sites in this type of catalyst, but also of enhancing selectivity for these types of catalysts by poisoning non-selective sites. We will correlate these results with the results of the spectroscopic work mentioned above and begin XAFS studies with collaborators at Argonne National Laboratory.

The focus of the work on photocatalysis will to shift to studies of the photoresponse of our CO_2 reduction catalysts into the visible light range. We are exploring the use of reactive DC magnetron sputtering to prepare nitrogen-doped TiO_2 materials and titania materials with controlled oxygen deficiencies. The solvothermal method will be utilized to prepare coupled semiconductors, including WO_3-TiO_2 and TiO_2-carbon nanotube as visible light photocatalysts for CO_2 reduction. At the same time, we continue to study the charge-transfer dynamics of the synthesized nanocomposite materials using EPR spectroscopy. We hope to prove by EPR studies that the solid-solid interfaces are locations for novel chemistry and highly active sites for photocatalysis in energy applications.

Representative Publications:

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Dash, A. K. F., H.; Elam, J.W.; Pellin, M.J.; Stair, P.C.; Marks, T.J.; "Product Selectivity in Oxidative Dehydrogenation of Cyclohexane by Single-Site Molecular Precursors of Vanadium Anchored in Nano-structured AAO-membranes"." **Manuscript in preparation**.

Dash, A. K. F., H.; Mucheri, S.; Marshall, C.L.; Stair, P.C.; Marks, T.J. "Supported Organovandium Species on Metal Oxide Surfaces and AAO-membranes for Oxidative Dehydrogenation of Propane." Manuscript in preparation.

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Harold H. Kung, “Nanotechnology: Opportunities for Chemical Engineering,” J. Chin. Inst. Chem. Engrs. 37 (2006)

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DE-FG02-97ER14789 **Peter C. Stair**

In-situ and Time-Resolved Characterization of Working Catalysts by Ultraviolet Resonance Raman Spectroscopy

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Students: Paula Allotta, Dana Sauter, Chao Zhang
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Goal

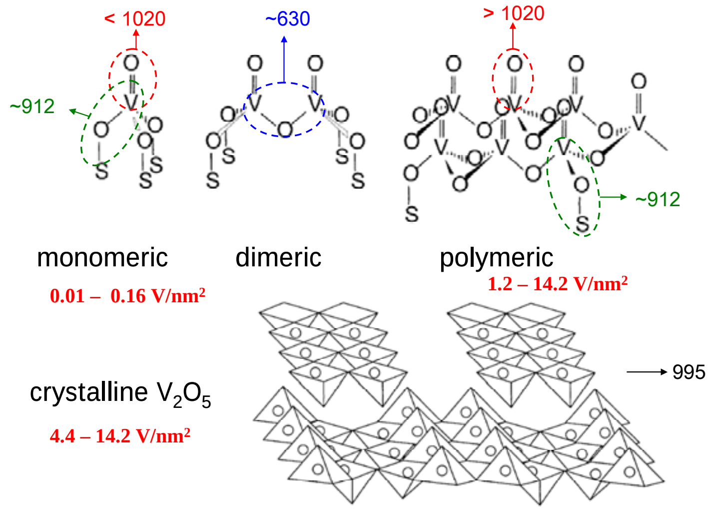
The objectives of this research are to better understand the nature of heterogeneous catalytic species, the interaction of reagent molecules with catalysts, and the catalytic and deactivating reaction pathways using in-situ and operando Raman spectroscopy excited at a series of laser wavelengths.

DOE Interest

The development of new and more efficient catalytic processes for energy conversion and utilization is advanced by the fundamental understanding of catalytic materials and reactions. Since most catalytic materials undergo transformation under reaction conditions, the application of measurement techniques that operate during reaction is essential to this understanding. Raman spectroscopy provides information on the nature of both catalytic materials and molecular reagents under reaction conditions in a single measurement. This project focuses on developing the measurement and interpretation of Raman spectra for quantitative and structural analysis of catalytic systems and in the application of Raman spectroscopy to understanding catalysis.

Recent Progress

Supported vanadium oxide monomers, clusters, and crystals have electronic absorptions at different wavelengths. By matching the excitation laser to the absorption wavelength resonance Raman spectra are obtained from the corresponding species. This behavior and the extension of detectable Raman signals to very low loadings of vanadia on alumina led to the band assignments shown in Figure 1.



Wu et al., J. Phys. Chem. B 109(2005)2793

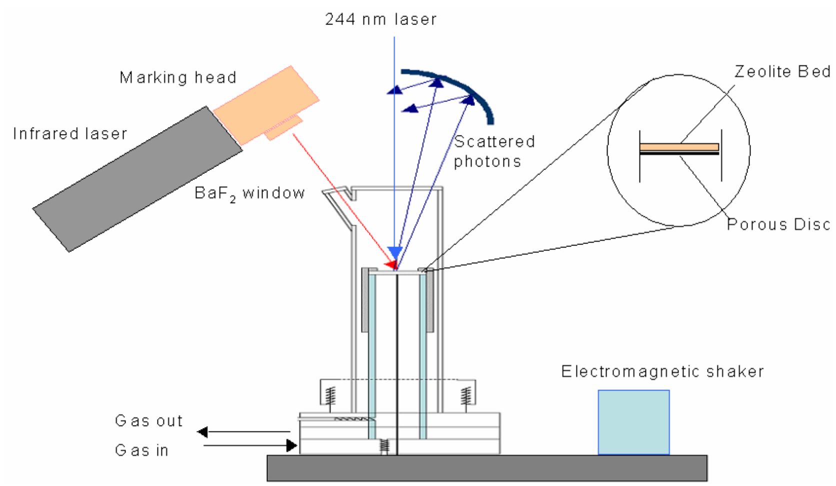
Figure 1

Selective resonance enhancement has been utilized to distinguish and quantify vanadium oxide monomers, clusters, and crystals at different loadings on θ-alumina. The activity and selectivity for butane dehydrogenation to butene, butadiene, and carbonaceous deposits (coke) was studied for these catalysts in order to investigate the structure-function relationship for this reaction. Monomers are highly selective for olefin formation with little production of coke and no deactivation. When the proportion of monomers to clusters was 1:1, the production of butadiene increased significantly with little or no deactivation. At higher vanadia loadings, where clusters dominated the distribution of supported species, the catalysts deactivated significantly over two hours on stream.

The mechanism of coke formation and the topological nature of the coke was a strong function of the nature of the vanadia species. At very low loadings where only monomers were present, coke formation was catalyzed by acidic sites on the alumina surface, and all the observed coke possessed a 2D topology. At somewhat higher vanadia loadings polystyrene was observed as an intermediate in the formation of polycyclic aromatic coke. As the vanadia loading increased, the coke assumed a 2D topology, which is associated with catalyst deactivation by blocking of the active sites.

Reports concerning the ability of Raman spectra to quantify the amount of coke deposited on a catalyst were checked by careful measurements of the Raman cross section for a series of substituted naphthalenes. These spectra reveal that the cross section can vary a factor 2 simply by changing the substitution position of the methyl group in methyl-naphthalene. This result indicates that quantitative analysis of coke deposits, without a detailed knowledge of the coke composition, are only reliable to within a factor 2 at best.

Experiments designed to clarify the coke formation reaction pathways during the methanol-to-hydrocarbons reaction catalyzed by H-MFI have been conducted for zeolites with differing Si/Al ratios and at a series of temperatures. New intermediate species have been observed by quenching the reaction at its early stages. New experimental data for very short times-on-stream in the millisecond regime were obtained using a fast IR heating experiment diagramed in Figure 2. Additional reaction intermediates have been observed.



Future Plans

The data set of time-resolved Raman measurements will be expanded with the objective of determining the number and spectra of independent components as coke layers are deposited using the SIMPLISMA algorithm. These results for zeolites with varying Si/Al ratios will provide detailed, in-situ spectra leading to a determination of reaction pathways.

Experiments are currently underway to clarify the nature of iron oxide clusters in H-MFI zeolite. The objective is to interrogate the mixture of cluster species formed during iron impregnation by vapor phase $FeCl_3$. Future experiments are designed to characterize the structure of a variety of supported metal oxide clusters and establish structure/function relationships.

Recent Publications

Jackson, S. D., S. Rugmini, et al. (2006). "A comparison of catalyst deactivation of vanadia catalysts used for alkane dehydrogenation." Chemical Engineering Journal (Amsterdam, Netherlands) **120**(1-2): 127-132.

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Zhang, C., G. Xiong, and P. C. Stair "UV Raman Spectroscopy Studies of Benzene Molecules Adsorbed inside Zeolite Pores" In preparation.

Zhang, C. and P. C. Stair "UV Raman Studies of Coke Formation During MTH Process over H-MFI" In preparation.

Zhang, C. and P. C. Stair "Quantitative UV Raman Analysis of Naphthalene Derivatives" In preparation.

Allotta, P. and P. C. Stair "Time-Resolved UV Raman Studies of Coke Formation in H-MFI" In preparation.

KC-03-04-01 **Peter C. Stair (Argonne National Lab)**
DE-FG02-03ER15457 **Peter C. Stair (Northwestern University)**

INSTITUTE FOR CATALYSIS IN ENERGY PROCESSES (ICEP): Model Catalytic and Photocatalytic Processes

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NU: M. Bedzyk, D. Ellis, J.-F. Gaillard, F. Geiger, M. Hersam, L. Marks, K. Poeppelemeier, R. Van Duyne

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Goals :

The overall scientific goals of ICEP are to understand at the molecular level catalytic and photocatalytic transformations relevant to energy harvesting, storage, and utilization and to further the discovery and development of highly efficient catalytic and photocatalytic processes. ICEP is organized into three (3) subtasks. The overall goal of this subtask is to develop fundamental, atomic level understanding of the relationship between catalytic chemistry and the surface atomic structure and electronic properties of the catalyst. The components of this subtask include:

- Synthesis of model catalytic materials for oxidation and photocatalysis.
- Catalyst surface structure determination by electron and x-ray diffraction.
- Catalyst surface structure by scanning probe microscopy.
- Surface science of catalytic chemistry.
- In-situ catalytic chemistry by Raman and SFG spectroscopy.
- Theory.

DOE Interest :

The understanding and control of reactions catalyzed on solid surfaces *at the molecular-level* is a “grand challenge” for 21st Century catalysis science. One component of the grand challenge is establishing catalytic structure/function relationships which depend on the knowledge of catalyst surface structures. This subtask brings together a team of university and national laboratory researchers who develop methods for the synthesis and characterization (both ex-situ and in-situ) of catalytic oxide surface structures and dynamics at the atomic scale.

Research plan:

Understanding surface structure and bonding, how they depend on surface chemical reactions, and how they influence catalysis and photocatalysis are the central themes of this subtask. If the surface structure of a given oxide or supported cluster could be predicted this would have an enormous impact upon our understanding of numerous chemical processes. The objective of this subtask is to address this outstanding experimental and theoretical problem for oxide surfaces and supported atoms and clusters on these surfaces. To tackle this problem we target critical and difficult theoretical challenges such as *ab-initio* predictions of multicomponent-oxide surface free energies, the structure of supported clusters, and reaction pathways. Experimental challenges include synthesizing well-defined oxide and supported cluster systems, determining surface structure as a function of environmental or reactive conditions, and evaluating the relationship between surface structure and specific chemical properties.

The investigation of bulk oxides focuses on synthesis and surface structure determinations of materials with the perovskite structure. Perovskite oxide surfaces have been used as heterogeneous catalysts and photocatalysts for reactions such as water splitting and photoreduction of carbon dioxide. Detailed knowledge of the surface structure at the atomic level is *critical* for a molecular level understanding of the reaction mechanisms involved, *i.e.* of the corresponding surface chemistry. This in turn allows for a rational design of a (photo)catalyst with an improved (photo)catalytic response. Much of the work on surface structure determination has been carried out on $SrTiO_3$ single crystals that are commercially available. In a parallel effort, the synthesis of $SrTiO_3$ powders consisting of nanoparticles of controlled size, shape and surface structure has been studied.

The atomic structure of model supported catalysts are determined by the X-ray standing wave (XSW) method, which combines diffraction and fluorescence data acquired in unison to generate 3D images representing the atomic density of adsorbates on a support. The morphology of adsorbed catalytic structures is measured using atomic force microscopy (AFM) and grazing incidence small angle X-ray scattering (GISAXS). The chemical oxidation state is measured by XPS. With the combination of the above techniques, comparisons may be drawn on the processing of a catalytic system and the relative impact of that processing on the performance of the system. The three systems we have worked on include tungsten on rutile, vanadium oxide supported on hematite, and platinum supported on strontium titanate. Samples are prepared in-house with molecular beam epitaxy (MBE) or with atomic layer deposition (ALD) in collaboration with Jeff Elam at Argonne National Laboratory.

