U.S. DEPARTMENT OF ENERGY | Office of Science

Basic Research Needs for Catalysis Science to Transform Energy Technologies

Introduction/Background

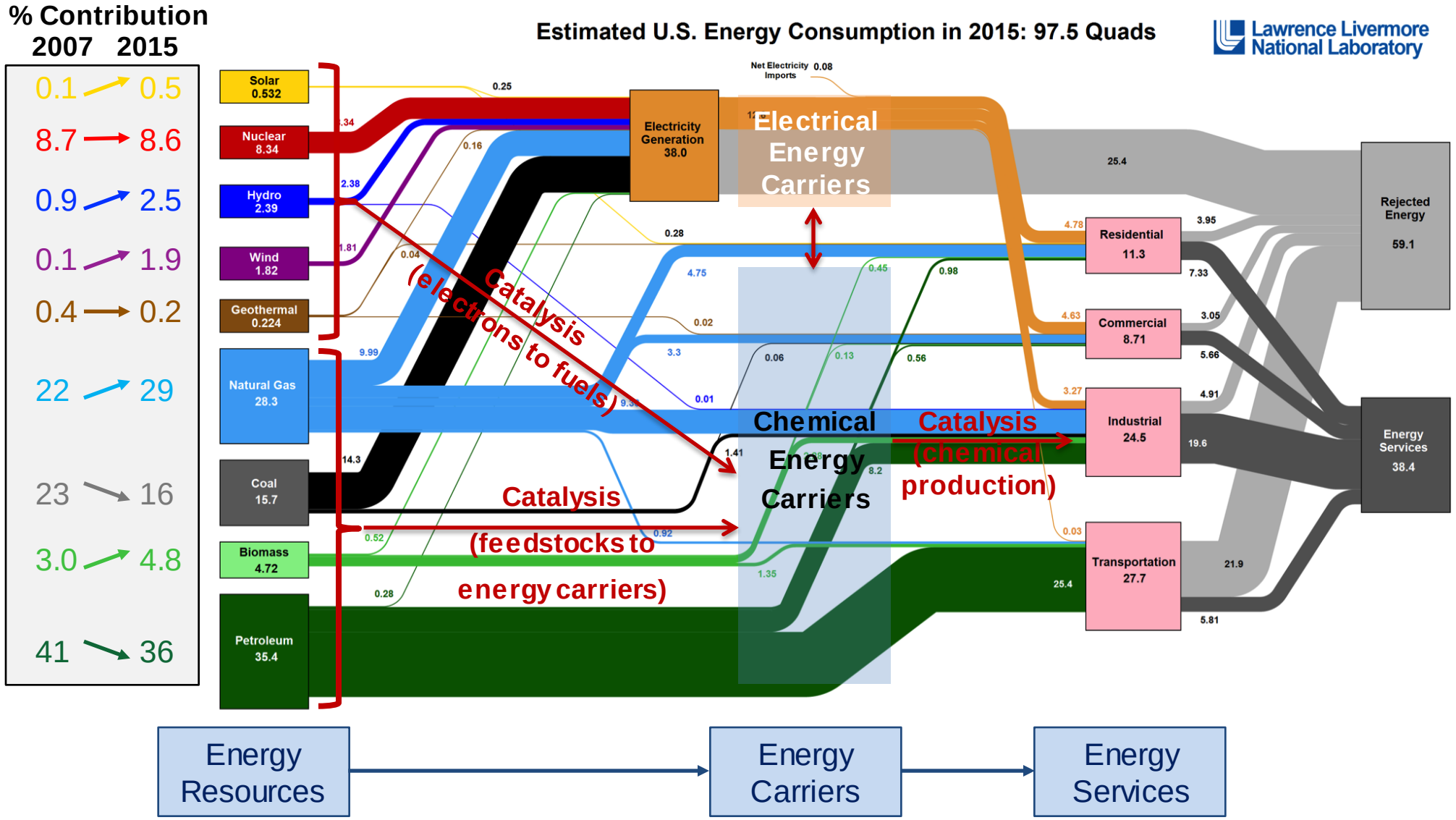
Highlights from May 2017 Workshop

Priority Research Directions

Progress on Final Report

Prof. Carl A. Koval – University of Colorado at Boulder

Changes in Our Energy Landscape Drive the Need for Advances in Catalysis



Impact of New Energy Technologies on the US Chemical Industry

U.S. Shale Just Triggered A Chemical Industry Renaissance

By Tsvetana Paraskova - Jul 03, 2017, 5:00 PM CDT

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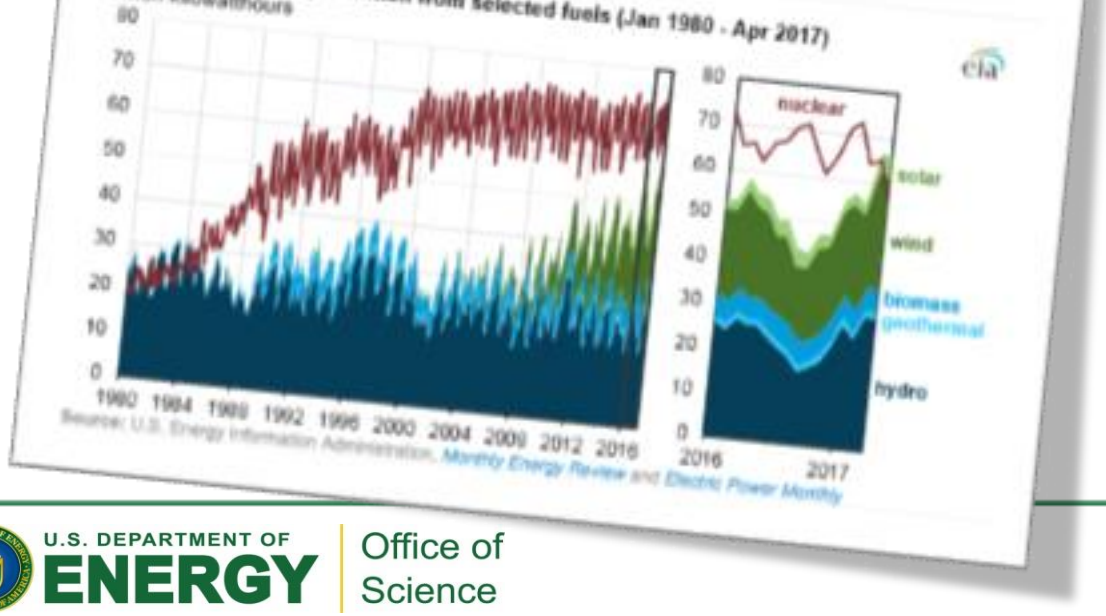
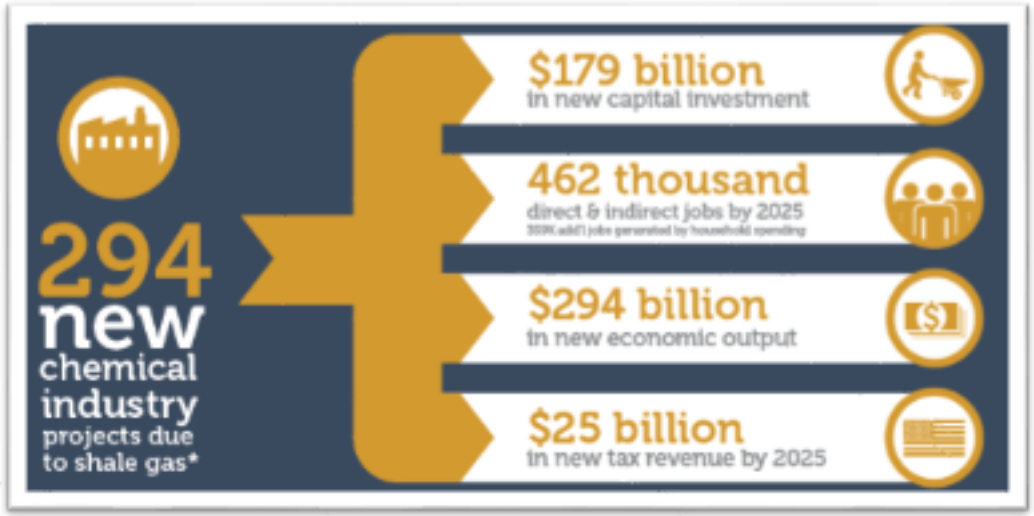
JULY 6, 2017

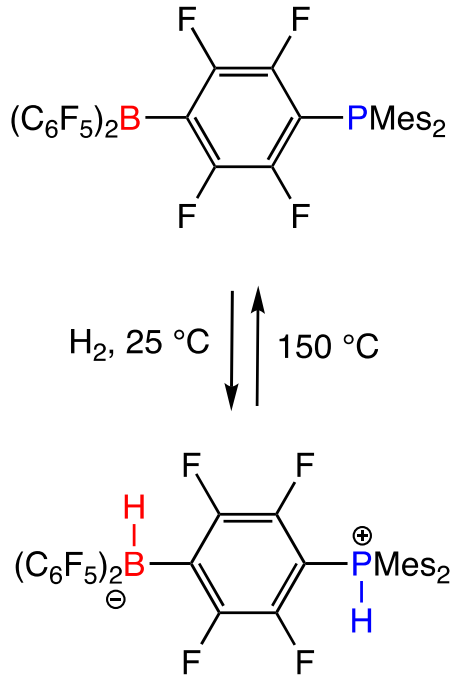
Monthly renewable electricity generation surpasses nuclear for the first time since 1984





New Paradigms in Catalysis Science

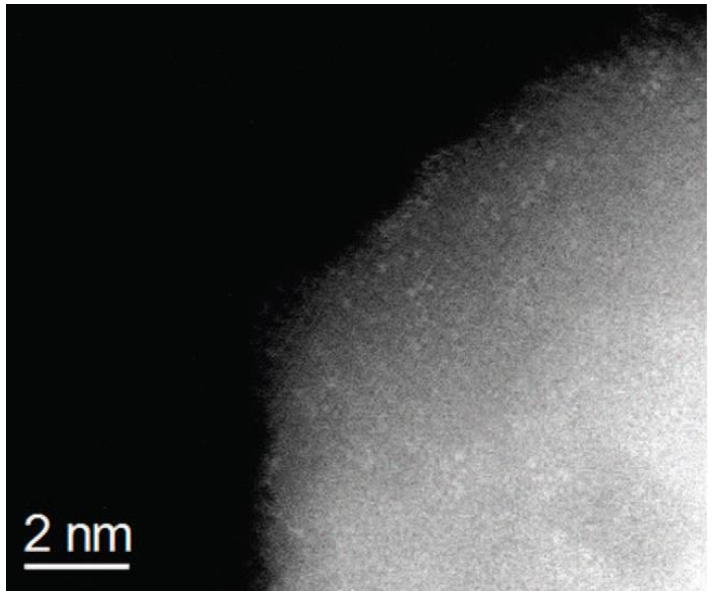
Metal-free redox catalysis using Frustrated Lewis Pairs (FLPs)



Room temperature H_2 activation leads to hydrogenation of unsaturated organic compounds.

Stephan, *Acc. Chem. Res.* **2015**, *48*, 306-316.

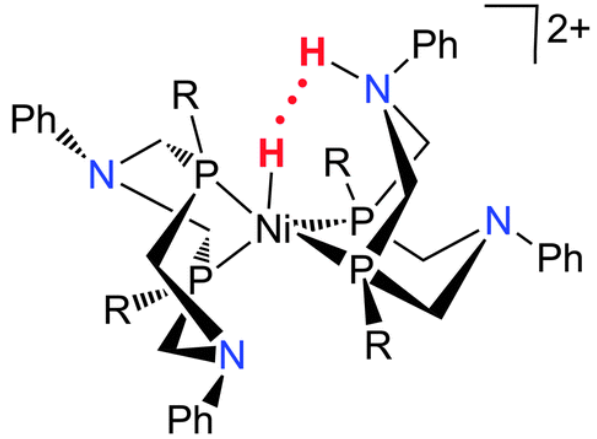
Stabilization of isolated metal atoms on oxide supports



Individual Pt atoms (bright dots) are stabilized on the surface of CeO_2 and catalyze CO oxidation without sintering.

Datye et al., *Science* **2016**, *353*, 150-154.

