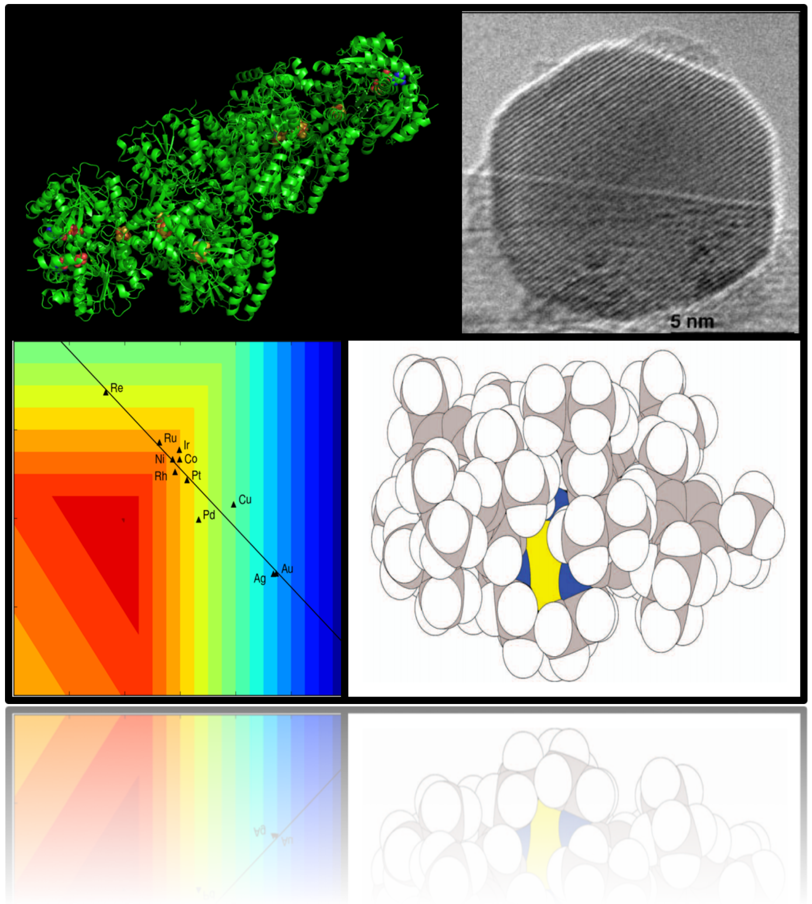
Sustainable Ammonia Synthesis

– Report from a DOE Roundtable



Jens Nørskov

SUNCAT
CENTER FOR INTERFACE SCIENCE AND CATALYSIS

Stanford | ENGINEERING

SLAC
NATIONAL ACCELERATOR LABORATORY

Workshop panel

Exploring the scientific challenges associated with discovering alternative, sustainable processes for ammonia production

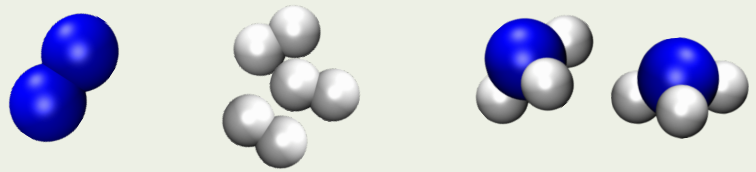
Co-chairs: Jens Nørskov, Stanford University and SLAC
Jingguang Chen, Columbia University and BNL

Panelists: Morris Bullock, PNNL
Paul Chirik, Princeton University
Ib Chorkendorff, Technical University of Denmark
Thomas Jaramillo, Stanford University
Anne Jones, Arizona State University
Jonas Peters, California Institute of Technology
Peter Pfromm, Kansas State University
Richard Schrock, Massachusetts Institute of Technology
Lance Seefeldt, Utah State University
James Spivey, Louisiana State University
Dion Vlachos, University of Delaware

Ammonia Synthesis

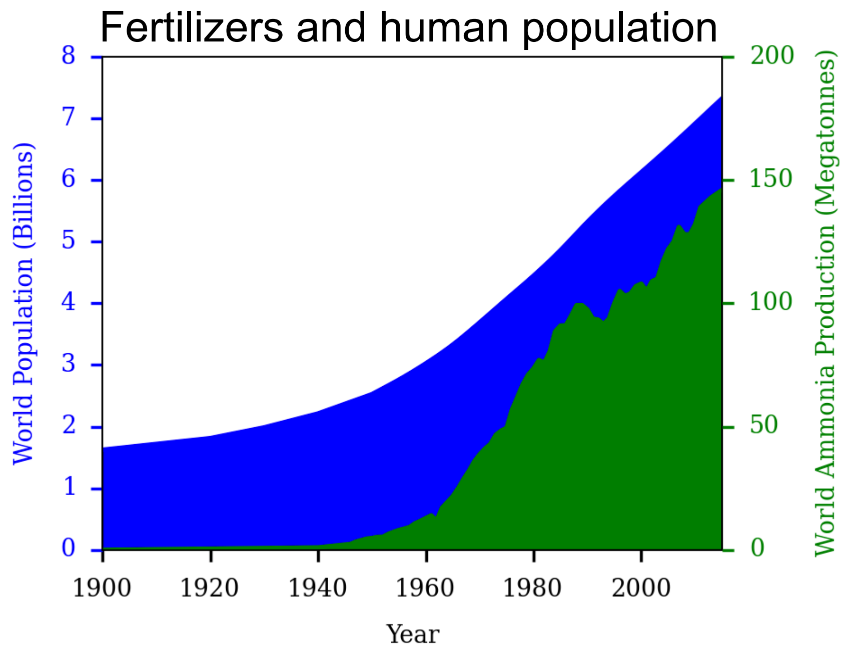
"Most important discovery in 20th century"

Smil, Nature **400**, 415 (1999)



$$N_2 + 3H_2 \rightarrow 2NH_3$$

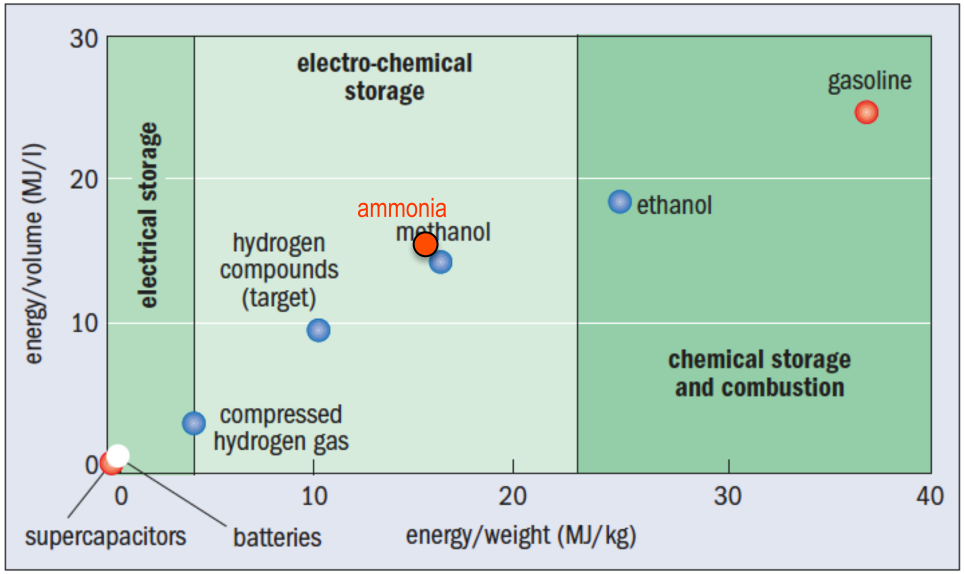
~1% of all energy use in the world



Data from:
http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/
http://www.geohive.com/earth/his_history3.aspx