Representative Recent Results:

$SrTiO_3$ surface

For the (001) surface of $SrTiO_3$, a model consistent with all available experimental evidence has been proposed by L. Marks and Poeppelmeier for the c(6x2) reconstruction. This model of the high temperature reconstruction is the third of the three reproducible reconstructions formed under oxidizing conditions and solved by this group. The atomic structure for the c(6x2) is obtained through a

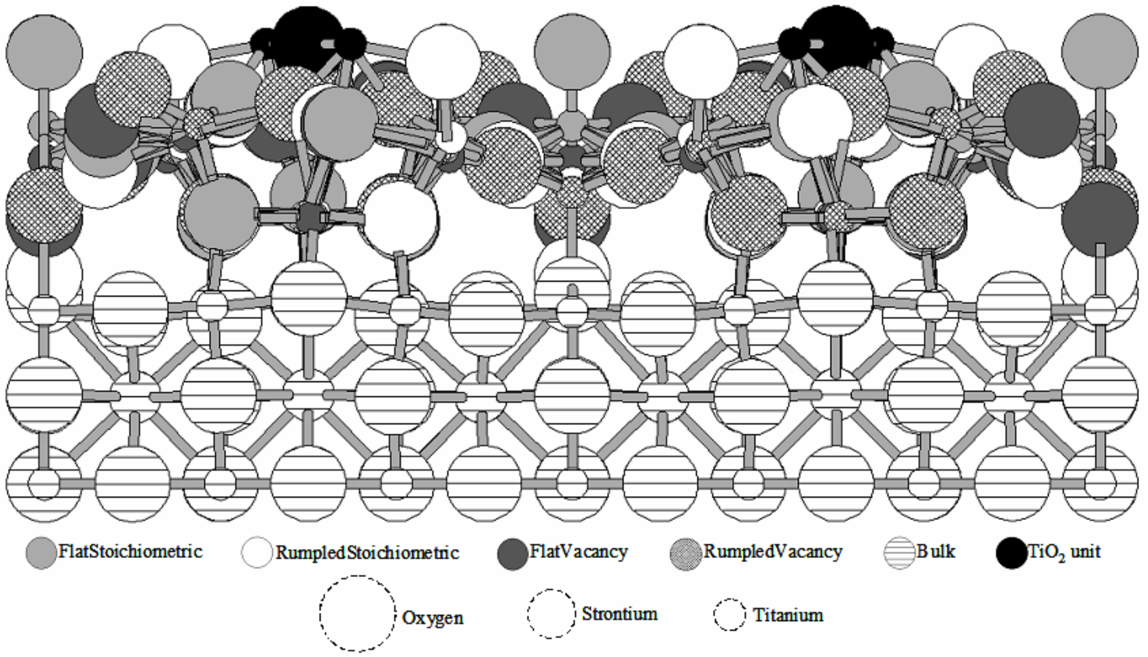

Figure 1. Cartoon combining onto one lattice the four DFT-relaxed structural motifs of the c(6x2) surface reconstruction on $SrTiO_3$, used as input for SXRD data refinement.

combination of results from transmission electron diffraction, surface x-ray diffraction, direct methods analysis, computational combinational screening, and density functional theory. Like the (2x1) and c(4x2) solved previously by the same groups, the c(6x2) is characterized by an overlayer of TiO_2 stoichiometry. However, this surface is complex and cannot be described by a single structure. Instead, it consists of short-range ordered microscopic domains composed of four main structural motifs, with additional non-periodic TiO_2 units distributed on the surface. This is one of the first, if not the first, demonstrations of the importance of configurational entropy dominating over enthalpy at high temperatures.

On the (110) surface of $SrTiO_3$ a large (4x3) surface reconstruction has been observed to form following 1100ºC annealing under flowing O_2. Using transmission electron microscopy combined with direct methods a scattering potential map has been constructed. Atoms were fit to this map to create a two-dimensional projection of the surface structure. The proposed solution, like reconstructions for other $SrTiO_3$ surfaces formed under oxidizing conditions, is composed of titanium and oxygen atoms. DFT calculations are being run to help determine the three dimensional structure.

For the (111) surface of $SrTiO_3$, a solution to the (3x3) surface structure has been obtained through a combination of transmission electron diffraction, direct methods, scanning tunneling microscopy, and electronic structure calculations. Like many other $SrTiO_3$ surface reconstructions formed in oxidizing conditions, there are no strontium atoms on the surface. The Ti-O coordination at the surface changes from octahedral to 4- and 5-fold, allowing the surface to have increased covalency while minimizing non-bonded O-O repulsions.

$LaAlO_3$ (001) surface

$LaAlO_3$, another perovskite, which has shown activity for oxidative coupling of hydrocarbons, has also been under investigation. For the (001) surface, the (√5×√5)R26.6º reconstruction has been identified as forming reproducibly under atmospheric conditions, and the L. Marks and Poeppelmeier groups have solved the (√5×√5)R26.6º surface reconstruction using transmission electron microscopy combined with direct methods. The structure is relatively simple, consisting of a lanthanum oxide termination with one lanthanum cation vacancy per surface unit cell, but results in an interesting electronic structure. To obtain charge neutrality there must be a fractional number of holes or atomic occupancies per surface unit cell. DFT calculations indicate that the charge compensation mechanism occurs by means of highly delocalized holes (Figure 2).

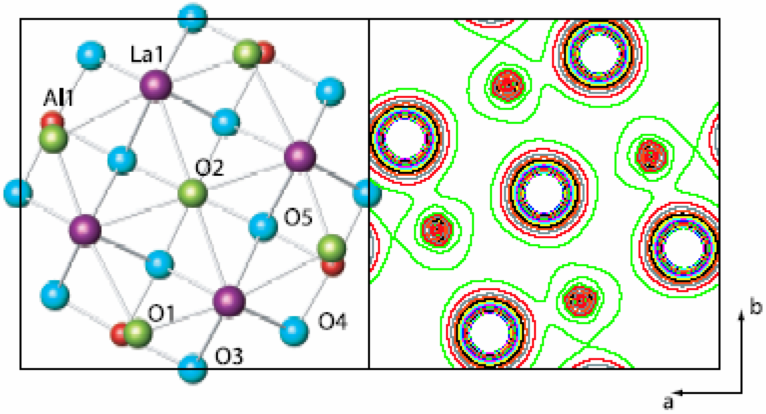

Figure 2. Top view of the RT5 surface reconstruction (left) with the surface unit cell outlined in black (a=8.537 °A). Contour map of the valence density in the surface plane (right) at 0.1 *e*/ °A3 showing the increased electron density between the surface oxygen (O1 and O2) and lanthanum atoms (La1) corresponding to increased covalent bonding. The La vacancy is located at the corner of the unit cell, atoms O1, O2 and La1 are in the surface layer, while Al1, O3, O4 and O5 are in the second layer.

Synthesis of $SrTiO_3$ nanoparticles

$SrTiO_3$ nanoparticles were obtained using a molten salt approach as described by Wong *et al.* Powder X-ray diffraction (PXRD) yields diffraction patterns that can be indexed to the cubic space group *Pm-3m*. The corresponding lattice constant is a = 3.906258(181)Å. Transmission electron microscopy (TEM) images of the as-prepared samples reveal that the $SrTiO_3$ nanoparticles are cubic shaped, with well defined edges of average length 120 nm (Figure 3). Moreover, electron diffraction and energy-dispersive

X-ray spectroscopy (EDX) show that the nanocubes are single crystalline and made up of Sr, Ti and O. Although these powders are not agglomerate-free, particle dispersion is greatly enhanced if compared to ceramics synthesized using conventional solid state reaction.

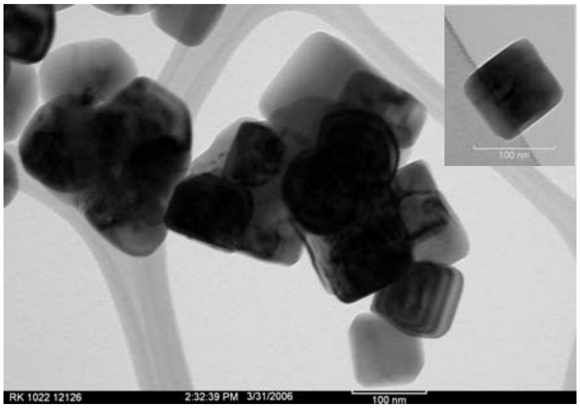

Figure 3. TEM image of the as-prepared $SrTiO_3$ nanostructures. Inset: an isolated $SrTiO_3$ nanocube.

A detailed theoretical study of the complete reaction pathway for propane ODH was carried out on a vanadium oxide surface following the steps of a Mars-van Krevelen mechanism. The calculations use the hybrid B3LYP density functional method and clusters with up to ten vanadium atoms. A schematic of the potential energy surface is given in Fig. 8. Energies of key points on the pathway were confirmed by periodic calculations. The results indicate that the (010) surface of V_2O_5 is unfavorable for propane ODH and other factors, such as the support material, are responsible for the observed catalytic activity of vanadia. The potential energy surface has large barriers, which are lowered if a singlet-triplet state crossing is considered. The triplet state is stabilized by breaking of surface bonds by adsorbates and transfer of charge to the surface. The reaction at a V-O-V bridging oxygen site is energetically similar to a V=O vanadyl site. The barriers on the reaction pathway are 45-80 kcal/mol above the energy of the reactants, which are larger than found experimentally (20-25 kcal/mol) for propane ODH on supported vanadia. The highest energy on the reaction pathway corresponds to an oxygen vacancy on the V_2O_5 surface, which forms on water desorption. The barriers for propane adsorption and propene elimination are also large (45-60 kcal/mol). Some of the barriers may be reduced by consideration of more complex reactions, such as a concerted reaction involving adsorption of O_2 during water elimination. The involvement of a support appears to be required to reduce other barriers, such as for propane adsorption.

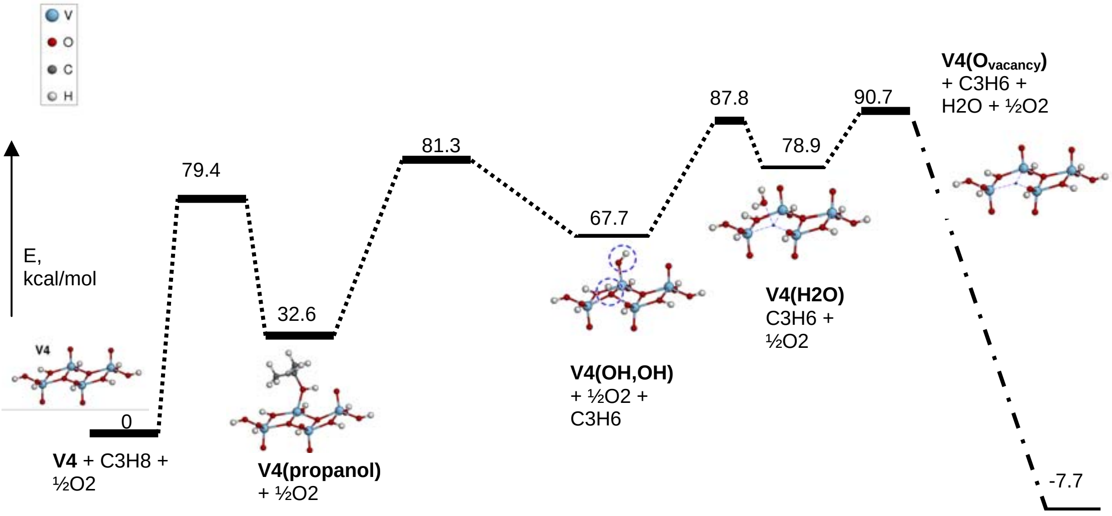

Figure 4: **Potential energy surface for propane ODH at a vanadyl site on V_2O_5 surface from density functional calculations.**

Our recent work on model supported catalysts includes tungsten on rutile, vanadium oxide supported on hematite, and platinum supported on strontium titanate. Samples are prepared in-house with molecular beam epitaxy (MBE) or with atomic layer deposition (ALD) in collaboration with Jeff Elam at Argonne National Laboratory.

$W/TiO_2(110)$

Submonolayer W deposited via ALD was shown to assume lateral adsorption sites consistent with Ti symmetry positions with a small (0.23 Å) outward displacement. AFM measurements confirmed that the W remained in a monolayer form with no cluster formation.

$V_20_5/Fe_2O_3(001)$

Recent work on this system extends the capability of the XSW method. ALD deposited vanadia was subjected to a redox cycle in conjunction with XSW measurements. The vanadia/hematite was first oxidized prior to an XSW measurement, which showed the vanadia to be incoherent and amorphous. Upon annealing in hydrogen, the vanadium species took up ordered positions.

$Pt/SrTiO_3(001)$

ALD deposited Pt is being investigated with AFM for the potential to form size selected catalyst particles as a function of surface treatments and ALD cycles. For MBE grown samples, preliminary XSW results indicate a bulk like structure for Pt and increased ordering through annealing. Fig. 4 depicts the structure of 0.6 ML Pt evaporated on $SrTiO_3(001)$ from XSW data. AFM and GISAXS results confirm the formation of clusters and their growth as a function of annealing.

Future Plans:

The overall goal of this subtask is to directly relate the experimentally observed chemical reactivity of oxide surfaces to their surface structure. Surface structure and chemistry studies will continue on $SrTiO_3$, but a significant effort in the future will be experimental and computational investigations of chemical and catalytic reactions on the model oxide surfaces. We will determine the $Pt/SrTiO_3$ nanocluster structure and combine it with morphological features from supporting AFM and GISAXS data. We will also continue studies of supported Pt ALD synthesis to develop control over catalyst particle size and the scalability of the process. Additional work will combine the approaches described above on mixed-metal catalyst systems. A particular focus will be photocatalytic reactions related to the reduction of CO_2 with water over $SrTiO_3$ and Pt supported on $SrTiO_3$. Computational studies of water adsorption and hydroxylation processes relevant to photocatalysis and ALD synthesis on defective and nonstoichiometric surfaces of hematite and related materials will be completed. Co-adsorption of small molecules, and their most basic associative and dissociative processes will be studied, using both atomistic and DFT approaches. Future work will also focus on conducting operando SERS experiments of model catalytic reactions such as the oxidative dehydrogenation of cyclohexane. Upcoming experiments will also involve the fabrication of other ALD films such as TiO_2 which is important for catalytic reactions such as the oxidation of propylene. Exploratory ALD chemistry will be performed to fabricate catalytic metal nanoparticles of gold and silver which are necessary for the oxidation of propylene.

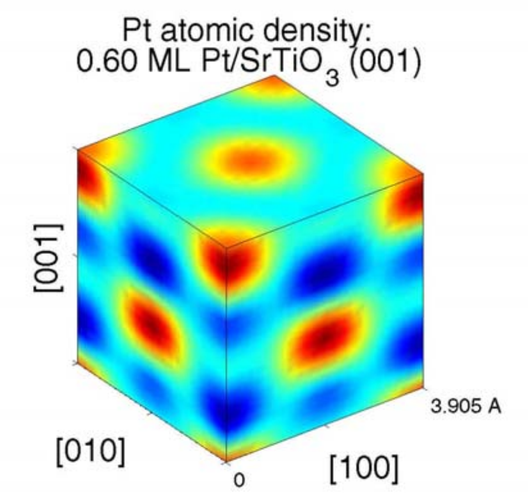

Figure 4: 3D Pt atomic map relative to $SrTiO_3$ cubic unit cell. This was produced by a summation of XSW measured Fourier components.

