Sustainable Ammonia Synthesis
– Report from a DOE Roundtable

Jens Nørskov
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 Pffromm, 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 20\textsuperscript{th} century”


\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]

\(~1\%~\text{of all energy use in the world~}~

Data from:
http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/
Ammonia for Energy Storage

High energy density

The nitrogen cycle

Crabtree, Serrao, Physics World Oct. 2009
Haber Bosch Process
\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]
100-150 bar
700-800K
H\textsubscript{2} from natural gas reforming

Ozaki and Aika, *Catalysis* 1
(Anderson and Boudart, Ed., 1982)
Catalytic rate map, Haber-Bosch process

Environmental impact

Galloway, Cowling, AMBIO, 31, 64 (2002)
Nature’s Ammonia Plant: Nitrogenase

\[ \text{N}_2 + 8(\text{H}^+ + \text{e}^-) + 16\text{ATP} \rightarrow 2\text{NH}_3 + \text{H}_2 \]

Nitrogenase mechanism

Turn-over frequency (rate)
TOF $\sim 2 \text{ s}^{-1}$

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)

Electro/photochemical $\text{N}_2$ 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)
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 H₂ 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
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

Haber-Bosch Heterogeneous Catalysis
200 atm, 400°C

Step catalysis or Chemical Looping
1 atm, <1500°C

Metal? Nitride

Nitride? Oxide

Concentrated solar energy
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
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
Workshop panel

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