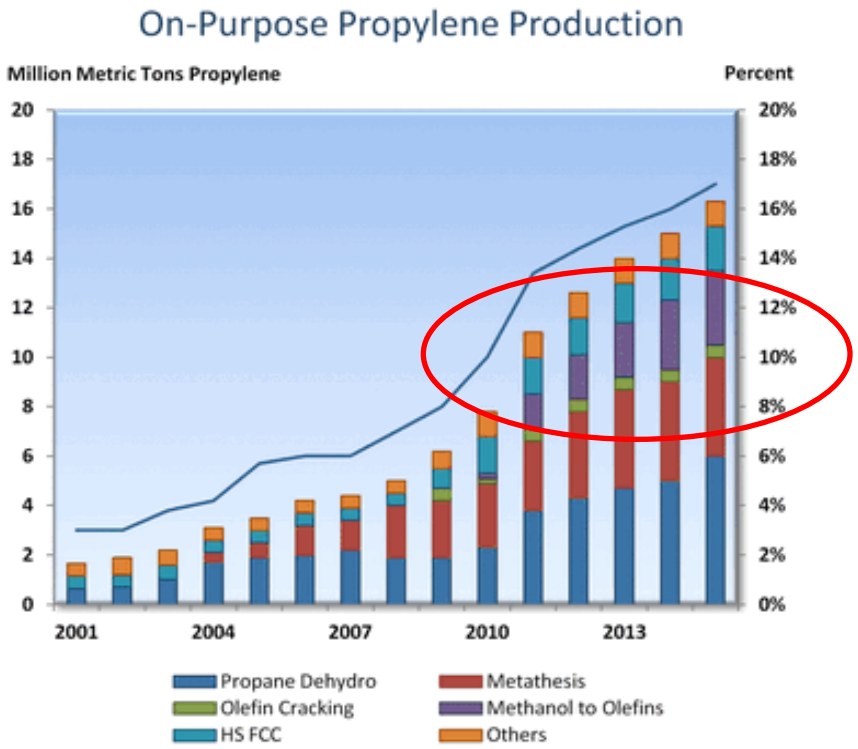
Outer coordination sphere assistance in multiproton, multielectron reactions

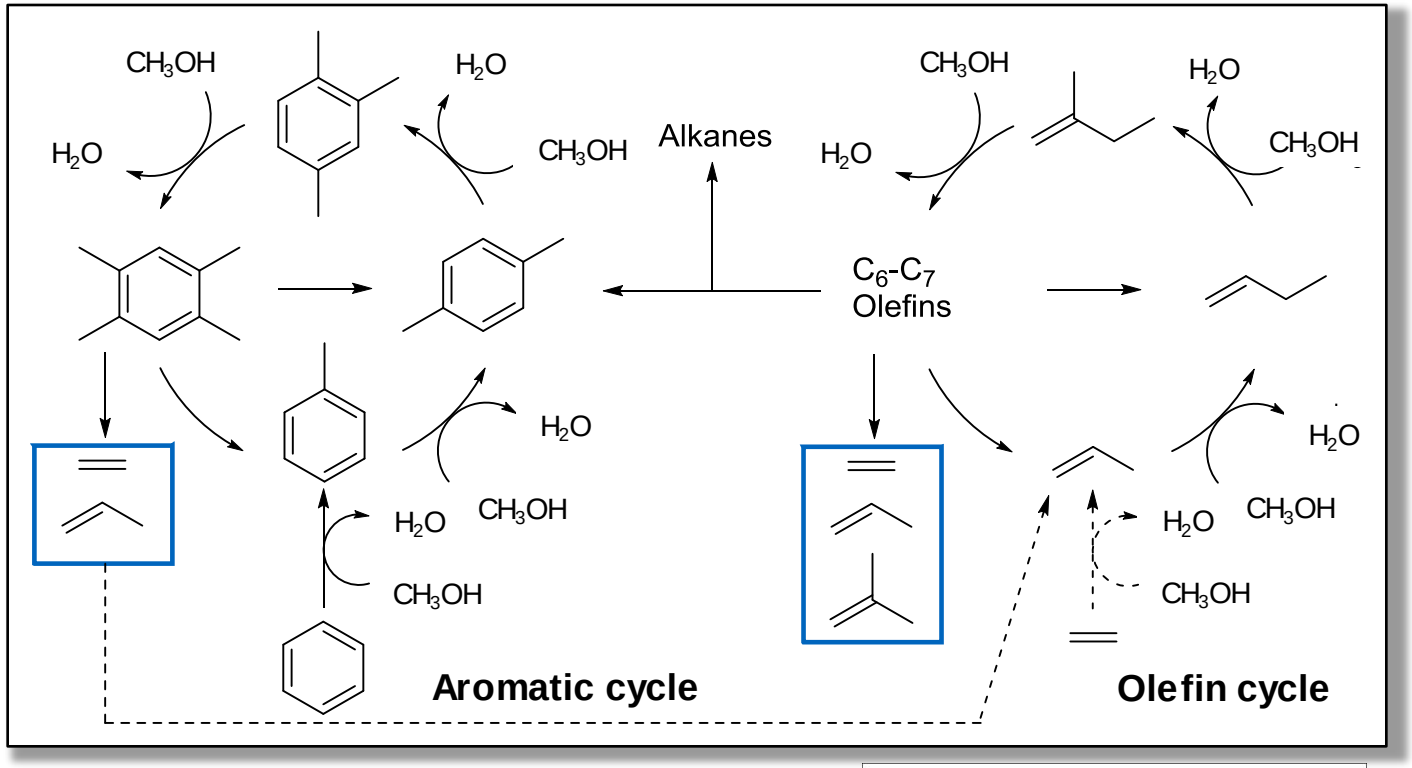


The rate of electrochemical H_2 evolution is dramatically enhanced by strategic placement of pendant amines that function as proton relays to a metal hydride.

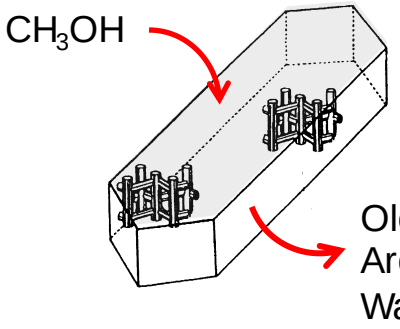
Bullock et al., *Chem. Commun.* **2014**, *50*, 3125-3143.

Dedicated Olefin Synthesis from Methanol



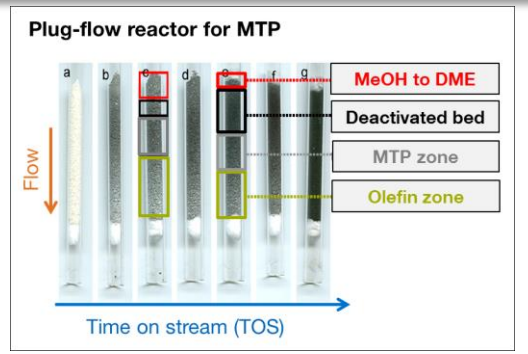


- Methanol-to-olefins technology has emerged (from a 50-year-old discovery) as one of the leading technologies for dedicated light olefin synthesis (>20 new plants worldwide)
- Fundamental science was indispensable for targeted catalyst development



Translation

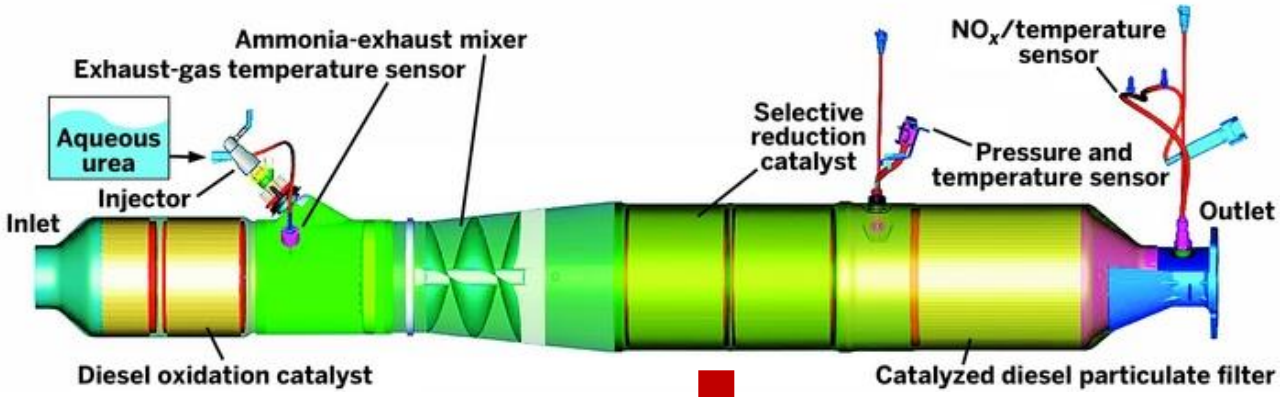
Inspiration



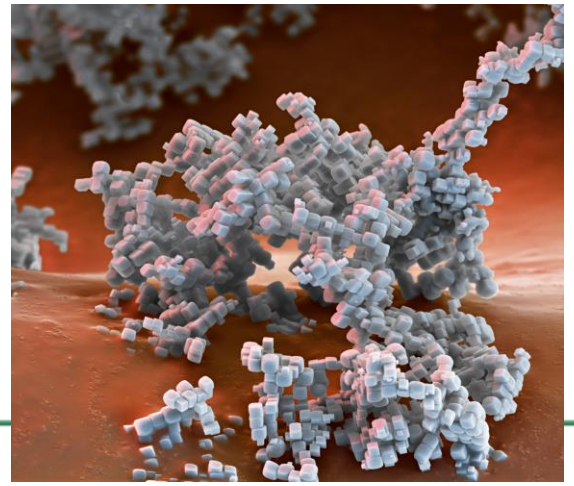
Patience et al., *Chem. Eng. Sci.* **2007**, *62*, 5527.

Low Temperature Catalysts for Diesel Exhaust Aftertreatment

Fuel-efficient diesel vehicles created new challenges for catalysis. Starting in 2007, NOx had to be removed from exhaust gases to meet stricter air quality standards. In selective catalytic reduction (SCR), a Cu/zeolite catalyst uses NH_3 to reduce NO_x to N_2.



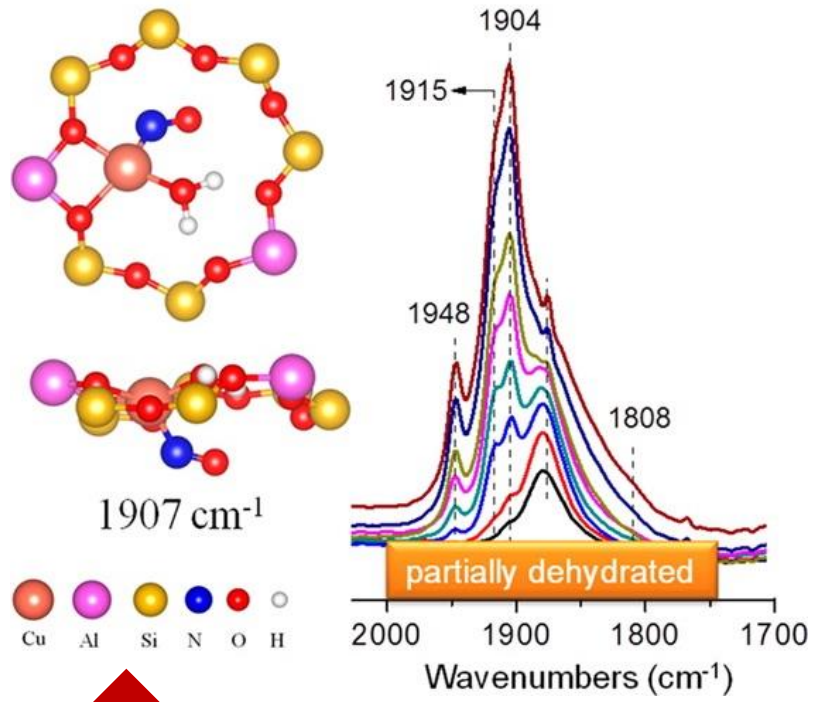
Ford DOC-SCR-DPF system layout
Beale et al., *Chem. Soc. Rev.* **2015**, *44*, 7371



www.basf.com

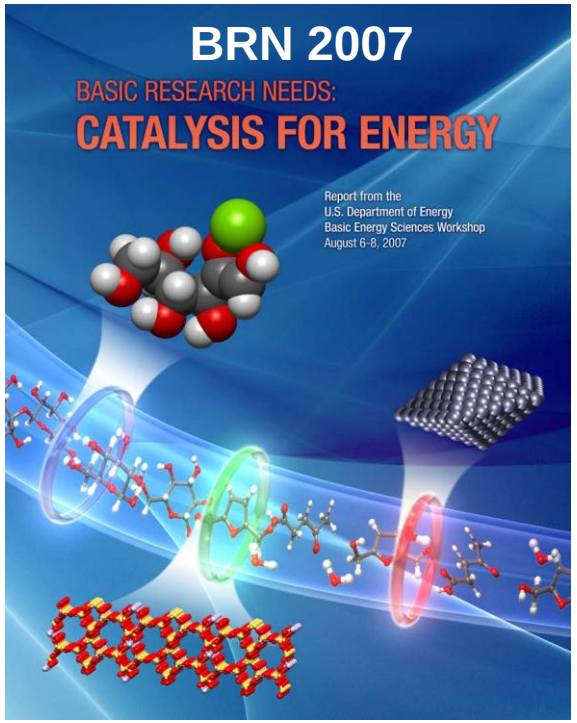
Bifunctional Cu/chabazite catalyst, selective for SCR and resistant to poisoning due to Cu^{2+} confinement in small zeolite pores

