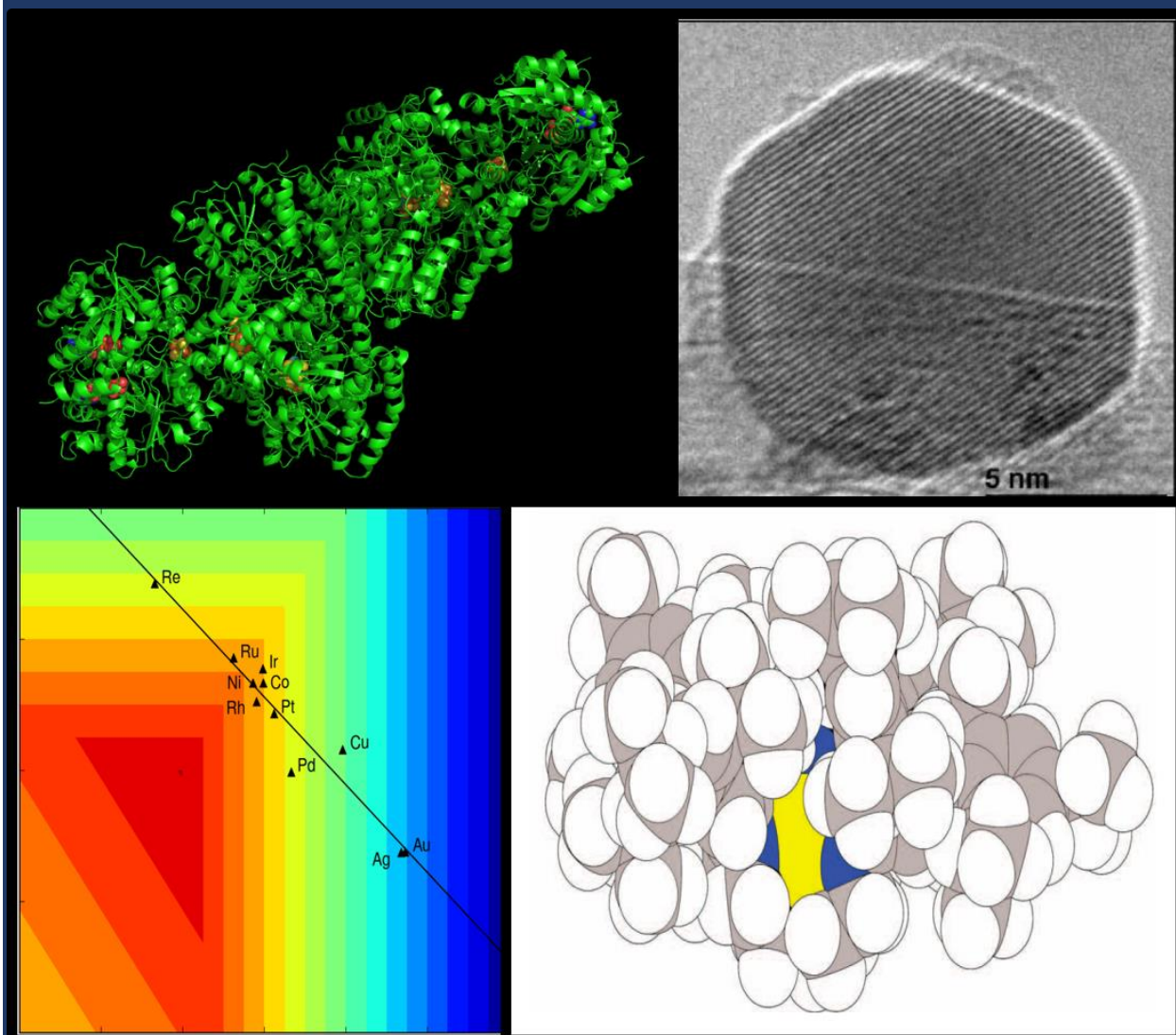# Sustainable Ammonia Synthesis

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

DOE Roundtable Report

Discussion Held February 18, 2016

Dulles, VA

U.S. DEPARTMENT OF
ENERGY

Office of Science

SUSTAINABLE AMMONIA SYNTHESIS

Roundtable Discussion held on February 18, 2016

Marriott Dulles Airport Suites Hotel, 45020 Aviation Drive, Dulles, VA 20166

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Cover:
Examples of ammonia synthesis catalysts: The Nitrogenase enzyme[1] (upper left), a Barium-promoted Ruthenium nanoparticle[2] for the Haber-Bosch process (upper right), the Schrock catalyst[3] for N_2 reduction at a single molybdenum center (lower right). The lower left image indicates why it is so difficult to reduce N_2 electrochemically. The calculated limiting potential activity map for N_2 electro-reduction at transition metal surfaces shows an optimum far from the usual metal catalysts.[4]

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[1] http://www.calvin.edu/academic/chemistry/faculty/arnoys/proteins/nitrogenase.png.

[2] From Hansen et al., *Science* **294**, 1508 (2001). Reprinted with permission from AAAS.

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SUSTAINABLE AMMONIA SYNTHESIS

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FIGURES

ACRONYMS AND ABBREVIATIONS

|	
AP-TPR	Ambient pressure temperature programmed reaction
AP-XPS	Ambient-pressure X-ray photoelectron spectroscopy
BEP	Brønsted-Evans-Polanyi relationship
BDFE	Bond dissociation free energy
CoMo	Cobalt and molybdenum
DFT	Density functional theory
DOE	U.S. Department of Energy
FeMo-co	FeMo cofactor in nitrogenase
FTIR	Fourier transform infrared spectroscopy
HER	Hydrogen evolution reaction
LT	Lowe and Thorneley kinetic model
N_2	Dinitrogen
NH_3	Ammonia
NMR	Nuclear magnetic resonance
N_2RR	Dinitrogen reduction reaction
OER	Oxygen evolution reaction
TOF	Turnover frequency
TON	Turnover number
UHV	Ultrahigh vacuum

I. INTRODUCTION

Ammonia (NH_3) is essential to all life on our planet. Until about 100 years ago, NH_3 produced by reduction of dinitrogen (N_2) in air came almost exclusively from bacteria containing the enzyme nitrogenase. In 1913 the first industrial production of ammonia from N_2 based on the Haber-Bosch process was introduced.[1] This has completely changed possibilities for human development, as illustrated in Figure 1. A large fraction of the current population on Earth is dependent on nitrogen from this process as fertilizer for food production, and it has been estimated that more than 50% of the nitrogen in an average human has been through this process. For this reason, among others, the Haber-Bosch process has been suggested to be the most important invention of the 20th century.[2] The process, $N_2 + 3H_2 \rightarrow 2NH_3$, requires a solid catalyst, and even with the best-known catalysts it is only feasible at high temperatures (~700 K) and pressures (~100 atm).[3] The process has been extremely well optimized over the years in very large industrial facilities.[4] The primary source of the dihydrogen in the process is natural gas, and it has been estimated that about 1% of all energy consumption in the world goes into this one process.[5] The economics of the fossil fuel-enabled Haber-Bosch process are favorable when no cost or penalty is attached to releasing fossil-derived CO_2 into the atmosphere. In the best case, about 1.9 metric tons fossil CO_2 are released per metric ton ammonia produced, using natural gas to obtain dihydrogen, dinitrogen, and energy.

Ammonia synthesis presents fascinating scientific and engineering challenges. Given that the reaction is exergonic at ambient conditions, a man-made catalyst should be able to facilitate this process at more benign conditions. Nitrogenase does that, albeit quite inefficiently; it uses 16 ATP per reduced N_2 molecule, corresponding to an energy expense of almost 5 eV per turnover of one N_2 molecule (~500 kJ/mole of N_2).[6] It is

therefore a grand challenge to chemistry to find new ways to activate the N-N bond. In heterogeneous catalysis, the Haber-Bosch process has been used as a vehicle to develop many of the concepts being employed today.[7] It was used to link well-defined surface science experiments to high-pressure heterogeneous catalysis and it has been named the "Bellwether reaction in heterogeneous catalysis".[8-11] In spite of many new insights, the industrial catalyst used today is surprisingly similar to the original one discovered by Mittasch in the beginning of the 20th century.[12]

The current industrial ammonia synthesis process has a substantial carbon footprint, so an
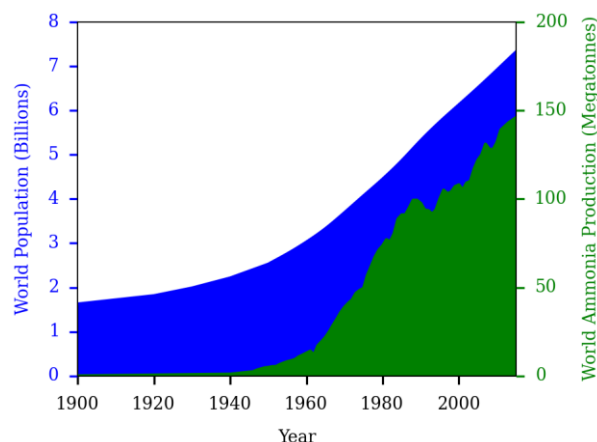
Figure 1. The correlated time evolution of the world population and annual ammonia production rate from 1900-2015. The data show how the industrial production of ammonia-based fertilizers by the Haber-Bosch process has enabled a sustained global population increase since the middle of the 20th century. Data from U.S. Geological Survey 2015 Mineral Commodity Summaries: Nitrogen (Fixed) -- Ammonia. http://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/ and Geohive Population Statistics -- Yearly Global Data, 2015. http://www.geohive.com/earth/his_history3.aspx

alternative, sustainable process based on the biological one would be highly desirable. It is unlikely that such a process would be more energy efficient than the Haber-Bosch process, but the energy could come from sustainable
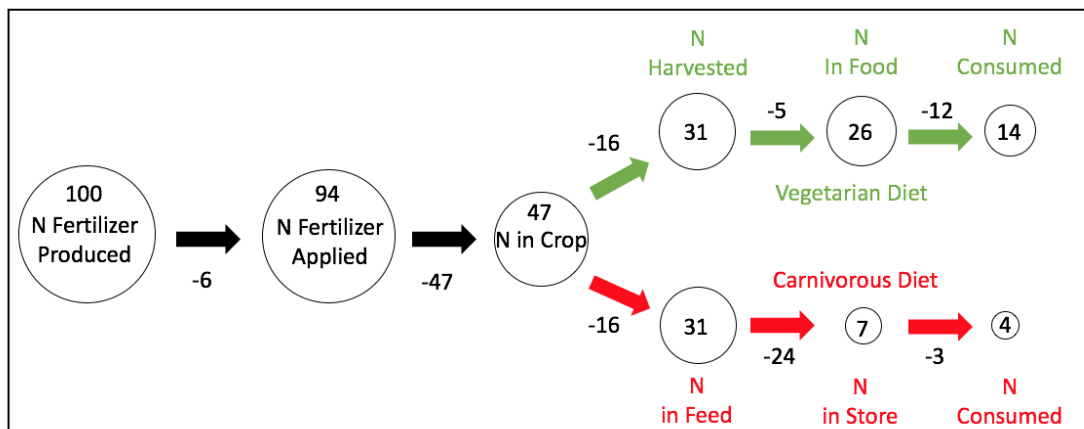
Figure 2. The overall efficiency of production, delivery, and uptake by organisms of fertilizer N produced by the Haber-Bosch process. Significant losses are shown for both Vegetarian and Carnivorous diets. Adapted with permission from J. N. Galloway, E. B. Cowling, AMBIO*, 31, 64 (2002).*

sources, such as solar or wind. It would also be desirable to be able to produce fertilizer close to the field and only when the crops need it: fertilizer production on demand would solve many transport and storage problems in the developing world and could help avoid the runoffs and nitrogen pollution that are associated with the use of fertilizer in the industrial world, see Figure 2.[13]