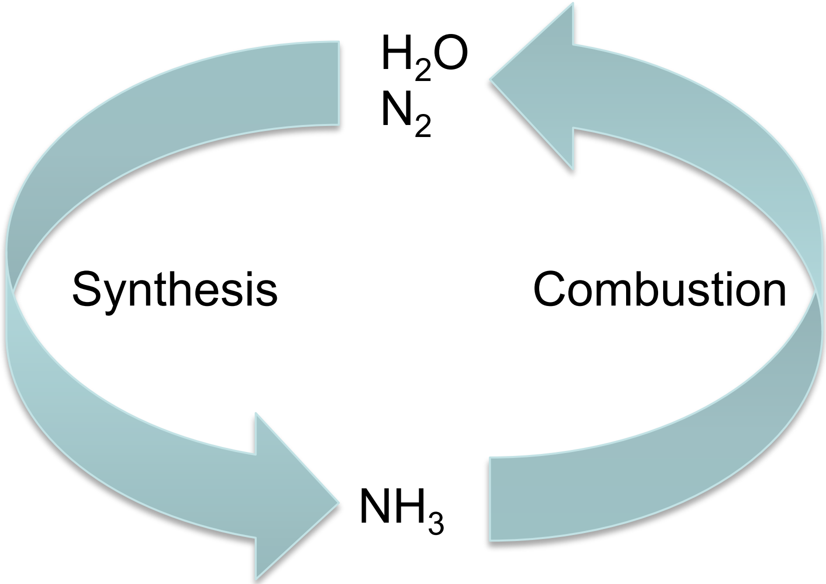
Ammonia for Energy Storage

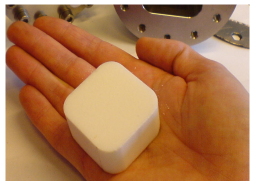
High energy density



Crabtree, Serrao,
Physics World Oct. 2009

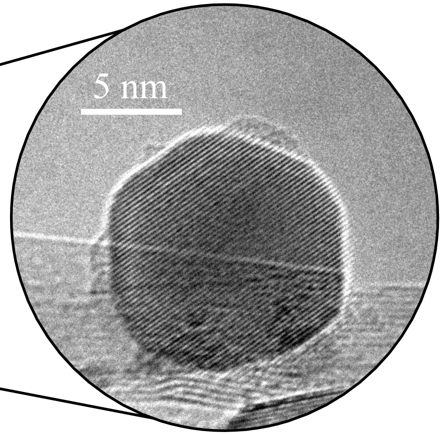
The nitrogen cycle





Safe storage

Today's Technology



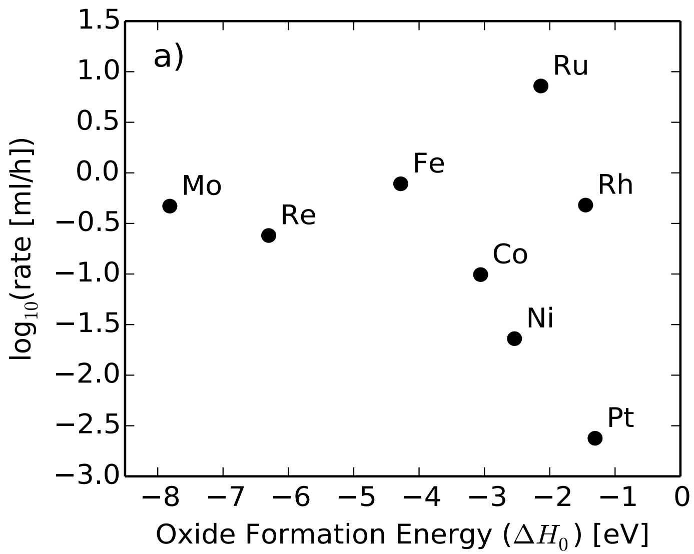
Haber Bosch Process

$N_2 + 3H_2 \rightarrow 2NH_3$

100-150 bar

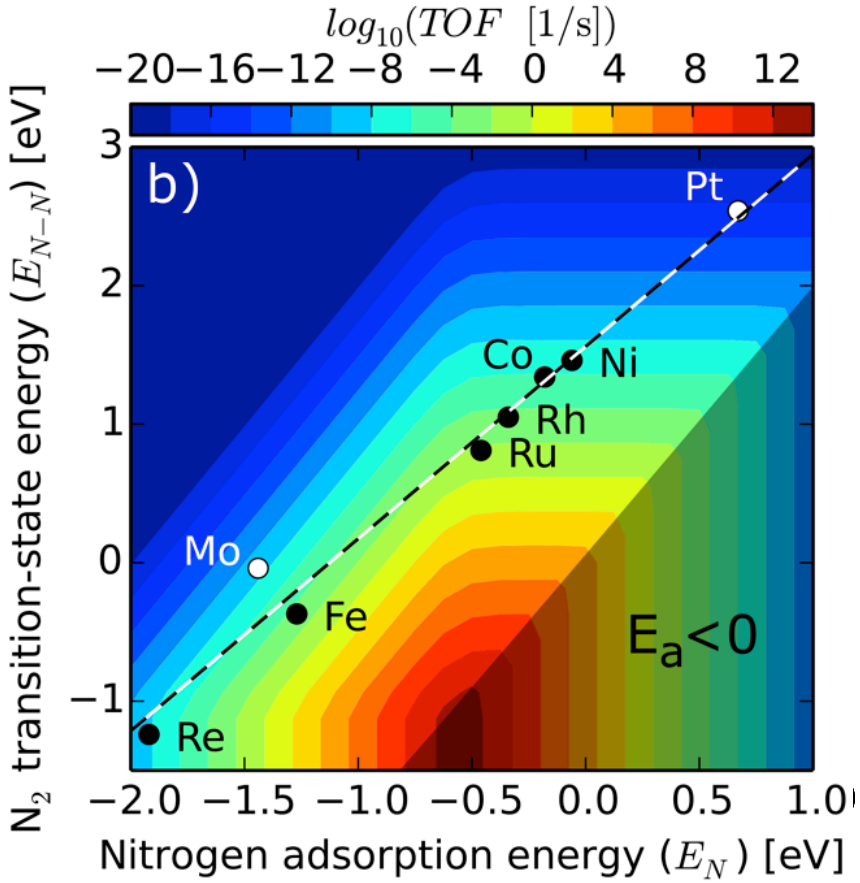
700-800K

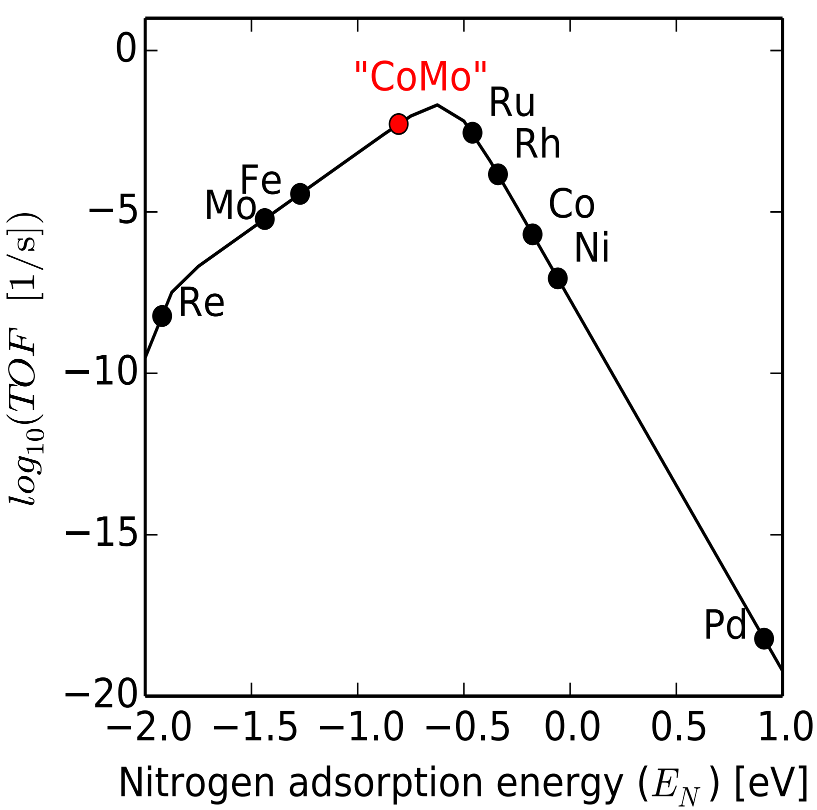
H_2 from natural gas reforming



Ozaki and Aika, *Catalysis* **1**
(Anderson and Boudart, Ed., 1982)