Representative Publications:

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Pless, J. D., H. S. Kim, et al. (2006). "Structure of $Mg_{2.56}V_{1.12}W_{0.88}O_8$ and vibrational Raman spectra of $Mg_{2.5}VWO_8$ and $Mg_{2.5}VMoO_8$." Inorganic Chemistry **45**(2): 514-520.

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P.C. Redfern, P. Zapol, M. Sternberg, S.P. Adiga, S.A. Zygmunt, and L.A. Curtiss (2006). "Quantum chemical study of mechanisms for oxidative dehydrogenation of propane on vanadium oxide.", J. Phys. Chem., B **110** 8363.

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S.A. Zygmunt, P.C. Redfern, P. Zapol, and L.A. Curtiss. "A density functional study of the structures and energies of vanadium oxide clusters on a (001) anatase support" **In preparation.**

KC-03-04-01 **Peter C. Stair (Argonne National Lab)**
DE-FG02-03ER15457 **Peter C. Stair (Northwestern University)**

INSTITUTE FOR CATALYSIS IN ENERGY PROCESSES (ICEP): Nanostructured Membrane Catalysis

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Goals :

The overall scientific goals of ICEP are to understand at the molecular level catalytic and photocatalytic transformations relevant to energy harvesting, storage, and utilization and to further the discovery and development of highly efficient catalytic and photocatalytic processes. ICEP is organized into three (3) subtasks. The overall goal of this subtask is to develop fundamental understanding of the relationship between catalyst structure at the nanoscale and the resulting catalytic chemistry. The components of this subtask include:

- Synthesis of highly uniform, nanostructured membranes.
- Synthesis of catalytic components.
- Catalytic testing.
- Structural and chemical characterization.
- Theory and modeling.

DOE Interest :

The understanding and control of reactions catalyzed on solid surfaces *at the molecular-level* is a “grand challenge” for 21st Century catalysis science. We expect that the fundamental results of this research will provide structure-function relationships between catalytically active sites and the chemical reactions they catalyze that are at the heart of this challenge. This project brings together a team of university and national laboratory researchers who develop methods for the design and synthesis of active catalytic sites at the atomic scale and tailored support structures at the nanometer scale, diverse spectroscopy, microscopy, and x-ray scattering techniques for detailed characterization (both ex-situ and in-situ) of catalyst structure and dynamics, elucidation of catalytic reaction mechanisms, and theory applied to catalytic processes.

Research plan:

Mesoporous and microporous catalytic material syntheses are often approached in a “one step” process. In this work we are using a new approach based on two steps: production of a stable mesoporous scaffold and then carefully controlled modification of the scaffold, where each step can be optimized independently. Our work involves gas phase deposition allowing directed control of the pore wall composition and diameter. The scaffold that is used is anodized aluminum oxide (AAO) and the deposition method is atomic layer deposition (ALD).

AAO membranes are an ideal scaffold with highly-aligned, parallel pores and narrow pore diameter distributions. Electrochemical conditions can be arranged to produce most probable pore diameters in the range 20 to 400 nm and membrane thicknesses in the range 0.5 to >250 μm. Prior catalytic studies using AAO showed interesting yield enhancements, but were limited to unreleased (pore blocked) films. Moreover, as-grown AAO membranes suffer from poorly defined pore wall morphology and composition with significant (5%) amounts of incorporated electrolyte anions.

ALD is a growth technique that uses alternating, saturating reactions between gaseous precursor molecules and a substrate to deposit films in a layer-by-layer fashion. By repeating the binary reaction sequence in an ABAB… fashion, films of micrometer thickness can be deposited with atomic layer precision. Current viscous flow reactor designs allow this monolayer by monolayer growth to proceed very rapidly, resulting in growth rates as high as 0.1 micron/hour.} Binary reaction sequences have been developed to deposit a wide variety of materials including oxides, nitrides, sulfides and metals. ALD composite oxides can also be formed by depositing alternating layers ("nanolaminates") or partial layers of the component oxides at a specific ratio that controls the composition of the composite layer. Because gas transport into mesoporous and microporous materials is diffusion-limited; surfaces at the entrance to the AAO membrane will receive reactant exposures that are ~10^3 larger than interior surface. Despite this, ALD has a demonstrated ability to coat mesoporous materials including AAO. The key to fabricating uniform nanoporous membranes from AAO templates is the "self-limiting" nature of the ALD binary reaction scheme.

The second part of this project utilizes state-of-the-art chemical, materials, and reaction characterization techniques along with advanced computing methodologies to systematically investigate catalytic reaction selectivity in prototypical selective oxidation reactions. In the first experiments membranes with catalytic phases deposited by conventional impregnation and novel ALD methods have been compared in order to make a connection with the extensive catalytic literature. Later, single catalytic particles will be deposited in each nanopore and reaction experiments performed to elucidate how elementary, catalytic reaction steps depend on the catalyst structure and composition at the atomic level. Membranes with a programmed series of catalytic particles in each pore will be used to study sequences of catalytic reactions. In collaboration with experiments, theoretical modeling at the ab initio and phenomenological level will be used to elucidate fundamental catalytic mechanisms.

Representative Recent Results:

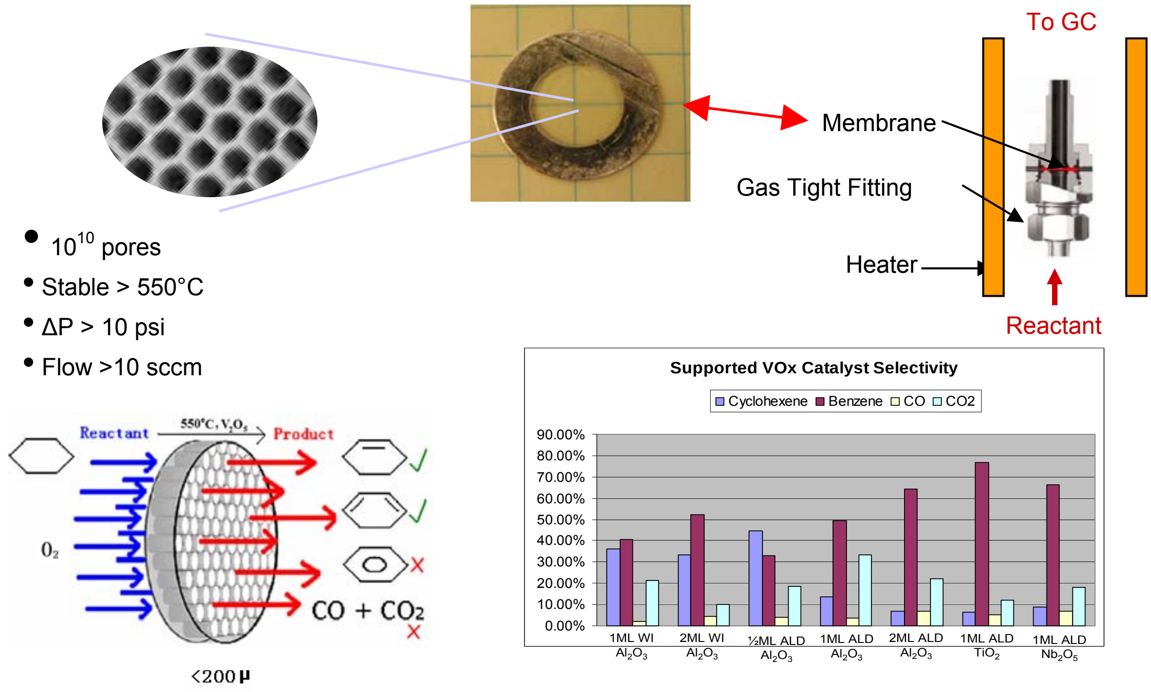

***Figure 1*: Nanostructured membrane catalysis experiments.**

Nanostructured membrane catalysts have been successfully fabricated and tested for the oxidative dehydrogenation (ODH) of propane (P) and cyclohexane (CH). The experimental arrangement and representative results for CH ODH are shown schematically in Figure 1. AAO membranes with 40 nm diameter pores are etched in the central portion of a high purity aluminum disk to form a mounted AAO structure shown in the photo (center top). A representative electron micrograph shows the typical uniformity. The mounted membrane pores are coated using ALD, first with 1 nm of Al_2O_3, which serves to cap the impure aluminum oxide formed during anodization. This alumina layer can be used as the support for catalytic materials deposited using conventional impregnation methods or by ALD. Catalytic reaction experiments are conducted by sealing the mounted membrane structure in a standard, gas-tight VCR fitting connected to a gas flow system and heated by a tube furnace. Product analysis following a single pass of the reagents through the membrane is performed using a gas chromatograph. The product distribution from cyclohexane oxidative dehydrogenation at 480°C are shown for several preparations of vanadium oxide prepared by wet impregnation and ALD and supported on alumina, titania, and niobia.

An extensive set of catalytic experiments have been conducted for the oxidative dehydrogenation of cyclohexane to cyclohexene, benzene, and carbon oxides and propane to propene and carbon oxides catalyzed by supported vanadium oxide. A number of interesting results have been obtained that can be summarized as follows:

- The catalytic TOF increases with vanadium loading even at loadings above 1 ML
- The vanadium loading is the most important variable for determining selectivity: selectivity to benzene increases with loading
- The selectivity to carbon oxides is low and relatively insensitive to conversion or vanadium loading
- Titania and niobia supports produce more active catalysts than alumina
- The membrane structure is more active and selective than the equivalent powder catalyst under the same operating conditions
- Vanadium oxide, under our reaction conditions, is active for single C-H bond breaking in the CH_2 groups that make up cyclohexane
- The number of V-O-V bonds in the catalysts has been characterized by UV-Vis absorption thresholds

ALD can also be employed to coat the AAO pores partially, thus creating pores with cylindrical sections of different diameters. Simulations in pores with these characteristics were performed. The results show that the number and distribution of hits between particles and the pore walls can be related to the distributions in the uniform diameter cases, as shown in Figure 2 for particles traveling through pores with cylindrical sections of 30 and 50 nm in diameter. The contact of the particles traveling inside the pores with the pore walls can be regulated by adjusting the aspect ratio (section length / section diameter) of the pore sections and the ratio of their cross-sectional areas. Analytical expressions were developed to relate the transmission probability in pores of multiple sections to the transmission probabilities of the constituent sections.

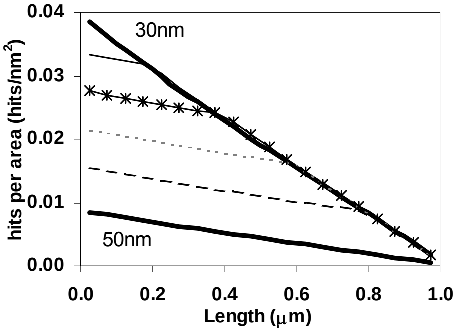

Figure 2: Average number of hits per area per segment for pores with d_1=50 nm, d_2=30 nm, total length = 1 μm and L_1= 0.2 μm (—),L_1= 0.4 μm (-*-), L_1= 0.6 μm (···) and L_1= 0.8 μm (---) for particles recovered on the downstream end of the membrane. The profiles for pores with uniform diameters of 50 and 30 nm are also shown.

Previously, we used theoretical expressions and molecular dynamics simulations to determine the role of convection, molecular diffusion, surface diffusion and Knudsen diffusion for ethane at 700 K and pressure near atmospheric in pores with diameters between 10 and 150 nm. The results showed that, under these conditions, the system is dominated by Knudsen diffusion. This dominance was then exploited to develop a model based on its principles: no interaction among particles and diffusive collisions between particles and the pore walls. This model allows studying the residence times and number of hits of particles on the wall, as well as the transmission probability (defined as the fraction of particles that enter the pore on one end and exit at the opposite end without going back to the initial side). The residence time and the number of hits are critical parameters for studying oxidation reactions in AAO membranes. Collisions with the pore walls lead to catalytic oxidation of the substrate, but they also can lead to oxidation of primary and higher order products. Thus, understanding the effect of the characteristics of the pores on the residence time and the number of hits is thus crucial to predicting product selectivity.

Molecular dynamics simulations have been employed to study the atomic structure of amorphous alumina surfaces that are characteristic of ALD layers. MD simulations of amorphous aluminum oxide was extended to include hydroxylation in the material. The simulations were done with 2 at. % to 8 at. % hydrogen content. Most of the hydrogen migrated to the surface after annealing in the MD simulations. The hydroxyl groups at the surface are either singly or doubly coordinated to aluminum. The presence of the hydrogen in alumina changes the surface morphology with increased roughness of ~2.3 Å at the highest hydrogen content. This is consistent with the aluminum oxide films made by ALD. The vibrational density of states was calculated for the hydroxylated amorphous aluminum oxide from the MD simulations. The results showed distinct OH stretching modes corresponding to the singly and doubly bonded OH groups. The vibrational density of states was investigated as a function of hydrogen content. The results indicate a broadening of the OH band with increase in density. This helps to explain the broad OH stretching peak observed in the FT-IR spectra of ALD aluminum oxide (subtask 1), which has a high hydroxyl content. Calculations have been initiated on VOx clusters on the hydroxylated amorphous aluminum oxide surface from the MD simulations, as well as for θ aluminum oxide.

Future Plans:

Synthesis, characterization, and evaluation of membrane nanostructures with shorter, smaller diameter pores will be conducted to investigate the influence of these properties on catalytic activity and selectivity. At a sufficiently small pore diameter, the chemical nature catalytic layers will be influenced by curvature of the pore wall. Structures with controlled and sequenced wall compositions will be investigated, particularly to determine the influence of wall composition at the end of the pores on possible gas phase chemical reactions. Reactors designed to probe changes in flow geometry, through flow, cross flow, reflected flow, have been constructed and will be evaluated. The computational effort will expand the modeling to include catalytic reaction effects.