McEwen, Peden et al., *ACS Catal.* **2014**, *4*, 4093

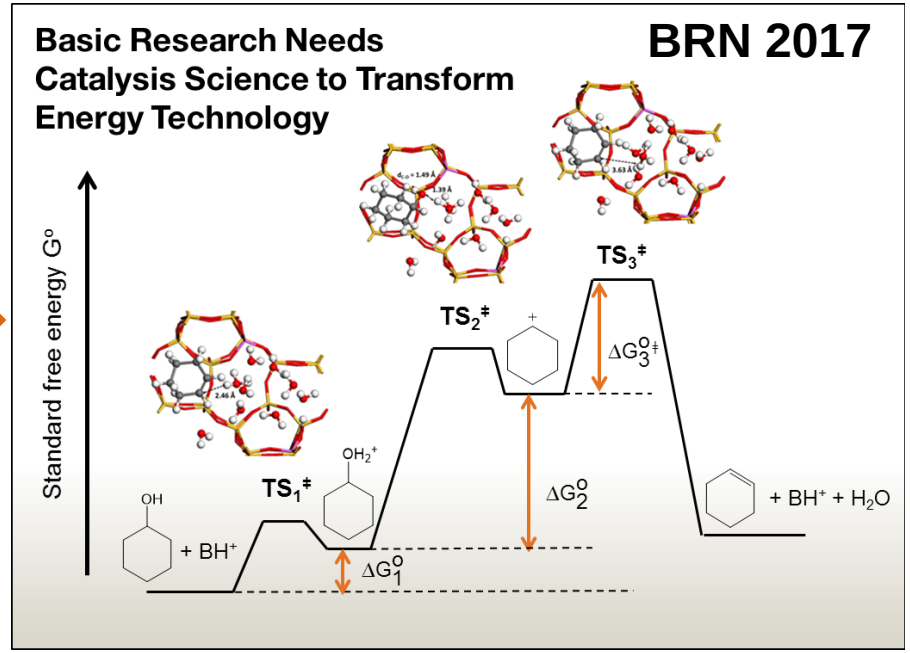


New Catalysis Science to Transform Energy Technologies

From feedstock focus to understanding and using chemical complexity.



Mechanisms and dynamics
Controlled catalyst synthesis
Heavy fossil energy feedstocks
Biologically derived feedstocks
Conversion of CO_2 and H_2O



Panel 1: Diversified Energy Feedstocks and Carriers
Panel 2: Novel Approaches to Energy Transformations
Panel 3: Advanced Chemical Conversion Approaches
Panel 4: Cross-cutting Capabilities and Challenges in Synthesis, Characterization, Theory and Computation

Carl Koval
University of Colorado, Boulder

Susannah Scott
UC Santa Barbara

Johannes Lercher
Pacific Northwest National Lab
Technical University Munich

Plenary Presentations at May Workshop


Catalyst Design for Sustainable Production of Fuels and Chemicals — Jens Norskov (Stanford)

The Nexus of Reaction Mechanism and Dynamic Materials Properties in Designing Catalytic Processes — Cynthia Friend (Harvard)


Opportunities for Catalysis in Utilization of Biomass Resources — Jim Dumesic (Wisconsin)

Creating New Economic Advantages from US Oil and Gas — Jim Rekoske (UOP)

Lessons From the Quest for Cellulosic Biofuels…… — Kim Johnson (Shell)



Impact of Catalytic Technology on Use of Renewable Energy Resources — Reuben Sarkar (EERE)

Frontiers, Challenges and Opportunities in Biological and Bio-Inspired Catalysis — Russ Hille (UC Riverside)

Panel Breakout Sessions at May Workshop


Panel 1: *Diversified Energy Feedstocks and Carriers*
Geoffrey Coates, Cornell University
Enrique Iglesia, University of California Berkeley, and Lawrence Berkeley National Laboratory


Panel 2: *Novel Approaches to Energy Transformations*
Morris Bullock, Pacific Northwest National Laboratory
Thomas Jaramillo, Stanford University, and Stanford Linear Accelerator Center



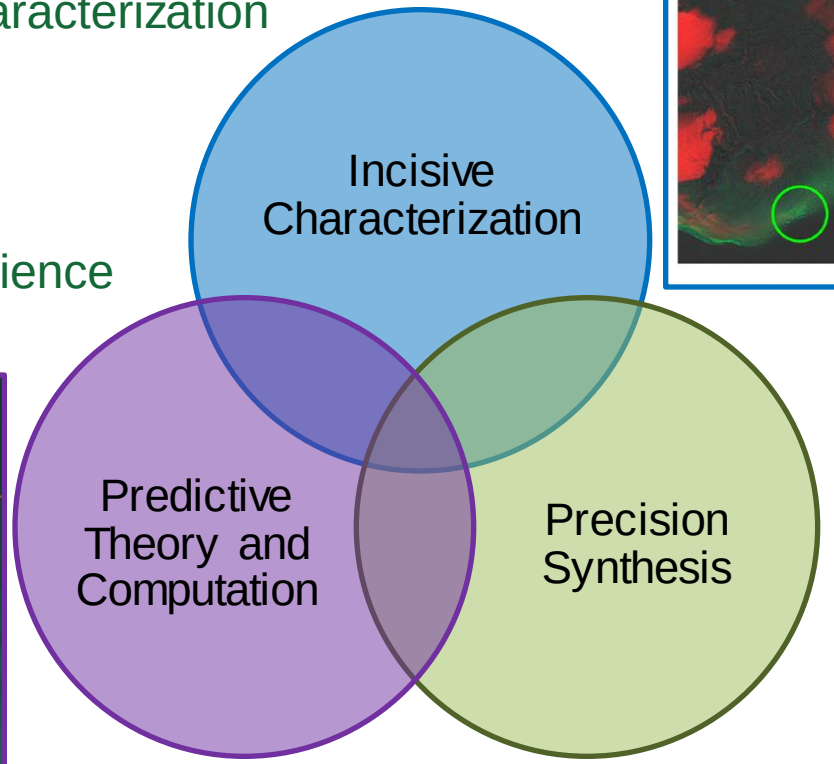
Panel 3: *Advanced Chemical Conversion Approaches*
Maria Flytzani-Stephanopoulos, Tufts University
Cathy Tway, Dow Chemical Company
Daniel Resasco, University of Oklahoma

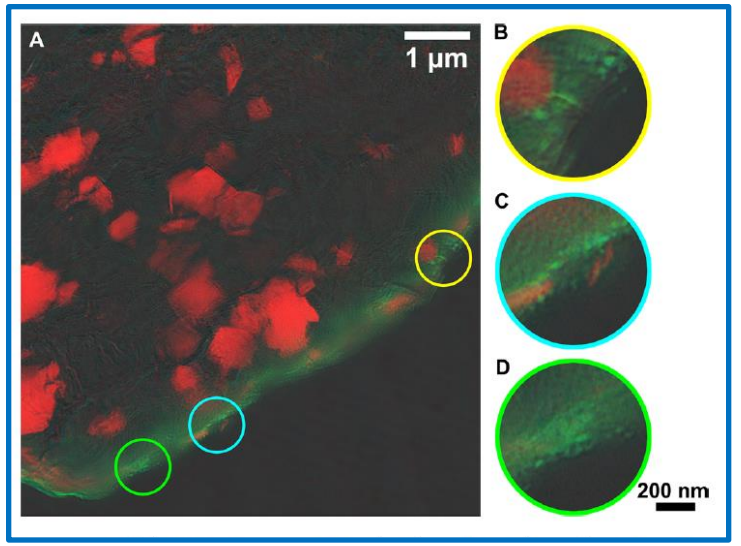


Panel 4: *Crosscutting Capabilities and Challenges: Synthesis, Theory, and Characterization*
Karena Chapman, Argonne National Laboratory
Victor Batista, Yale University
Sheng Dai, Oak Ridge National Laboratory

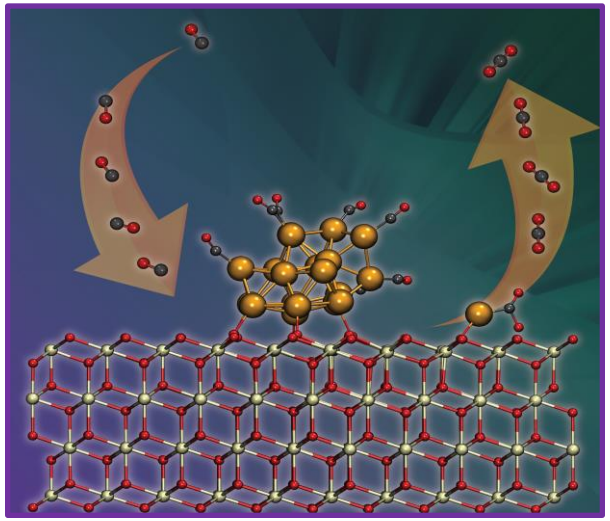
Transformative Capabilities for Catalysis: Synthesis, Computation, and Characterization

- Identify rare and/or metastable active states
- Span multiple time/length-scales
- Conduct multimodal *operando* characterization
- Resolve reaction mechanisms
- Control interfacial interactions
- Incorporate cooperativity and resilience

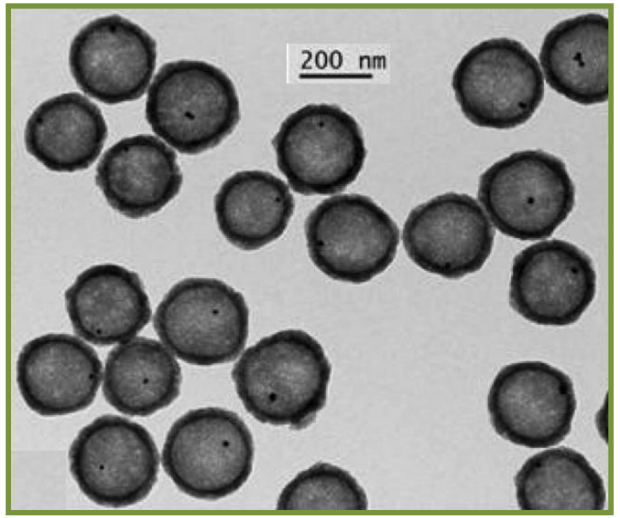




Meier, Weckhuysen et al., *ACS Catal.*, **2016**, *6*, 2178.