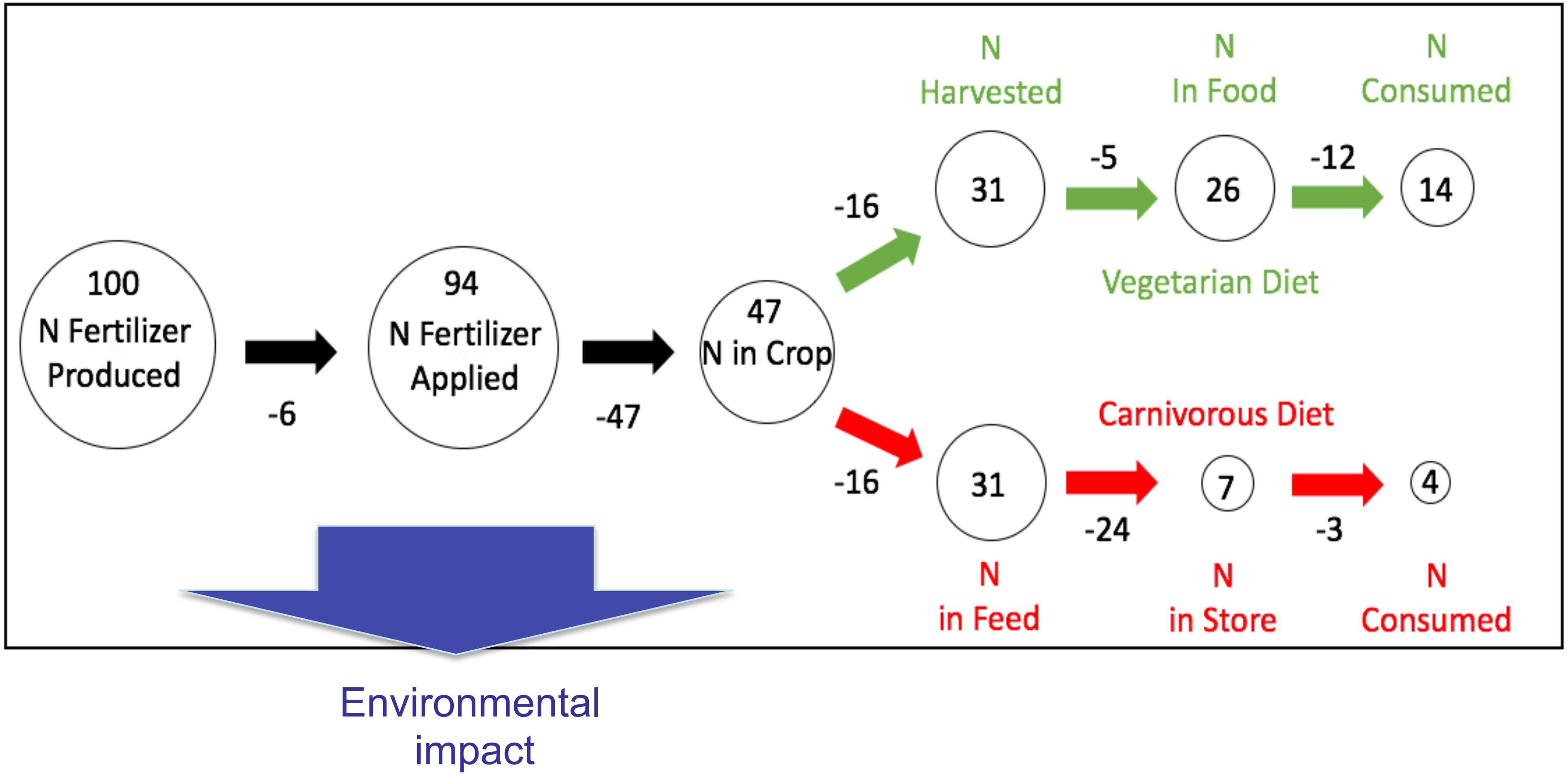
Catalytic rate map, Haber-Bosch process





Medford, Vojvodic, Hummelshøj, Voss, Abild-Pedersen, Studt, Bligaard, Nilsson, Nørskov, J.Catal. **328**, 36 (2015)

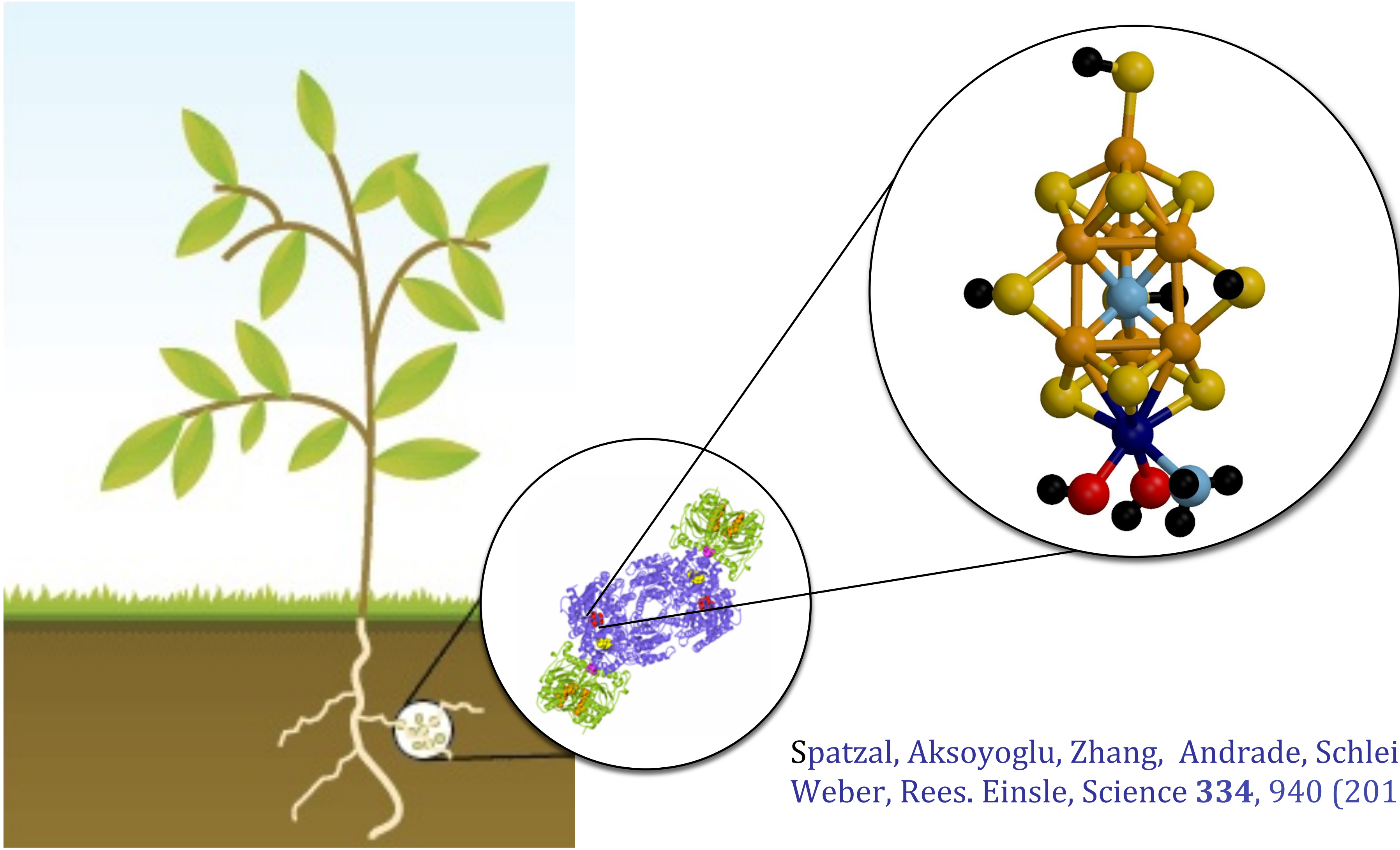
Environmental impact



Galloway, Cowling, AMBIO, 31, 64 (2002)

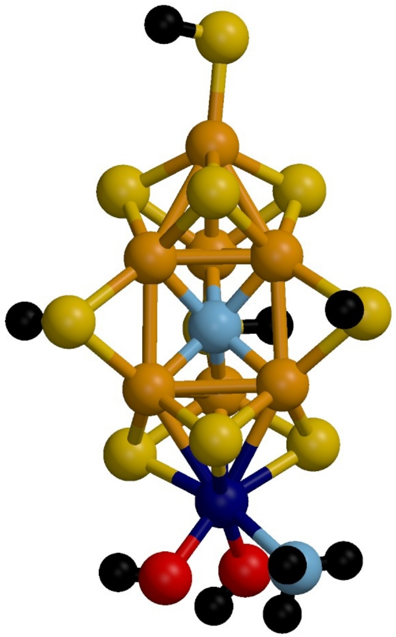
Nature's Ammonia Plant: Nitrogenase

$N_2 + 8(H^+ + e^-) + 16ATP \rightarrow 2NH_3 + H_2$



Spatzal, Aksoyoglu, Zhang, Andrade, Schleicher, Weber, Rees. Einsle, Science **334**, 940 (2011)