Publications:

Pellin, M. J., P. C. Stair, et al. (2005). "Mesoporous Catalytic Membranes: Synthetic Control of Pore Size and Wall Composition." Catalysis Letters **102**(3-4): 127-130.

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DE- FG02-86ER13622.A000 **Steven L. Suib**

Title - Porous Nano-Size Transition Metal Oxides Preparation, Characterization and Applications.

Students: Chunhu Chen, Vincent Crisostomo, Jason Durand, Aimee Morey.
Collaborators: Joe DiCarlo, Yardney; Jon Hanson, Brookhaven National Labs; Dave Mullins, Oak Ridge National Labs; P. Thiyarajaran, Argonne National Labs.
Contact: Steven L. Suib, Unit 3060, Dept. of Chemistry, University of Connecticut, Storrs, CT 06269-3060.

Goals of the Work:

- To prepare and characterize single and multiple framework substitutions in various OMS and OL systems.
- To prepare and characterize new OMS and OL structures and compositions.
- To understand factors that control conductivity, magnetic, and structural properties of nano-sized OMS systems.
- To fully characterize physical and chemical properties of the above-mentioned systems and to develop novel characterization methods for OMS systems.
- To use nanosize porous metal oxides for selective oxidations, shape selective oxidations, and membrane applications.

Recent Progress :

Our major efforts have focused on the use of several OMS and OL materials in the selective oxidation of alcohols. These catalysts are outstanding materials for the selective aerobic catalytic oxidation of alcohols. The selectivity in almost all cases is 100%. Not many examples of oxidations are known to occur by the Mars van Krevelen pathway in the liquid phase due to competition from readily generated free radicals. A multi-electron redox event occurring in the liquid phase coupled with the potential of shape-selectivity in the regularly ordered tunnels makes these OMS-2 materials an interesting new class of oxidation catalysts. Hollow sphere OMS-2 catalysts which display high activity, clearly show that morphology plays an important role in enhancing rates of selective oxidations.

Cryptomelane-type manganese oxides octahedral molecular sieve (K-OMS-2) were used for the acid-catalyzed condensation of phenylhydroxylamine with aniline to produce 2-aminodiphenylamine. The H^+-exchanged K-OMS-2 was found to be an efficient catalyst for this reaction. The reaction showed high selectivity (> 96%) for the *ortho* isomer of aminodiphenylamine compared with the *para* product. Effects of the amount of H^+ exchange and temperature were investigated. These materials were used for the condensation reaction of phenylhydroxylamine with aniline. H-K-OMS-2-catalyzed reactions gave higher selectivity for 2-ADPA than for 4-ADPA. The reaction is a simple one-step process and is completed in only 35 min. H-K-OMS-2 is a unique catalyst that gives predominantly the *ortho* isomer. To the best of our knowledge, this is the only catalyst that yields the *ortho* isomer with high selectivity compared with the *para* isomer. A proposed mechanism is given in Fig. 1.

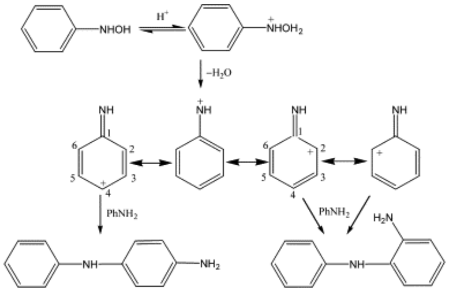


Fig. 1. Mechanism of Acid Catalyzed Condensation of Phenylhydroxylamine with Aniline.

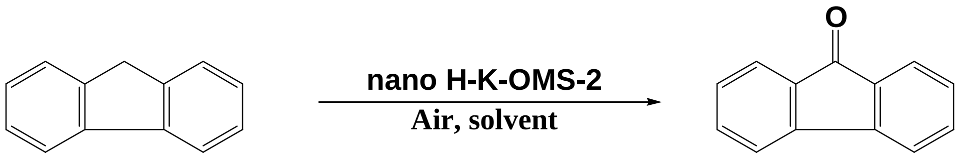
DOE Interest:

Fundamental knowledge in the areas of synthesis, new characterization methods, structural analysis, mixed valency, electron transfer, magnetic behavior, conductivity, catalysis, electrocatalysis, and photocatalysis has been obtained in our studies of OMS and OL materials. The novelty of porous semi-conducting molecular sieves has allowed fundamental studies of effects of electron transfer and unique electrocataytic systems based on nano-films of OL and OMS. Control and understanding of conductivity of all of these materials is important for redox catalytic cycling, sensing devices, and in several spectroscopic and microscopic experiments where charging can be significantly reduced. Catalytic oxidations are the focus of proposed catalysis studies because excellent preliminary results and selected high impact targets have been obtained. Recent work from other groups concerning generation of 3x3 materials using bacterial catalysis, production of single crystal multipods of MnO, generation of macroporous manganese oxides with regenerative mesopores, and production of redoxable nanosheet crystallites of MnO_2 via delamination and others have provided insight for much of our work. The unique combination of availability of numerous structural types, good electrical properties, high permeability, and high porosity is rare.

Future Plans:

The following section summarizes some recent novel unpublished results in the area of selective oxidations that we are pursuing. All these reactions are catalyzed by various OMS catalysts. One theme that is being continued is the effect of morphology on selective oxidations. With OMS-2 alone there are various morphologies such as hollow spheres, helices, papers/membranes, stars, multipods, and dendrites that have the same composition but very different rates. These rate differences cannot be accounted for solely based on surface areas. Correlations of types and sizes of pores, chemical compositions, and average oxidations states with rates need to be studied for all the reactions given below. These reactions are environmentally friendly, generally one-pot, and use air or oxygen as oxidizing agents. Systematic studies of various single and multiple framework substituted OMS systems with and without H^+ sites are being done.

Oxidations of Fluorene or Isophorone are currently being studied. Reaction [1] below shows that 9-fluorene can be converted in high yield to 9-fluorenone.



No Peroxide

9-Fluorene **9-Fluorenone** ***[1]***

Conversion 97 %
Selectivity 100 %

A detailed mechanism of the above reaction **[1]** will provide ideas for several oxidation applications. Nano-H-K-OMS-2 particles are critical to this reactivity. Almost no conversion occurs with larger particles (> 500 Å) of H-K-OMS2. A proposed mechanism involves a 9-fluorenol intermediate, shown in Figure 2, which has not yet been isolated. Fluorenone has been identified as a model compound capable of modifying a wide variety of polymeric substrates. For example, fluorenone chromophore has been incorporated into the backbone of Nylon. Mass spectrometry, FTIR, and NMR methods are being used to

study this mechanism. Production of oxygenates at a saturated position without peroxide is extremely difficult and this is an impetus for studying this reaction mechanism.
The first step is not well established, but hydrogen is most likely coming from H-K-OMS-2.

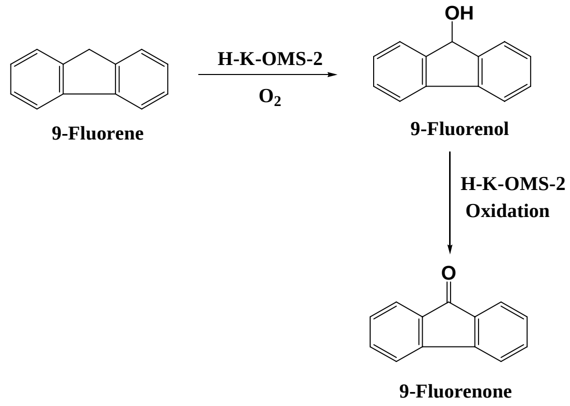


Fig. 2, Proposed Mechanism for Selective Oxidation of 9-Fluorene.

Another possible target using the above -size catalyst is Ketoisophorone (KIP). KIP is a useful intermediate for starting materials for medicinal purposes (Vitamin E, Carotenoids). Heterogeneous oxidations of these and similar alkylarenes have been done often at high temperature (> 200^{o}C) however, expensive noble metal or mixed metal oxide catalysts with selectivities less than 100% are generally observed. Often such catalysts are active with only some substrates, not a whole family. Similar methods are being used to study the mechanism of this reaction**.**

Representative Publications 2006-2007:

Li, W., Yuan, J.; Shen, X. F.; Gomez-Mower, S.; Xu, L. P.; Sithambaram, S.; Aindow, M.; Suib, S. L. Hydrothermal Synthesis of Structure and Shape Controlled Manganese Oxide Octahedral Molecular Sieve (OMS) Nano-materials, *Adv. Funct. Mat*., 2006, **16**, 1247-1253.
Li, W.; Yuan, J.; Gomez-Mower, S.; Sithambaram, S. Synthesis of Single Crystal Manganese Oxide Octahedral Molecular Sieve (OMS) Nanostructures with Tunable Tunnels and Shapes, *J. Phys. Chem*., 2006, **110**, 3066-3070.
Malinger, K. A.; Ding, Y.; Sithambaram, S.; Espinal, E.; Gomez, S.; Suib, S., Microwave Frequency Effects on Synthesis of Cryptomelane-type Manganese Oxide and Catalytic Activity of Cryptomelane Precursor, *J. Catal*., 2006, **239**, 290-298.
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Ghosh, R.; Shen, X.; Villegas, J. C.; Ding, Y.; Malinger, K.; Suib, S. L., Role of Manganese Oxide Octahedral Molecular Sieves in Styrene Epoxidation, *J. Phys. Chem*., 2006, **110**, 7592-7599.
Durand, J. P.; Villegas, J. C.; Gomez-Mower, S.; Giraldo, O.; Suib, S. L. Colloidal Manganese Oxide Precursor to Octahedral layered OL-3 Materials, *J. Inorg. & Organomet. and Polm. Materials*, 2007, in press.
Ngala, K.; Dobley, A.; Suib, S. L., Characterization and Electro-catalytic Behavior of Layered Li_2MnO_3 and its Acid-Treated form, *Chem. Mat*., 2007, **19**, 229-234.
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Katikaneni, S., Patel, P.; Suib, S.; OMS-2 catalysts in PEM fuel cell applications, US Patent Application 20060019130, January 26, 2006.
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DE-AC05_76RL01830 **János Szanyi**

Chemistry on base-metal oxide nano structures on oxide substrates: A model system approach

Post-docs: Emrah Özensoy, and Cheol-Woo Yi

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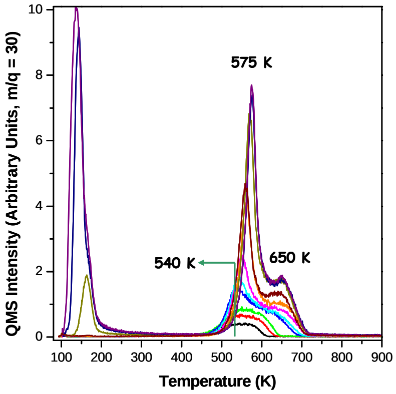
Goal

Investigate and understand the fundamental aspects of NOx chemistry on base-metal oxide nano structures prepared on well-characterized model oxide surfaces. The two main objectives are (i) to prepare and characterize (both composition and structure) base-metal oxide (BaO) nano structures on well ordered oxide substrates, and (ii) to investigate the surface chemistry of small molecules containing unpaired electron density (NOx) on these model oxide systems.

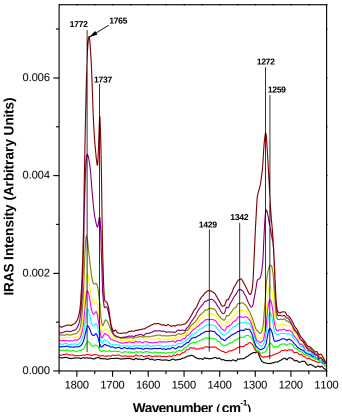
Recent Progress

Interaction of BaO with Al_2O_3 Films: Using a reactive layer assisted deposition (RLAD) we attempted the preparation of BaO nanostructures on ultrathin, well-ordered, as well as thick Al_2O_3 films grown on a NiAl(110) metal alloy substrate. Ba metal, at different coverages, was deposited onto a thick (~30 ML) N_2O_4 ice on alumina films, then the thus formed $BaNO_x$ layer was thermally decomposed to form the $BaO/Al_2O_3/NiAl(110)$ systems. Up to high nominal BaO coverages (~20 ML) BaO reacted with the alumina films (regardless of the Al_2O_3 film thickness) to form Ba-aluminate layers even at low annealing temperatures. Above 30 ML BaO coverages several pure BaO layers formed that allowed the investigations of the NOx chemistry of pure BaO.

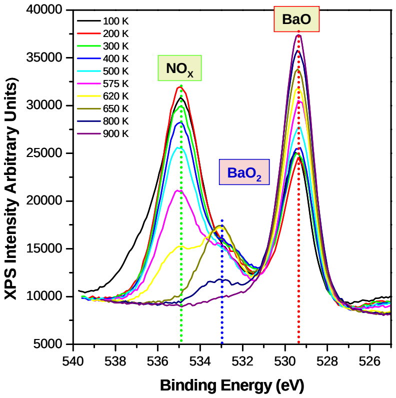
Interaction of NO_2 with BaO: We experimentally demonstrated that NO_2 adsorbed cooperatively on BaO in accord to predictions of theoretical calculations. The pairwise NO_2^-/NO_3^- formation was observed at 85 K up to a monolayer covarege. The formation of both nitrite and nitrate species were substantiated by the presence of two N 1s features in the XP spectra, and well as by the characteristic bands in the IR spectra. Thermal desorption results also suggested the formation of both nitrites and nitratres. NO_2 adsorption at elevated temperatures resulted in the conversion of all the initially-formed nitrite species into nitrates, in agreement with results reported for real, high surface area catalyst materials. In the course of thermal decomposition of the elevated temperature-formed nitrate species we observed the formation and the subsequent decomposition of BaO_2 above 650 K.