The present report is based on a roundtable meeting held under the auspices of the Department of Energy, Basic Energy Sciences, to explore the scientific challenges associated with discovering alternative, sustainable processes for ammonia production. A panel of scientists spent a day discussing the current state-of-the-art and the potential challenges and research opportunities. In the following we summarize the findings for heterogeneous catalysis and homogeneous and enzyme catalysis separately. We also discuss a number of cross-cutting themes in catalyst synthesis, characterization and theory. Finally, we outline a number of research challenges and opportunities in the field.

One major finding is that the Haber-Bosch process is very well understood and well optimized. Alternatives that do not rely on fossil resources as the source of energy and dihydrogen are far from a stage where they can contribute to

fertilizer production. Substantial progress has been made to understand aspects of N_2 reduction by heterogeneous, homogeneous, and enzyme catalysts under ambient conditions, or by alternative high temperature processes. Yet many questions remain that must be addressed to build foundational principles upon which the design of the next generation of sustainable N_2 reduction catalysts will be built.

The overarching grand challenge identified by the Roundtable Panel is to devise new approaches to the discovery of active, selective, scalable, long-lived catalysts for sustainable ammonia synthesis. This entails integrating theory and experiment to understand mechanisms and identify catalyst descriptors that can be used in catalyst design. It also requires integrating knowledge from heterogeneous, homogeneous, and enzyme catalysis. A number of new tools in computational and in-situ and operando characterization of catalysts also need to be invoked to ensure success.

II. STATE-OF-THE-ART AND CHALLENGES OF AMMONIA SYNTHESIS

Here we summarize the current status of three catalysis areas for N_2 activation and ammonia synthesis: heterogeneous catalysis, homogeneous and enzyme catalysis, and cross-cutting approaches. In each subsection we will discuss both the state-of-the-art and challenges associated with the development of sustainable ammonia synthesis. The specific results cited below are meant to exemplify and support the arguments made in this report and are not an exhaustive review of the field.

2.1 Heterogeneous Catalysis

In this section, we describe heterogeneous approaches to ammonia production that utilize hard materials as the basis for different processes. First, we describe the conventional approach to ammonia synthesis, the Haber-Bosch process that dominates ammonia production today. We discuss how this process works, and the challenges that exist in improving a process that has been optimized over approximately the last 100 years. Next, we describe approaches to ammonia synthesis that are renewable in nature. One type of process is based on electrocatalysis and/or photocatalysis, employing renewable energy as inputs in making a sustainably-derived H_2 that can be used in the Haber-Bosch process. Another approach is to directly produce ammonia via electrocatalysis or photocatalysis. Another concept is based on chemical looping, in which heterogeneous materials can be designed to undergo specific phase transitions at high temperatures.

2.1.1. Thermochemical Processes for Ammonia Production

State-of-the-art

Commercial ammonia production is today carried out via the Haber–Bosch process based on an iron catalyst structurally promoted with Al_2O_3 and electronically promoted with potassium. The ammonia synthesis reaction only represents a small fraction of the overall process. First, natural gas is converted through the steam reforming process to synthesize dihydrogen. In a similar manner, oxygen has to be removed from the atmosphere in order to produce pure dinitrogen. In order to remove any oxygen-containing compounds such as CO from the N_2 and H_2 mixture, methanation is employed whereby the oxygen is removed as water.[14] While methane does not severely influence the ammonia production, even ppm levels of oxygen are detrimental. Ammonia is today produced in large centralized plants, typically 2500 tons a day, at locations where natural gas and water are present in large amounts. The total annual production amount is about 146 million tons at an energy cost of roughly 28GJ/ton.[14] Ammonia is therefore responsible for roughly 1% of our annual global energy consumption of $5.6*10^{20}$ J/year, equivalent to 18 TW of power.[15]

Substantial resources have been invested in understanding and improving the ammonia catalyst. Surface science studies have elucidated important elementary steps in the ammonia synthesis process and it was one of the first catalytic processes to be modeled in detail.[10,16] It has been shown that atomic steps (or very open surfaces) completely dominate the reactivity of catalyst surfaces for N_2 activation.[17-19] New catalysts have been proposed. For example, ruthenium has been used in the Kellogg's Advanced Ammonia Process, since it is a better catalyst than iron (albeit much more expensive) for approaching equilibrium once substantial

amounts of ammonia have already been synthesized.

It is now well accepted that the activity of the elements can be explained through a volcano relationship involving the N-binding energy on different surfaces; some metals bind N too strongly and others bind it too weakly, representing each side of the volcano.[20, 21] For less reactive catalysts, N_2 dissociation is rate-limiting since the activation barrier is too high, combined with the large entropy loss when going from the gas phase to the transition state for dissociation. For more reactive surfaces, N_2 dissociation can occur but the process is limited by the small number of free sites available for dissociation, as atomic nitrogen and other intermediates block the surface.

Based on these insights, new catalysts were identified, for example by combining elements from each side of the volcano, such as cobalt and molybdenum (CoMo).[22] Nevertheless, the activity was not sufficiently improved to compete with the much cheaper iron-based catalysts. Recent theoretical calculations have revealed that the activation barrier for the dissociation and the bonding energy of all the intermediates are scaling with each other since the bonding involved is of the same nature. Thus for conventional catalyst formulations, it has not yet been possible to obtain a situation where the barrier is very low and at the same time the bonding energies of the relevant intermediates are also low. If this could be realized by breaking the known scaling relations, reaction rates could be orders of magnitude higher than what is seen today.[21]

Challenges and Opportunities

Improvements made to the ammonia synthesis process have mostly been related to optimizing the overall plant design and utilizing the energy balance of the plant. As mentioned above, it would be extremely difficult to discover a new ammonia catalyst that is more efficient and cost-effective than the existing iron-based catalysts. Nevertheless, it might be possible to find a reaction pathway where the barrier for the initial dissociation of the dinitrogen is decoupled from the bonding energy of the intermediates, i.e., by breaking the scaling relation between the two adsorbate-surface interaction energies. This could lead to much more active catalysts that could potentially operate at lower temperatures and thus lower the process pressure, one of the most significant factors contributing to the cost. If such highly active catalysts could be developed, both the capital cost and the energy consumption would be reduced significantly, particularly if the dihydrogen were made from sustainable energy sources. Such an approach would open possibilities for producing ammonia closer to the agricultural field of use and to the point of generation of such sustainable energy sources.

The route for obtaining such very active catalysts likely requires a shift away from the conventional catalyst surfaces employed today, which are two-dimensional in nature. Instead we must be able to introduce three-dimensional bonding, as has been explored in homogeneous catalysis and in biocatalysts, where the enzymes utilize this effect to obtain an optimized balance between activation and bonding. Promising options include introducing confined active sites such as those found in carbon nanotubes or similar systems, or creating interfaces between two different types of sites. It is, however, worth noting that such very specialized sites often come with serious transport problems or lack of high active site densities.

2.1.2 Electron-driven Processes for Ammonia Production: Electrocatalysis and Photocatalysis

Figures 3 and 4 show two different schemes in which electrocatalysis and/or photocatalysis can play a role in ammonia production. Renewable electricity derived from

wind or solar has grown substantially in recent years, and energy storage from these intermittent sources has become an increasingly important challenge. The concepts shown in Figure 4 reflect the use of renewable electricity to drive key electrochemical transformations, notably the hydrogen evolution reaction (HER) to produce H_2, the oxygen evolution reaction (OER) to produce O_2, and the nitrogen reduction reaction (N_2RR) for the direct production of ammonia. It is conceivable that any of the aforementioned reactions can be carried out by electrolysis coupled to renewable electricity sources, or by photocatalytic processes that harvest sunlight directly to drive the redox reactions.

Figure 3 shows a direct electrocatalytic or photocatalytic ammonia production process in which N_2RR catalysts are employed to directly produce ammonia, with OER catalysts balancing the reaction by oxidizing water to produce the protons and electrons needed for the N_2RR. The overall reaction is: $2N_2 + 6H_2O \rightarrow 4NH_3 + 3O_2$.