Nitrogenase mechanism

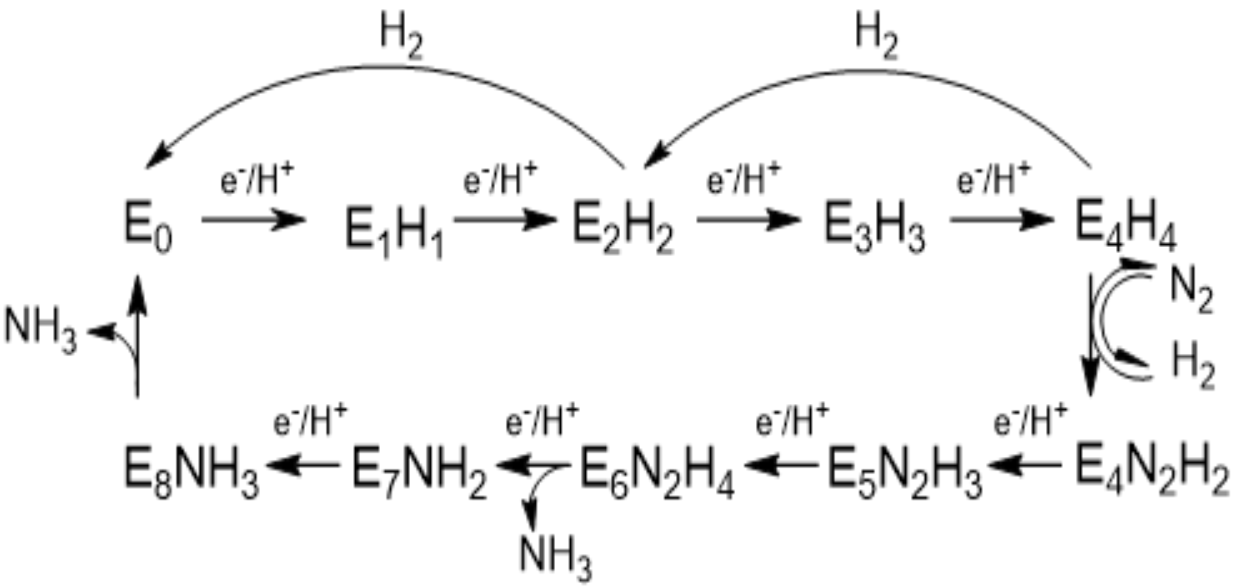


Turn-over frequency (rate)

TOF ~2 s^{-1}

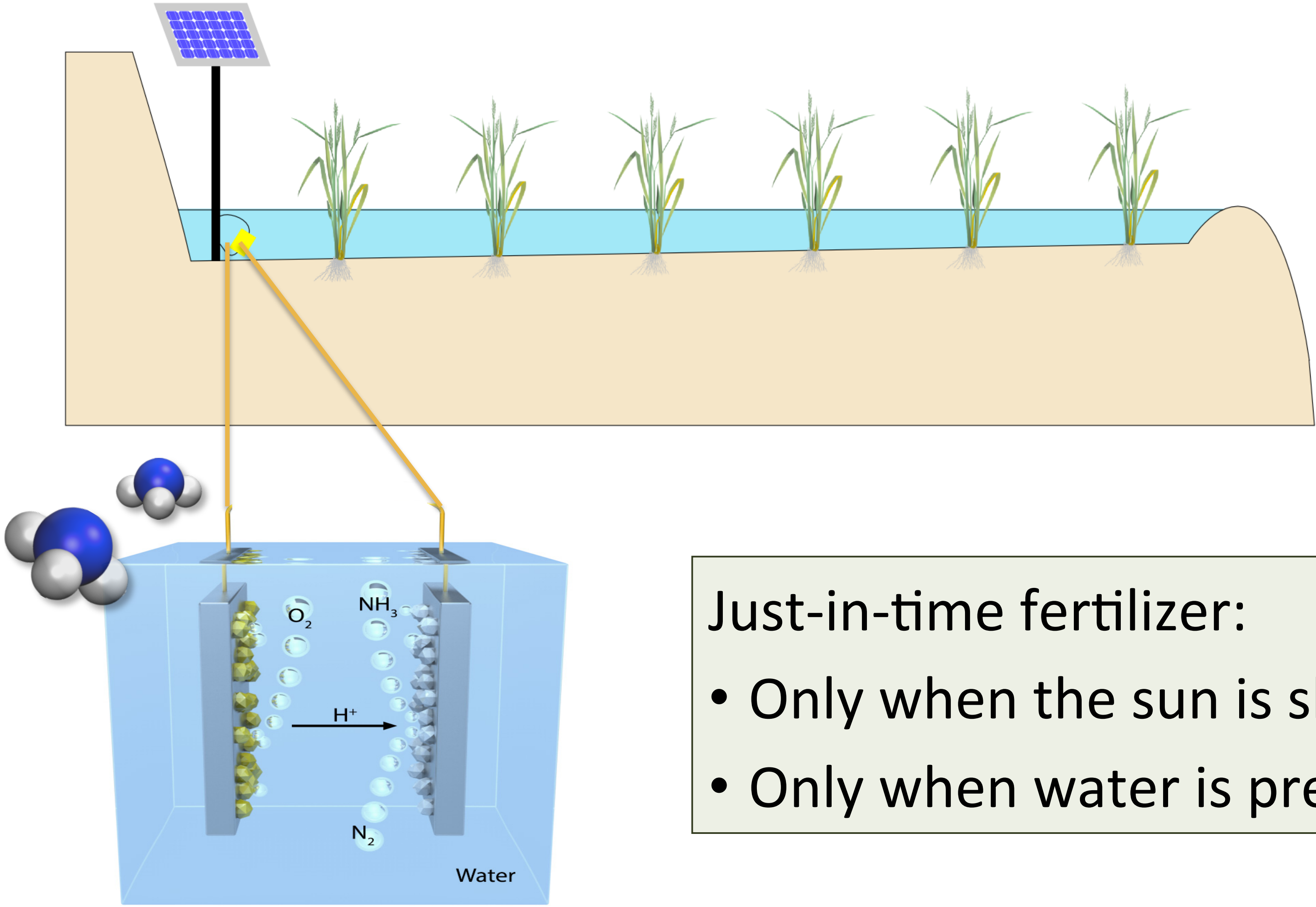
Energy input:

16 ATP/N2



Thorneley; Lowe, in *Molybdenum Enzymes* (Spiro, T. G., Ed.), p 221, Wiley, New York: **1985**

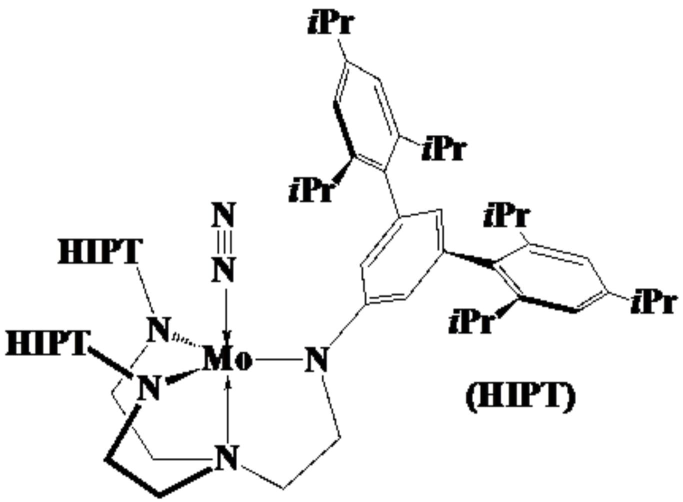
Delocalized Ammonia production



Just-in-time fertilizer:

- Only when the sun is shining
- Only when water is present

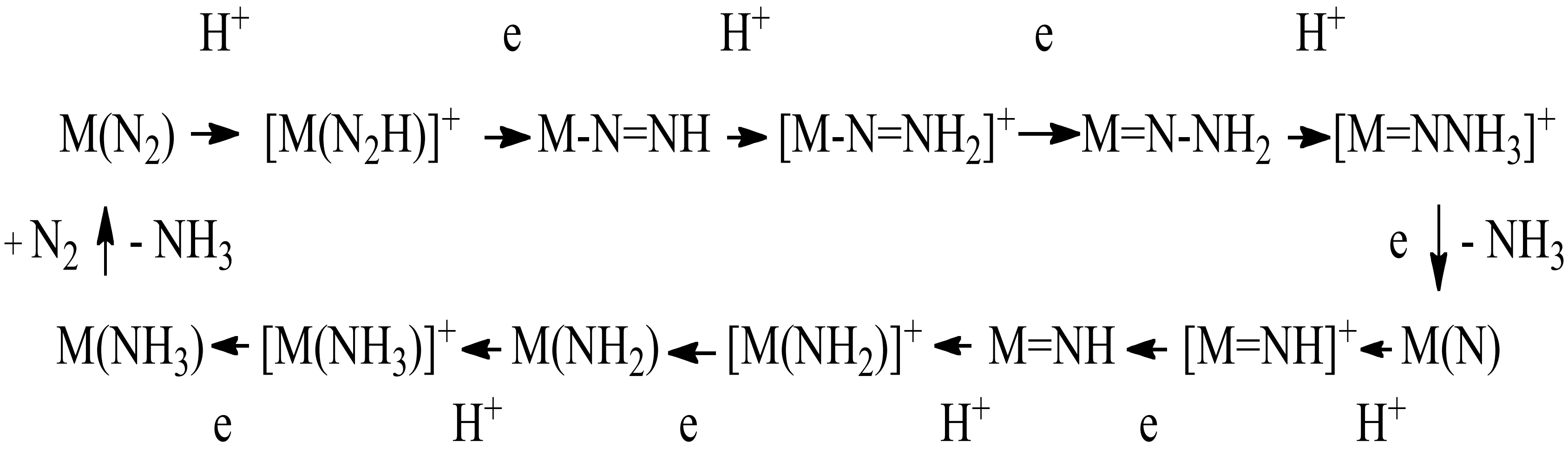
The Schrock catalyst



Turn-over number
TON ~ 10

Strong reducing agents

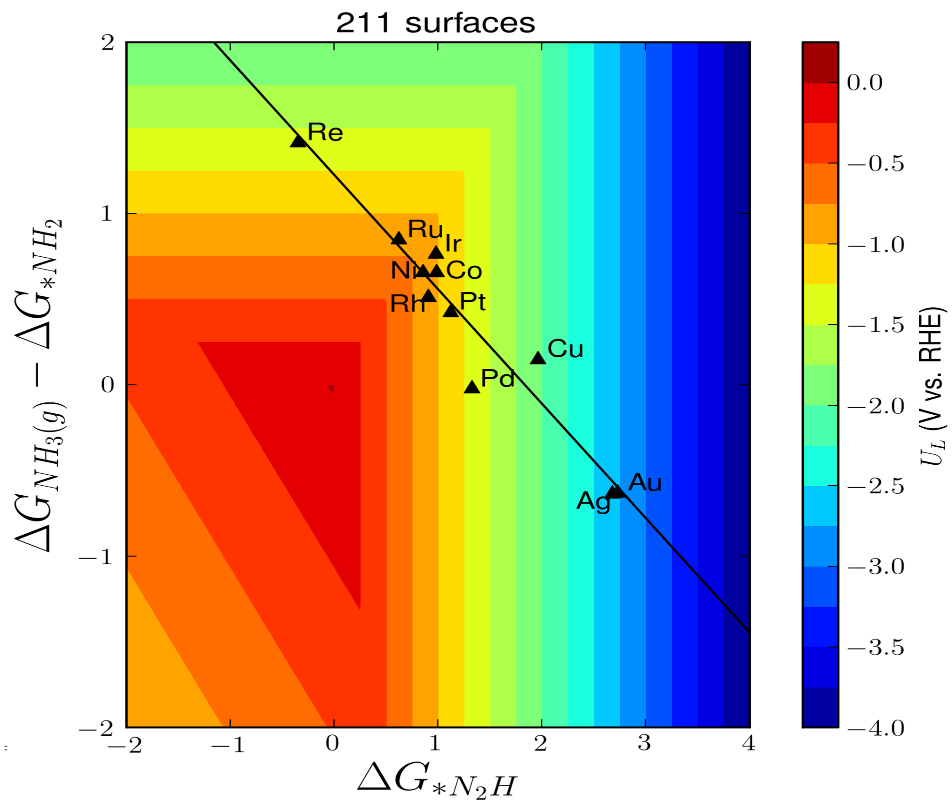
Recently Fe based complexes, TON ~100, (Peters)



Schrock, Acc Chem Res **38**, 955 (2005).

Electro/photochemical N_2 reduction

- Many catalysts tested
- Ambient temperature: Low rate and/or high overpotentials
- High temperature: Higher rates but high overpotentials

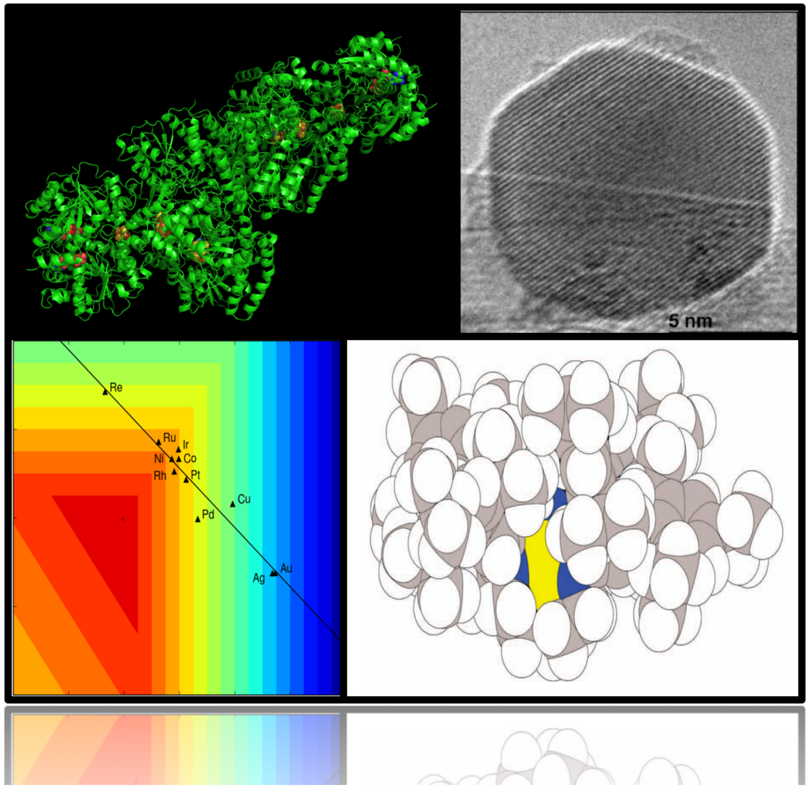


van der Ham, Koper, Hetterscheid, Chem. Soc. Rev. **43**, 5183 (2014)
Montoya, Tsai, Vojvodic, Nørskov, ChemSusChem **8**, 2180 (2015)

Conclusion, sustainable NH_3 syntehsis

Currently there is no viable heterogeneous, homogeneous, or enzyme catalyst known that fulfills all of the requirements:

- active
- selective
- scalable
- long-lived



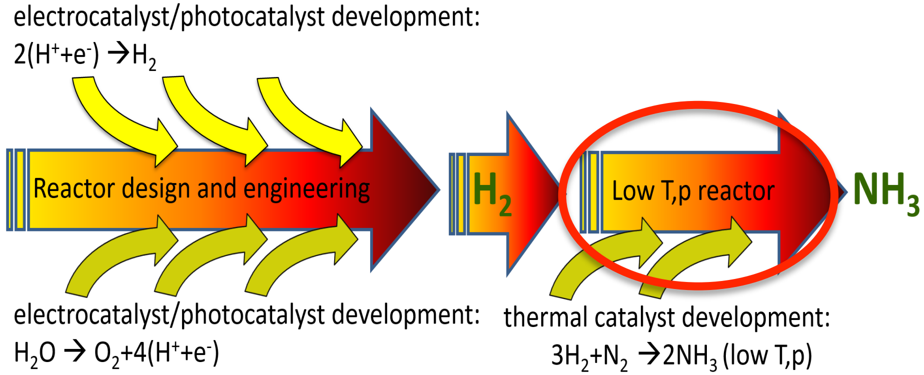
The grand challenge

Discovery of new catalysts (and processes) for sustainable ammonia synthesis.