1. TPD spectra obtained after NO_2 adsorption on a thick $BaO/Al_2O_3/NiAl(110)$

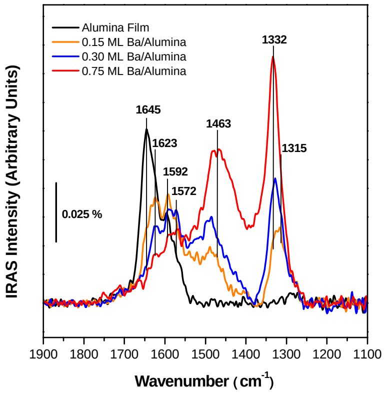


2. RAIR spectra collected during NO_2 adsorption on a thick $BaO/Al_2O_3/NiAl(110)$ sample at 85 K.



3. O 1s XP spectra obtained during annealing of a NO_2-saturated (85 K) thick $BaO/Al_2O_3/NiAl(110)$ sample

NO_2 Adsorption on Ba-aluminate: The interaction of NO_2 with the alumina film grown on NiAl(110) as well Ba-aluminate layers with varying Ba contents were also investigated. In agreement with our studies on high surface area γ-Al_2O_3 support materials only surface nitrates are produced when NO_2 reacts with the Al_2O_3 film. As Ba is deposited onto the alumina film, it readily forms Ba-aluminates. These Ba-aluminate layers, under the experimental conditions we applied in the studies of NO_2 adsorption on pure BaO, do not react with NO_2 to form nitrates, only nitrites, even at very high exposures. However, at higher NO_2 pressures (>5×10^{-6} Torr), upon the interaction of NO_2 with Ba in the Ba-aluminate layers, ionic nitrates are formed. Our data suggest that the Ba ions are "pulled out" from the Ba-aluminate layer as they interact with NO_2 and form the nitrate species.



4. RAIR spectra collected after NO_2 adsorption/reaction on alumina, and Ba-alumina layers on a NiAl(110) substrate at 300 K.

DOE Interest

Energy efficiency of internal combustion engines is of major economic and environmental importance. Significant fuel saving (~50 %) can be achieved by operating these engines at high air-to-fuel ratios, in contrast to the currently used stoichiometric ones. However, under these lean (oxygen rich) conditions traditional three-way catalysts are unable to reduce NOx to an increasingly lower level required by federal regulations. Therefore, the demand for new catalyst materials that are able to eliminate NOx from the automotive exhaust gas stream is high. Alkaline and alkaline earth metal oxide-based NOx storage-reduction catalysts are the most promising materials for the reduction of NOx under lean conditions. The basic scientific understanding of the functioning of these materials, however, is still rather poor. Addressing the interactions of the active NOx storage phase and support materials, and its consequences on the NOx storage/release processes are critically important. Developing catalysts that can operate under the demanding conditions of lean-burn engines (high water content, presence of both CO_2 and SO_2) is still a great challenge. Addressing the fundamental scientific issues of this emerging technology is critical in the successful development of new catalytic systems.

Future Plans

After completing our studies on the BaO/alumina systems we will investigate the effect of different support materials on the NOx chemistry of BaO. We will also extend our studies on the alumina-based model NOx storage systems using scanning probe microscopy techniques (STM, and/or AFM) to obtain atomically resolved information about the structures formed in the preparation of these model systems, as well as, more importantly, about the structural changes that are taking place during NOx chemistry in these systems. We also plan to investigate the influences of H_2O, SO_2 and CO_2 on the interaction of NOx with the nano-structured base-metal oxide, as well as the planar oxide supports.

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DE-FG02-05ER15700 **Wilfred T. Tysoe**

Investigating the Reaction Pathways for Vinyl Acetate Formation on Pd(111) and Gold-Palladium Alloys

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Goal

Understand the elementary steps in the reaction pathways for the palladium and palladium/gold catalyzed formation of vinyl acetate monomer (VAM) by probing the surface chemistry in ultrahigh vacuum and at moderate pressures. Establish how the composition and local atomic configuration of the alloy influences the elementary steps that control activity and selectivity. Use density functional theory (DFT) calculations to understand adsorption on Pd(111) and Au/Pd alloys and explore reaction pathways.

Recent Progress

The formation of vinyl acetate monomer (VAM) from ethylene, acetic acid and oxygen is catalyzed by supported palladium and palladium gold alloys, where the selectivity improves from ~85% on palladium to over 90% on the alloy. Two reaction pathways have been proposed [1,2]. In the first [1], adsorbed acetate species react with ethylene to form an acetoxyethyl-palladium intermediate that decomposes via β-hydride elimination to yield VAM. An alternative pathway suggests that a vinyl species is initially formed from ethylene and inserts into a surface acetate species to form VAM directly [2]. The elementary step of this reaction is probed by monitoring the infrared spectrum of adsorbed acetate species on Pd(111) when pressurized by ethylene (P(ethylene) ~ 1×10^{-4} Torr). Acetate species are titrated from the surface by reaction with ethylene and separate temperature-programmed reaction (TPR) experiments reveal that this results in VAM formation. Reaction with C_2D_4 reveals a strong deuterium isotope effect (k_H/k_D~6). An infrared spectrum collected of the surface immediately following complete removal of the acetate species reveals the formation of an acetoxyethyl-palladium intermediate when reaction is carried out using C_2D_4, providing support for the Samanos pathway [1]. Measuring the acetate titration rate using ethylene isotopomers, 1,2-dideuteroethylene and 1,1-dideuteroethylene reveals that they have different isotope effects. Such behavior cannot be explained using the Moiseev pathway. However, if it is assumed that the acetoxyethyl-palladium intermediate of the Samanos pathway blocks the adsorption of ethylene, this difference can be explained by the relative β-hydride elimination rates of the different d_2-acetaoxyethyl-palladium isotopomers. Finally, the reaction pathway was explored using density functional theory (DFT), which showed that the elementary-step activation energies of the Moiseev pathway are consistently higher than those for the Samanos route, in accord with the above conclusions. The calculations further predicted an activation energy for the rate-limiting β-hydride elimination step of ~60 kJ/mol. This value was determined experimentally by measuring the rate of acetate titration by ethylene as a function of sample temperature yielding a value of ~55 kJ/mol, in excellent agreement with calculation. The results provide compelling evidence for VAM synthesis proceeding via the Samanos pathway.

In order to investigate the effect of alloy formation on VAM synthesis, gold palladium alloys are formed by depositing several (~5 monolayers) of gold on a clean Pd(111) substrate and heating to various temperatures. This causes gold to diffuse into the bulk of the Pd(111) sample to form alloys, where the gold to palladium ratio in the near-surface region on the Pd(111) single crystal can be controlled by varying the annealing temperature, thus allowing the surface chemistry on a wide range of alloy surface to be compared. This system displays no additional low-energy electron diffraction (LEED) features implying that the alloy is relatively disordered. Significant chemical shifts are found in the gold and palladium features by X-ray photoelectron spectroscopy (XPS) confirming alloy formation and these are in good agreement with corresponding bulk alloys. Since the surface energy of gold is substantially lower than that of palladium, the surface of the alloy is expected to be enriched with gold compared to the bulk. This effect is explored using LEED intensity versus beam energy (I/E) curves of various alloys and the data fit as a function of the gold compositions in the outermost and second layers, and the bulk. This reveals that the outermost and second layers are substantially enriched in gold compared to the bulk, as expected. We have examined the surface chemistry of ethylene and acetic acid on Au/Pd(111) alloys. It is found that the degree of ethylene hybridization varies as a function of alloy composition, from π-bonded at high gold mole fractions to di-σ-bonded as the alloy becomes palladium rich. A similar trend is found for acetic acid, which adsorbs molecularly on gold-rich alloys, forms η^1-acetate species for intermediate gold concentrations, and only forms the η^2-acetate species, the reactive species for the formation of VAM on clean Pd(111), at gold mole fractions in the near-surface region below ~10%. Studies of the reaction of ethylene with Au/Pd(111) at room temperature reveal that ethylidyne formation, found to occur on the clean Pd(111) surface, is suppressed by alloying with gold. Ethylidyne is found to form on the clean palladium surface after acetate species have been titrated by ethylene. Since this can only be removed by total oxidation, suppression of ethylidyne formation may be one of the reasons for the increased selectivity of the alloy.

The kinetics of reaction between ethylene and acetate species have also been measured on various Au/Pd(111) alloys as a function of temperature. These experiments were carried out for relatively low gold concentration, where acetate species were found to form. This showed a considerable reduction in reaction activation energy from ~60 kJ/mol for the clean surface to a low value of ~30 kJ/mol. This further implies that alloying with gold not only suppresses the formation of side products that potentially lead to total combustion products (ethylidyne), but also lowers the surface reaction activation energy, possibly further leading to higher selectivity.

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DOE Interest

Understanding the fundamental surface catalytic pathways and the influence of alloying is central to improving the selectivity and activity of catalytic reaction pathways. Linking such fundamentals studies to DFT calculations will provide additional insights into the bonding and chemistry of reactants on surfaces and will also provide stringent tests of the precision of DFT calculations in predicting adsorbate geometries and energetics, as well as elementary step activations energies.

Future Plans

We will supplement our low-energy electron intensity versus beam energy (I/E) analyses of the structure and composition of the outermost layer of the Au/Pd(111) alloy with low-energy ion scattering (LEIS) experiments to directly measure the composition of the outermost layer and carry out scanning tunneling microscopy experiments to confirm these results and measure the gold and palladium distribution. Similar surface science and structural and composition measurements will also be made on Pd(100) surfaces to examine the structure sensitivity of the reaction. The goal is to identify the nature of the active sites on the (111) and (100) surfaces and to understand the origin of this activity and to disentangle electronic and structural effects. DFT calculations will be carried out, both for clean surfaces and for alloys to rationalize the experimental results and to gain insights into how accurately DFT predicts these data. This work will be expanded to examining alloy surfaces to gauge the effect of surface versus subsurface gold on the catalytic activity of the alloy systems. This work will provide fundamental insights into the origin of the increased activity and selectivity of alloy catalysts for the synthesis of VAM.

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DOE DEF-G02-93ER14350 **Israel E. Wachs**

Propane Oxidation to Acrylic Acid and Propane Ammoxidation to Acrylonitrile over Mixed Metal Oxide Catalysts

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Goal

Determine reaction mechanisms and catalyst molecular/electronic structure-catalytic activity/selectivity relationships for activation of propane and its derivatives (propylene) to valuable intermediates (acrolein and acrylic acid) over well-defined model supported vanadia-based catalysts.

Recent Progress

Molecular/Electronic Structures and Surface Acidic/Redox Characteristics of Supported Vanadia Catalysts: An *in situ* UV-vis spectroscopic method, coupled with Raman spectroscopy, was developed to quantify the speciation of the surface vanadia species on oxide supports. For the first time, it was found that (i) isolated surface VO_4 species are almost exclusively present on all oxide supports at low surface vanadia coverage (<2 V/nm^2), (ii) both isolated and polymeric surface VO_4 species coexist at intermediate surface vanadia coverage (2-6 V/nm^2), and (iii) polymeric surface VO_4 species are the dominant surface vanadia species at monolayer surface coverage (~8 V/nm^2). Above monolayer coverage, crystalline V_2O_5 nanoparticles are also present on the surface vanadia monolayer. Pyridine-IR chemisorption studies revealed that the isolated surface VO_4 species only possess Lewis acid character and that the appearance of Bronsted acid sites coincides with the formation of polymeric surface VO_4 species. The crystalline V_2O_5 nanoparticles possess both Lewis and Bronsted acid sites. Corresponding H_2-TPR measurements showed that the polymeric surface VO_4 species reduce more easily than the isolated surface VO_4 species, and that the crystalline V_2O_5 nanoparticles are the least reducible. This is the first time that it has been possible to directly relate the molecular structures of the surface vanadia species with their acidic and reducibility characteristics.

Oxidative Dehydrogenation (ODH) of Propane to Propylene: The propane ODH TOF values are (1) constant below monolayer coverage for a given support revealing, (2) increase in the presence of secondary surface metal oxide additives, and (3) vary dramatically when the specific oxide supported is altered. The constant TOF for the surface VO_4 species with surface coverage also reveals that (*i*) only one surface VO_4 site is involved in propane ODH, (*ii*) propane activation is not related to presence of bridging

V-O-V bonds (*iii*) propane activation is not related to the terminal V=O bond length, (*iv*) the acidity of the surface vanadia species doesn't affect propane activation, (*v*) the reducibility of the surface vanadia species doesn't affect propane activation.

The crystalline V_2O_5 nanoparticles present above monolayer are not able to activate propane, but are active in further oxidation of propylene to COx. The significant effect of the specific oxide support on the TOF values demonstrates that the bridging V-O-Support bond is the catalytic active site and that the support cation controls the electron density on the bridging oxygen. The promotion of the supported vanadia catalysts by the inactive surface WOx and MoOx promoters shows that propane is adsorbing in a precursor state on these secondary surface sites that are supplying the weakly adsorbed propane to the catalytic active vanadia sites.

Oxidation of Propylene to Acrolein over Model Supported Vanadia Catalysts: Conversion of propane to oxygenates proceeds via the propylene intermediate and, consequently, it is critical to also investigate the oxidation of propylene to oxygenates in order to better understand how this catalytic reaction proceeds. Similar to propane ODH, the acrolein formation TOF varied by a factor of $\sim10^2$ with the specific oxide support, which reflects the catalytic role of the bridging V-O-Support bond. Among the supported V_2O_5 catalysts (V_2O_5/ZrO_2, V_2O_5/TiO_2, V_2O_5/Nb_2O_5, V_2O_5/Al_2O_3 and V_2O_5/SiO_2), only supported V_2O_5/Nb_2O_5 was found to be highly selective towards production of acrolein. Thus, the detailed investigation of the selective oxidation of propylene to acrolein was undertaken over well-defined model supported V_2O_5/Nb_2O_5 catalysts.

Whereas propane ODH requires only one O atom to remove the two H atoms, the selective oxidation of propylene to acrolein requires two O atoms (one to remove the two H atoms and a second to form the C=O functionality). Not surprisingly, a plot of log [rate of acrolein formation] vs. log [V atoms/g] that yields a slope of ~2, which demonstrates the increase in acrolein TOF is solely related to the requirement of two surface VO_4 sites. This also implies that the Bronsted acid sites associated with the polymeric surface VO_4 species don't affect the selective oxidation of propylene to acrolein. This was further confirmed by the addition of secondary acidic WOx species did not affect the propylene consumption TOF.