Figure 4 shows an indirect electrocatalytic/photocatalytic ammonia production process in which a thermally catalyzed ammonia production process is coupled to renewable H_2 production by electrocatalysis or photocatalysis. In this case, HER catalysts and OER catalysts are employed to produce H_2 in a renewable, sustainable manner: $2H_2O \rightarrow 2H_2 + O_2$. The H_2 is then fed into a thermal reactor for Haber-Bosch chemistry: $N_2 + 3H_2 \rightarrow 2NH_3$. In principle, this could be accomplished in conventional Haber-Bosch plants by replacing the H_2 that is normally derived from fossil fuel-based steam methane reforming with H_2 derived from renewable resources. This could have a significant impact in reducing the CO_2 emissions in the Haber-Bosch process. An intriguing opportunity would emerge if catalysts for a low temperature, low pressure Haber-Bosch process could be developed; the technology shown schematically in Figure 4 could be deployed in a distributed manner to provide ammonia directly
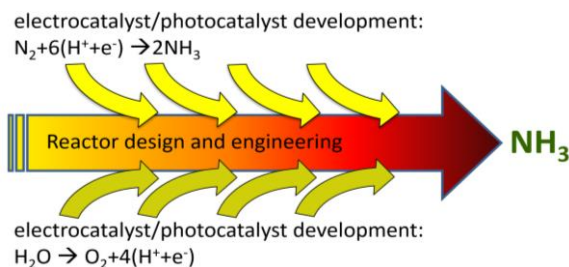
Figure 3. A direct electrocatalytic / photocatalytic pathway to ammonia production that employs renewable energy, e.g. wind or solar, to drive the catalysis.
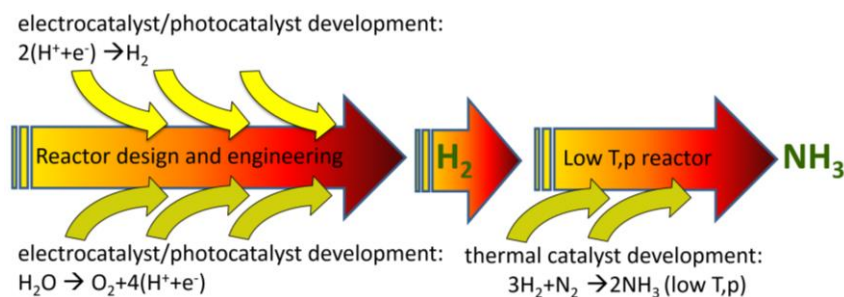
Figure 4. An indirect electrocatalytic / photocatalytic pathway to ammonia production that employs renewable energy, e.g. wind or solar, to produce H_2 that is then fed into a thermal reactor for NH_3 production.

and just-in-time in agricultural fields where the fertilizer is needed.

2.1.2.1 Electrochemical Ammonia Synthesis

State-of-the-Art

Electrochemical NH_3 synthesis from N_2 in H_2O below 373 K was reported to occur at a cell potential of -1.1 V vs. Ag/AgCl with an NH_3 partial current density of 0.015 mA/cm^2, resulting in a 0.24% current efficiency.[23] Since this discovery, various attempts to improve efficiency have been applied, with some success.

For example, it was reported that the addition of lithium salts increased current efficiencies up to 8% in non-aqueous electrolytes and to 1.3% for aqueous systems.[24,25] Using a molten salt (LiCl-KCl-CsCl eutectic) with a porous nickel cathode at ambient pressures and a temperature of 650 K, a current efficiency of 72% was achieved, though a non-zero ammonia signal while using an argon control was observed. [26]

Proton-conducting ceramic oxides have also been explored for electrochemical ammonia synthesis across a broad range of temperatures in fuel cell electrolyzer systems. Using humidified N_2 and H_2, a polymer electrolyte membrane, and $SmFe_{0.7}Cu_{0.3-x}Ni_xO_3$ (x = 0–0.3) as a cathode catalyst, one group reported up to 90% current efficiency towards NH_3 at 5.97 mA. The process required 2 V at 353 K.[27] Such systems, while impressive in current efficiency, require careful control experiments due to low overall yields and observed ambient ammonia absorption by polymer electrolyte membranes.

Few reports exist of ambient temperature and ambient pressure ammonia synthesis from air and water. One study used a platinum anode and cathode with a Nafion polymer membrane that was treated with NH_3. Ammonia was produced with a partial current density of 0.028 mA/cm^2 and current efficiency of 0.5% at cell voltages of 1.2 to 1.6 V, though NH_3 was not confirmed to be produced from N_2 except by calculation of NH_3 previously contained in the Nafion membrane.[28]

Challenges and Opportunities

Electrochemical reduction of N_2 to NH_3 at low temperatures and pressures has been reported, though very poor efficiency has impeded a concerted effort in this area. Even the best reported data required large overpotentials to yield only low current densities, indicating inefficient catalysis. Future research in this area needs to focus on theory-guided screening and discovery of new ammonia catalysts, as well as developing novel methods for ammonia synthesis at low temperatures and pressures. One important issue that has hindered development in the field is the difficultly in employing proper controls, standards, and experimental methods to definitively show that ammonia is truly synthesized by N_2 reduction as opposed to emerging from contamination or other sources. There are many sources of non-N_2 nitrogen and ammonia contaminants reported throughout the literature, as described in the state-of-the-art section. Overcoming nitrogen and ammonia contamination is paramount to the successful demonstration of ammonia synthesis and should be done with $^{15}N_2$ dinitrogen, FTIR analysis, choice of system materials, and careful controls using argon.

2.1.2.2 Photocatalytic Ammonia Synthesis

State-of-the-Art

Photocatalytic routes to ammonia synthesis have been explored since it was demonstrated that TiO_2 powders doped with Fe_2O_3 could produce NH_3 from N_2 and H_2O.[29] As with many photocatalytic research areas, TiO_2 became the workhorse photocatalyst for subsequent studies, though other light-absorbing materials such as WO_3, FeO_x, and cuprous chloride have been examined as possible photocatalysts.[21,30-33] Co-catalysts such as Ru and

Pt have been added to photoactive materials for improved NH_3 production.[34] Researchers have added conductive polymer overlayers to light-absorbing materials to raise the energy of the conduction band, thereby increasing the driving force of N_2 reduction.[35-37]

Many of the above studies include powders that are not attached to electrodes for further electrochemical characterization. However, a recent study on diamond and boron-doped diamond photoelectrodes reported that the high band gap of the material actually allowed for detectable solvated electrons for improved ammonia synthesis.[38] This study also used $^{15}N_2$ to confirm that the $^{15}NH_3$ IR signal originated from N_2 gas and not from other possible sources, serving as an important control.

Challenges and Opportunities

The most significant challenge for photocatalytic ammonia synthesis is the general requirement for high-energy UV light to reduce N_2. The partial current densities reported to produce NH_3 are also typically 3 to 5 orders of magnitude below those reported for electrochemical methods. This may be overcome with appropriate catalysts or light-absorbing systems. Importantly, further studies with catalysts attached to electrodes will provide a greater understanding of material capabilities via photoelectrochemical characterization. Similar to electrochemical ammonia synthesis, photocatalytic approaches must employ proper methods and controls (e.g. $^{15}N_2$ labeling studies) in order to prove definitively that any NH_3 reported indeed comes from the catalytic reduction of N_2 as opposed to contamination or other sources.

2.1.2.3 Electrocatalytic Oxygen Evolution Reaction

State-of-the-Art

The oxygen evolution reaction is the primary reaction that occurs at the counter electrode in aqueous electrochemical ammonia synthesis and via the positive holes from charge separation in aqueous photochemical ammonia synthesis. Thus, efficient OER catalysis is important to the overall efficiency of NH_3 production in aqueous solutions. State-of-the-art catalysts in alkaline media include $NiFeO_x$, CoO_x and specific perovskite-type materials, which are considered highly active and stable in alkaline media, though they require overpotentials above 0.3 V to operate; in acid IrO_x is the only OER catalyst with reasonable activity and stability.[39-41]

Challenges and Opportunities

Despite significant efforts to improve OER catalysis and catalytic materials, required overpotentials remain high due to kinetic losses. Decreasing the observed "wall" of 0.3 V of required overpotential is a significant challenge to overcome, but may be accomplished by using novel catalyst systems to break scaling relations. In addition to the challenge of decreasing this overpotential barrier, there remain no earth-abundant OER catalysts that are operationally stable in acidic media. Further breakthroughs in this field would enable greater overall efficiency for many catalytic reduction reactions and thus represent a great opportunity.

2.1.2.4 Electrocatalytic Hydrogen Evolution Reaction

State-of-the-Art

Catalysis of the hydrogen evolution reaction (HER) has been improved by several key advances in recent years. A substantial effort to replace scarce and precious metal HER catalysts such as Pt, which is highly active and stable, has given rise to the discovery of effective earth-

abundant alternatives. A growing number of earth-abundant transition metal sulfides, carbides, and phosphides have been found to be active for the HER with varying levels of stability in acidic or alkaline aqueous solutions under standard operating conditions.

High surface area CoP, FeP, Ni_2P, MoP, and WP, along with other phases of these materials, have recently been discovered to be among the best performing earth-abundant catalysts.[42-48] They require overpotentials of only 0.12 V to 0.05 V in acid media to produce a geometric current density of 10 mA/cm^2, and most exhibit excellent stability under standard operating conditions, losing only a few mV over many hours of applied current and voltage cycling. For comparison, polycrystalline platinum standards achieve a 10 mA/cm^2 current density with about 0.02 V overpotential. Less than a decade ago, few earth-abundant materials could operate at under 0.3 V overpotential, and fewer were identified as acid-stable alternatives.

Carbides, nitrides, and sulfides of the transition metals listed above were among the additional identified acid-stable alternatives to precious metals.[49-52] MoS_2 is a well-studied catalyst with high activity and reasonable stability under operating conditions. In-depth studies have identified edge sites of MoS_2 layers that are particularly active for the HER.[53] Subsequent studies aiming to maximize MoS_x active sites via compositional and structural control show improved activity (<0.15 V at 10mA/cm^2) and exemplify the progression of practical science with improved understanding of a system. [54,55]

One remaining challenge is identifying and optimizing reactive sites in more active catalysts to close the gap with Pt HER catalysis. Importantly, an acid-stable, earth-abundant OER would enable the practical use of these HER catalysts. Alternatively, the state-of-the-art alkaline HER catalysts include NiMo, NiFe, CoMo, and TiCu, though a challenge remains in the long-term stability and performance of anion exchange membranes for separation of HER and OER half reaction catalysts and products in these systems.[56-59]

Challenges and Opportunities

Improved understanding of the HER is an important component of current and future research. The HER is in competition with NH_3 synthesis in aqueous electrochemical systems. Therefore, promoting the reduction of dinitrogen is dependent upon controlling the HER occurring on catalyst surfaces. When synthesizing NH_3 with N_2 and H_2O, mitigation of the HER while accessing surface protons for nitrogen reduction will be a key challenge to overcome for these competing reactions. The discovery of novel catalysts, via theory-guided screening with improved selectivity for NH_3 production over H_2 production, will be important for aqueous ammonia synthesis.