Discovery of new ways to reduce the inert N_2 molecule is the overarching grand challenge for sustainable ammonia synthesis.

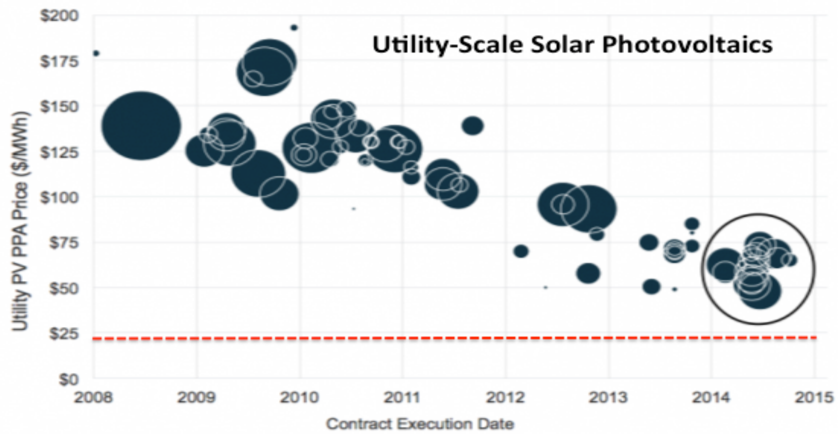
Challenges I

Development of relatively low pressure (<10 atm) and relatively low temperature (<200 C) thermal processes.



- Sustainable H_2 production

- Need new catalysts enabling catalysis at non-Haber-Bosch conditions

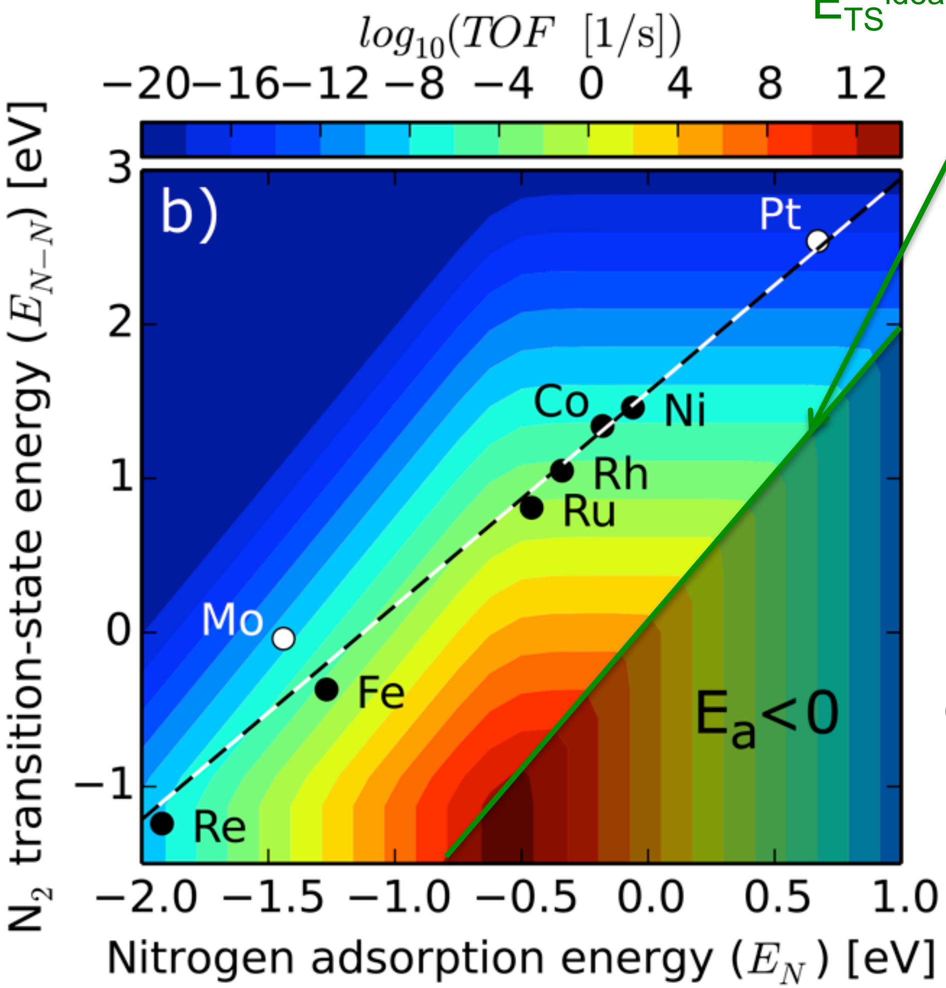


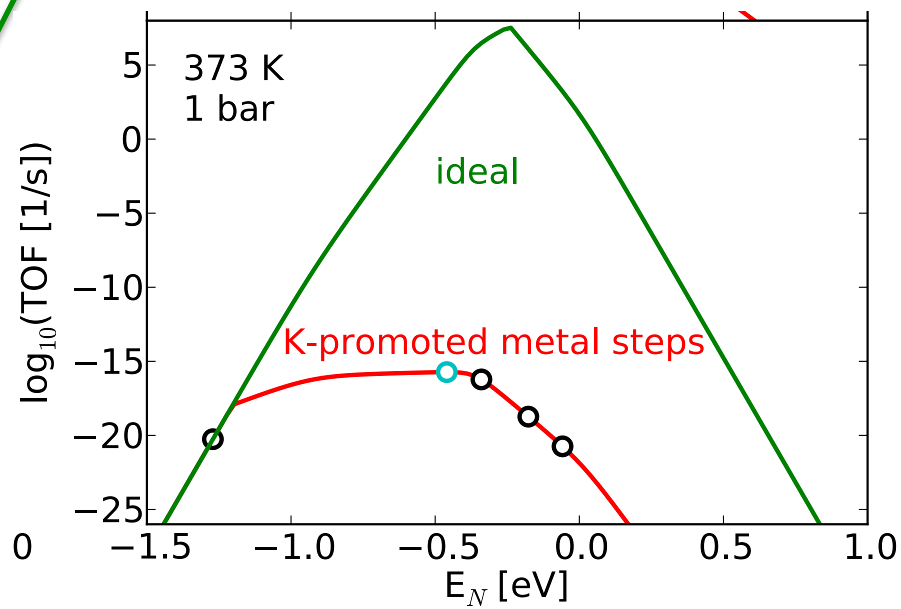
Source of PV data: GTM Research, Arun Majumdar

Low T,p thermal catalysis

The ideal catalyst:

$E_{TS}^{ideal}(E_N)=2E_N$





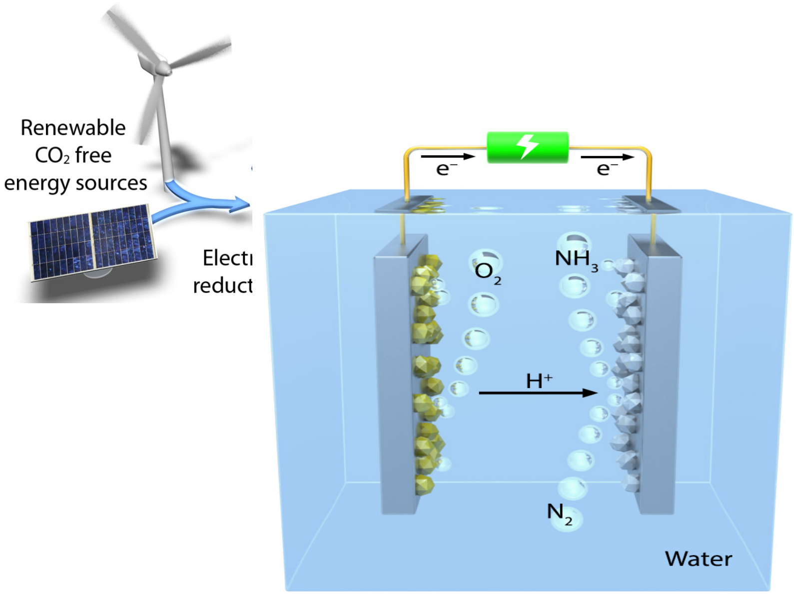
Vojvodic, Medford, Khan, Studt, Abild-Pedersen, Bligaard, Nørskov, CPL **598**, 108 (2014)