Mechanistic studies reveal that the surface allyl, H_2CCHCH_2*, is the most abundant reaction intermediate (mari) during propylene oxidation. Isotopically labeled propylene, C_3D_6 and C_3H_6, demonstrated that the rate-determining-step (rds) involves breaking of the terminal allyl C-H bond with the oxygen insertion step following the rds. Studies with isotopically labeled oxygen, $^{18}O_2$ and $^{16}O_2$, showed that the oxygen inserted into the surface intermediate exclusively comes from the catalyst lattice and not from gas phase molecular O_2 (Mars-van Krevelen mechanism). Gaseous O_2, however, is required to remove the H* as H_2O formed upon propylene dissociative chemisorption (Langmuir-Hinshelwood). Thus, for the first time a combined Langmuir-Hinshelwood-Mars-van-Krevelen (LH-MvK) mechanism has been discovered.

DOE Interest

The conversion of inexpensive propane to valuable intermediates is currently of great industrial interest since it would reduce manufacturing costs, fixate the carbon in a usable form and avoid the combustion or flaring of propane to global warming CO_2 emissions. The synthesis of well-define model catalysts and *in situ*/*operando* spectroscopy characterization studies are developing new general methods for synthesizing and investigating mixed metal oxide catalysts and their reactions. The current fundamental studies are also advancing the catalysis science of mixed metal oxide catalyst systems that find wide applications in the energy industry.

Future Studies

The propylene oxidation studies are being successfully extended to the selective oxidation of propylene in the presence of steam to yield acrylic acid ($H_2C=CHCOOH$), which is the next reaction step in the conversion of propane to valuable intermediates.

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Novel Nano-Dispersed Early Transition Oxide Catalysts on Mesoporous Silica

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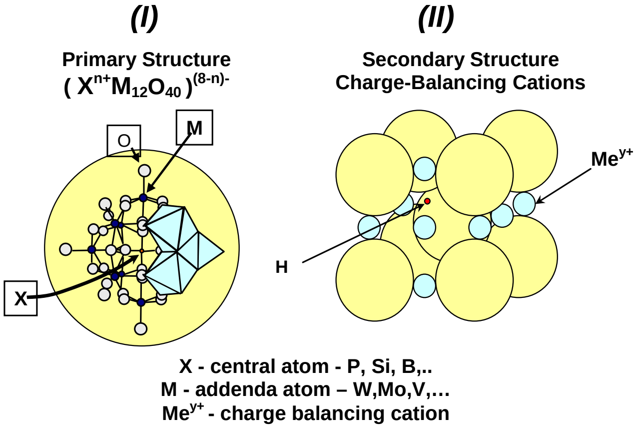
Dispersion of catalyst particles on high surface area supports with precise control of domain size, composition, and atomic level connectivity are critical for understanding the fundamental properties of the catalysts and for developing efficient catalysts. To date, catalysts particles are dispersed on the support using controlled infiltration or controlled surface hydrolysis. Although these methods are widely investigated, more development effort is needed to synthesize the nano structured catalysts with better control of structure, composition, and spatial dispersion. We recently developed new approaches to achieve such control and these will be described in this poster along with catalyst characterization and kinetics studies.

Polyoxometalate (POM)-based clusters exhibit well-defined size and atomic connectivity, diverse chemical composition, and relatively high stability. Thus, they represent ideal structures to examine rigorously the effects of chemical composition, atomic connectivity, and cluster size on acid and redox properties, as well as the catalytic consequences of these properties in catalysis by transition metal oxides. These materials crystallize into secondary structures (structure II in the below figure) with intracrystalline sites accessible to different extents by reactants, and with transition states of varying size and polarity. We have addressed these challenges by developing site titration protocols that allow measurements of the number of acid sites accessible during catalysis and by exploring synthetic approaches that isolate intact POM Keggin clusters on inert mesoporous supports with minimal fragmentation of Keggin clusters into smaller lacunary structures. Highlights from this work will also be presented in the poster.



Primary and secondary structures in polyoxometalates.

DE-FG02-03ER15478 **Jason F. Weaver**

Non-Thermal Reactions of Gas-Phase Oxygen Atoms with Atoms Adsorbed on Transition Metal Surfaces

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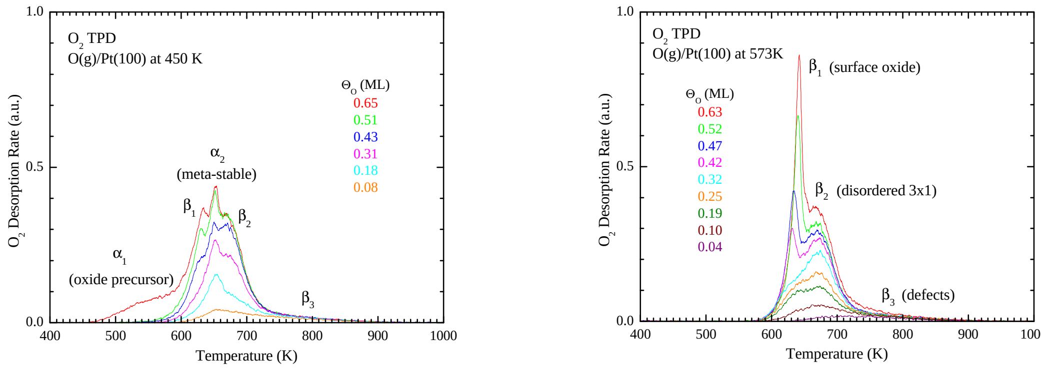
Goals

The reactions of gas-phase oxygen atoms at transition-metal surfaces are important in catalytic oxidation processes occurring at high temperature and with plasma activation. Due to the strong bonding of oxygen on metals, the collision of an oxygen atom with a metal surface results in significant energy release that can stimulate non-thermal reactions such as direct atom abstraction and adsorption-induced reactions. A primary goal of this project is to elucidate the mechanisms and quantify the kinetics of non-thermal reactions between gas-phase oxygen atoms and atoms adsorbed on transition-metal surfaces, and to further the fundamental understanding of the effects of adsorbate and surface properties on the predominant non-thermal processes. Additionally, oxygen atom beams are being utilized to oxidize transition metal surfaces in ultrahigh vacuum. This approach enables detailed characterization of high-coverage surface oxygen phases that affect catalyst performance under realistic conditions, but which have not been widely explored under well-controlled conditions.

Recent Progress

Oxidation of Pt(100). We have recently completed investigations of the oxidation of the Pt(100)-hex-*R*0.7° surface by gaseous oxygen atoms. Key findings that have emerged from this work are 1) that a meta-stable phase develops at low surface temperature, and transforms to a surface oxide, and 2) that an oxygen precursor species mediates the transition from surface to bulk oxide growth. The O_2 TPD spectra shown below illustrate that population of the meta-stable phase is enhanced relative to the surface oxide when adsorption is conducted at 450 K versus 573 K. The meta-stable phase converts to the surface oxide more rapidly at higher temperature, resulting in a more intense desorption peak from the surface oxide after adsorption at 573 K.



O_2 TPD spectra following oxygen atom adsorption at surface temperatures of 450 K and 573 K

Further increasing the oxygen atom exposure results in the growth of Pt oxide particles, with concurrent diminution of the low temperature desorption feature labeled as α_1. This oxygen feature appears to originate from oxygen atoms adsorbed on top of the surface oxide. We have recently shown that this adsorbed state serves as a precursor in the formation of bulk oxide particles, and developed a kinetic model based on this idea that quantitatively reproduces the initial kinetics of bulk oxide formation. The model assumes that oxygen atoms adsorb on top of the surface oxide, and that a kinetic competition exists between desorption of the precursor oxygen and reaction with the surface oxide to produce a bulk oxide nucleus. By analyzing rate data, we find a fourth-order dependence of the bulk oxide formation rate on the coverage of the precursor oxygen species, which implies a critical size for oxide nucleus formation involving four oxygen atoms adsorbed on top of the surface oxide. This general mechanism may be applicable for describing the transition from surface to bulk oxide growth on other transition metal surfaces as well. We are currently investigating this possibility.

Hot precursor reactions during O-atom collisions on D-covered Pt(100). We also recently completed a study of the reactions induced by the collisions of gaseous oxygen atoms with deuterium chemisorbed on Pt(100). These collisions result in facile production of D_2O at surface temperatures as low as 90 K, with about 20% of the heavy water desorbing during the low temperature reaction. The production of water at such low temperatures must occur by non-thermal reactions. We find that the D_2O production kinetics is well described by considering that hot OD radicals, produced by direct reactions between incident O atoms and adsorbed D atoms, serve as intermediates in reaction pathways that produce water. Due to the high exothermicity of OD production, the OD radicals are highly energetic and react readily with adsorbed D and OD species to generate D_2O. This work demonstrates that gaseous oxygen atoms can efficiently access low temperature reaction pathways during collisions with adsorbate-covered metal surfaces.

DOE Interest

Understanding of the mechanisms that govern the surface reactions of gaseous oxygen atoms, and quantification of the associated kinetic parameters, is important to the design and modeling of catalytic processes that occur under extreme conditions, including processes such as surface combustion and plasma-assisted oxidation catalysis. Also, understanding the growth and properties of high-concentration oxygen phases on late transition metal surfaces is important for describing many applications of oxidation catalysis, such as remediation of exhaust gases in lean-burn engines, fuel processing and selective oxidation of organic compounds.

Future Plans

Atom abstraction from Pd(111) and other metal surfaces. We are currently investigating the interactions of gaseous oxygen atoms with adsorbed species on Pd(111). Through experiments with oxygen isotopomers, we have preliminary evidence that gaseous oxygen atoms directly abstract oxygen atoms adsorbed on Pd(111) at surface temperatures below 150 K. We plan to further characterize this non-thermal reaction, and pursue studies of oxygen-induced abstraction of other adsorbed atoms, including D and S, on Pd(111). We also plan to investigate similar reactions on other late transition metal surfaces. The general aim is to elucidate the non-thermal reaction pathways and mechanisms and determine how adsorbate and surface properties affect the reaction kinetics.

Growth and reactive properties of oxygen phases on transition metal surfaces. We also plan to continue investigating the mechanisms for oxidation of late transition metal surfaces, and the reactive properties of the various oxygen phases that develop. Our investigations of Pt(111) and Pt(100) oxidation reveal common characteristics in the progression of oxygen phases leading to bulk oxide growth, and the oxidation of Pd(111) also exhibits similar trends. A key aim of this effort is to determine the mechanisms governing surface oxidation, and establish a more general description of the oxygen phase development on various metal surfaces. We will also continue to study the reactive properties of the high-coverage oxygen phases that form on these surfaces using probe molecules such as CO, NO and small hydrocarbons. We aim to obtain insights for understanding the origins for reactivity differences among the various oxygen phases. Such information is useful for understanding catalytic behavior of transition metal surfaces under realistic conditions.

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DE-FG02-04ER15587 **J. M White and C. B. Mullins**

The Surface Chemistry of Size-Controlled Oxide-Supported Ir Nanoclusters

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Goal

Our primary goal is to study the basic chemistry of size-controlled, oxide-supported nanoclusters. We are particularly interested in investigating supported iridium clusters to activate C-H and C-halogen bonds. We are also interested in exploring the promotional effect of a second metal on/in iridium to form bimetallic nanocluster catalysts.

Recent Progress

Preparation of Iridium and Gold Decorated Metal Oxide Surfaces: Using a commercial nanocluster source (the Nanogen® source and the MesoQ® mass filter by Mantis) purchased through this grant, we have been able to reproducibly prepare three different types of model catalysts for further study: (i) size-selected iridium nanoparticles supported on $TiO_2(110)$, (ii) size-selected bimetallic iridium-gold clusters supported on $TiO_2(110)$, and (iii) size-selected iridium nanoparticles supported on Au(111). We have also conducted surface chemical studies of gold particles supported on $TiO_2(110)$ as well as reactivity studies of the Au(111) surface.

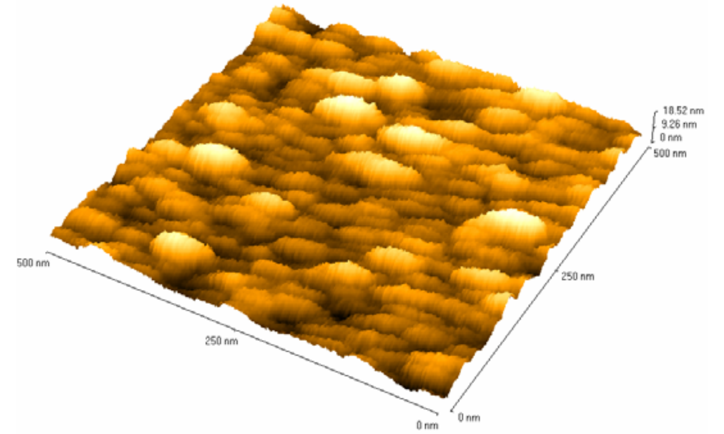

Figure 1. AFM Image of Ir/TiO_2 (110) showing particles with 4-6 nm diameter

Physical and Chemical Characterization of Supported Ir Nanoclusters: Both in-situ and ex-situ physical characterization of many of the samples we prepared were performed using XPS, SEM, EDX, AFM, and AES to determine the structure of the ensemble of nanoparticles. For example, Fig. 1 shows an AFM image of 4-6 nm (diameter) iridium nanoparticles supported on $TiO_2(110)$ (equivalent of 10 monolayers of Ir was deposited). Fig. 2 shows an SEM image of bimetallic iridium-gold nanoclusters supported on $TiO_2(110)$. The accompanying table shows the elemental surface composition. In order to chemically characterize the various samples, we performed *in situ* temperature programmed desorption (TPD) measurements after exposure to molecules such as oxygen, hydrogen, carbon monoxide, and water. Surprisingly, the size-selected iridium nanoparticles supported on titania appeared largely inert based on a comparison with the Ir-bare titania samples. We speculate that the Ir nanoparticles might be migrating sub-surface due to strong metal-support interactions. This led us to prepare iridium nanoclusters on a gold single crystal [Au(111)]. We deposited iridium nanoparticles (coverages ranging from 0.5 ML–10 ML) on Au(111) and performed similar TPD measurements to those performed on Ir/TiO_2(110). Results from these measurements also suggested that the iridium nanoparticles were fairly inert. These results are quite interesting (and puzzling) considering the aggressive chemical nature of single-crystalline iridium[1] (especially the highly corrugated Ir(110) surface) and the recent experimental results of a Japanese group studying a few gold layers placed conformally on Ir(111).[2] We have also studied the surface chemistry of TiO_2 supported gold clusters as well as Au(111) including: (i) the reactivity of molecularly chemisorbed oxygen with CO on TiO_2 supported gold nanoparticles at low temperature, (ii) we have shown that water is directly involved in enhancing CO oxidation on atomic oxygen covered Au(111) at 77 K, and finally, (iii) we have demonstrated the selective oxidation of ammonia to nitrogen on atomic oxygen covered Au(111).

