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Catalysts for Nitrogen Reduction to Ammonia

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Abstract

The production of synthetic ammonia remains dependent on the energy- and capital-intensive Haber-Bosch process. Extensive research in molecular catalysis has demonstrated ammonia production from di-nitrogen, albeit at low production rates. Mechanistic understanding of di-nitrogen reduction to ammonia continues to be delineated through study of molecular catalyst structure, as well as through understanding the naturally-occurring nitrogenase enzyme. The transition to Haber-Bosch alternatives through robust, heterogeneous catalyst surfaces remains an unsolved research challenge. Catalysts for electrochemical reduction of di-nitrogen to ammonia are a specific focus of research, due to the potential to compete with Haber-Bosch and eliminate associated carbon dioxide emissions. However, limited progress has been made, as most electrocatalyst surfaces lack specificity towards nitrogen fixation. In this review, we discuss the progress of the field in developing a mechanistic understanding of nitrogenase-promoted and molecular catalyst-promoted ammonia synthesis and provide a review of the state-of-the-art and scientific needs for heterogeneous electrocatalysts.

1 Introduction

Ammonia is essential to the global economy as a fertilizer feedstock, industrial and household chemical, and chemical precursor in addition to also being considered a future fuel alternative and hydrogen storage molecule. Despite drawbacks, such as energy use, process complexity, greenhouse gas emissions, and limiting economies of scale in production, there remain no viable alternatives to the incumbent Haber-Bosch process (HBP). In this review, we discuss progress in the fields of biocatalysis, homogeneous catalysis, and heterogeneous catalysis to understand the reaction of di-nitrogen (N_2) reduction to ammonia (NH_3) and to enable a more sustainable path to NH_3 production.

NH_3 is predominately used as an agricultural feedstock in the production of synthetic fertilizers. High yield nutritious crops are dependent on the addition of these fertilizers and the associated nitrogen supply due to the degradation of agriculturally-usable soil. The need for NH_3 production continues to increase in order to support a growing global population, and abundant and low-cost NH_3 production is ultimately necessary to provide a stable and affordable food supply. Demand for NH_3 is also likely to increase with additional future uses as a carbon-neutral fuel and hydrogen storage molecule, as a result of superior energy density and easy handling and storage.

The current industrial production method, the HBP, produces 500 million tons of NH_3 per year.¹ In the HBP, a mixture of hydrogen gas (H_2) and nitrogen gas, termed synthetic gas, is passed over an iron-based catalyst commonly promoted with K_2O and Al_2O_3 . Steam reforming of coal and/or natural gas to produce the inlet H_2 stream leads to 1.87 tons of the greenhouse gas carbon dioxide (CO_2) released per 1 ton of NH_3 .² The exothermic N_2 reduction reaction, shown below, requires temperatures of 300-500°C to improve the kinetics and pressures of 150-200 atm

to shift the reaction equilibrium to be in favor of the products.



Recycling of unreacted synthetic gas is required, because each pass results in a conversion efficiency of only 15%. However, a 97% overall conversion is achieved by the utilization of these unreacted gases. Even with a high conversion efficiency, the HBP remains energy intensive, and the entire process scheme needed to achieve reaction conversions of 97% is complex. Overall, the HBP accounts for ~1% of the world's yearly natural gas consumption and is responsible for ~1% of global energy consumption.² Further, the large plant infrastructure is only economically viable at large economies of scale, where natural gas feedstock is responsible for 50% of the production cost

Today, there is a need for alternative technologies, and there is a growing interest as to whether an electrochemically-based system may possibly succeed as a replacement to the HBP. Electrochemical reduction of N_2 to NH_3 is thermodynamically predicted to be more energy efficient than the HBP by about 20%.³ Additionally, an electrochemical process could provide the advantage of eliminating fossil fuels as the source of H_2 and energy via the use of water molecules as the H_2 source and integration with renewable energy technology. In this scenario, ammonia would be synthesized directly from humidified air in a carbon-neutral manner. Electrochemical systems offer additional advantages including modularity, scalability, and on-site, on-demand NH_3 generation. The HBP is restricted in economies of scale due to its natural gas feedstock dependence. A smaller plant infrastructure, electrochemical or otherwise, that utilizes renewable resources would result in the ability to decentralize ammonia production and provide availability in remote areas.