Alternatively, cost-effective catalysis of the HER has the potential to provide a clean stream of H_2 for direct input into Haber-Bosch reaction streams, thereby reducing the requirement for carbon-based fuels as hydrogen sources. Correspondingly, the study of thermal catalyst systems, but with decreased temperature and pressure requirements compared to the traditional Haber-Bosch process, has additional potential to reduce the environmental impact of ammonia production. For situations where the cost or scalability of the HER catalyst are of little concern, platinum is a tremendously active catalyst that can be implemented immediately, in either acidic or alkaline media. If non-precious metal based HER catalysts are desired, there is significant room for improvement in both acidic and basic media. While the activities of the best electrodes consisting of non-precious metal HER catalysts are promising based on performance per unit area, these electrodes possess an extremely high loading of catalyst material compared to those containing Pt. On a turnover frequency

(TOF) basis, Pt is 5 to 6 orders of magnitude more active than the very best non-precious metal catalysts for the HER. This could have an impact both for photocatalytic and electrocatalytic approaches to H_2, since in photocatalysis a high loading could block incoming light and cause mass-transport problems of water/protons in and gaseous product out, an issue that could also be of concern for electrolysis devices that operate in the dark. Thus, challenges remain in developing further improved non-precious metal HER catalysts, in both acidic and basic media.

2.1.3 Solar Thermochemical Looping for Ammonia Production

The thermochemical looping process represents one of the potential approaches for the sustainable production of ammonia without fossil CO_2 release. As compared in Figure 5, the Haber-Bosch process (left) consists of several steps: (1) adsorbing and splitting of dinitrogen while providing dihydrogen and (2) forming and then releasing ammonia from the surface to make the catalytic surface available again to repeat the process. These steps occur simultaneously on the surface of the Haber-Bosch catalyst at steady-state. In chemical looping, these steps are essentially separated in time and performed in three discrete operations, forming a cycle (Figure 5, right): (1) N_2 cleavage by forming a bulk metal nitride from a metal and dinitrogen, (2) nitrogen protonation to ammonia by supplying dihydrogen or a hydrogen source such as water, and (3) recovery of the metal for re-use in step (1) to again form the metal nitride. Figure 5 (right) shows one particular implementation where the metal oxide is reduced back to the metal as natural gas is converted to dihydrogen and carbon monoxide (syngas) in step (3). Step 3 requires energy input, which can come from concentrated solar energy.

The tradeoff between dissociation of dinitrogen and binding of N in the nitride vs. ammonia formation upon contact with hydrogen or a hydrogen donor bears similarities to the tradeoffs experienced in optimizing Haber-Bosch catalysts (section 2.1.1. above). Doping or use of metal alloys may optimize this tradeoff.

State-of-the-Art

Thermochemical looping catalysis is currently performed by contacting a solid bed of particles of a metal or metal compound sequentially with different gases. Potential advantages of such a scheme include:

- Atmospheric pressure operation, simplifying the process and allowing down-scaling.
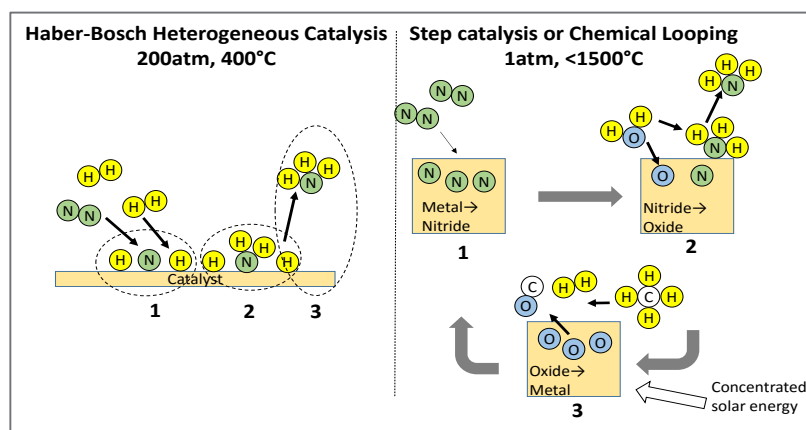
Figure 5. *The steps of Haber-Bosch catalysis (left) are separated in step catalysis or chemical looping (right) to form stable intermediates.*

- Decoupling and separate optimization of the three steps (above) by manipulating temperature and gas phase composition for each step.
- Ability to accept oxygen impurities in nitrogen, causing a small oxide dead load, rather than the strict requirement of the Haber-Bosch process whose catalysts need costly, high-purity nitrogen and meticulous operation due to the high degree of sensitivity to oxygen.
- Easier start up and shut down since chemically stable and robust materials are formed (metal nitrides, metal oxides etc.).

Recently the synthesis of NH_3 at atmospheric pressure using this technology was explored via a three-step solar thermochemical cycle based on (1) nitridation of aluminum, (2) hydrolysis of aluminum nitride with steam to ammonia and aluminum oxide, and (3) carbo-thermal reduction of aluminum oxide (with an option to use carbon from renewable biomass) to enable nitride formation and return to step (1).[60] The approach has the potential to produce ammonia sustainably, using abundant solar radiation to drive the inorganic synthesis cycle. This approach does present two issues: the need to continuously supply and handle large amounts of solid carbon-containing reducing agents and impractical maximum required temperatures of up to 2300 K.

Chemical looping catalysis for ammonia synthesis at atmospheric pressure using nitrides has been explored both from an economic point of view, and by studying the thermodynamics, materials science, and kinetics of the process.[61-63] Supplying hydrogen to the ammonia synthesis process using water is an attractive approach, although the overall process would require additional energy input (from concentrated solar energy) to reduce the metal oxide and close the chemical looping scheme. The maximum temperature can be kept below 1800 K by using manganese instead of aluminum.

Challenges and Opportunities

Challenges arise from the tradeoff required between steps 1-3 (Figure 5, right) when substituting a different metal oxide. For example, manganese may form a nitride quite readily and at acceptable conditions, but it may be difficult to reduce the manganese oxide, and ammonia formation from manganese nitride may be limited by mass transfer and/or kinetics. The thermodynamics of pure metals have been investigated for these chemical transformation reactions and some recommendations have been derived.[64] However, it may be possible to improve issues such as vacancies for nitrogen hosting in metal lattices and reactive properties by modification of pure metals. Several approaches may prove beneficial:

New alloys and doped materials. Employing alloys or doped materials may open opportunities not afforded by pure materials by modification of the kinetics and thermodynamics of the various compounds to be formed in step catalysis. Basic thermodynamic measurements will likely be necessary since the specific conditions and material compositions that may be desirable have not been at the center of attention. Advanced characterization to determine the presence and distribution of various atoms in the solid materials offer the opportunity to take advantage of exceptional properties found at the nano-scale.

Mass transfer. Converting bulk solid materials results in challenges pertaining mass transfer in solids and regarding to the question of how the solid materials will be used in the process. Several strategies may be employed to address this issue: using nanoparticles instead of macroscopic particles, adding a carrier matrix, and determining the limiting steps in the chemical looping process.

Process integration and optimization. One of the hallmarks of today's Haber-Bosch implementations is an extremely high degree of process integration. Mass and energy flows are used so efficiently that the thermodynamic efficiency of the overall process is approaching theoretical limits. Integration of energy flows and potential use of mass flows in different experimental configurations should also be investigated in order to optimize these new processes.

2.2 Homogeneous and Enzyme Catalysis

Homogeneous and enzyme catalysts for N_2 reduction to ammonia offer many advantages that warrant expanded efforts to advance the efficiency and understanding of these catalysts. Nitrogenase catalyzes N_2 reduction at relatively high rates (turnover frequency, TOF ~ 2 NH_3 s^{-1}) with relatively high turnover numbers (TON) at room temperature and atmospheric pressure.[6] Fifty years of study on nitrogenase has laid the foundation for defining the mechanism of this catalyst that achieves N_2-to-NH_3 conversion under benign conditions. Many challenges remain to define a complete mechanism, including identifying key intermediates, understanding the roles of ATP hydrolysis in driving electron transfer, and building a reaction mechanism using computational approaches in concert with experimental data.

Homogeneous catalysts for N_2 reduction offer systems that can be trapped in uniform states and can be analyzed by diverse spectroscopic techniques to provide atomic level details of intermediate states, thus providing one of the best opportunities to define a molecular mechanism for N_2 reduction to ammonia.[65] For example, rational ligand design can result in next generation catalysts with improved efficiency, lifetime, or selectivity. Excellent progress is being made in developing small molecule systems that can activate and reduce N_2. Going

forward, challenges include developing more stable and active systems that can be analyzed in situ, and using calculations to define a complete reaction mechanism constructed from spectroscopically observed states. The state-of-the-art and challenges and opportunities in building a foundation for understanding N_2 activation are reviewed below.

2.2.1 Homogeneous Catalysts

State-of-the-Art

The discovery of a nitrogen-fixing enzyme (a nitrogenase) that contains iron and molybdenum along with a transition metal compound that contains dinitrogen bound to ruthenium (in 1965) initiated a race to prepare ammonia catalytically at low pressure and temperature with a transition metal complex.[66,67] Entire institutes were created in England and Russia in the late 1960s for this purpose. While stoichiometric N_2-to-NH_3 conversion was demonstrated using low-valent Mo-N_2 complexes in the 1970s, only in 2003 was N_2 finally reduced catalytically to ammonia with protons and electrons using a well-characterized molybdenum catalyst (298 K and 1 atm pressure; Figure 6).[68]
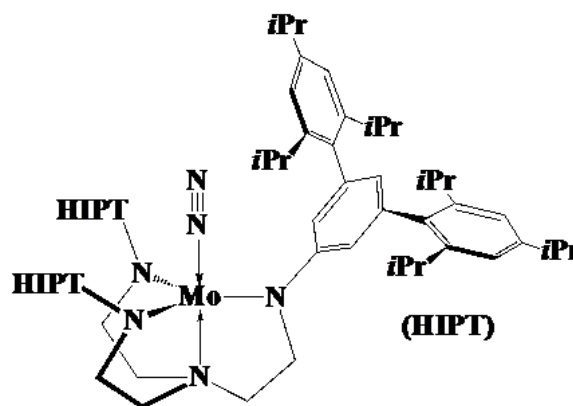
Figure 6. *Structure of a homogeneous Mo-based nitrogen reduction catalyst. Reprinted with permission from Schrock,* Acc Chem Res *38 (12), 955 (2005). Copyright 2005 American Chemical Society.*