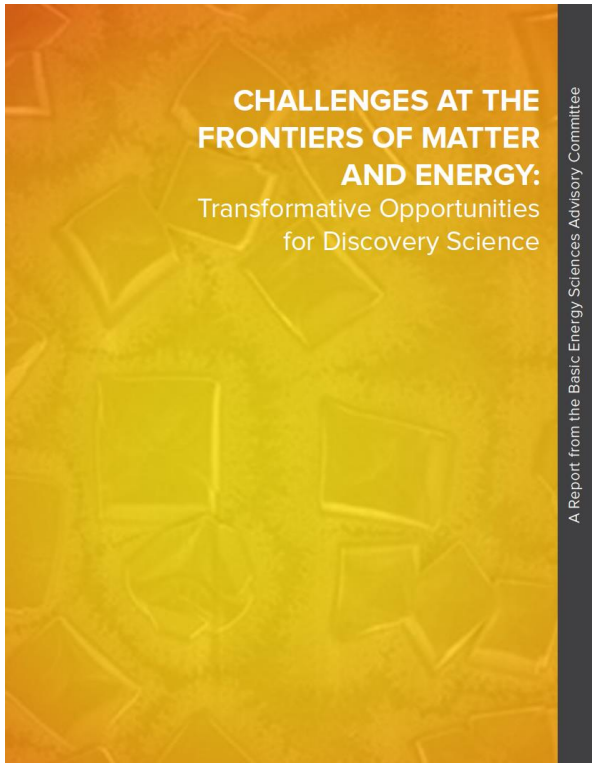


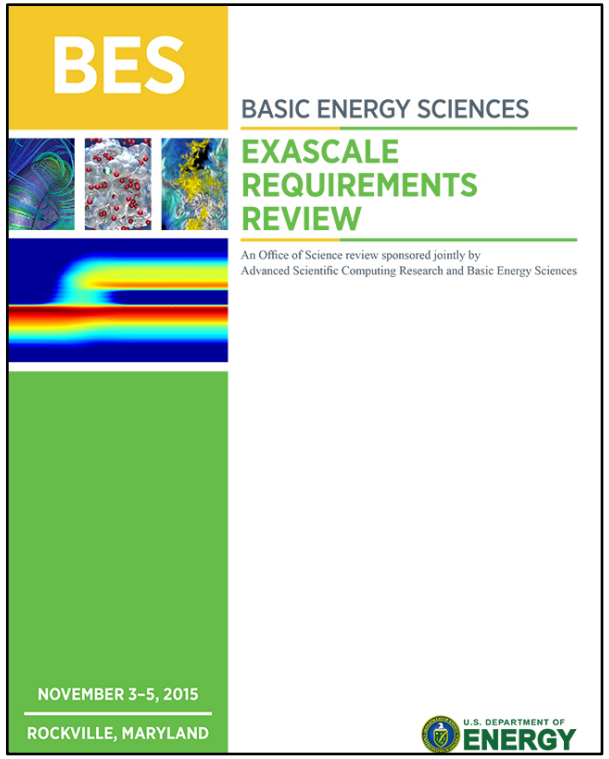
Li, Rousseau et al. *Nature Commun.* **2015**, *6*, 6511

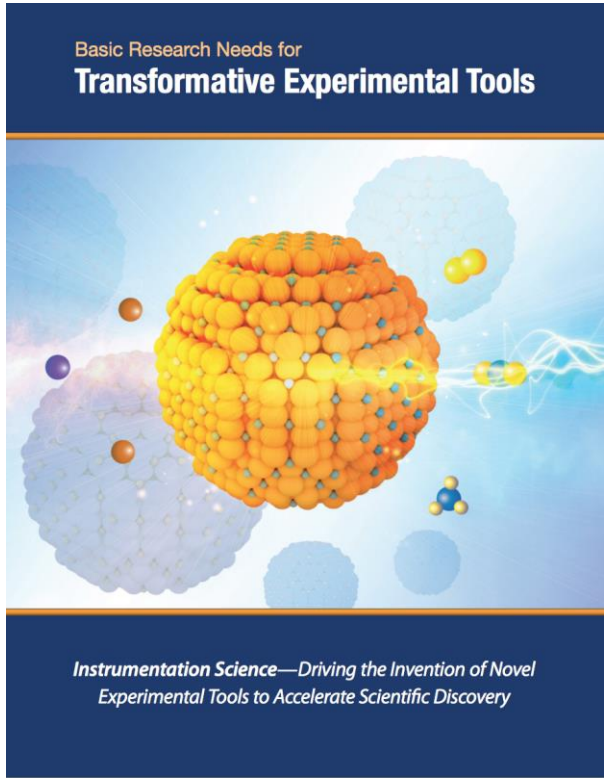


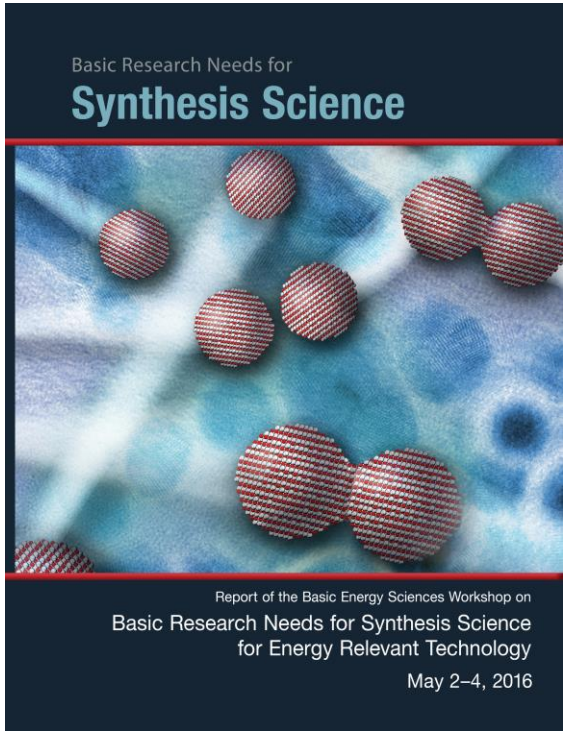
Zaera et al., Surf. Sci. 2016, 648, 150

Recent DOE Reports Emphasizing Synthesis, Computation, and Characterization





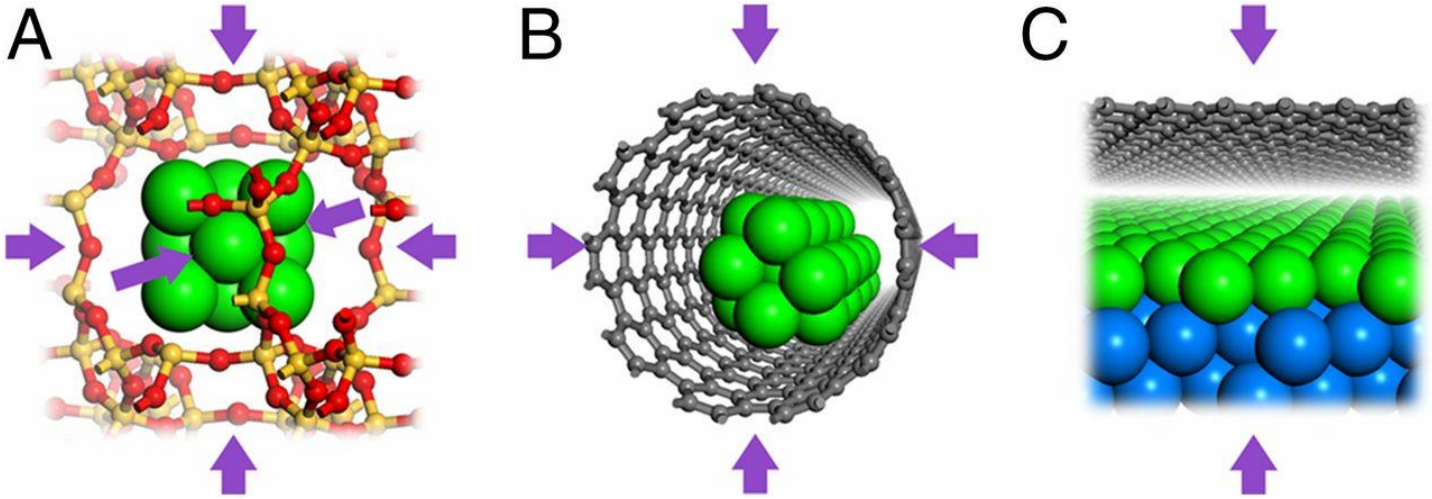




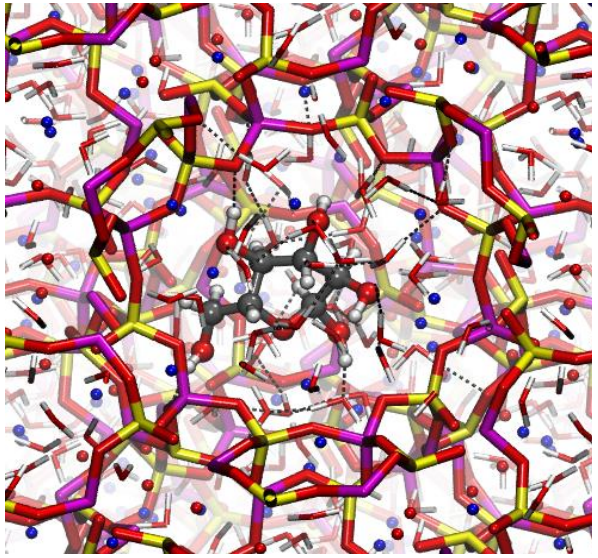
Construct catalyst architectures to incorporate strong and weak interactions that organize matter and space beyond the binding site

The extended structure of the active site includes not only the locations where the molecular orbitals of the reactants interact directly with the catalyst, but also nearby regions in space where the atomic organization in 3-dimensions serves to assemble and precisely position both reacting molecules and non-reacting components such as solvent molecules and counter-ions to achieve selective chemical transformations at high rates.

Metal nanoparticle catalyst confinement, (A) inside a zeolite pore; (B) inside a carbon nanotube; (C) beneath a graphene sheet



Glucose solvation by water in a zeolite supercage



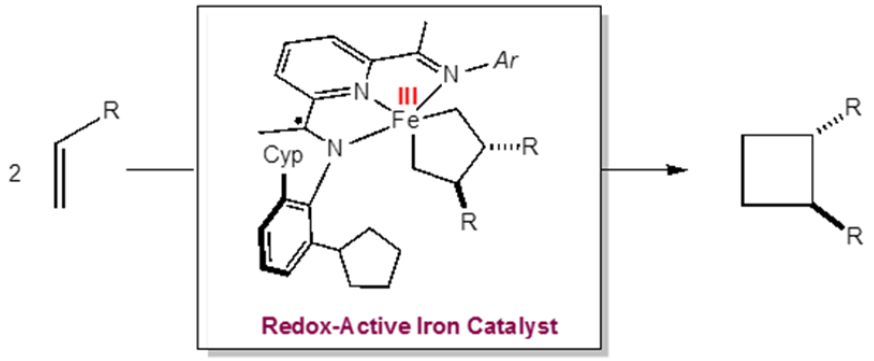
Fu et al. *Proc. Natl. Acad. Sci.* **2017**, *114*, 5930.

Scott et al. *ACS Catal.* **2017**, *114*, 5930.

Constructing Cooperative Catalyst Architectures

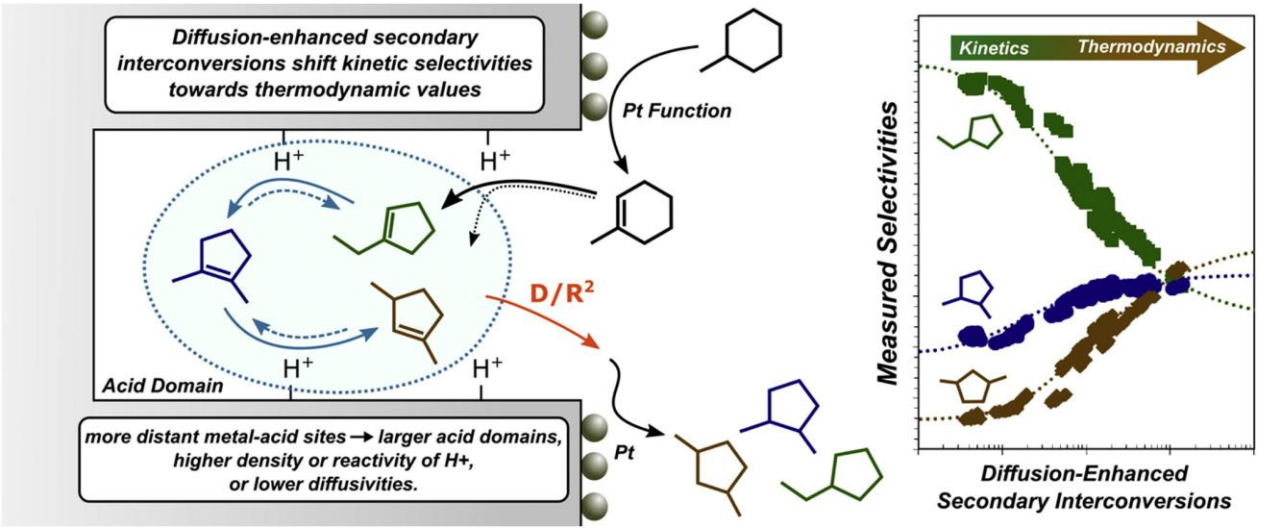
- *How do we map the cooperative roles in catalyst-substrate ensembles at an atomistic level, using powerful emerging characterization and theory methods?*
- *How do we design synthesis methods that direct the organization of structural and functional motifs in the extended catalyst architecture so as to influence the ground and transition states of reacting molecules?*

Redox-active ligands enable thermally-forbidden cyclodimerization



Chirik et al., *Science* **2015**, *349*, 960.