Challenges II

Development of electrochemical and photochemical routes for N_2 reduction based on proton and electron transfer

- Need active and selective catalyst for N_2 electro-reduction (solid or molecular)

- Need good water splitting catalysts

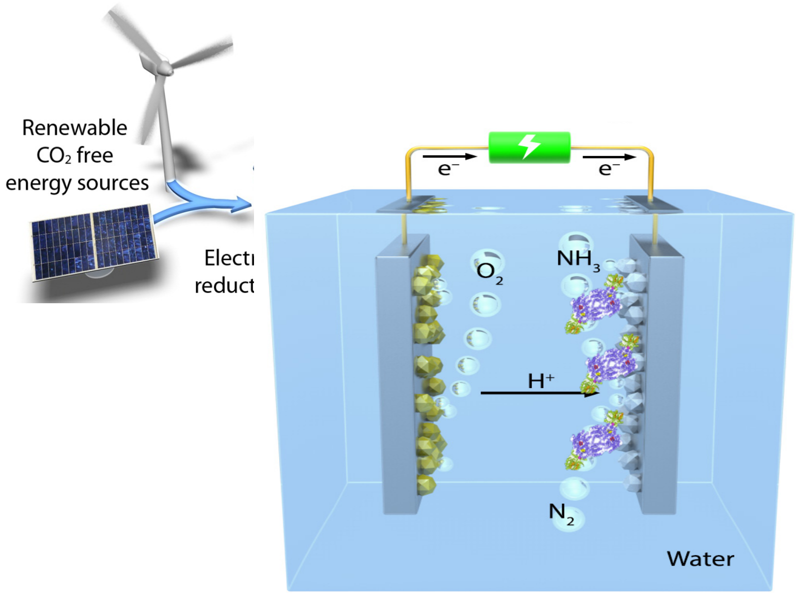


Challenges III

Development of biochemical routes to N_2 reduction

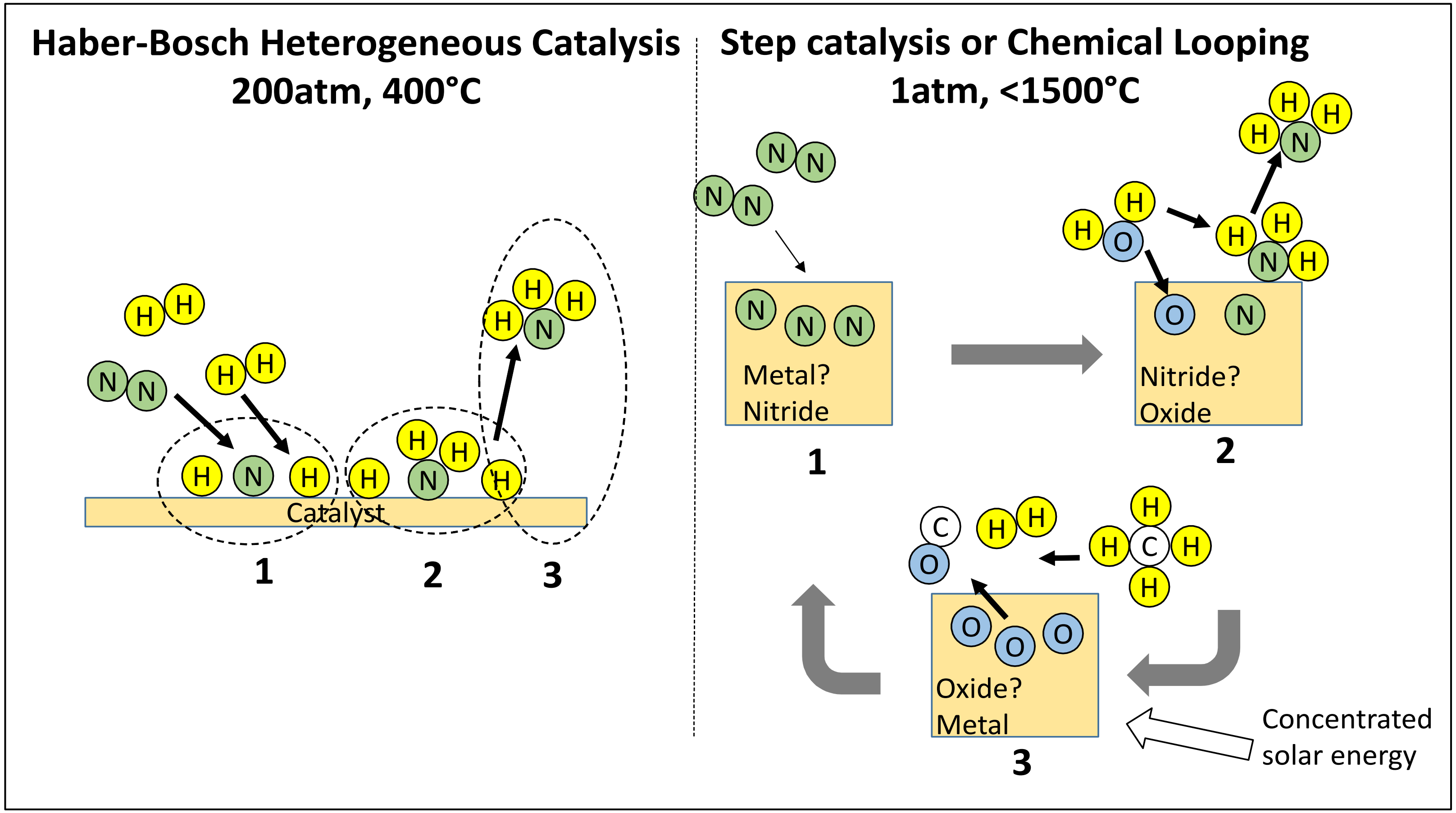
- Immobilize redox enzymes on electrode surfaces

- Immobilize cells on electrode surfaces



Challenges IV

Development of chemical looping (solar thermochemical) approaches



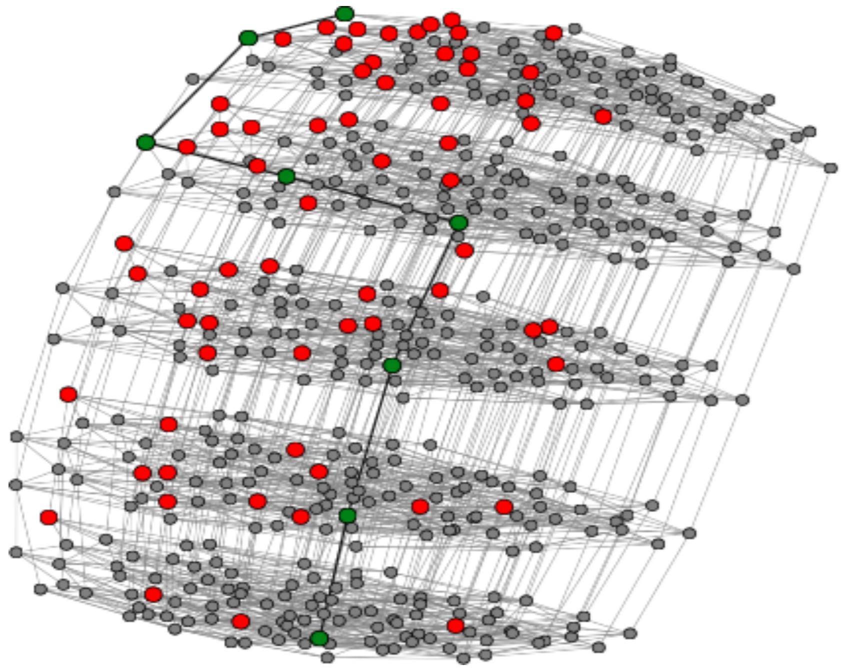
Challenges V

Identification of descriptors of catalytic activity using a combination of theory and experiments