The electrochemical catalysis community has, for the most part, made incremental progress towards enabling efficient electrochemical N₂ reduction although efforts are plagued by low Faradaic efficiencies due to the competing hydrogen evolution reaction, which dominates all metal-based catalyst surfaces. Few catalysts have resulted in efficiencies greater than 1%, with efficiencies of >30% achieved only at high temperature and for limited time and/or current produced,⁴ or when used in combination with ionic liquids.⁵ In this review, we discuss the key research efforts to delineate the mechanistic aspects of natural biocatalysts (nitrogenases) that catalyze N₂ reduction, as well as homogeneous (molecular) catalyst systems and current computational theory. The findings of recent and ongoing nitrogenase research continue to direct current homogeneous catalyst research. The synergy of these two fields suggests that a fundamental understanding of the roles of specific species (ligands) and the local catalyst environment in the adsorption and desorption of nitrogen species will ultimately lead to the development of a better heterogeneous catalyst. Therefore, the last section of the review offers potential insights for selectivity in heterogeneous catalyst design.

Biocatalysis - Nitrogenase

Biological nitrogen fixation occurs naturally in diazotrophic microorganisms through the enzyme nitrogenase. Notably, nitrogenase operates at mild conditions (<40°C, atmospheric pressure) compared to catalysts operating in the traditional HBP (300°C - 500°C, >150 bar). The study of this enzyme is thus of great interest in meeting the grand challenge of sustainable and efficient ammonia synthesis. The synthesis of ammonia from dinitrogen by nitrogenase follows reaction (2) under optimal conditions.



The reaction involves the obligatory hydrolysis of adenosine triphosphate (ATP) to release stored chemical energy and thermodynamic or kinetic barriers of nitrogen reduction. For every molecule of nitrogen that is reduced two molecules of ammonia are generated, and protons are also reduced to form one molecule of H₂. Therefore, 25% of the energy consumed results in hydrogen production. In the absence of nitrogen or other substrates, nitrogenase reverts to the reduction of protons.

Three distinct nitrogenase enzymes sharing similar characteristics have been found; they are distinguished by their metal-centered catalytic cofactors (co): FeMo-co, FeFe-co, and VFe-co. The most widely studied and understood nitrogenase enzyme contains the FeMo-co, and is known as MoFe nitrogenase. Therefore, this review will provide a brief overview on the structure and functions of the MoFe nitrogenase.

X-ray crystallography has given insight into the crystal structure of the MoFe nitrogenase enzyme, and a representation of the structure is shown in Fig. 1.⁶ Nitrogenase consists of two multi-subunit proteins, both of which are oxygen sensitive, with one protein serving as a catalytic domain and the other serving as a reducing domain. The MoFe protein is the catalytic protein to which nitrogen binds and is reduced to NH₃, whereas the second protein, or the Fe protein, hydrolyzes MgATP molecules and transfers electrons to the MoFe protein (more specifically, to the FeMo-co) for catalysis. Table 1 outlines the basic components of these proteins and their functions.

Table 1. Basic components and functions of the nitrogenase enzyme.

Protein	Domain	Function
Iron (Fe) Protein Homodimer (~66 kDa)	Fe ₄ S ₄ , F-cluster	Facilitates hydrolysis of MgATP and electron transfer to the MoFe protein
	Nucleotide binding sites	Facilitates binding of MgATP
Molybdenum-Iron (MoFe) Protein $\alpha_2\beta_2$ Tetramer (~240 kDa)	Molybdenum-Iron Cofactor Clusters (FeMo-co)	Catalyzes reduction of nitrogen to ammonia, buried to prevent access to H ₂ O and improve nitrogen selectivity over hydrogen evolution
	Fe ₈ S ₇ , P-clusters	Responsible for transferring electrons to the FeMo-co from the Fe ₄ S ₄ cluster of the Fe protein

The Fe protein is a homodimer and each subunit in the protein contains a nucleotide binding site for a MgATP molecule and 2x cysteine residues to which the bridging [4Fe4S] cluster binds. The MoFe protein is a larger $\alpha_2\beta_2$ tetramer containing two Fe₈S₇ “P-clusters” (one bridging cluster between each α and β subunit dimer) and two FeMo cofactors (Fe₇MoS₉C, located in the α subunit). The P cluster is thought to play an exclusive role in transferring electrons originating from coupled ATP-hydrolysis in the Fe protein to the FeMo-co of the MoFe protein. The electron transfer to each component is depicted in Fig. 1a.