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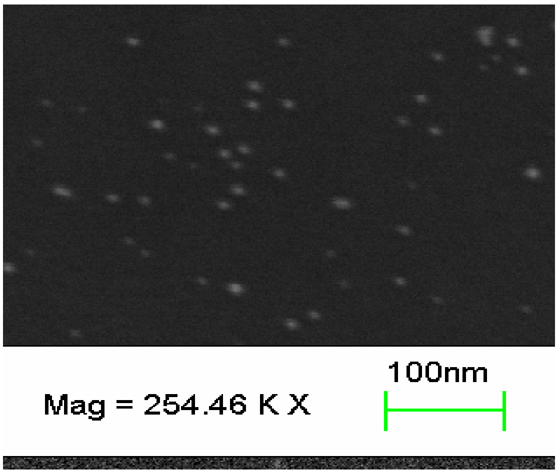

Figure 2. SEM Image of Ir-Au Nanoparticles

Table. EDX Analysis of Ir-Au Nanoparticles (shown in Figure 2)

Elt.	Line	Intensity c/s	Conc. wt.%	Comp. Atom %
C	Ka	0.00	0.000	0.000
O	Ka	11.35	36.30	64.029
Ti	Ka	22.70	60.12	35.451
Ir	Ma	1.09	1.913	0.281
Au	Ma	0.89	1.667	0.239
	Total		100	100

DOE Interest

There is great interest regarding the effects of size and composition of metallic particles supported on metal oxide materials and their surface chemical properties.

Future Plans

Thus far we have used rutile titania and gold as our support materials; in the future, we intend to prepare samples using alumina and silica as supports. By repeating the same set of experiments we have performed on the titania supported samples, we hope to get information about the influence of support materials on the surface chemistry and morphology of iridium nanoparticles. We will also study the adsorption and desorption of inorganic and organic substances such as carbon monoxide, water, ammonia, methanol, methane, and carbon tetrachloride. Additionally, we plan to capitalize on the combination of iridium's relative ease of breaking bonds and gold's relative ease of releasing adsorbed species, to design bimetallic nanoparticles of iridium and gold that are capable of unique chemistry.

Publications Acknowledging DOE (2005-2007)

- "Physical Characterization of Ir Nanoparticles Deposited on TiO_2(110)," Rotimi A. Ojifinni, Jinlong Gong, J. Mike White, and C. Buddie Mullins, in preparation.
- "Desorption Kinetics and Oxidation of Methanol on Clean and Atomic Oxygen Pre-covered Gold," Jinlong Gong, David W. Flaherty, Rotimi A. Ojifinni, J. Mike White, and C. Buddie Mullins, *Journal of Physical Chemistry C* to be submitted in April 2007.
- "Water Enhanced Low Temperature CO Oxidation and Isotope Effects on Atomic Oxygen Covered Au(111)," Rotimi A. Ojifinni, Jinlong Gong, Tae S. Kim, J. Mike White, and C. Buddie Mullins, *Journal of the American Chemical Society* to be submitted in May 2007.
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DEFG02-88ER13864 **John T. Yates, Jr.**

Li Promoter Action on CO and N_2 Chemisorption and Dissociation on Ru Single Crystal Surfaces

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Goal

To use transition metal single crystal surfaces as model catalytic surfaces, exploring the role of atomic step sites on the surface chemistry of important feedstock molecules and the role of an alkali metal promoter atom (Li).

Recent Progress

The promotion of the dissociation of CO and N_2 on Ru model catalyst surfaces has been investigated using temperature programmed desorption and infrared reflection absorption (IRAS) methods.

It has been found that atomic step sites on the Ru(109) surface are the active sites for CO dissociation[1,2]. Using Li atoms as promoters of dissociation, it is found that Li exhibits a dipole moment at zero coverage of 10 D on the atomically-smooth Ru(001) surface and that on the atomic step sites of Ru(109) the dipole is screened by the steps giving a dipole moment of only 6 Debye [3]. Despite the screening by steps, Li actively promotes CO dissociation at about 500 K. Evidence (IRAS) for a CO_xLi_y complex is found on Ru(001), but not on Ru(109), presumably because bonding of CO and Li at the step sites prevents complex formation[4].

The thermally-activated dissociation of N_2 has been shown to occur exclusively on atomic step sites and the activation energy for dissociation has been measured as 0.26 ± 0.05 eV. The N atoms produced are associated with the atomic step sites and recombination occurs near 550 K [5]. By artificially dissociating adsorbed N_2 on terrace sites, an additional recombination process occurs beginning at about 400 K, and is attributed to the N(a) + N(a) process on the flat terrace sites [6]. Using measurements of the N-N stretching frequency, we could separate N_2 species present on atomic step sites from N_2 species on terrace sites, finding that N_2 bonds primarily by a σ-donor mechanism [7]. DFT investigations indicate that on atomic step sites, N_2 species bound through both ends of the molecule will form with greatly reduced N-N bond energies compared to σ-bonded species, and these may be the species which proceed to dissociation. They are unobserved by IRAS[7].

DOE Interest

Alkali metal promoter atoms are used in the catalytic conversion of CO to hydrocarbons and in the conversion of N_2 into ammonia. It is thought that the local electric field associated with an alkali promoter atom is responsible for its action in lowering the activation energy barrier for desirable catalytic surface reactions. Thus, understanding how this happens should be of generic interest to DOE in its research program on catalysis. Since the active sites for dissociation for CO and N_2 on Ru surfaces are those with the smallest Ru-Ru coordination number (atomic steps and kinks), it is important to understand how alkali metal atoms interact with these active sites on model stepped single crystal surfaces, and to understand the behavior of active sites influenced by alkali metal adsorbates. This work has been done using surface probes which are specific for understanding these issues, namely the measurement of the kinetics of thermal desorption, the measurement of the vibrational frequency of the molecules upon intereaction with step sites, terrace sites and Li atoms, and the measurement of the surface dipole moment of the Li promoter atoms.

Future Plans

We plan to change the program to one focused on the activation of C-H bonds by metals. This research will be done using our newly-discovered method for detecting the spillover of atomic hydrogen from C-H bond scission onto a high surface area semiconductor surface. A very sensitive optical method will be employed to monitor the formation of conduction band electrons from spilled-over hydrogen atoms. The temperature dependence of the rate of hydrogen spillover will be used to monitor the rate of C-H bond scission on metals supported on the semiconductor support.

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CATALYSIS SCIENCE INITIATIVE: Molecular Level Design of Chiral Heterogeneous Catalysts

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Goals:

The main goal of this project is to determine the mechanisms by which enantioselectivity can be bestowed on heterogeneous catalysts. Specifically, chirality is to be imparted to achiral surfaces either by exposing chiral planes or by using chiral modifiers.

DOE Interest:

Enantioselectivity is critical in the production of numerous fine chemicals for bioactive applications such as pharmaceuticals. Chiral heterogeneous catalysis has a number of attractive features to offer for its use in fine chemical synthesis, but has so far not be incorporated in any commercial process. This is mostly due to the difficulty in designing such processes without an understanding of the parameters that control chirality and enantioselectivity on surfaces. The basic knowledge generated from the studies being carried out by our research team is expected to advance the development of heterogeneous chiral catalysis, and in more general terms, selectivity in catalysis.

Research Plan:

The hypothesis underpinning our collaborative research effort is that there are three possible origins to chirality and enantioselectivity on catalytic metal surfaces:

- chirality arising from 1:1 interactions between the reactant and individual adsorbed chiral molecules, and
- chirality arising from adsorbates that form long-range chiral ensembles on the surface,
- natural chirality arising from the atomic structure of the metal surface,

Our collaborative program is aimed to understand the relative importance of each of these three mechanisms in enantiospecific adsorption and catalytic reactions.

Recent Progress:

In order to understand the 1:1 modifier:reactant interaction mechanism for imparting chirality on surfaces, our studies have focused on the use of infrared spectroscopy to characterize the adsorption of cinchonidine and other related modifiers in situ on Pt surfaces. In general, we have concluded that the enantioselective properties of the catalyst are defined by the nature of the adsorption of the chiral modifier, and that those in turn are influenced by the details of the cinchona/Pt system, by parameters such as the concentration of the modifier in solution, the type of solvent used, and the nature of the gasses dissolved in the liquid phase.

Vibrational assignments for the cinchonidine were first made using a combination of experimental spectroscopic measurements and ab initio computational methods. Several bands in both the IR and Raman spectra were identified as useful in providing information regarding the mode of adsorption of cinchonidine on metal surfaces. It was then determined that the adsorption of the cinchona chiral template on Pt is very sensitive to the concentration in solution: while at low and intermediate concentrations the cinchonidine is bonded with the quinoline ring parallel to the surface, at high concentrations the ring is tilted away from the surface. The optimum enantioselectivity occurs under conditions consistent with a template adsorption geometry having the quinoline ring parallel to the surface.

The influence of dissolved gases on the adsorption of cinchonidine from CCl_4 solutions onto polycrystalline platinum surfaces was also characterized. It was observed that most of the gases studied, which included Ar, N_2, O_2, air and CO_2, neither enhance the adsorption of cinchonidine nor damage the cinchonidine adlayers once they have formed on the surface. On the other hand, H_2 was observed to play a unique role, initially facilitating the uptake of cinchonidine, but later removing some of the resulting adsorbed cinchonidine from the platinum surface. The solvent was also determined to have a strong influence on the adsorption of the chiral modifier on the catalyst surface. In particular, the polarity of the solvent was found to influence the kinetics of cinchonidine desorption into solution in a manner that correlated well with its influence on the enantioselectivity of the chirally modified catalyst. It appears that cinchonidine adsorbs irreversibly on platinum from non-polar solutions such as cyclohexane, but can be easily removed by more polar solvents such as dichloromethane. The evolution of the adsorbed cinchona overlayer upon flushing with different solvents is illustrated in Figure 1. The behavior observed in our studies correlates well with the solubility of cinchonidine in different solvents and with the performance of the cinchona/platinum catalyst in the same solvents.

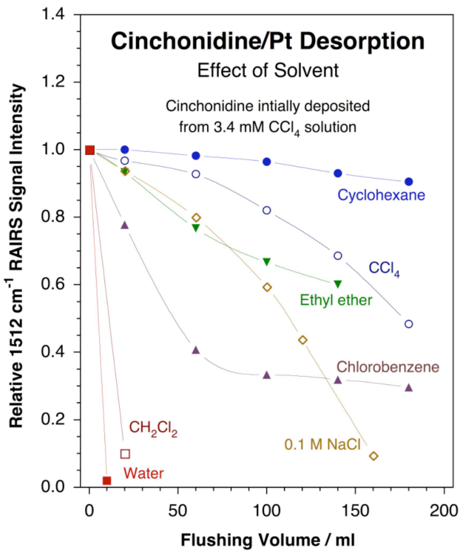
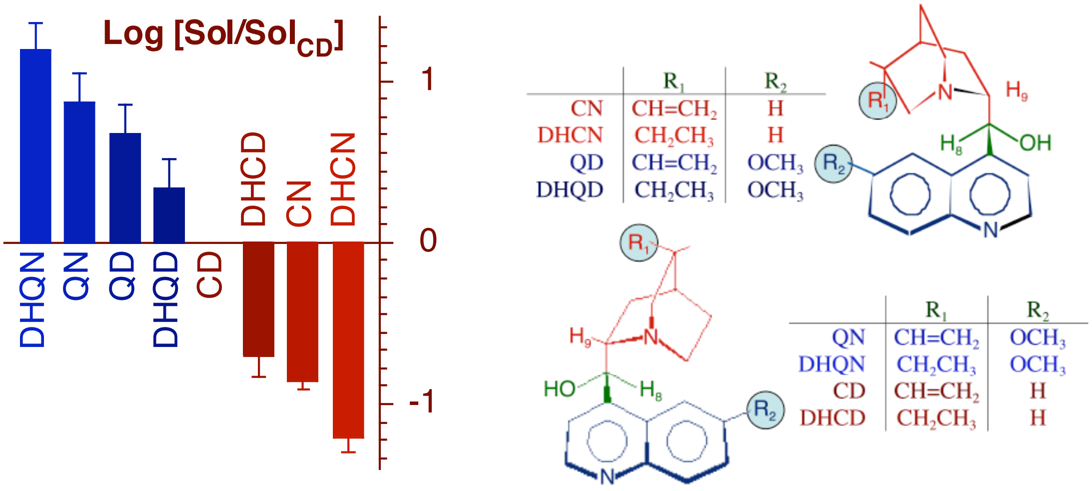


Figure 1. Desorption of adsorbed cinchonidine from a platinum surface into different solvents as a function of rinsing volume. In these experiments the cinchonidine was first adsorbed from a carbon tetrachloride-saturated solution, and then flushed with sequential 20 ml aliquots of the stated solvents. The coverage of the adsorbate remaining on the surface was determined in-situ by following the infrared absorption signal at 1512 cm^{-1}, which corresponds to an in-plane deformation of the quinoline ring. The data show that the desorption kinetics are severely affected by the nature of the solvent, varying from fast desorption in water and dichloromethane to irreversible adsorption in cyclohexane and other alkanes. This trend correlates well with the chirality-imparting ability of cinchonidine for enantioselective hydrogenation reactions on platinum catalysts.