- Identify the most important properties determining catalytic activity

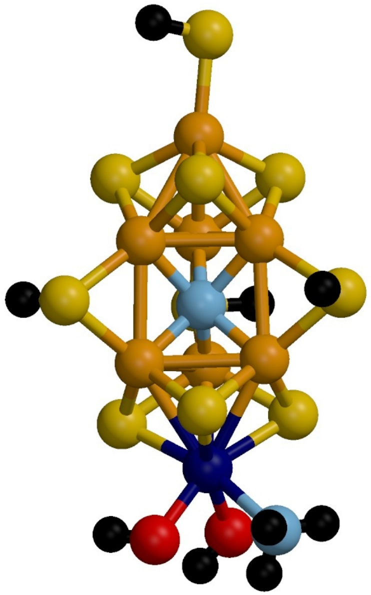
- Understand active site motifs

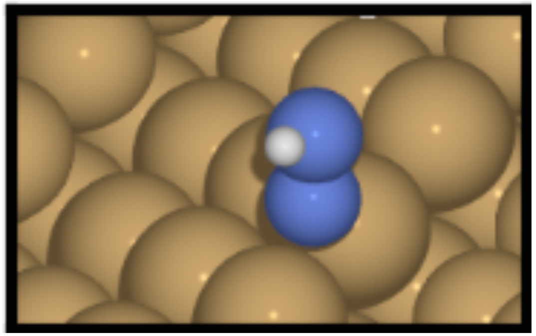
- Basis for catalyst design

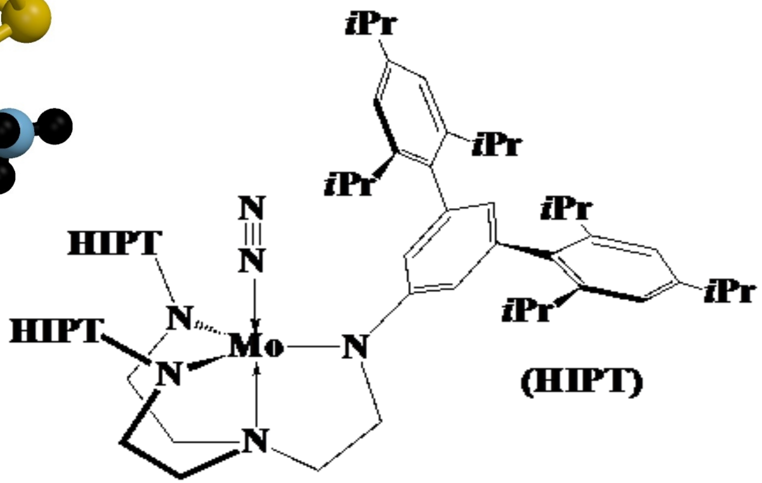


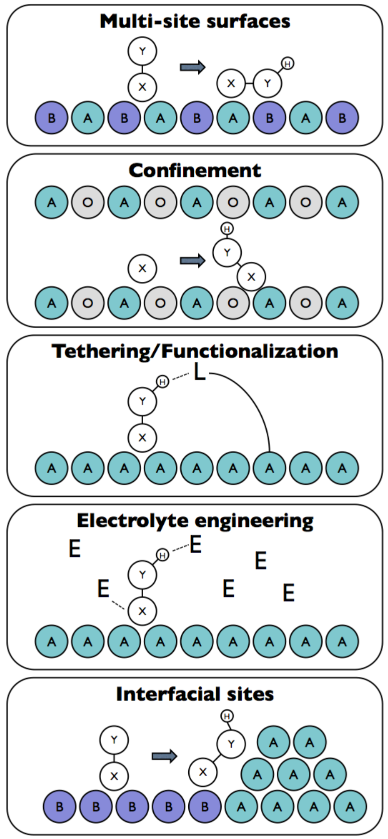
Challenges VI

Integration of knowledge from nature (enzyme catalysis), molecular/homogeneous, and heterogeneous catalysis.









Challenges VII

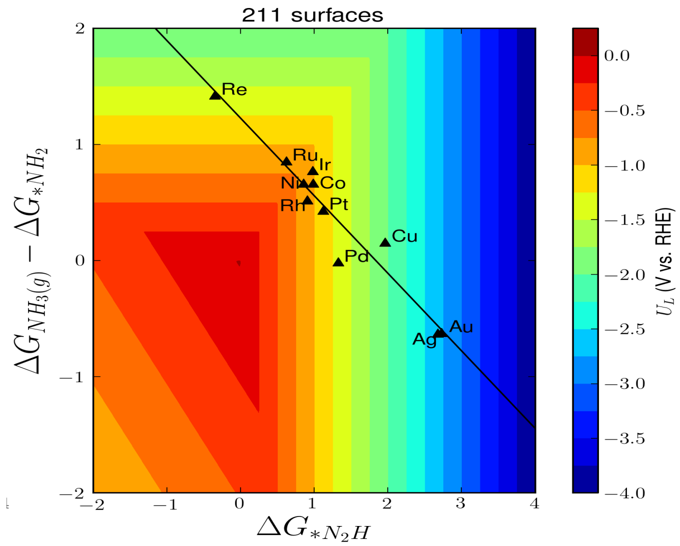
Characterization of surface adsorbates and catalyst structures (chemical, physical and electronic) under conditions relevant to ammonia synthesis.

- Ambient-pressure techniques needed

- *In-situ* and *operando* synchrotron techniques needed

Sustainable ammonia synthesis

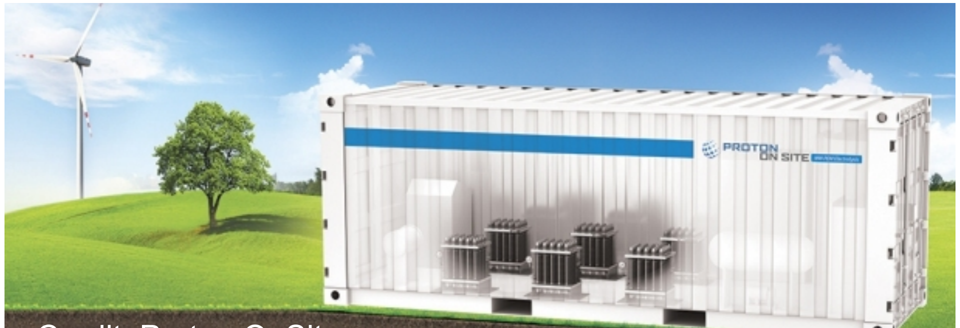
- Significant scientific challenge
- Large potential impact on energy, environment, and food supply
- Example of "new chemistry" for sustainable, distributed production



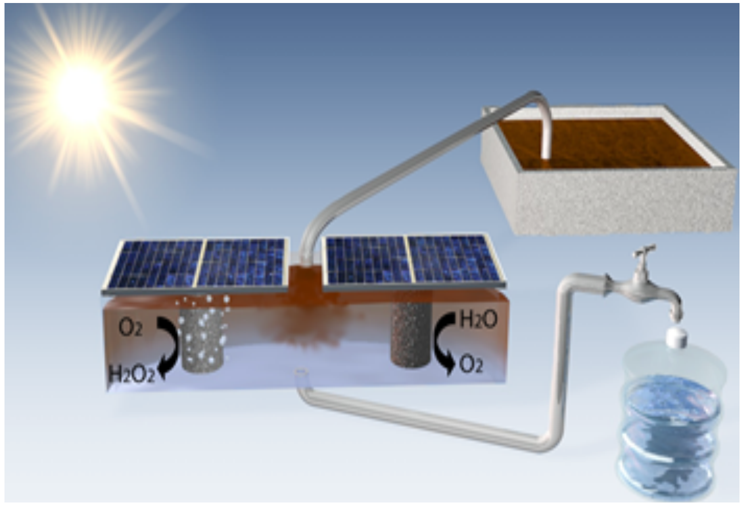
http://landresources.montana.edu/soilfertility/ndeficiency.html

Distributed, sustainable chemical production

- Energy: Distributed sources vs. fossil
- Safety: On-site and on-time vs. transport and storage
- Economics: Efficiency of scale vs. mass production
- Innovation: small vs. large economic risks



Credit: Proton OnSite



Workshop panel

Co-chairs: Jens Nørskov, Stanford University and SLAC
Jingguang Chen, Columbia University and BNL

Panelists: Morris Bullock, PNNL
Paul Chirik, Princeton University
Ib Chorkendorff, Technical University of Denmark
Thomas Jaramillo, Stanford University
Anne Jones, Arizona State University
Jonas Peters, California Institute of Technology
Peter Pfromm, Kansas State University
Richard Schrock, Massachusetts Institute of Technology
Lance Seefeldt, Utah State University
James Spivey, Louisiana State University
Dion Vlachos, University of Delaware