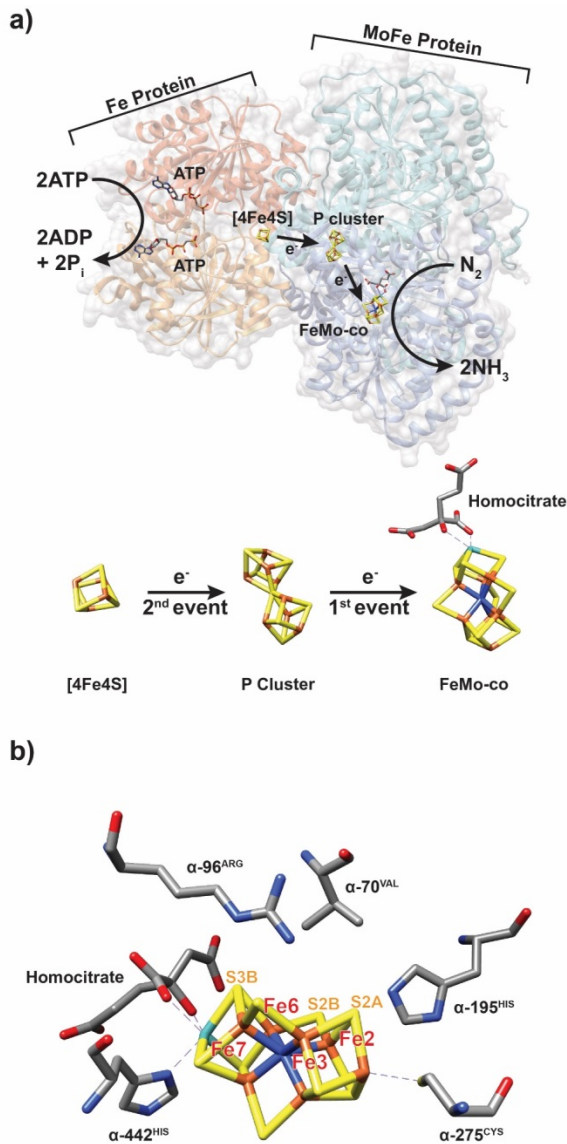


Figure 1. Nitrogenase enzyme structure and functions a) Diagram of one half of the nitrogenase complex and electron transfer. b) Detailed diagram of the FeMo cofactor and surrounding environment. Images redrawn from Ref.⁶

Electron Transfer Three models exist to describe the electron transfer process between the Fe protein and the MoFe protein: the ‘sequential’, ‘direct’, and ‘deficit-spending’ models. In the sequential model, for each Fe protein that complexes with the MoFe protein, a single electron is transferred from the F-cluster to the P-cluster, where it is then transferred to the FeMo-co. This

model would require the P-cluster in the MoFe protein to reach a super-reduced state, which has not been observed. The direct electron transfer model involves the FeMo-co being reduced directly by the Fe protein, meaning that the P-cluster is not involved. As the P-cluster has been shown to change oxidation states during the reaction,⁷ this model is unlikely. The deficit spending model proposes that an electron is first transferred from the P-cluster to the FeMo-co within the MoFe protein, and only after this is the P-cluster reduced again by F-cluster of the Fe-protein. This mechanism for electron transfer is consistent with recent stopped-flow kinetic experiments.⁸

Dissociation of the Fe protein from the MoFe protein after electron transfer has been considered the rate limiting step.⁹ More recent studies, however, indicate that the hydrolysis of ATP at the Fe protein, and more specifically, the release of phosphate from the protein, is the rate-limiting step.¹⁰

FeMo-co Structure Researchers have recently made great strides in determining the structure of nitrogenase, specifically FeMo-co. The complete molecular structure of the FeMo-co has been determined with the identification of an interstitial carbon atom at the center (Fig 1b).¹¹ Despite this progress, the understanding of the electronic structure of the FeMo-co is still debated. Electronic studies suggest that FeMo-co only cycles through one redox couple, with one resting stage M^N and a one electron reduced stage M^R .¹² Although studies have often accepted Mo(IV) to be the oxidation state of the molybdenum, recent studies propose the reassignment of the oxidation state to Mo(III).¹³ This finding has prompted studies that clearly assign the charges of the iron and molybdenum atoms in the FeMo-co so that substrate reactivity with the Fe and Mo atoms in the FeMo-co can be better understood.¹⁴ Studies have shown that three of the seven

iron atoms in the FeMo-co (iron atoms labeled one, three and seven in Fig. 2a) are relatively reduced compared to the remaining four iron atoms. Given this information, a FeMo-co with three iron atoms in the 2+ oxidation state, four iron atoms in the 4+ oxidation state, and a molybdenum atom with a 3+ oxidation state would agree with these observations of the FeMo-co.