The reducing agent was a chromium complex and the acid a lutidinium complex in hexane as a solvent. Up to eight equivalents of ammonia (per Mo) are formed along with four equivalents of molecular hydrogen (H_2). The mechanism was shown (through experiment and calculations) to consist of the step-wise addition of six protons and six electrons to molecular nitrogen bound initially to a Mo(III) metal center (Figure); eight of these proposed intermediates were prepared and characterized through structural (X-ray) studies.[69-71] The catalytic reaction is limited by loss of the triamidoamine ligand attached to the metal. The only significantly endothermic step, which should be surmountable in the first successful system through binding of the acid (BaseH$^+$) to the distal end of the nitrogen ligand, is the delivery of the first proton, which sets up a subsequent proton-coupled electron transfer upon addition of an electron to that hydrogen bonded pair.
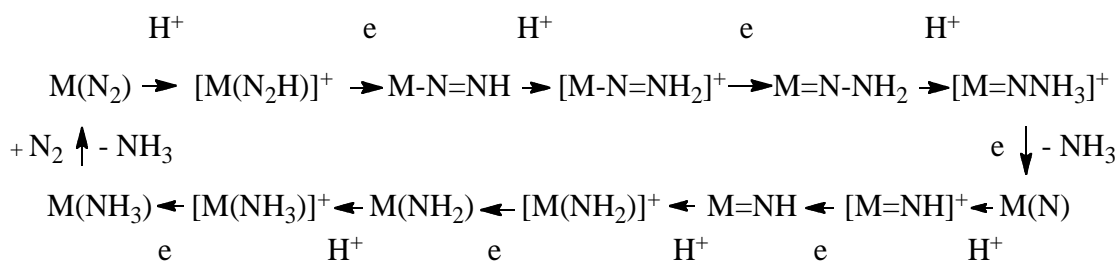
Two other systems capable of dinitrogen reduction have been reported. A low oxidation state precursor to a molybdenum catalyst for reduction of nitrogen was reported by Nishibayashi in 2011, but the electron and proton sources are similar to those employed in the earlier studies.[72] More ammonia is produced in the Nishibayashi system, but the mechanism has not been elucidated. The total amount of ammonia formed is again limited by the loss of ligand from the metal in the presence of protons and electrons. In 2013, Peters discovered iron complexes that catalyze N_2-to-NH_3 conversion at

195 K in the presence of a strong reducing agent (KC_8) and a strong acid at -78 °C.[73,74] Molecular hydrogen (H_2) is a byproduct in all molecular catalytic systems, as it is in nitrogenases, with the minimum amount being approximately one equivalent of H_2 for each N_2 reduced.

Challenges and Opportunities

The development of molecular catalysts for N_2-to-NH_3 conversion in the last 10-15 years employing protons and electrons is a remarkable achievement, but dramatic further improvements are needed to produce catalysts with high catalytic rates and long lifetimes. New catalysts must also be stable in the presence of protons, electrons, ammonia, and hydrogen. An example of a potential ligand of this type has been published recently.[75] Selective formation of ammonia without formation of dihydrogen as a byproduct is the most desirable, but has not yet been observed. Dihydrogen formation presumably can be minimized if milder sources of protons and electrons are employed; currently the least reducing conditions are ~ -1V vs. the normal hydrogen electrode.

Since catalytic reduction of nitrogen to ammonia at room temperature and pressure is a reality, the development of sustainable, carbon-neutral electrocatalysts for the synthesis of NH_3 with protons and electrons derived from water splitting is promising. Basic requirements to propel advances in this area include the design of $M(N_2)$ complexes that can accommodate multiple proton and electron transfers, and fundamental

$$M(N_2) \xrightarrow{H^+} [M(N_2H)]^+ \xrightarrow{e} M\text{-}N\text{=}NH \xrightarrow{H^+} [M\text{-}N\text{=}NH_2]^+ \xrightarrow{e} M\text{=}N\text{-}NH_2 \xrightarrow{H^+} [M\text{=}NNH_3]^+$$

$$_{+}N_2 \uparrow \text{-} NH_3 \qquad\qquad e \downarrow \text{-} NH_3$$

$$M(NH_3) \xleftarrow{e} [M(NH_3)]^+ \xleftarrow{H^+} M(NH_2) \xleftarrow{e} [M(NH_2)]^+ \xleftarrow{H^+} M\text{=}NH \xleftarrow{e} [M\text{=}NH]^+ \xleftarrow{H^+} M(N)$$

Figure 7. The thirteen proposed intermediates in the step-wise catalytic reduction of dinitrogen by protons and electrons in the presence of a Molybdenum catalyst. Adapted from D.V. Yandulov and R.R. Schrock, Science **301, 76** (2003). Reprinted with permission from AAAS.

studies on how to achieve controlled delivery of protons and electrons. Proton-coupled electron transfers or even hydrogen atom transfers may be involved in such multi-proton, multi-electron reactions, thus lowering the barrier that may be encountered by sequential addition of protons and electrons.

Because reduction of N_2 to NH_3 is a multiple-proton, multiple-electron process, many intermediate chemical species $[M-N_xH_y^{n+}]$ are involved in the synthesis of ammonia. Assessing the viability of possible catalytic cycles would be greatly enhanced by developing an understanding of the strength of the bonds that need to be formed and broken in the reaction. Specifically, determination of the bond dissociation free energies (BDFEs) of N-H bonds is needed to understand the properties of likely intermediates including M-N=NH, M=N-NH$_2$, M=N-NH$_3$, etc. and would guide rational synthesis of potential catalysts.

Initial experimental estimates have shown that N-H BDFEs of coordinated ammonia can vary from approximately 40 to 100 kcal/mol and demonstrate the importance of metal identity and oxidation state as well as the possibility of ligand control to tune stability of potential intermediates. In addition, determining the energies of these bonds would allow for evaluation of the energetic requirements of the individual chemical steps that ultimately lead to NH$_3$. Such thermodynamic data, together with kinetic data on the rates of protonation reactions and electrochemical studies on the plausible intermediates, would provide critical insights to guide the rational design of new molecular catalysts and may open new pathways for N_2 fixation with milder reagents and lower overpotential. It is also important to identify features that tune the reduction potentials of relevant complexes to ensure that the multiple reductions required for catalysis are energetically feasible. Thus, research should focus on exploring complexes designed to simultaneously promote N_2 binding and multiple reductions at the metal site.

2.2.2 Nitrogenase

State-of-the-Art

The bacterial enzyme responsible for N_2 reduction, nitrogenase, has been the focus of studies to elucidate its mechanism since the enzyme was first purified to homogeneity over 50 years ago. It was clear from the earliest studies that nitrogenase is capable of reducing N_2 to ammonia using electrons and protons with a TOF of about 2 NH_3 s^{-1} and very high TON ($>10^6$). The first enzyme to be purified (and the most widely distributed) is the Mo-dependent nitrogenase that contains an active site metal cluster with Mo, Fe, S, C, and homocitrate (called FeMo-co), shown in Figure 8. Later studies demonstrated "alternative" nitrogenases that contain V or Fe instead of Mo.[76-79] These latter two enzymes, while not as well studied as the Mo-enzyme, appear to be composed of homologous proteins and metal clusters, presumably with either V or Fe replacing the Mo in the active metal cluster (called FeV-co and FeFe-co).
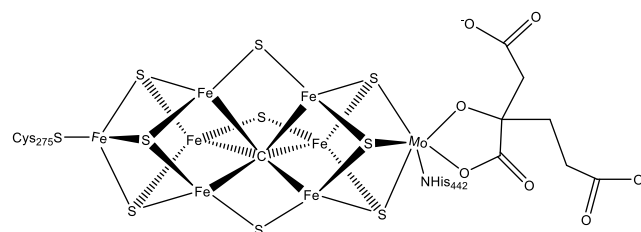
Figure 8. FeMo-co active site of nitrogenase. The structure of FeMo-co is shown as elucidated by X-ray crystallography of the MoFe protein. The central atom was recently established to be a carbide (C4-). The organic acid homocitrate (right) provides two ligands to the Mo, while the protein provides Cys and His ligands.

A range of studies on Mo-nitrogenase have advanced knowledge on several aspects of the mechanism. A large number of studies are consolidated into the well accepted Lowe and Thorneley (LT) kinetic model that defines how

electrons and protons are accumulated at the active site FeMo-co (Figure 9).[80] This model captures several important aspects of the mechanism of nitrogenase, including the need to accumulate multiple electrons and protons on the FeMo-cofactor before N_2 can bind, and the constitutive relaxation of the system by loss of electrons and protons through the formation of H_2.

$$E_0 \xrightarrow{e^-/H^+} E_1H_1 \xrightarrow{e^-/H^+} E_2H_2 \xrightarrow{e^-/H^+} E_3H_3 \xrightarrow{e^-/H^+} E_4H_4$$

$$E_8NH_3 \xleftarrow{} E_7NH_2 \xleftarrow{e^-/H^+} E_6N_2H_4 \xleftarrow{e^-/H^+} E_5N_2H_3 \xleftarrow{e^-/H^+} E_4N_2H_2$$
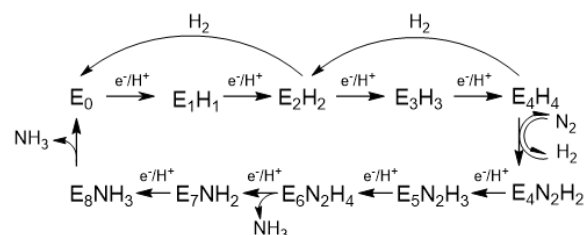
Figure 9. *Lowe and Thorneley (LT) kinetic scheme for nitrogenase catalysis. Accumulation of electrons and protons on FeMo-co is represented by En states where n represents the total number of electrons and protons accumulated. Reaction scheme from R. Thorneley and D. Lowe, in* Molybdenum Enzymes *(Ed. T. G. Spiro), p. 221, Wiley, NY (1985).*

Many recent mechanistic studies have aimed at trapping and characterizing intermediates of the LT kinetic model. Using a combination of rapid-freeze trapping and advanced spectroscopic analysis of the trapped states, a number of different intermediates have been characterized.[81] However, the utility of these trapped states in defining mechanism has been limited because none could be mapped to specific states of the LT model.

A breakthrough was achieved when one trapped state was mapped to the E_4 state of the LT model.[82] Characterization of this trapped E_4 state has provided considerable insights into this state that is poised to bind and activate N_2. A key finding is the direct observation of bridging hydrides (Fe-H-Fe) in the E_4 state. Studies on the reactivity of the hydrides in the E_4 state have suggested a reductive elimination of two hydrides as H_2 with activation of the metal core by two electrons and prompt binding and reduction of N_2 to a metal-bound diazenido species (HN=N-Fe).[81]

These studies have provided molecular level insight into one state along the nitrogenase N_2 reduction pathway. Much remains to be done to completely understand the mechanism, as detailed in the next section.