Effect of metal-acid site proximity on activity and selectivity in bifunctional catalysts



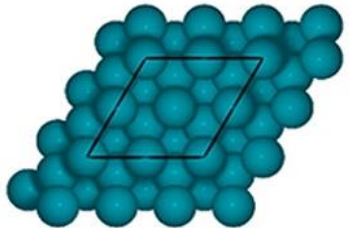
Bimetallic cooperativity in polyol dehydration

Iglesia et al., *J. Catal.* **2016,** *344*, 817**.**

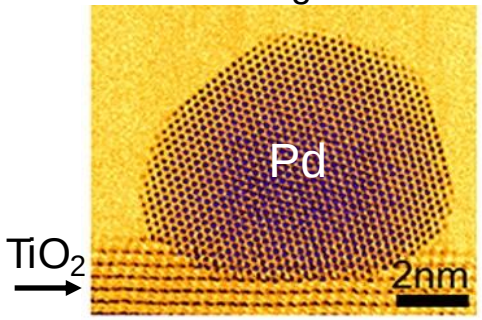
Davis et al., ACS Catal. 2015, 5, 5679

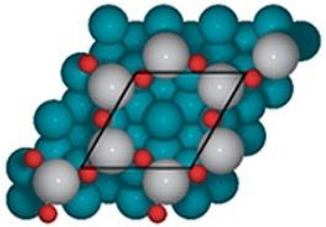
Control the dynamic evolution of catalysts by influencing the rates and directing the pathways for reorganization

Catalysts are inherently dynamic materials whose local and extended structures change continuously, beginning when the components are assembled into a catalytically active architecture and continuing as materials interact with reaction mixtures.

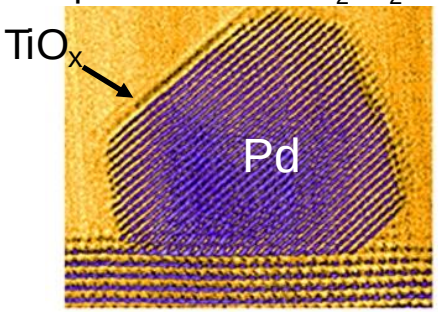


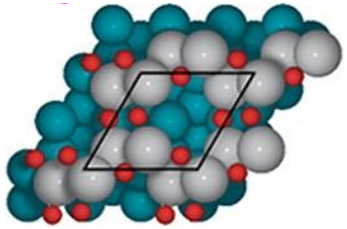
No TiO_x layer on Pd nanoparticle under oxidizing conditions



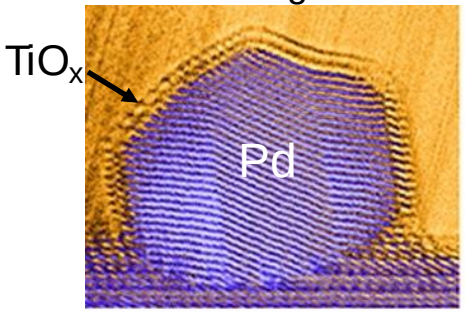


TiO_x monolayer on Pd nanoparticle under H_2/O_2 mixture





TiO_x bilayer on Pd nanoparticle under reducing conditions

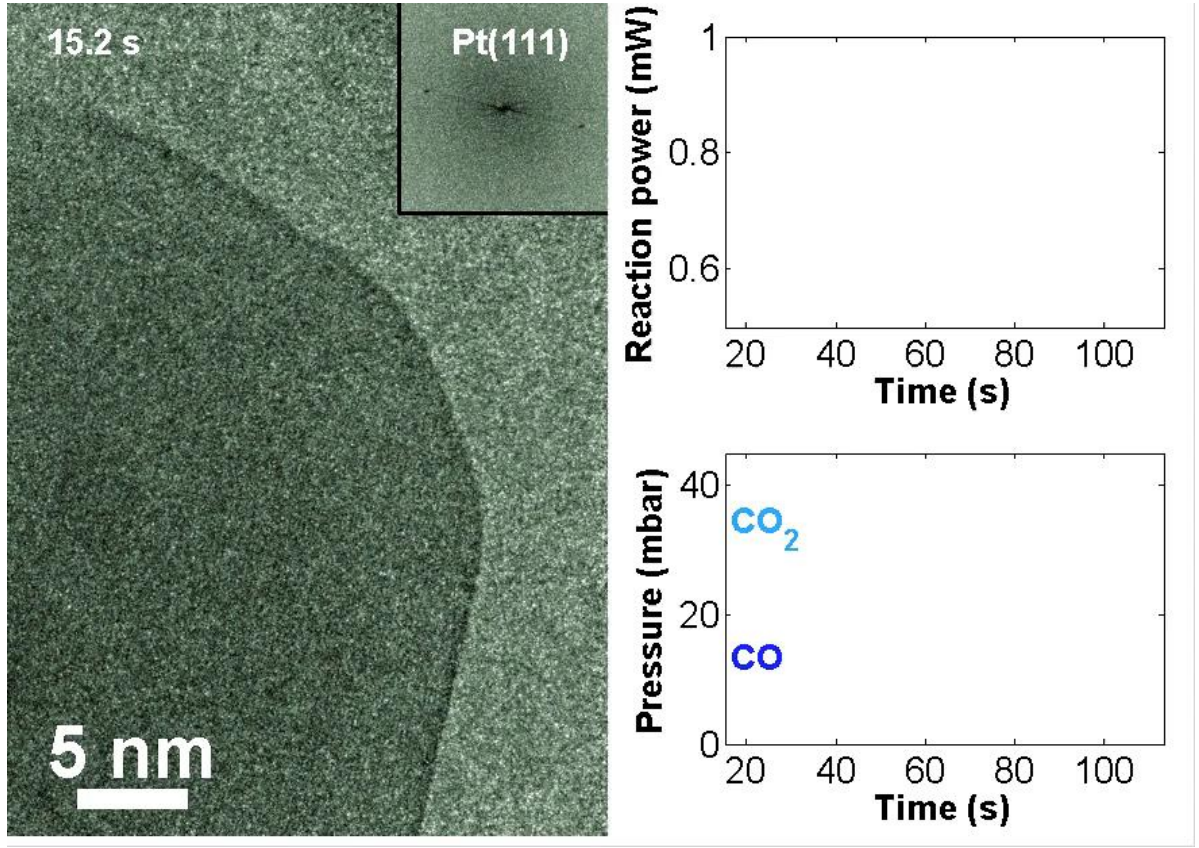


Pan et al. *Nano Lett.*, **2016**, *16*, 4528-4534.

Observing and Directing Complex Catalyst Behavior

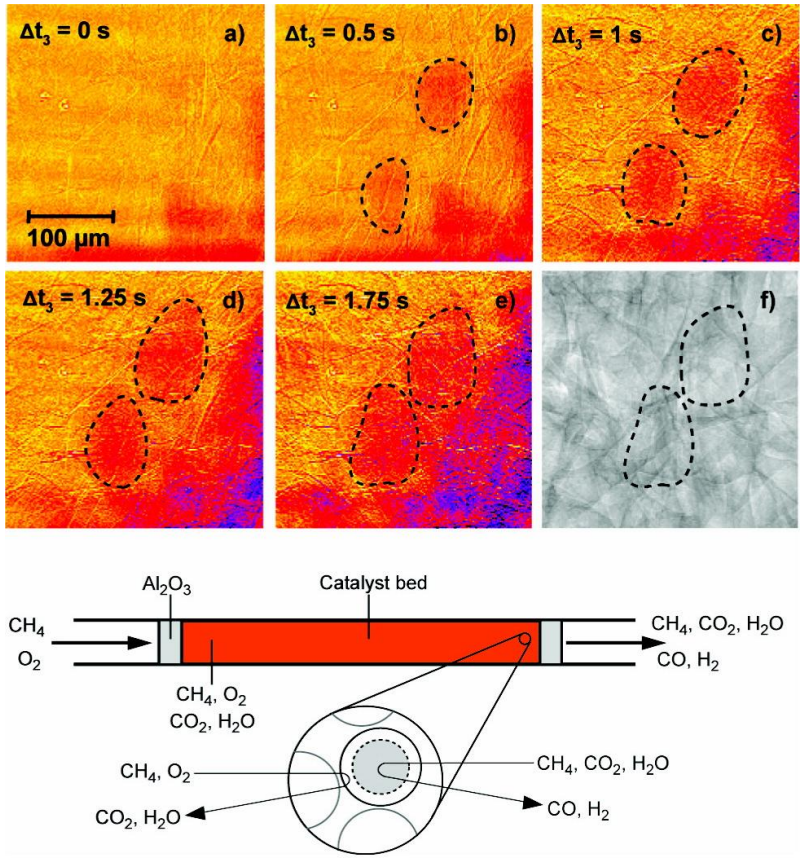
- *How do we monitor changes in catalysts in real time and relate their consequences to reactivity and selectivity?*
- *How do we design catalysts to control their rates of activation, deactivation, and reactivation?*

Time-resolved TEM images of Pt nanoparticle exposed to CO/O_2 at 727 K



Kooyman, Helveg, et al. *Nature Mater.*, **2014**, *13*, 884-890.

Reduction/ignition of individual Pt-Rh nanoparticles during catalytic partial oxidation of methane



Grunwaldt et al. *J. Phys. Chem. C*, **2009**, *113*, 3037.

Decode complex networks of reactions, and integrate catalytic reactions with molecular transport and separations

Emerging chemical fuels and feedstocks are often mixtures that present challenges for catalysis in terms of their inherent complexity and variability. In addition, their highly distributed nature will require entirely new approaches to catalytic processing.

Agriculture Residues

Flared Gas

Municipal Solid Waste

Pulp Waste

Wet Sludges

Fats, Oils, and Greases

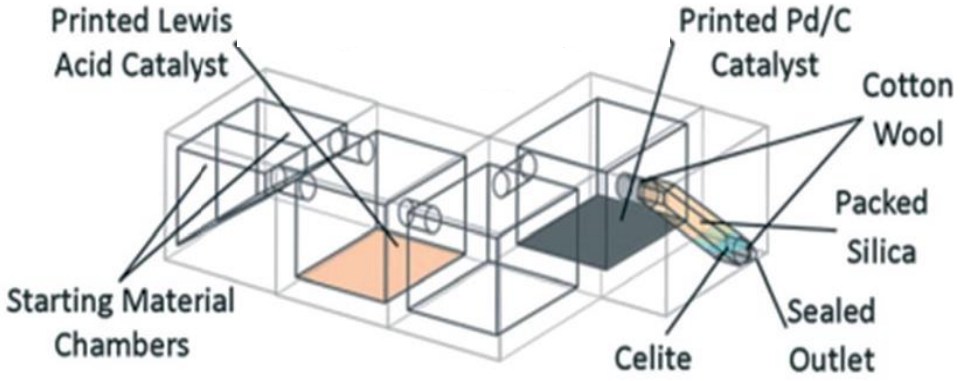
Alternative feedstocks have huge energy potential, and pose unique challenges for catalyst technology.

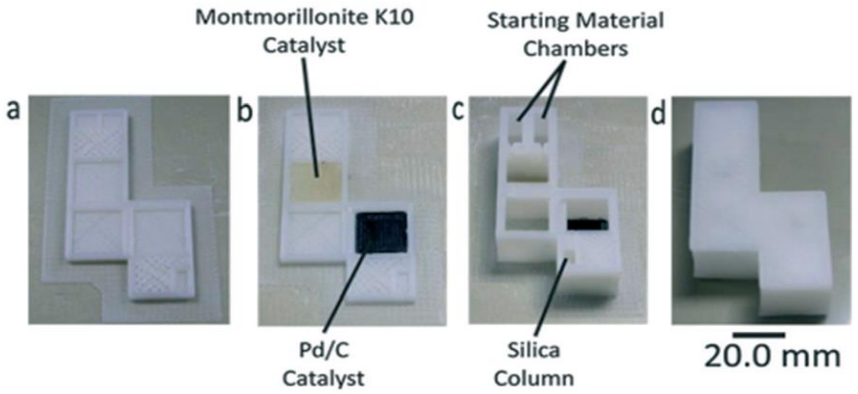
Complex mixtures
Distributed sources
Solids handling