Reaction Mechanism With the existence of three types of metal-centered catalytic cofactors (FeMo-co, FeFe-co, and VFe-co), the precise substrate binding site is still debated. With respect to the FeMo-co, the involvement of amino acids in the catalysis and the spatial positioning (Fig. 2b) suggests the active site to be the Fe-S face, but determining the location and binding mode of dinitrogen within the nitrogenase remains a challenge.

Despite knowledge of the nitrogenase structure and active site, the mechanism of nitrogenase-mediated N_2 reduction to NH_3 remains unsolved. Amino acid substitutions and freeze-quench trapping, however, has isolated intermediates in support of draft mechanisms. Lowe and Thorneley developed an 8-step kinetic model for reduction of nitrogen to ammonia by nitrogenase (Fig. 2).

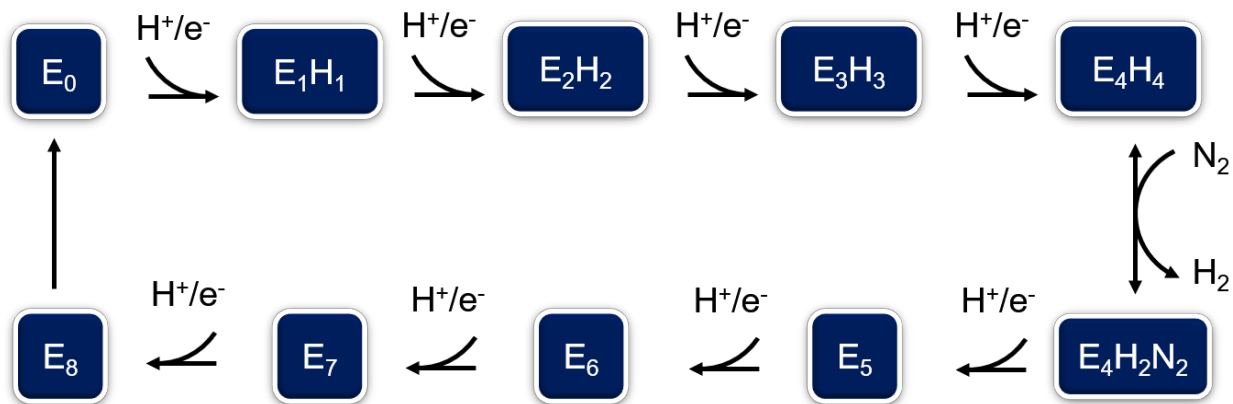


Figure 2. Single electron-proton transfer model for nitrogenase-mediated nitrogen fixation Simplified representation of Lowe Thorneley kinetic scheme for nitrogen reduction.¹⁵ The full mechanistic model also features N_2 binding at E3.

More recently, Hoffman et al. proposed a nitrogenase mechanism of N_2 activation and reduction that unifies with the Lowe-Thorneley (LT) kinetic model. In the LT kinetic model, one proton and one electron bind to the cofactor during each stage from one to eight, designated from E_0 to E_8 . This draft mechanism proposes H_2 generation to proceed through a reductive elimination of hydrides producing a highly reduced FeMo-co intermediate stage (E_4). At stage E_4 , four protons are bound to the FeMo-co including two protons that are bound to two iron atoms each (Fe-H-Fe). At this stage, N_2 is able to bind to the FeMo-co and the dinitrogen triple bond can be split.