Challenges and Opportunities

Great progress has been made in developing homogeneous catalysts for N_2 reduction and in understanding aspects of the reaction catalyzed by the complex enzyme nitrogenase. As highlighted here, these systems offer unprecedented opportunities to gain molecular level insight into the mechanism of N_2 activation and ultimately ammonia synthesis. Achieving such insights will require a wave of new fundamental studies, aided by application of innovative approaches and techniques. Such studies, while challenging, should provide the mechanistic foundation that will contribute to the design of new catalysts possessing all of the attributes needed for sustainable N_2 reduction. Approaches need to be devised to trap more intermediates along the reaction pathway and characterize them, using a range of methods, to provide a more complete molecular picture. Success in such studies will require creative approaches to trapping the intermediates and application of powerful techniques such as X-ray crystallography and spectroscopic techniques that exploit the paramagnetic nature of the metal clusters. Application of robust computations guided by known intermediates will be essential for building a comprehensive reaction mechanism.

Additional work also needs to focus on understanding how electrons and protons are delivered to the active site FeMo-co and how energy (e.g., ATP) is coupled to each step in the N_2 activation process. Progress in this arena will require a range of approaches to trap states, to measure pre-steady state events (e.g., conformational changes), and ultimately to "watch" the entire process in real time.

Computation, along with the application of new cutting edge characterization techniques, will be critical to building a comprehensive picture.

Electrochemical techniques offer a powerful approach to addressing aspects of the nitrogenase mechanism. Direct electron transfer has been demonstrated between electrodes and a number of redox enzymes. However, to date, nitrogenase has proven resistant to this approach. Ordinarily, electron flow to the N_2-activating site of nitrogenase is strictly controlled by cleavage of ATP, but recent studies have shown that this coupling can be overcome and nitrogenase can be reduced by strong europium-based chemical reductants or photogenerated electrons from nanoparticles.[83,84]

This finding suggests that it may also be possible to find conditions in which electrons can be transferred from an electrode to the nitrogenase active site without addition of a soluble electron shuttle. Such direct, unmediated electrochemistry offers an unparalleled opportunity to control and tune the electrochemical potential of an experiment, gaining both thermodynamic and kinetic mechanistic information. Importantly, these properties are not obscured by the diffusion of a chemical redox mediator. Developing creative means to functionally immobilize recalcitrant redox enzymes, including nitrogenase, on electrode surfaces is essential for realizing this approach. When successful, direct electrochemical studies of nitrogenase will provide an unprecedented picture of the catalytic properties of this important enzyme driven only by electricity. This will provide foundational information essential for the development of stable and efficient electrocatalysts for N_2 reduction using solar energy.

2.3 Cross-Cutting Approaches

2.3.1 Synthesis

State-of-the-Art

Heterogeneous Catalysts. The objective in synthesis of heterogeneous catalysts is to produce an ensemble of atomically-precise catalytic sites that match the structures that are known from practice or computation to be active, selective, and stable for sustainable ammonia synthesis, simultaneously minimizing or eliminating CO_2 emissions.[85] Substantial progress in describing these sites has been attributed to computational catalysis, which allows the synthesis specialist to attempt to reproduce the specific sites of interest. A recent review of synthesis techniques for producing heterogeneous catalysts describes a wide range of methods.[86] Only three have been widely reported for ammonia catalysts: colloidal, reverse micelle, and wet impregnation.[87-91] The synthesis step is complicated by a poor fundamental understanding of the significance and exact role of various promoters, many of which are likely to be commercial secrets. However, given the wide range of methods that have not yet been employed to synthesize ammonia catalysts, substantial progress is possible.

Homogeneous Catalysts. One synthesis approach that may have significant promise is to take inspiration from biocatalysis. For example, the current model for how the enzyme nitrogenase catalyzes N_2 reduction suggests a fundamentally different mechanism compared to heterogeneous catalysts. Nitrogenase appears to reduce N_2 by sequential addition of electrons and protons, with cleavage of the N-N bond occurring late, after the addition of five electrons and protons. This contrasts with the accepted mechanism for heterogeneous catalysts, where N-N bond cleavage occurs early and is rate-limiting. A key challenge is to take advantage of the

mechanistic insight from the enzymes in designing new heterogeneous catalysts.

The synthesis of nitrogenase in bacterial cells is complex, requiring an array of dedicated proteins that are involved in regulation of protein expression, mobilization of Fe, Mo, and S, building of complex metal clusters, and maturation of the final active protein. While the basic outline of this multi-step process is in place, additional studies are necessary to understand this process at a molecular level. Significant progress has been made in framing the basic outlines of how nitrogenase catalyzes N_2 reduction, but, again, many fundamental questions remain, as outlined in other sections in this report. A key challenge for the design of next generation homogeneous catalysts will be to apply fundamentals of how nitrogenase catalyzes N_2 reduction.

Challenges and Opportunities

Given the fact that only a few of the available atomically precise methods to synthesize heterogeneous catalysts have been attempted for ammonia catalysts, significant progress is likely. It is probably that the optimum catalysts for sustainable ammonia production will be complex mixtures of promoters, supports, pre-treatment processes and other components. It is necessary to demonstrate atomically precise synthesis techniques for constructing complex active sites that are catalytically well-understood and demonstrable.

There is a significant incentive to take advantage of homogeneous catalysis of dinitrogen reduction. Combined with characterization and theory, the science and practice of synthesis can greatly improve the activity, selectivity, and stability of ammonia catalysis.

2.3.2 Characterization

Fundamental understanding of catalytic mechanisms requires the characterization of

physical and chemical properties of both catalysts and surface species (adsorbed reactants, intermediates, products) under in-situ reaction conditions. Several in-situ techniques are currently available for catalytic studies, including laboratory-based FTIR and NMR, as well as synchrotron-based XRD and X-ray absorption spectroscopies. Significant progress has also been made in microscopic measurements of structures and morphologies under conditions relevant to catalytic reactions. Catalysis researchers can gain access to most of these techniques through the general user programs at the synchrotron facilities and nano-science centers located at several national laboratories.

State-of-the-Art

Heterogeneous Catalysts. Due to the weak interaction between N_2 and the heterogeneous catalyst surface, in-situ surface science techniques, instead of the conventional ultrahigh vacuum (UHV) ones, are necessary to achieve sufficient adsorbate coverage. Synchrotron-based ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) allows the characterization of the identity and coverage of surface adsorbates, and at the same time the elemental composition and oxidation state of the catalyst surface. A related technique, ambient pressure temperature programmed reaction (AP-TPR), allows measurements of gas-phase products. The AP-XPS and AP-TPR measurements can be performed on both well-characterized single crystal surfaces and powder catalysts. The former provide comparison between experimental studies and density functional theory (DFT) calculations on model surfaces, while the latter represent realistic catalysts for catalytic studies. These two methods, together with the other in-situ techniques mentioned in the preceding paragraph, should allow the correlation between DFT calculations on model surfaces and catalytic performance over industrially relevant catalysts.

Homogeneous Catalysts. The characterization of trapped intermediates on nitrogenase relies mostly on paramagnetic spectroscopy. The metal clusters of nitrogenase are paramagnetic in certain oxidation states, enabling application of the powerful electron paramagnetic resonance spectroscopy technique. Advancing our understanding of the mechanism by which nitrogenase catalyzes N_2 reduction will require the application of a range of cross-cutting approaches. These should include rapid kinetic methods that allow characterization of key intermediates The field would benefit from applying methods used in the characterization of homogeneous and heterogeneous catalysts including electrochemistry, spectroscopic methods (e.g., FTIR), and microscopy methods. Spectroscopic methods that take advantage of paramagnetic states of the nitrogenase metal clusters have been valuable to the studies that have been achieved so far, but such approaches have limitations. For example, diamagnetic states are not observed by these methods. Going forward, spectroscopic methods that include both non-destructive FTIR and paramagnetic interrogation of the metal centers are necessary.

Challenges and Opportunities

Gaining rapid and sufficient access to in-situ characterization techniques at national laboratories presents a real challenge. In particular, due to the very limited number of end stations for AP-XPS and AP-TPR measurements in the U.S., it is likely to be very difficult to obtain enough beamtime for meaningful mechanistic studies. The development of more end stations for ambient pressure measurements, as well as the improvement of reactor cells for other in-situ spectroscopic and microscopic techniques, would significantly facilitate the understanding of reaction mechanisms on alternative catalysts for N_2 activation and ammonia synthesis.

2.3.3 Theory

State-of-the-Art

Ammonia synthesis is one of the chemistries for which first-principles techniques were employed early on. Linear scaling relations predicting thermochemistry on various materials, along with Brønsted-Evans Polanyi (BEP) relations predicting activation energies from thermochemistry on low index and stepped surfaces of single metals, are well established.[92,93] Theory and experiments have demonstrated that the chemistry is structure-sensitive and steps are active sites for this chemistry.[17,94,95] Microkinetic models have been developed for both synthesis and decomposition and a volcano curve has been employed to predict mixed metal alloys (e.g., a CoMo catalyst), using the interpolation principle to show that activity is superior to a single metal Ru catalyst.[19,22,96] A microkinetic/informatics approach for predicting core/shell bimetallics has also been introduced. For homogeneous catalysts, the N-H bond dissociation energy has been estimated via DFT and several thermochemical cycles have been computed.[97,98]

Overall, significant progress has been achieved. Yet, it has become clear that in the case of heterogeneous catalysts there is a maximum activity dictated by thermodynamic and kinetic considerations (scaling relations).[98,99] For homogeneous catalysts, the structure of the catalyst and the choice of ligands play an important, but rather poorly understood, role.

While there have been a number of theoretical studies on nitrogenase, most of these studies have been limited by the lack of key insights from experiment. It is only recently that the field has gained key insights including the identity of the central atom C of FeMo-co and the roles of Fe-hydrides in the N_2 binding and reduction mechanism. It will be critical for theory studies going forward to embrace these experimental findings and to extend the

mechanism in ways that are testable by experiments.

Challenges and Opportunities

Given the following challenges, theory can be instrumental in our ability to build fundamental principles and to predict catalytic materials for ammonia synthesis whose activity goes beyond the best materials known today. Topics of interest include improved activity, stability at finite temperatures, ligand design for homogeneous catalysts, prediction of intermediates, and inclusion of medium effects.