Integration of Reaction with Separation and Design for Catalyst Resilience

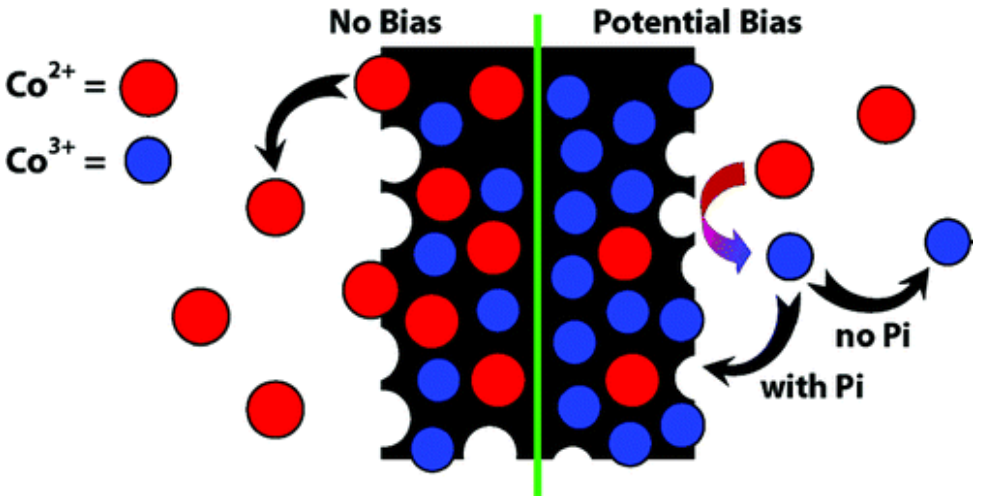
- *How do we design catalysts that adapt to transients in feed composition and reaction conditions, and that are capable of operating in highly distributed systems with minimal external control?*

Achieving spatial control over catalysts, reactions and separations





Self-healing oxygen-evolving catalyst

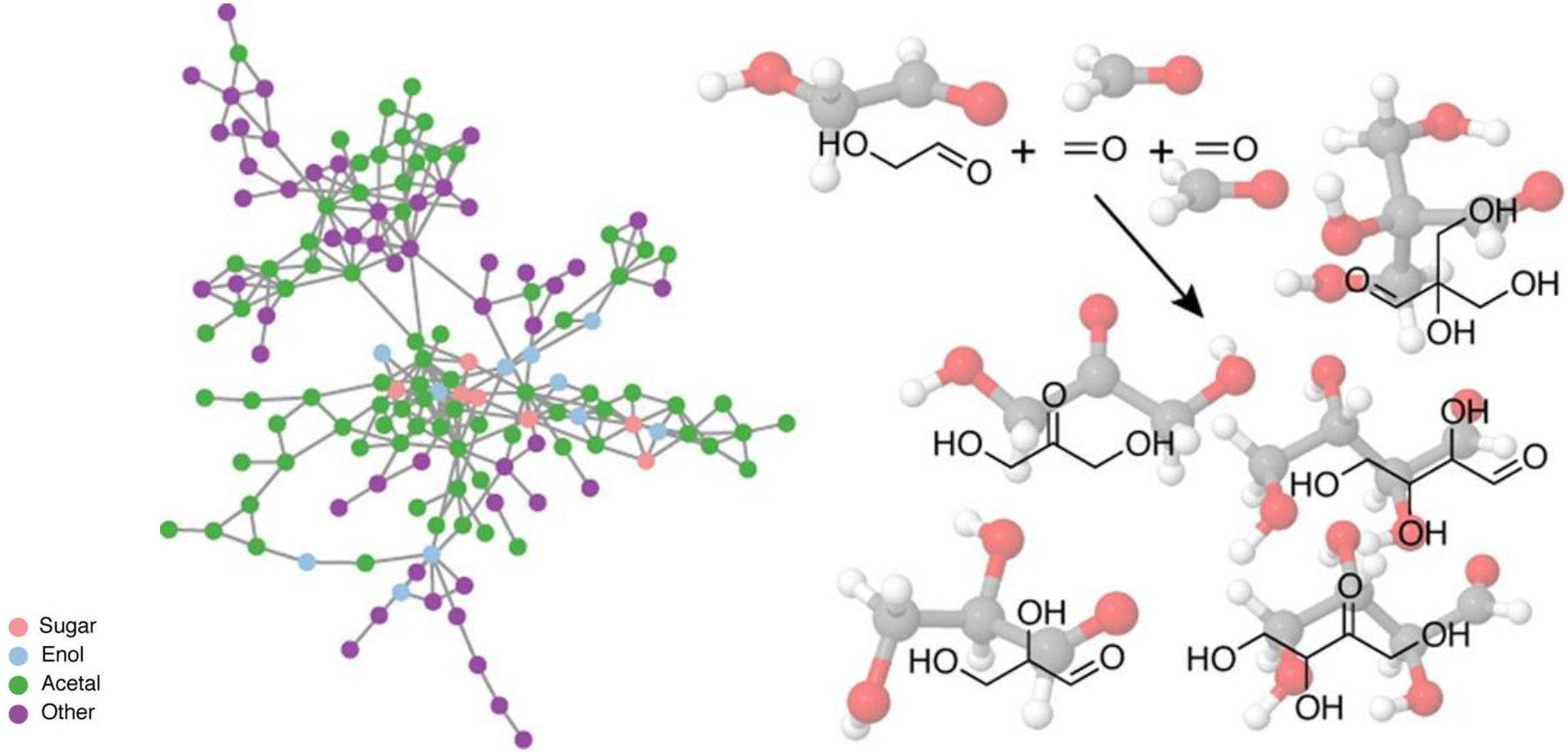


Nocera et al. *J. Am. Chem. Soc.* **2009**, *131*, 3838.

Cronin et al. *Chem. Sci.* **2013**, *4*, 3099.

Combining Catalyst Discovery and Mechanisms with Systems-Level Insight

- *How do we direct chemical transformations in multicomponent mixtures towards specific desired chemical products, via systems-level control of all the micro- and macro-kinetic factors that dictate rates in catalytic reaction cascades?*



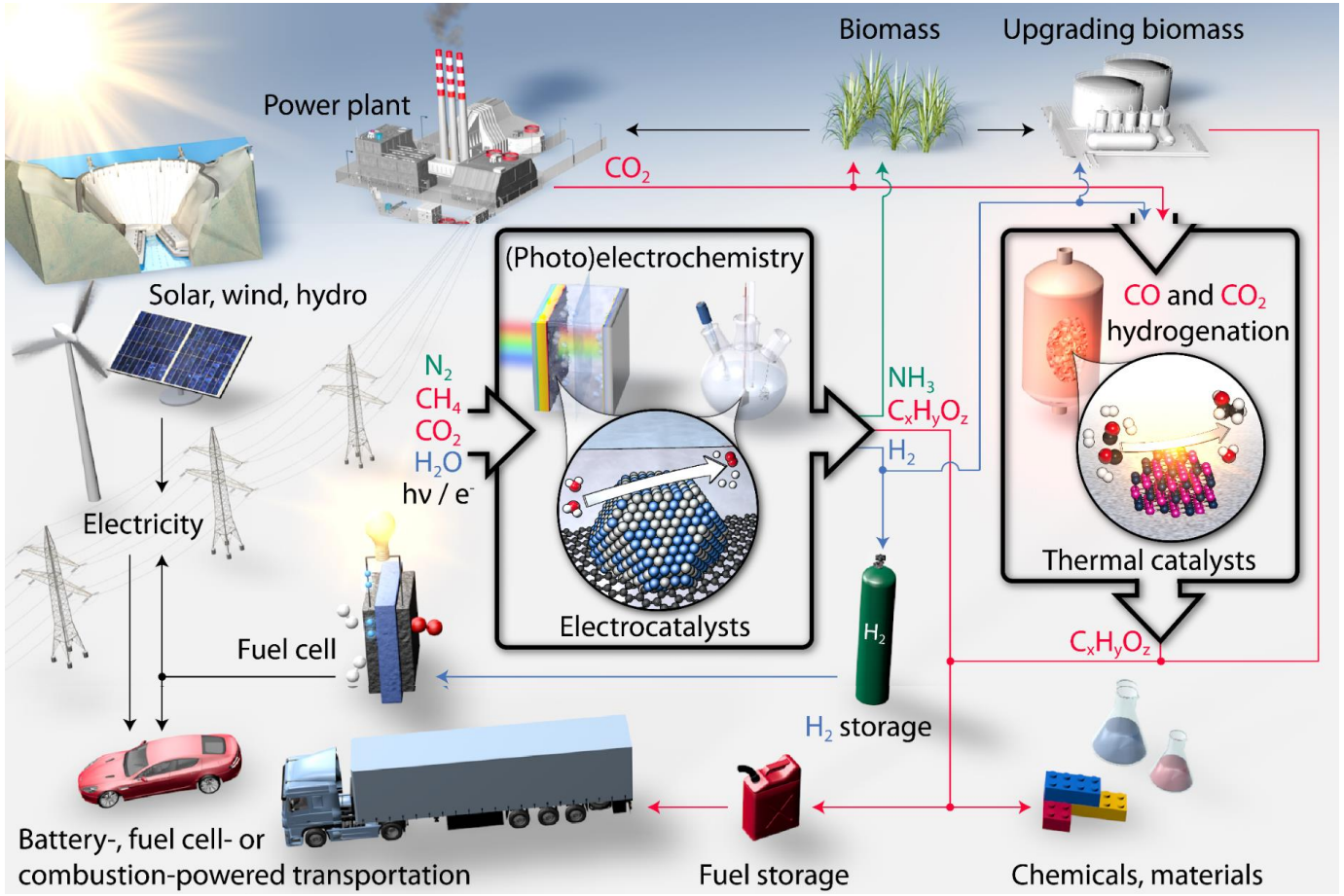
Construction of a reaction network for the *formose* reaction (self-condensation of formaldehyde in alkaline solution, resulting in a complex mixture of aldose and ketose sugars) using heuristic transformation rules.

Rappoport, Aspuru-Guzik et al. *J. Chem. Theor. Comput.* **2014**, *10*, 897.

Design electrocatalyst systems to optimize electron-driven processes for precise chemical transformations efficiently under mild conditions

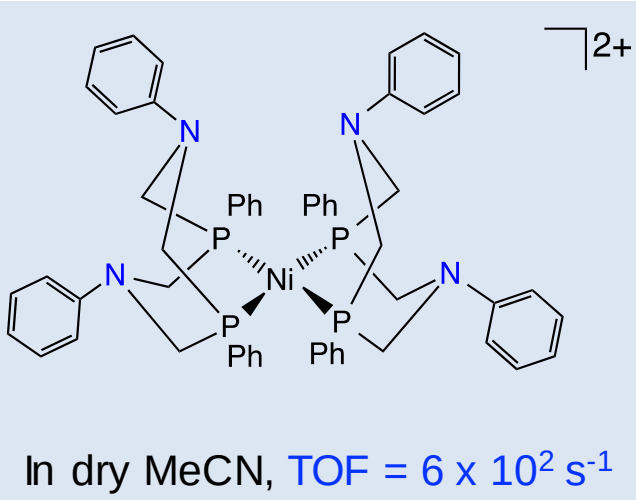
The interconversion of chemical and electrical energy is based on the ability to store energy in chemical bonds and retrieve energy from those bonds by using the electron potential to control the directions and rates of chemical processes.

Electrochemical systems offer the possibility to drive chemical transformations under mild conditions, where thermal catalysis is inefficient.



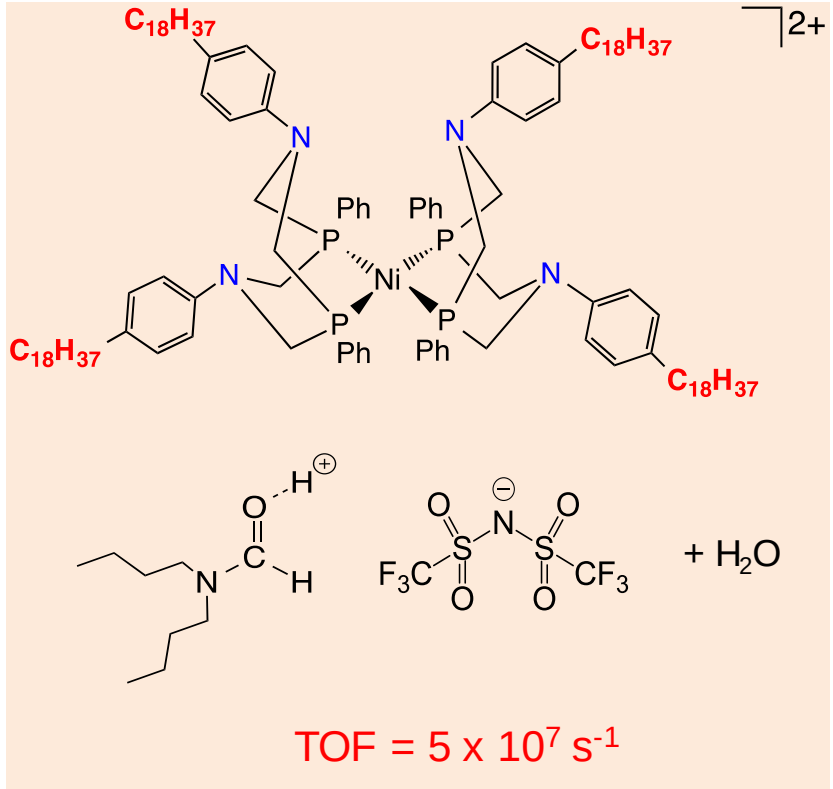
Enhancing Activity in Molecular Electrocatalysts for H_2 Production

- *How do we design conducting solid/solution interfaces, and coupled redox reaction chemistries, that catalyze electron-driven chemical processes with high precision and efficiency under mild conditions?*
- *How do we improve electrocatalysts for critical multi-electron, multi-proton reactions, and also expand the repertoire of chemical transformations that can occur effectively in electrochemical systems?*
- *How do we develop new electrocatalytic systems that circumvent known scaling relationships through detailed mechanistic understanding of catalytic pathways?*



In dry MeCN, TOF = 6 x 10^2 s^{-1}

Detailed mechanistic understanding



TOF = 5 x 10^7 s^{-1}

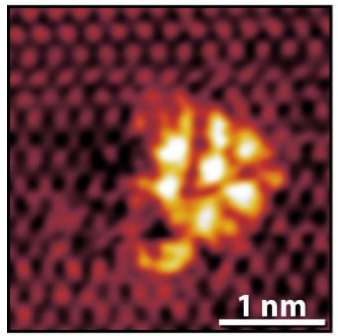
Roberts, DuBois et al., *J. Am. Chem. Soc.* **2011**,*133*, 5861.