Multiple computational studies have also proposed possible mechanisms for dinitrogen reduction. A model proposed by Varley *et al.*¹⁶ uses density functional theory (DFT) calculations to explain how the dissociation of belt-sulfur-atoms as H_2S (S2B sulfur, Fig. 1b) from the FeMo-co unveils the reactive Fe sites. The work was based on structural experiments supporting the displacement of a belt-sulfur atom by CO.¹⁷ According to the model, this step is critical to the initiation of the N_2 reduction process. The subsequent re-sealing of the active Fe site by H_2S re-absorption, required to free the second NH_3 product, releases H_2 which can account for the

requisite H₂ produced per reduced N₂ by nitrogenase in the LT kinetic model.¹⁶ Mechanisms determined in additional studies discuss the vital role played by the interstitial carbon and protein environment in initiating the reduction process, which was not considered by the previous work.¹⁸

Role of Protein Environment and Interstitial Carbon Polypeptides and amino acids located near the FeMo-co have been found to affect the reactivity of the MoFe protein. Using mutant enzymes and modeling, several important residues have been determined, as summarized in Table 2. Many key amino acids are near the active center, but studies have also determined that the activity of the enzyme can be modified by making certain amino acid substitutions in the β -chain, away from the FeMo-cofactor. Specifically, substituting histidine for tyrosine at position β -98 improved reactivity of the MoFe protein compared to the wild-type for the conversion of hydrazine to ammonia while using unnatural reducing agents.¹⁹ Given the position of the substitution, near where the Fe protein would transfer an electron to the MoFe protein, it is believed that this amino acid substitution modifies the structure of the MoFe protein in a way that mimics the conformational change that occurs when the Fe protein binds to the MoFe protein.

Table 2. Important primary and secondary structural features in the MoFe protein with their function.

Amino Acid/Helix	Function
α -70 ^{Val}	Controls access of substrates to the active sites on FeMo-co. ²⁰
α -helix containing α -70 ^{Val}	Blocks water from the active site through orientation of hydrophobic amino acids. ²¹
α -96 ^{Arg}	Contributes to the control of substrates to the FeMo-co. Hydrogen bonds to S5A sulfur atom in the FeMo-co. ¹⁸
α -195 ^{His}	Facilitates the delivery of protons to the active site. Stabilizes the protonated nitrogen intermediate. ²²

α -helix containing α -195 ^{His}	Presents hydrophobic residues to the active site. ²¹
α -191 ^{Gln}	Impacts reactivity of the FeMo-co. ²³
β -98 ^{Tyr}	Facilitates electron transfer between the Fe protein and the MoFe protein. ¹⁹

The peptide environment and the presence of interstitial carbon may play an even greater role as theorized by recent computational studies.¹⁸ Current proposals suggest that the first hydrogen binding takes place at the interstitial carbon atom rather than at the S2B sulfur, as originally predicted by Dance.²⁴

Additionally, high-resolution crystal structure analysis has revealed that polypeptide chains around the FeMo cofactor are likely blocking water from the active site.²¹ This analysis suggests that the α -helix containing α -70^{Val} is arranged such that the hydrophobic amino acids face the active site, and the more hydrophilic amino acids, and thus water molecules, are arranged on the opposite side. The chain containing α -195^{His} is also thought to be arranged where hydrophobic residues are facing the active site.²¹ This same study also postulates an interesting feature of the nitrogenase enzyme: a chain of water molecules from the surface of the enzyme to the FeMo-co. This water chain consists of a “proton bay” and a chain of eight water molecules that acts as a pathway for transmitting protons from the outer layers of the enzyme to the FeMo-co. This structural feature may also be interpreted as a conduit for ammonia product to escape, as H₂O and NH₄⁺ are hard to distinguish.

Homocitrate, represented in (Fig. 2b), is a bidentate ligand that binds to the molybdenum atom.¹⁵ The homocitrate located next to the FeMo-co also has an effect on the catalytic activity of the MoFe nitrogenase. Studies have shown that the lysine residue at the α -426 position in the MoFe protein may hydrogen-bond with the homocitrate located with the FeMo-co.²⁵ It is

believed that the hydrogen bonding between the α -146^{Lys} and the homocitrate orients the homocitrate in the direction that best allows N₂ to bind with the FeMo-co, thus optimizing the catalysis of nitrogen to ammonia.