Models and concepts have been developed by considering a single active site, either a low index crystallographic plane or a step. Currently, there is a lack of predictive theory that describes multiple active sites along with the synergy among multiple sites in homogeneous, heterogeneous, and enzymatic catalysts.

There is also a lack of guiding principles and predictive models capturing medium effects (e.g., electrolytes, ionic liquids), support effects of heterogeneous catalysts such as interfacial sites, and confinement effects as encountered in microporous materials. Similarly, there is a lack of cross-cutting principles describing homogeneous, heterogeneous, and electrocatalytic materials.

Improved theoretical methods that efficiently and properly describe the intermediate charge-transfer states and simultaneously treat pi-bonded reactants and sigma-bonded products with equal accuracy are needed. In addition, methods that merge the accuracy of quantum-chemical methods with the capabilities in density-functional methods for treating reference metal-ion states with multiple unpaired electrons are expected to be an important ingredient for success.

III. GRAND CHALLENGES

Participants in the Roundtable discussions concluded that the scientific basis for sustainable processes for ammonia synthesis is currently lacking, and it needs to be enhanced substantially before it can form the foundation for alternative processes. The Roundtable Panel identified an overarching grand challenge and several additional scientific grand challenges and research opportunities:

Discovery of active, selective, scalable, long-lived catalysts for sustainable ammonia synthesis.

Discovery of new catalysts is the overarching grand challenge for sustainable ammonia synthesis. Currently there is no viable heterogeneous, homogeneous, or enzyme catalyst known that fulfills all of the requirements for an active, selective, scalable, long-lived catalyst. This is true for homogenous redox or electrochemical processes, as well as for electrochemical or photochemical surface processes.

The Panel also identified a number of additional scientific challenges and research opportunities:

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

Given the possibility of delocalized dihydrogen production through electrolysis or a photoelectrochemical device, it is desirable to find alternative catalysts that can enable a thermal process at relatively low temperature. Such a catalyst opens the door to developing a low-pressure process compatible with low-pressure dihydrogen generation and small scale production.

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

Essential to most non-thermal alternatives to the Haber-Bosch process, it is critical to develop electrochemical processes for N_2 reduction using electrons generated from solar or wind resources. There is a need to build upon molecular level mechanisms for electrochemical and photochemical N_2 reduction and the associated energetics that were demonstrated on molybdenum-based catalysts.

Development of biochemical routes to N_2 reduction

New, creative means to functionally immobilize recalcitrant redox enzymes, including nitrogenase, on electrode surfaces will open new possibilities for feeding sustainable energy into a biological process.

Development of chemical looping (solar thermochemical) approaches

Fundamental understanding is required to identify new alloys and doped materials and to achieve process integration and optimization for the N_2 activation through metal nitridation/reduction cycles using heat/photons generated by solar thermal processes.

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

Given that there has been only limited success so far in identifying new catalysts that could form the basis for sustainable ammonia production, new catalyst design approaches are needed. Computational methods should be combined with atomic-scale controlled synthesis, operando characterization, and catalytic testing. A key element is the identification of the most important descriptors of catalytic activity and selectivity.

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

Insight from heterogeneous, homogeneous and enzyme catalysis, if combined, could strengthen the possibilities for a breakthrough in catalyst design. The field of ammonia synthesis could provide a "test bed" for a more integrated approach to catalyst discovery in general.

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

There is a strong need to invoke all the new tools in computational and *in situ* and operando characterization of catalysts. This includes chemical, physical, and electronic characterization of the active catalyst, reaction intermediates and the relevant bond energies, as well as the effects of reaction media, such as gas, solution, ionic liquid, or electrolyte.

REFERENCES

1. T. Kandemir; M. E. Schuster; A. Senyshyn; M. Behrens; R. Schlögl *Angew. Chem. Int. Ed.* **2013**, *52*, 12723.
2. V. Smil *Nature* **1999**, *400*, 415.
3. R. Schlögl *Ammonia synthesis*; Wiley Online Library, 2008.
4. K. Tamaru *Catalytic ammonia synthesis: fundamentals and practice*; Plenum Press: New York 1991.
5. G. Booth; H. Zollinger; K. McLaren; W. Sharples; A. E. Westwall *B. Elvers, S. Hawkins and G. Schulz Eds* **2002**, *17*.
6. B. K. Burgess; D. J. Lowe *Chemical reviews* **1996**, *96*, 2983.
7. A. J. Medford; A. Vojvodic; J. S. Hummelshøj; J. Voss; F. Abild-Pedersen; F. Studt; T. Bligaard; A. Nilsson; J. K. Nørskov *J. Catal.* **2015**, *328*, 36.
8. G. Ertl; S. Lee; M. Weiss *Surf. Sci* **1982**, *114*, 527.
9. S. R. Bare; D. Strongin; G. Somorjai *J PHYS CHEM* **1986**, *90*, 4726.
10. P. Stoltze; J. Nørskov *Physical Review Letters* **1985**, *55*, 2502.
11. M. Boudart *Top. Catal.* **1994**, *1*, 405.
12. R. Schlögl *Angew. Chem. Int. Ed.* **2003**, *42*, 2004.
13. J. N. Galloway; E. B. Cowling *AMBIO: A Journal of the Human Environment* **2002**, *31*, 64.
14. I. Chorkendorff, I.; J. W. Niemantsverdriet *Concepts of Modern Catalysis and Kinetics*, pp. 327-335, Wiley-VCH, New York: **2003**
15. *www.eia.gov*.
16. G. Ertl *Angew. Chem. Int. Ed.* **2008**, *47*, 3524.
17. S. Dahl; A. Logadottir; R. Egeberg; J. Larsen; I. Chorkendorff; E. Törnqvist; J. K. Nørskov *Physical Review Letters* **1999**, *83*, 1814.
18. C. J. Jacobsen; S. Dahl; P. L. Hansen; E. Törnqvist; L. Jensen; H. Topsøe; D. V. Prip; P. B. Møenshaug; I. Chorkendorff *J. Mol. Catal. A: Chem.* **2000**, *163*, 19.
19. K. Honkala; A. Hellman; I. Remediakis; A. Logadottir; A. Carlsson; S. Dahl; C. H. Christensen; J. K. Nørskov *Science* **2005**, *307*, 555.
20. A. Logadottir; T. H. Rod; J. K. Nørskov; B. Hammer; S. Dahl; C. Jacobsen *J. Catal.* **2001**, *197*, 229.
21. A. Vojvodic, A.J. Medford, F. Studt, F. Abild-Pedersen, T.S. Khan, T. Bligaard, and J.K. Nørskov, Chem. Phys. Lett. **2014**, *598*, 108.
22. C. J. Jacobsen; S. Dahl; B. S. Clausen; S. Bahn; A. Logadottir; J. K. Nørskov *J. Am. Chem. Soc.* **2001**, *123*, 8404.
23. V. Kordali; G. Kyriacou; C. Lambrou *Chem. Commun.* **2000**, 1673.
24. A. Tsuneto; A. Kudo; T. Sakata *Journal of Electroanalytical Chemistry* **1994**, *367*, 183.
25. F. Köleli; D. B. Kayan *Journal of Electroanalytical Chemistry* **2010**, *638*, 119.
26. T. Murakami; T. Nishikiori; T. Nohira; Y. Ito *J. Am. Chem. Soc.* **2003**, *125*, 334.
27. G. Xu; R. Liu; J. Wang *Science in China Series B: Chemistry* **2009**, *52*, 1171.
28. R. Lan; J. T. Irvine; S. Tao *Sci Rep-Uk* **2013**, *3*.
29. G. Schrauzer; T. Guth *J. Am. Chem. Soc.* **1977**, *99*, 7189.
30. E. Endoh; J. K. Leland; A. J. Bard *J. Phys. Chem.* **1986**, *90*, 6223.
31. V. Augugliaro; A. Lauricella; L. Rizzuti; M. Schiavello; A. Sclafani *International Journal of Hydrogen Energy* **1982**, *7*, 845.
32. M. M. Khader; N. N. Lichtin; G. H. Vurens; M. Salmeron; G. A. Somorjai *Langmuir* **1987**, *3*, 303.
33. K. Tennakone; S. Punchihewa; R. Tantrigoda *Solar Energy Materials* **1989**, *18*, 217.
34. K. Ranjit; T. Varadarajan; B. Viswanathan *Journal of Photochemistry and Photobiology A: Chemistry* **1996**, *96*, 181.
35. K. Hoshino; M. Inui; T. Kitamura; H. Kokado *Angew. Chem. Int. Ed.* **2000**, *39*, 2509.
36. K. Hoshino *Chemistry–A European Journal* **2001**, *7*, 2727.