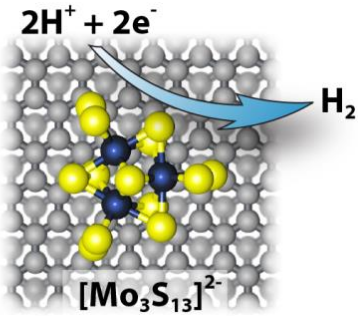
O'Hagan et al., *Angew. Chem. Int. Ed.* **2016**, *55*, 13509.

Designing Nano-Structured Catalysts for H_2 Production

Increasing fraction of edge sites = higher activity

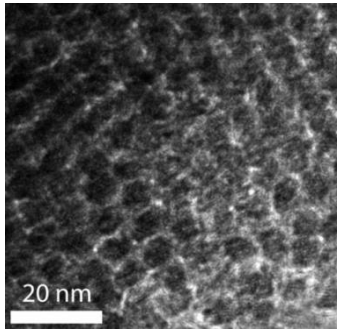
3





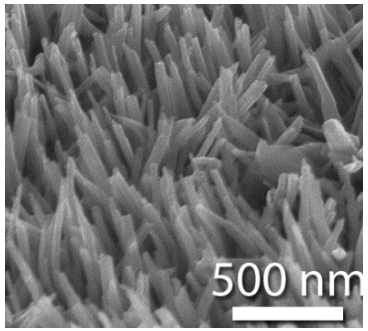
$[Mo_3S_{13}]^{2-}$ clusters

2

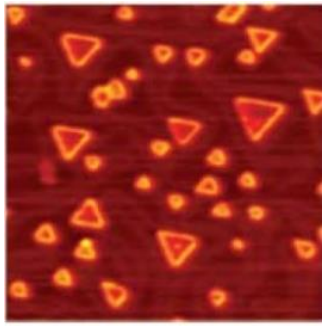


Mesoporous MoS_2 thin films

1

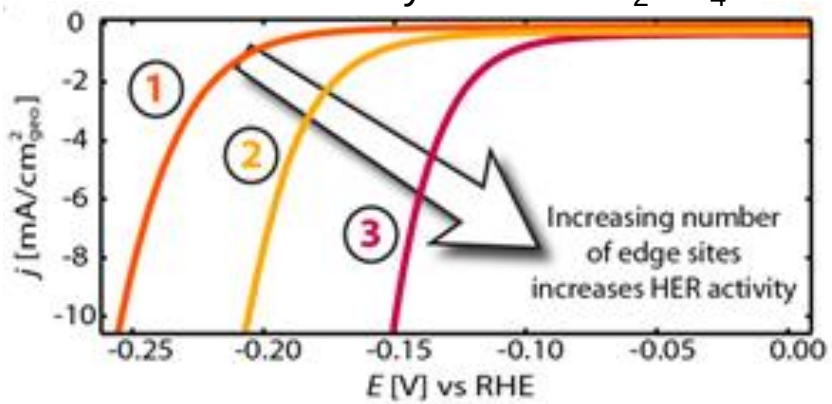


Core-shell MoO_3-MoS_2 nanowires



MoS_2 nanoparticles

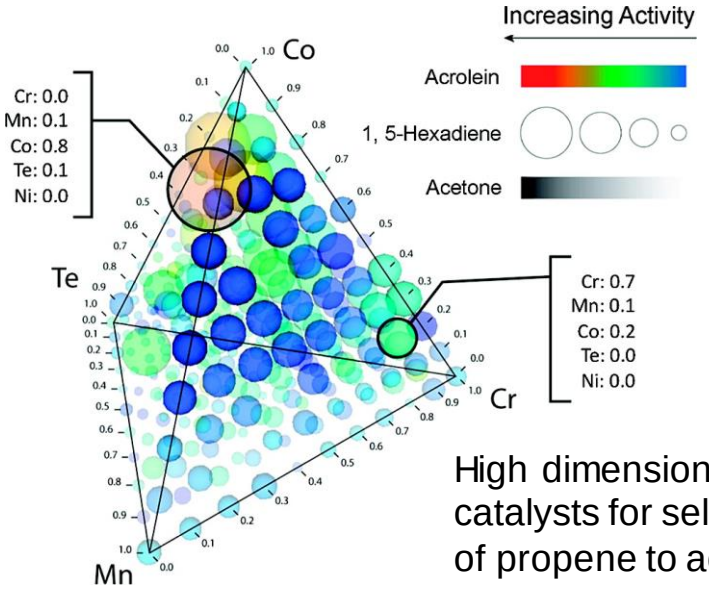
HER activity in 0.5 M H_2SO_4



Jaramillo, Besenbacher et al., *Nat. Chem.*, **2014**, *6*, 248.

Drive new catalyst discoveries using data science to resolve complex structure-function relations, predict new catalyst properties, and design more incisive experiments

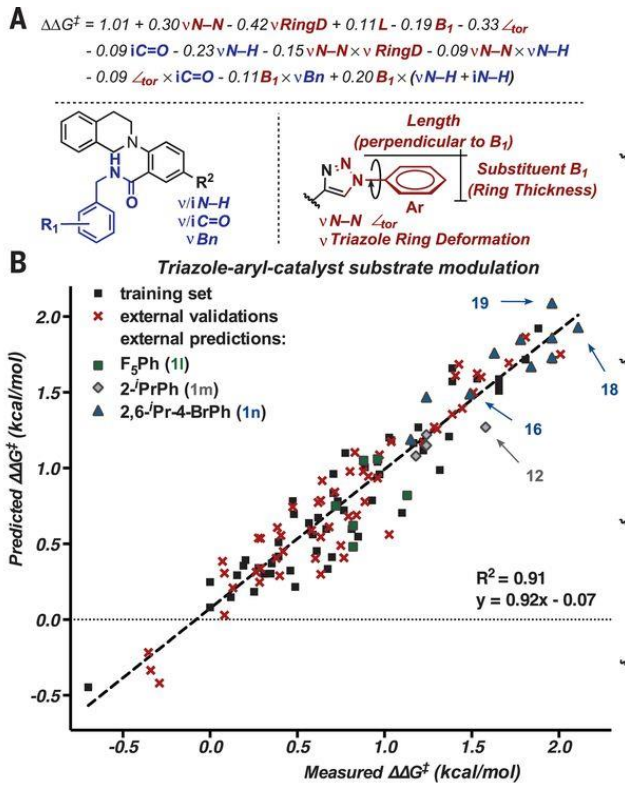
The complex coupling of many variables that govern catalyst reactivity and its evolution in time makes it challenging to discern relationships between catalyst structure/composition and performance.

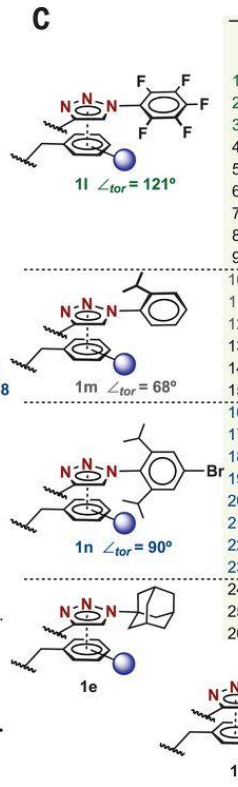


High dimensional screening of catalysts for selective oxidation of propene to acrolein

Rajan et al. *J. Comb. Chem.* **2009,** *11*, 385

Multivariate analysis of catalytic C-N bond formation





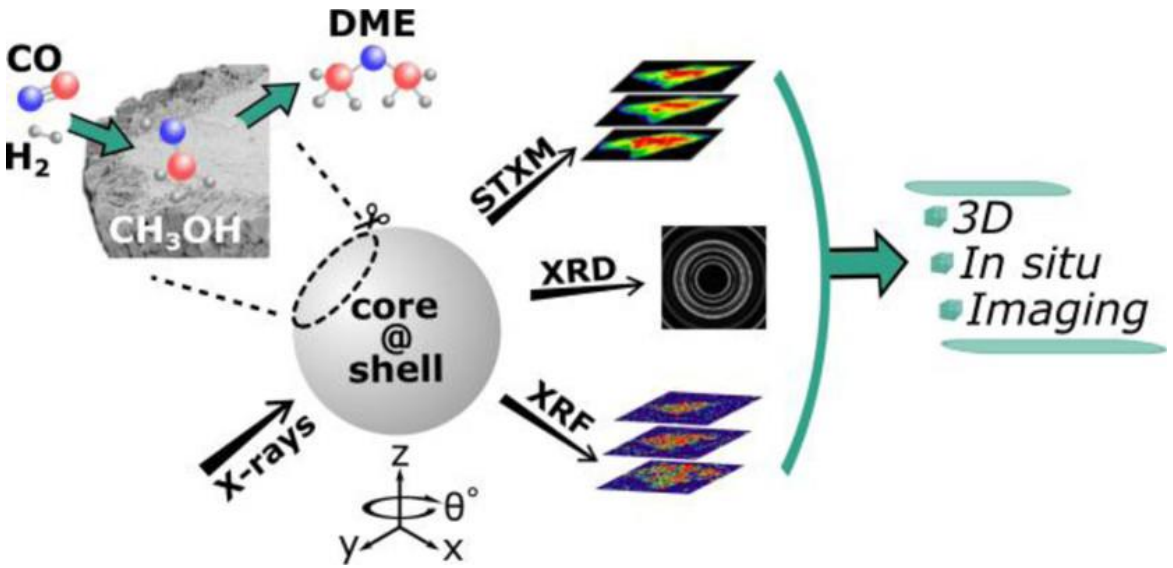
	catalyst Ar	substrate R_1	substrate R_2	predicted %ee ($\Delta\Delta G^{\ddagger}$)	measured %ee ($\Delta\Delta G^{\ddagger}$)
1	F_5Ph (**1l**)	**2a** 4-H	H	60 (0.82)	74 (1.13)
2	F_5Ph (**1l**)	**2b** 4-Me	H	72 (1.06)	67 (0.96)
3	F_5Ph (**1l**)	**2e** 2-OMe	Ph	56 (0.75)	54 (0.72)
4	2,6-F_2Ph (**1k**)	**2a** 4-H	H	52 (0.68)	58 (0.79)
5	2,6-F_2Ph (**1k**)	**2b** 4-Me	H	66 (0.96)	54 (0.71)
6	2,6-F_2Ph (**1k**)	**2e** 2-OMe	Ph	50 (0.64)	44 (0.57)
7	2,6-$(OMe)_2$Ph (**1j**)	**2a** 4-H	H	68 (0.98)	63 (0.88)
8	2,6-$(OMe)_2$Ph (**1j**)	**2b** 4-Me	H	73 (1.10)	58 (0.78)
9	2,6-$(OMe)_2$Ph (**1j**)	**2e** 2-OMe	Ph	67 (0.96)	67 (0.97)
10	2-^{i}PrPh (1m)	**2b** 4-Me	H	77 (1.22)	78 (1.24)
11	2-^{i}PrPh (1m)	**2c** 4-OMe	H	75 (1.15)	78 (1.24)
12	2-^{i}PrPh (1m)	**2d** 4-NO_2	H	79 (1.27)	87 (1.58)
13	2,4,6-$(^i$Pr$)_3$Ph (**1c**)	**2b** 4-Me	H	58 (0.79)	66 (0.93)
14	2,4,6-$(^i$Pr$)_3$Ph (**1c**)	**2c** 4-OMe	H	58 (0.78)	63 (0.89)
15	2,4,6-$(^i$Pr$)_3$Ph (**1c**)	**2d** 4-NO_2	H	76 (1.17)	76 (1.17)
16	2,6-$(^i$Pr$)_2$-4-BrPh (**1n**)	**2a** 4-H	H	85 (1.49)	85 (1.49)
17	2,6-$(^i$Pr$)_2$-4-BrPh (**1n**)	**2e** 2-OMe	H	90 (1.76)	88 (1.63)
18	2,6-$(^i$Pr$)_2$-4-BrPh (**1n**)	**2f** 2-Me	H	93 (1.96)	95 (2.11)
19	2,6-$(^i$Pr$)_2$-4-BrPh (**1n**)	**2g** 2-Br	H	94 (2.09)	93 (1.96)
20	2,6-$(^i$Pr$)_2$-4-BrPh (**1n**)	**2h** 2-^{i}Pr	H	92 (1.88)	93 (1.96)
21	2,6-$(^i$Pr$)_2$-4-BrPh (**1n**)	**2j** 2-OMe	Br	90 (1.73)	93 (1.96)
22	2,6-$(^i$Pr$)_2$-4-BrPh (**1n**)	**2k** 2-OMe	^{i}Pr	92 (1.88)	91 (1.78)
23	2,6-$(^i$Pr$)_2$-4-BrPh (**1n**)	**2i** 2-OMe	Ph	89 (1.67)	92 (1.88)
24	1-Ad (**1e**)	**2a** 4-H	H		81 (1.32)
25	1-Ad (**1e**)	**2b** 4-Me	H		78 (1.24)
26	1-Ad (**1e**)	**2c** 2-OMe	Ph		55 (0.72)