More recent work has been directed at probing the parameters that control the adsorption geometry of the cinchona modifiers, and with that, their efficiency in imparting enantioselectivity to catalytic processes. A comparative study was carried out using cinchonidine, cinchonine, quinine, quinidine, and the dihydro analogs of those four molecules. Significant differences were observed not only in their adsorption properties on the platinum surface, but also in their solubility in a number of solvents. Those differences were deemed due to intrinsic molecular properties associated with their structure, because the relative solubilities of the different cinchona modifiers remain approximately constant in different solvents (Figure 2). Correlations between the conformation of cinchona and their chemical and biological behavior have been identified in several cases already, but have not been properly explained to date. Preliminary NMR and DFT data suggest that the most stable configuration of each molecule may be determined by the steric effects exerted by the groups (vinyl, methoxy) bonded to the outside molecular frame. This behavior may account for the differences in catalytic enantioselectivities reported with cinchonidine versus cinchonine. In a related way, it was determined, also by using NMR, that protonation of the cinchona modifiers affects both their molecular configuration and their chemical performance.



	R$_1$	R$_2$
CN	$CH=CH_2$	H
DHCN	CH_2CH_3	H
QD	$CH=CH_2$	OCH_3
DHQD	CH_2CH_3	OCH_3

	R$_1$	R$_2$
QN	$CH=CH_2$	OCH_3
DHQN	CH_2CH_3	OCH_3
CD	$CH=CH_2$	H
DHCD	CH_2CH_3	H

Figure 2. Solubilities of different cinchona (cinchonine, CN, quinine, QN, quinidine, QD, dihydrocinchonidine, DHCD, dihydrocinchonine, DHCN, dihydroquinine, DHQN, and dihydroquinidine, DHQD) relative to those of cinchonidine (CD). The structures of these compounds are provided in the right-hand side. The numbers reported are averages over the values measured in more than 30 solvents, with error bars that correspond to 95% confidence intervals. No significant variations in relative solubilities were observed as a function of the nature of the solvent, implying that the changes observed are intrinsic to the structure of the cinchona. 2-D NMR experiments lead us to propose a connection between those changes and variations in the configurations available to each compound, which are in turn affected by the end groups in the quinuclidine and quinoline rings, R_1 and R_2 respectively.

In terms of the formation of chiral superstructures on the surface upon adsorption of chiral modifiers, we have shown that such a mechanism is indeed operative with a series of enantiopure compounds, including 2-butoxide, 2-methylbutanoic acid and (1-naphtyl)ethylamine (NEA) as well as a few aminoacids. Several metal surfaces have been used here, including those of Pd(111), Pt(111) and Cu(111) single crystals. The enantioselectivity of these systems has been tested by using (R)- and (S)-propylene oxide as probes, by both quantifying their thermal desorption spectra and identifying the adsorbed species with infrared-absorption spectroscopy.

In general, it has been observed that enantioselective adsorption of the propylene oxides is observed over a narrow range of 2-butoxide coverages near $\theta_{2\text{-ButO}} \sim 1/2$, where it shows a preference for the homochiral surfaces, that is, for surfaces covered with moieties of the same chirality as the propylene oxide probe. This preference can reach enhancement ratios (ER) of about two. An example of the data obtained from these studies, in this case for the adsorption of (S)-NEA on Pt(111), is provided in Figure 3. To note in that figure is the additional contribution from the energetics of the adsorption to the enantioselectivity of the surface. This places NEA as an intermediate case acting as both a 1:1 complex-forming modifier and a templating agent for chiral suprastructure formation.

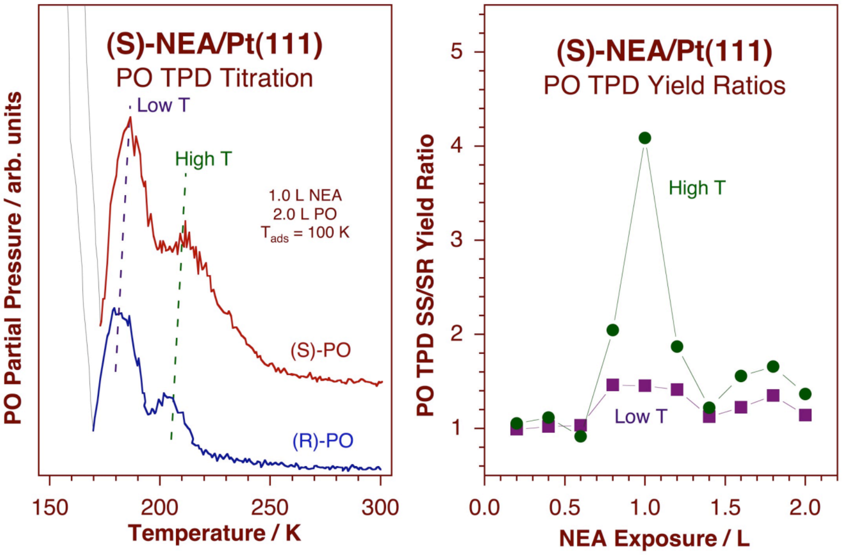


Figure 3. Left: TPD traces for the molecular desorption of (R)- and (S)-propylene oxide (PO) after saturation on a Pt(111) surface predosed with 1.0 L of (S)-(1-naphtyl)ethylamine (NEA). Two peaks are seen in each case, but with different yields and peak maxima due to the enantiopreference of adsorption for (S)-PO on the (S)-NEA templated surface. Right: Plot of the SS/SR yield ratios of (S)- vs. (R)-PO on (S)-NEA covered Pt(111) as a function of exposure of the latter. The contributions from the two TPD peaks were separated to highlight the fact that it is the high T peak the one responsible for the enantioselectivity. This example points to both energetic and entropic contributions to the chirality of the surface.

The effect reported here have proven quite general, except for the case of the adsorption of 2-methylbutanoic acid on Pd(111) (but not on Pt(111)). In order to try to understand this anomaly, the experimental work has been complemented with Density Functional Theory (DFT) calculations. Specifically, since density functional theory calculations show that 2-butoxy and 2-methylbutanoate species exhibit identical chiral footprints, the loss of enantioselectivity of the 2-methybutanoate species on Pd(111) has been explained by the freer rotation of the 2-butyl species in 2-methylbutanoate compared to 2-butoxy species. In order to test this hypothesis, a methyl group was replaced by an NH_2- group, which should bond to the surface to inhibit azimuthal rotation. A series of experiment to measure the chemisorptive enantioselectivity of (R)- or (S)-PO on surfaces modified by 2-aminobutanoic acid, where the PO coverages were measured using beams of propylene oxide by the King and Wells method, revealed that the enantioselectivity was restored. In this case, the variation in enantioselectivity varied as a function of 2-aminobutanoate coverage, also reaching a maximum at ~50% of saturation as found above for 2-butoxide species, and reaching a maximum enhancement ratio of 1.7 ± 0.1.

Experiments were carried out for a number of amino acids to gauge the effect of altering the aminoacid functional group. It was found that there is a slight decrease in ER from 2.0 ± 0.2 to 1.6 ± 0.1 in going from alanine, to 2-aminobutanoic acid to norvaline, where the function group varies in the homologous series, methyl, ethyl to propyl. This implies that the size of the chiral "pocket" is not strongly affected by the length of the alkyl group. Aminoacids with branched side groups (valine and leucine) resulted in a compete loss in enantioselectivity, presumably due to steric hindrance by the bulky, branched side chains preventing the aminoacids from approaching sufficiently close to properly define a chiral pocket. Isoleucine, where branching occurs at the second carbon, exhibits intermediate enantioselectivity (ER = 1.3 ± 0.1).

Further work has proceeded to determine the structure of aminoacids on Pd(111) and to measure their thermal stability, reaction pathways and chemisorptive enantioselectivity. Low-energy electron diffraction (LEED) intensity versus beam energy (I/E) experiments are being used to measure the structure of amino acids. Initial experiments were carried out using a conventional LEED system with an incident electron beam current of ~1 μA. It was however found that aminoacids on Pd(111) are extremely susceptible to damage in the electron beam and completely decompose before an I/E curve could be collected. In order to circumvent this problem, data were collected for glycine and alanine using a system in which the incident beam current is ~200 fA, thus allowing LEED I/E curves to be collected for an electron exposure much lower than the adsorbate coverage, thereby obviating electron beam decomposition problems. Aminoacid surface structures were calculated using density functional theory (DFT) to compare with the measured LEED I/E data.

Additional X-ray photoelectron spectroscopy (XPS) shows that aminoacids adsorb on Pd(111) in both their zwitterionic (~70-80%) and anionic forms (20-30%), where the ratio of each depends only slightly on coverage. Glycine, alanine and proline each thermally decompose at slightly above 300 K by scission of the C-C bond in the aminoacid framework, and evolve CO and CO_2 originating from the carboxylate group. A small amount of the amine is found to desorb, with the amine depending on the nature of the side group in the aminoacid. The majority, however, decomposes to form HCN. These results confirm that the chemisorptive enantioselectivity measurements made above for propylene oxide on various aminoacids were carried out for surfaces covered by a mixture of zwitterionic and anionic forms. The chemisorptive enantioselectivity of propylene oxide was also measured on aminoacid-covered surfaces by monitoring the propylene oxide coverage by TPD, and yielded ER values in good agreement with those found above when using the King and Wells method. Lastly, experiments were carried out to examine the selectivity of β-hydride elimination of (R)- or (S)-2-butoxide species compared to rehydrogenation to yield 2-butanol in the presence of (R)- or (S)-propylene oxide. In this case, propylene oxide acts as the chiral modifier rather than the probe. It was found that, at least on Pd(111), the surface 2-butoxy hydrogenation and β-hydrogenation reactions are enantioselective, with the yield of 2-butanol due to 2-butoxide rehydrogenation increasing when co-adsorbed with propylene oxide of the same chirality. Thus, such experiments should allow us to explore not only how chiral pockets affect the adsorption of chiral molecules but also their subsequent surface reactivity.

Finally, in terms of naturally chiral surfaces, our most recent work has extended the past research to studies of reactivity on these surfaces. Using chiral 2-bromobutane, it was possible to create chiral 2-butyl groups on naturally chiral Cu surfaces, and to show that the kinetics of their β-hydride elimination is enantioselective. The next step will be to investigate the possibility of imprinting chirality on achiral surfaces by using chiral adsorbate agents.

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Poster Presentations Addendum

Characterization of Multidimensional Porous Networks for Membrane Applications

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Abstract

Multidimensional Nanoporous Networks are porous materials with both micropores (d < 2 nm) and mesopores (2 nm < d < 50 nm). Typically porous materials fall into the following categories:

- Zeolite: Microporous alumina silicate
- MCM-41: Mesoporous silica
- SBA-15: Mesoporous silica with micropores in the walls
- PHTS (Plugged Hexagonal Templated Silica): Like SBA-15 with microporous plugs.

Multidimensional porous networks, could be used as model materials for membrane systems which can comprise both micropores and mesopores.

These materials require new careful techniques to separate the microporous and mesoporous components of the structure, in order to give valid estimations of the surface areas and pore distributions. We have developed a combination of three techniques to achieve this purpose. Namely, employing pre-adsorption to separate the mesoporous nature of the materials from the micropore component (<2 nm). Secondly the use of an accurate empirical model to estimate the micropore size distribution of a non-crystalline microporous solids, such as SBA-15.[1,2] Thirdly, incorporating a novel technique which has been developed to measure porous structure of intact membranes and supported catalyst materials. The technique involves a specially designed re-sealable cell in which the membrane can be placed followed by the measurement of high resolution adsorption. This technique has been successfully demonstrated on alumina supported silicalite membranes of differing geometries.[3,4]

SBA-15 samples exhibit high micropore volumes within well-ordered mesoporous silica walls. This could be considered a model material for studying multidimensional nanoporous networks, i.e. membranes. Sequential adsorption techniques used to estimate the external surface area for microporous samples, and a surface area for mesoporous samples with varying micropore volumes.

This sequential adsorption technique can be applied to membranes and other micro-meso-porous systems.

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Transport via Adsorption on Intact Zeolite Membranes

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Abstract

Zeolite membranes promise energy-efficient separations of mixtures that arise in the energy and chemical industries. Optimizing zeolite membrane separation processes requires a good model of transport in membranes, however. Such models require accurate information about the pore sizes and equilibrium sorption properties of real membranes, which may contain crystal defects that affect transport significantly. These defects, which only go part of the way through the membrane in so-called "defect free" membranes, could range from a few nanometers in size up to tens of nanometers. Defects in this size range, if present in sufficient quantity, should be detectable by physical adsorption.

We compare the adsorption properties of intact supported silicalite membranes with those of silicalite powder and alumina supports and find that the support contributes significantly to the quantity adsorbed, presumably due to the relatively large thickness of the support relative the thin membrane. The micropore filling regions of the adsorption isotherms of the powder and supported membrane are nearly identical, suggesting that we can deconvolute contributions from the zeolite and the support by comparing them in the low-pressure region. At higher pressures, however, the supported membranes exhibit a much higher quantity adsorbed than the powders. Despite this difference, no hysteresis is observed in the isotherms, indicating a general lack of mesoporosity (pores 2–50 nm in diameter) in the samples.

Using the measured adsorption isotherms to determine the thermodynamic factors, we estimate the argon transport flux at steady state by assuming surface diffusion with a constant Maxwell-Stefan diffusion coefficient in the support and both a constant and a variable Maxwell-Stefan diffusion coefficient in the zeolite layer. The estimated flux is virtually the same using adsorption data from powders and membranes. For the relatively thin membranes used here, we find that the support exerts a much greater influence on the predicted fluxes for a wide range of values of the ratios of the support to zeolite diffusion coefficients.

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