REFERENCES

37. T. Ogawa; T. Kitamura; T. Shibuya; K. Hoshino *Electrochem Commun* **2004**, *6*, 55.
38. D. Zhu; L. Zhang; R. E. Ruther; R. J. Hamers *Nature materials* **2013**, *12*, 836.
39. M. G. Walter; E. L. Warren; J. R. McKone; S. W. Boettcher; Q. Mi; E. A. Santori; N. S. Lewis *Chemical reviews* **2010**, *110*, 6446.
40. C. C. McCrory; S. Jung; J. C. Peters; T. F. Jaramillo *J. Am. Chem. Soc.* **2013**, *135*, 16977.
41. J. Suntivich; K. J. May; H. A. Gasteiger; J. B. Goodenough; Y. Shao-Horn *Science* **2011**, *334*, 1383.
42. E. J. Popczun; C. G. Read; C. W. Roske; N. S. Lewis; R. E. Schaak *Angew. Chem.* **2014**, *126*, 5531.
43. J. F. Callejas; J. M. McEnaney; C. G. Read; J. C. Crompton; A. J. Biacchi; E. J. Popczun; T. R. Gordon; N. S. Lewis; R. E. Schaak *ACS nano* **2014**, *8*, 11101.
44. E. J. Popczun; J. R. McKone; C. G. Read; A. J. Biacchi; A. M. Wiltrout; N. S. Lewis; R. E. Schaak *J. Am. Chem. Soc.* **2013**, *135*, 9267.
45. J. M. McEnaney; J. C. Crompton; J. F. Callejas; E. J. Popczun; A. J. Biacchi; N. S. Lewis; R. E. Schaak *Chem Mater* **2014**, *26*, 4826.
46. J. M. McEnaney; J. C. Crompton; J. F. Callejas; E. J. Popczun; C. G. Read; N. S. Lewis; R. E. Schaak *Chem. Commun.* **2014**, *50*, 11026.
47. L. Feng; H. Vrubel; M. Bensimon; X. Hu *PCCP* **2014**, *16*, 5917.
48. P. Xiao; M. A. Sk; L. Thia; X. Ge; R. J. Lim; J.-Y. Wang; K. H. Lim; X. Wang *Energy & Environmental Science* **2014**, *7*, 2624.
49. T. G. Kelly; J. G. Chen *Chemical Society reviews* **2012**, *41*, 8021.
50. D. Kong; J. J. Cha; H. Wang; H. R. Lee; Y. Cui *Energy & Environmental Science* **2013**, *6*, 3553.
51. H. Vrubel; X. Hu *Angew. Chem.* **2012**, *124*, 12875.
52. W.-F. Chen; J. T. Muckerman; E. Fujita *Chem. Commun.* **2013**, *49*, 8896.
53. T. F. Jaramillo; K. P. Jørgensen; J. Bonde; J. H. Nielsen; S. Horch; I. Chorkendorff *Science* **2007**, *317*, 100.
54. J. Kibsgaard; Z. Chen; B. N. Reinecke; T. F. Jaramillo *Nature materials* **2012**, *11*, 963.
55. C.-L. Hsu; Y.-H. Chang; T.-Y. Chen; C.-C. Tseng; K.-H. Wei; L.-J. Li *International Journal of Hydrogen Energy* **2014**, *39*, 4788.
56. J. R. McKone; B. F. Sadtler; C. A. Werlang; N. S. Lewis; H. B. Gray *ACS Catalysis* **2013**, *3*, 166.
57. C. C. McCrory; S. Jung; I. M. Ferrer; S. M. Chatman; J. C. Peters; T. F. Jaramillo *J. Am. Chem. Soc.* **2015**, *137*, 4347.
58. J. M. McEnaney; T. L. Soucy; J. M. Hodges; J. F. Callejas; J. S. Mondschein; R. E. Schaak *J Mater Chem A* **2016**.
59. Q. Lu; G. S. Hutchings; W. Yu; Y. Zhou; R. V. Forest; R. Tao; J. Rosen; B. T. Yonemoto; Z. Cao; H. Zheng *Nature communications* **2015**, *6*.
60. M. Galvez; A. Frei; F. Meier; A. Steinfeld *Ind Eng Chem Res* **2008**, *48*, 528.
61. R. Michalsky; B. J. Parman; V. Amanor-Boadu; P. H. Pfromm *Energy* **2012**, *42*, 251.
62. R. Michalsky; P. H. Pfromm *J PHYS CHEM C* **2012**, *116*, 23243.
63. R. Michalsky; P. H. Pfromm; A. Steinfeld *Interface focus* **2015**, *5*, 20140084.
64. R. Michalsky; P. H. Pfromm *Aiche J* **2012**, *58*, 3203.
65. N. Lehnert; J. C. Peters *Inorg Chem* **2015**, *54*, 9229.
66. A. Allen; C. Senoff *Chemical Communications (London)* **1965**, 621.
67. J. Chatt; J. R. Dilworth; R. L. Richards *Chemical reviews* **1978**, *78*, 589.
68. D. V. Yandulov; R. R. Schrock *Science* **2003**, *301*, 76.
69. R. R. Schrock *Angew. Chem. Int. Ed.* **2008**, *47*, 5512.
70. S. Schenk; B. Le Guennic; B. Kirchner; M. Reiher *Inorg Chem* **2008**, *47*, 3634.
71. W. Thimm; C. Gradert; H. Broda; F. Wennmohs; F. Neese; F. Tuczek *Inorg Chem* **2015**, *54*, 9248.
72. S. Kuriyama; K. Arashiba; K. Nakajima; H. Tanaka; N. Kamaru; K. Yoshizawa; Y. Nishibayashi *J. Am. Chem. Soc.* **2014**, *136*, 9719.
73. G. Ung; J. C. Peters *Angew. Chem.* **2015**, *127*, 542.
74. J. S. Anderson; J. Rittle; J. C. Peters *Nature* **2013**, *501*, 84.

75. S. Zahim; L. A. Wickramasinghe; G. Evano; I. Jabin; R. R. Schrock; P. Müller *Org Lett* **2016**, *18,* 1570

76. T. Spatzal; M. Aksoyoglu; L. Zhang; S. L. Andrade; E. Schleicher; S. Weber; D. C. Rees; O. Einsle *Science* **2011**, *334*, 940.

77. V. K. Shah; W. J. Brill *Proceedings of the National Academy of Sciences* **1977**, *74*, 3249.

78. T. R. Hoover; A. D. Robertson; R. L. Cerny; R. N. Hayes; J. Imperial; V. K. Shah; P. W. Ludden, *Nature*, **1987**, *329*, 855.

79. R. R. Eady *Chemical reviews* **1996**, *96*, 3013.

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

81. B. M. Hoffman; D. Lukoyanov; Z.-Y. Yang; D. R. Dean; L. C. Seefeldt *Chemical reviews* **2014**, *114*, 4041.

82. D. Lukoyanov; Z.-Y. Yang; B. M. Barney; D. R. Dean; L. C. Seefeldt; B. M. Hoffman *Proceedings of the National Academy of Sciences* **2012**, *109*, 5583.

83. L. E. Roth; J. C. Nguyen; F. A. Tezcan *J. Am. Chem. Soc.* **2010**, *132*, 13672.

84. K. Danyal; B. S. Inglet; K. A. Vincent; B. M. Barney; B. M. Hoffman; F. A. Armstrong; D. R. Dean; L. C. Seefeldt *J. Am. Chem. Soc.* **2010**, *132*, 13197.

85. N. Saadatjou; A. Jafari; S. Sahebdelfar *Chem. Eng. Commun.* **2015**, *202*, 420.

86. W. Yu; M. D. Porosoff; J. G. Chen *Chemical reviews* **2012**, *112*, 5780.

87. N. Yahya; P. Puspitasari; K. Koziol; P. Guiseppe In *Carbon and Oxide Nanostructures: Synthesis, Characterisation and Applications*; Springer Berlin Heidelberg: Berlin, Heidelberg, 2011, p 395.

88. C. Fernández; C. Sassoye; D. P. Debecker; C. Sanchez; P. Ruiz *Applied Catalysis A: General* **2014**, *474*, 194.

89. A. Jafari; N. Saadatjou; S. Sahebdelfar *International Journal of Hydrogen Energy* **2015**, *40*, 3659.

90. B. Lin; K. Wei; X. Ma; J. Lin; J. Ni *Catalysis Science & Technology* **2013**, *3*, 1367.

91. J. Lin; L. Zhang; Z. Wang; J. Ni; R. Wang; K. Wei *J. Mol. Catal. A: Chem.* **2013**, *366*, 375.

92. F. Abild-Pedersen; J. Greeley; F. Studt; J. Rossmeisl; T. Munter; P. G. Moses; E. Skulason; T. Bligaard; J. K. Nørskov *Physical Review Letters* **2007**, *99*, 016105.

93. H. Falsig; J. Shen; T. S. Khan; W. Guo; G. Jones; S. Dahl; T. Bligaard *Top. Catal.* **2014**, *57*, 80.

94. A. M. Karim; V. Prasad; G. Mpourmpakis; W. W. Lonergan; A. I. Frenkel; J. G. Chen; D. G. Vlachos *J. Am. Chem. Soc.* **2009**, *131*, 12230.

95. W. Chen; I. Ermanoski; T. E. Madey *J. Am. Chem. Soc.* **2005**, *127*, 5014.

96. D. A. Hansgen; D. G. Vlachos; J. G. Chen *Nature chemistry* **2010**, *2*, 484.

97. I. Pappas; P. J. Chirik *J. Am. Chem. Soc.* **2015**, *137*, 3498.

98. H. Tanaka; K. Arashiba; S. Kuriyama; A. Sasada; K. Nakajima; K. Yoshizawa; Y. Nishibayashi *Nature communications* **2014**, *5*, 3737.

99. D. Hibbitts; E. Iglesia, *Acc. Chem. Res.* **2015**, *48*, 1254.

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APPENDIX:
ROUNDTABLE AGENDA

February 18, 2016, Washington-Dulles Marriott Suites Hotel

8:00-8:10	*Welcome from DOE and Charge to the Roundtable Participants* Harriet Kung

Introduction

8:10-8:20	*Opening Remarks* Jingguang Chen
8:20-9:00	*Ammonia Synthesis beyond Haber-Bosch* Jens Norskov
9:00-9:10	*Break*

Alternative Pathways (20 min presentation followed by 10 min discussion)

9:10-9:40	*Transition Metal Activation of Dinitrogen* Richard Schrock
9:40-10:10	*Nitrogenase Pathways to Ammonia* Lance Seefeldt
10:10-10:40	*Surface activation of N_2, electrochemical and thermal* Ib Chorkendorff
10:40-10:55	*Fe-mediated N_2 reduction catalysis* Jonas Peters (on teleconference)
10:55-11:10	*Water splitting as a source of hydrogen or protons and electrons* Tom Jaramillo
11:10-11:25	*Break: participants pick up lunch*
11:25-12:20	*Working Lunch: Guided Discussion* Cross-cutting challenges: theory, synthesis and characterization of catalysts Leads: Seefeldt, Spivey, Vlachos, Chen
12:20-12:30	*Break*

<u>Challenges for N$_2$ Activation</u> (10 min presentation of important scientific challenges followed by 5 min discussion):

12:30-12:45   *Homogeneous Catalysis for N$_2$ activation*
                     Paul Chirik

12:45-1:00   *Redox Enzyme Activation of N$_2$*
                     Anne Jones

1:00-1:15   *Electrochemical Activation of N$_2$ in solution*
                     Morris Bullock

1:15-1:30   *Thermal N$_2$ Activation Pathways*
                     Peter Pfromm

1:30-1:45   *Catalyst Design Strategies*
                     Dion Vlachos

1:45-2:00   *Break*

<u>Discussion and Conclusions</u>

2:00-4:30   *Discussion of the emerging research directions*
                     Leads: Jens Norskov and Morris Bullock

4:30-5:00   *Separate group meetings on writing assignments*
                     Leads: Norskov, Chen, Seefeldt, Spivey

5:00-5:15   *Concluding remarks*