Milo, Neel et al. *Science* **2015,** *347*, 6223

Mining Complex Information Using Data Science Approaches

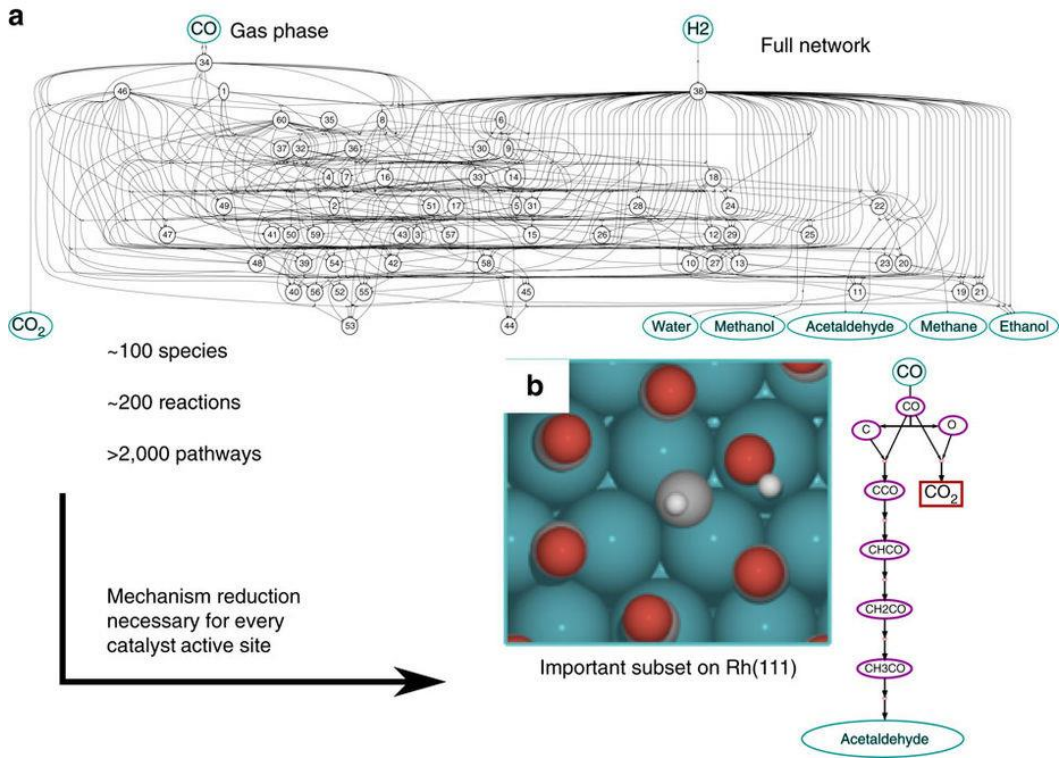
- *How do we deploy the tools of machine learning to find and extract robust, often unexpected structure-activity relations from large, heterogeneous datasets?*
- *How do we use this information to predict effective combinations of catalytic structural components and reaction cascades, leading to entirely new catalyst formulations?*

In situ multimodal 3D chemical imaging of a hierarchically structured core@shell catalyst for methanol synthesis



Grunwaldt et al. *J. Am. Chem. Soc.* **2017,** *139*, 7855

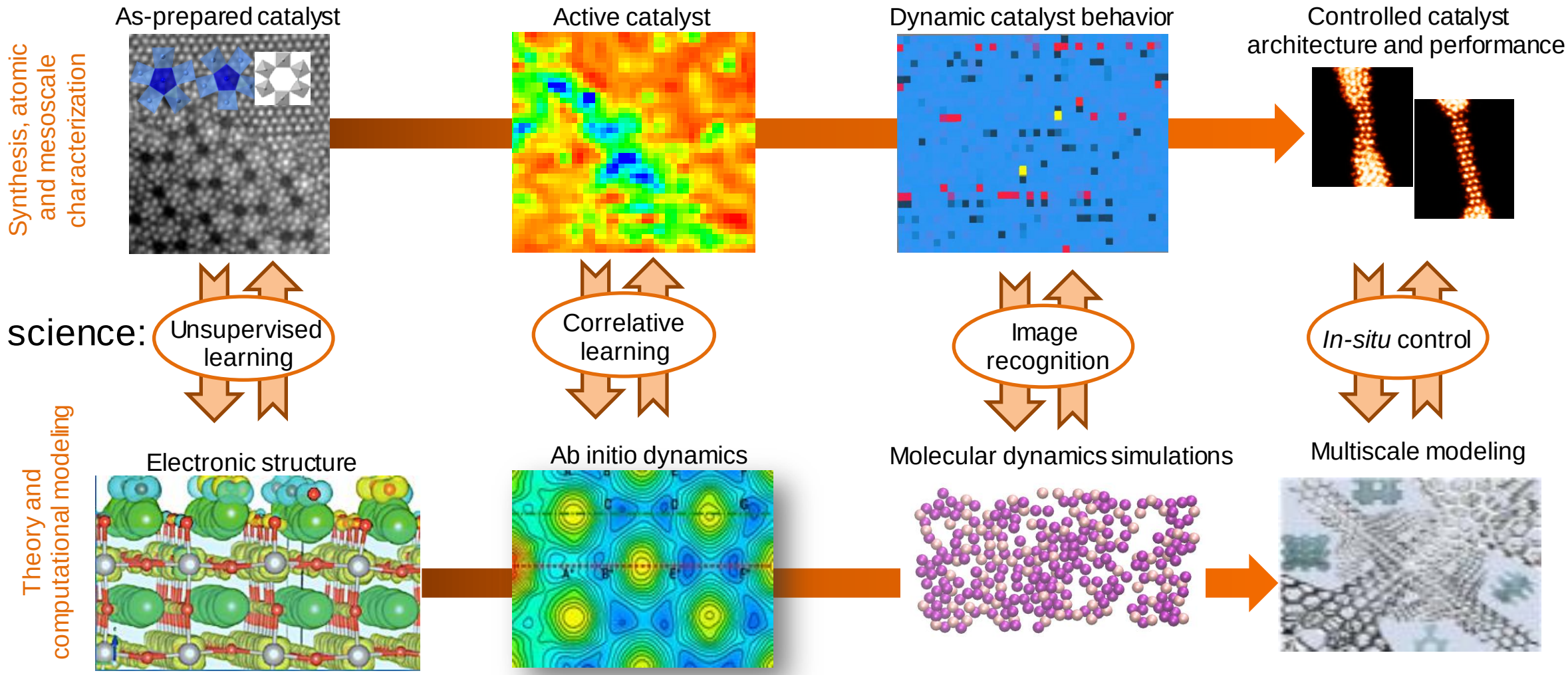
Machine learning simplifies reaction network for syngas ($CO+H_2$) conversion to acetaldehyde over Rh(111)



Bligaard, Nørskov, et al. *Nat. Commun.* **2017,** *8*, 14621

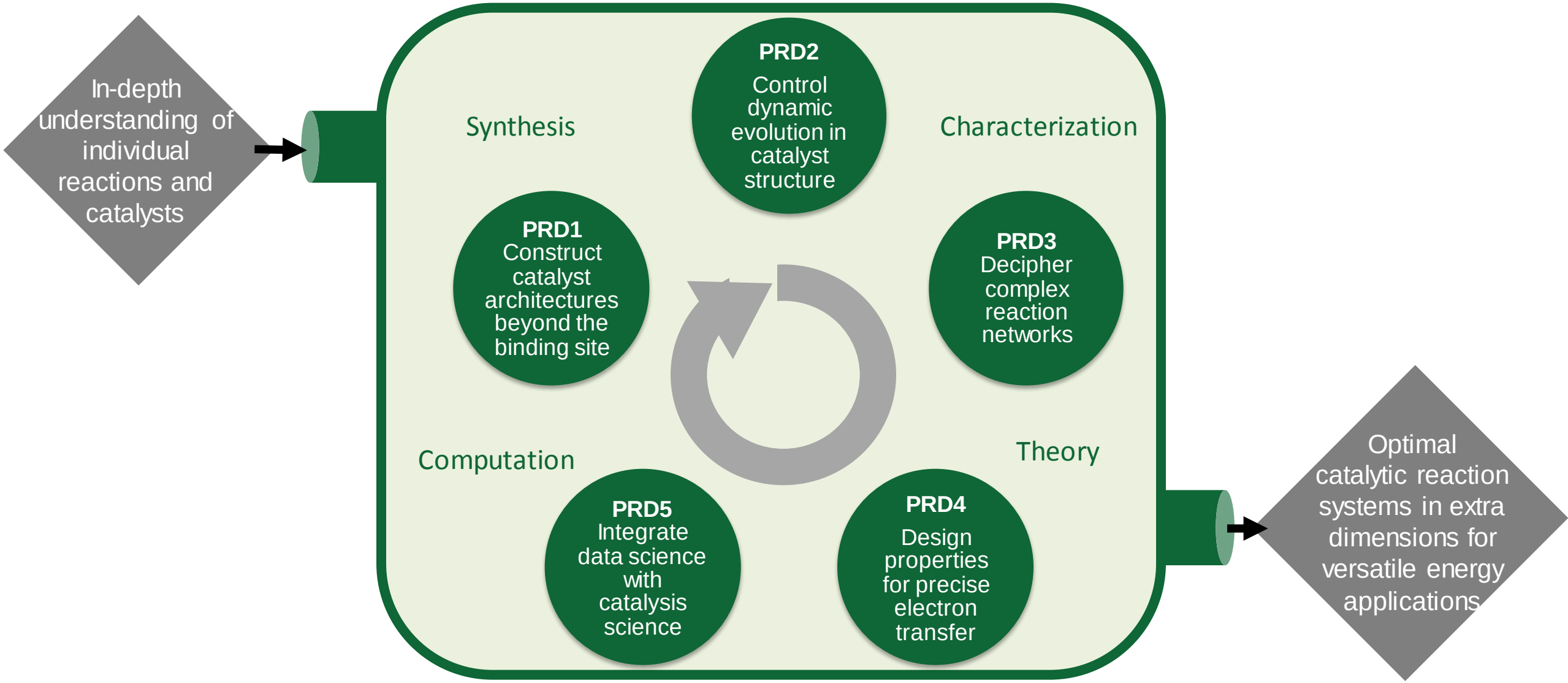
Extracting More Detailed Information from Experiments

- *How do we use data science tools to design better experiments with higher resolution and greater sensitivity, and extract more information from them?*



after Olga Ovchinnikova, ORNL

Embracing Complexity in Catalysis Science



Progress towards Final Report

Appendix I: Technology Perspectives Resource Document

Draft Panel Reports and PRDs on Sharepoint Site

Weekly videoconferences involving ca. 30 people involved in writing

Goal is to have first drafts of Brochure and Final Report by end of July