Nitrogenase Enzymes in Electrochemistry Recent work has studied the MoFe protein in electrochemical applications, with multiple substrates and reducing agents. In one key study, the MoFe protein was immobilized on a glassy carbon electrode surface and demonstrated electrochemical activity.²⁶ The cobaltocene/cobaltocenium redox couple was used to mediate electrons between the electrode surface and the MoFe protein where it was found that under an applied voltage, the immobilized nitrogenase could reduce azide or nitrite to ammonia. While this system was unable to reduce dinitrogen into ammonia, the results demonstrate that mediated electron transport to MoFe nitrogenase immobilized on an electrode surface is possible and represents a promising step toward being able to produce ammonia from nitrogen in electrochemical systems. Further, this method provided a novel approach to study substrate turnover by the MoFe protein free of the rate limiting steps associated with Fe protein-coupled catalysis.

Nitrogenase has also been incorporated in an enzymatic fuel cell. Using a proton exchange membrane as a separator, a NH₃-producing nitrogenase cathodic compartment was coupled with a hydrogenase-based anodic compartment, where hydrogen was employed as the terminal electron donor.²⁷ In this configuration, the enzyme was not immobilized at the electrode surface and the Fe protein of nitrogenase was also included. When using methylviologen as an electron mediator between the cathode and nitrogenase (via the Fe protein), it was found that a

current could be generated while small quantities of ammonia were produced; the hydrolysis of ATP was required for nitrogenase turnover.

Molecular Catalysts

Synthetic molecular complexes provide an arguably less complex model to study the mechanism of N_2 fixation, as compared to biological or heterogeneous surface systems. Molybdenum was long thought to be the essential transition metal for nitrogen fixation by the nitrogenase enzyme. Using single Mo- based molecular catalyst, first non-enzymatic system was developed to reduce dinitrogen to ammonia at ambient conditions through a distal type mechanism²⁸ The only other reported molybdenum based catalytic system for dinitrogen reduction at ambient conditions is di-Mo based catalyst with PNP-type pincer ligands. Using DFT calculations a distal type pathway was proposed and it also explained the key role played by di-nuclear complex for catalytic activity by allowing stable bridging of nitrogen ligand which acts as a medium to transfer e^- from one Mo core to the active site of the other core.²⁹ Although work has continued for molybdenum-based molecular catalysts including recent advancements with PNP-type (with the highest turnover number for molecular catalysts of 415 per Mo atom), PCP-type, and NNN-type pincer ligands,³⁰⁻³² more bio-inspired mimic catalysts have become an emerging area.

Bio-Inspiration & Mechanistic Investigation Recent biochemical and spectroscopic studies on the nitrogenase enzyme provide convincing evidence that dinitrogen reduction occurs at the Fe atom in the FeMo-co.^{20,33-37} Similarly, the industrial production of ammonia utilizes an iron-based catalyst. In the field of Fe-based complexes, research has focused on nitrogenase

enzyme mimics,³⁸⁻⁴¹ HBP mimics,⁴¹⁻⁴³ and the environmental influence of the ligand structure.⁴⁴⁻⁴⁶

In a single Mo atom system, binding of N₂ occurs through the reduction of Mo^{IV} to Mo^{III},⁴⁷ the reduction of Mo^I to Mo⁰,²⁹ or Mo^{II or IV} to Mo^I.^{30,31} In Fe, Ni, and Co systems, binding of N₂ is apt to occur through the reduction of the metal from the M^{II} to the M^I oxidation state, where further reduction to the M⁰ oxidation state will yield a different binding alignment. Experiments performed on synthesized complexes with intermediate species already attached showed that a single Fe atom stabilizes significant intermediates.⁴⁶ However, DFT and experimental studies show that additional metal centers increase N-N activation through bond lengthening.^{43,48,49} More specifically, low coordinate complexes (i.e., electronically unsaturated)⁴¹ containing three Fe atoms demonstrated cooperation between the centers to make N-N cleavage thermodynamically feasible.^{48,49}

Different mechanisms have been presented over time, including the Chatt-type (including either the alternating (or symmetric) reaction pathways or the distal (or asymmetric) pathway) (Fig. 3).^{38,50} The symmetric pathway has been favored as the mechanism for the nitrogenase enzyme^{15,33}, as well as catalysts producing hydrazine. However, recent findings^{30,51} demonstrate the production of N³⁻ as the N-N bond is cleaved and reduced to NH₃ in a multi-iron complex and that iron nitrides have been observed for single iron complexes⁵², resulting in growing support for the asymmetric pathway. Therefore, much of the recent research in the field of molecular catalysts is focused toward designing molecular catalysts for the competing symmetric pathway or asymmetric pathway.

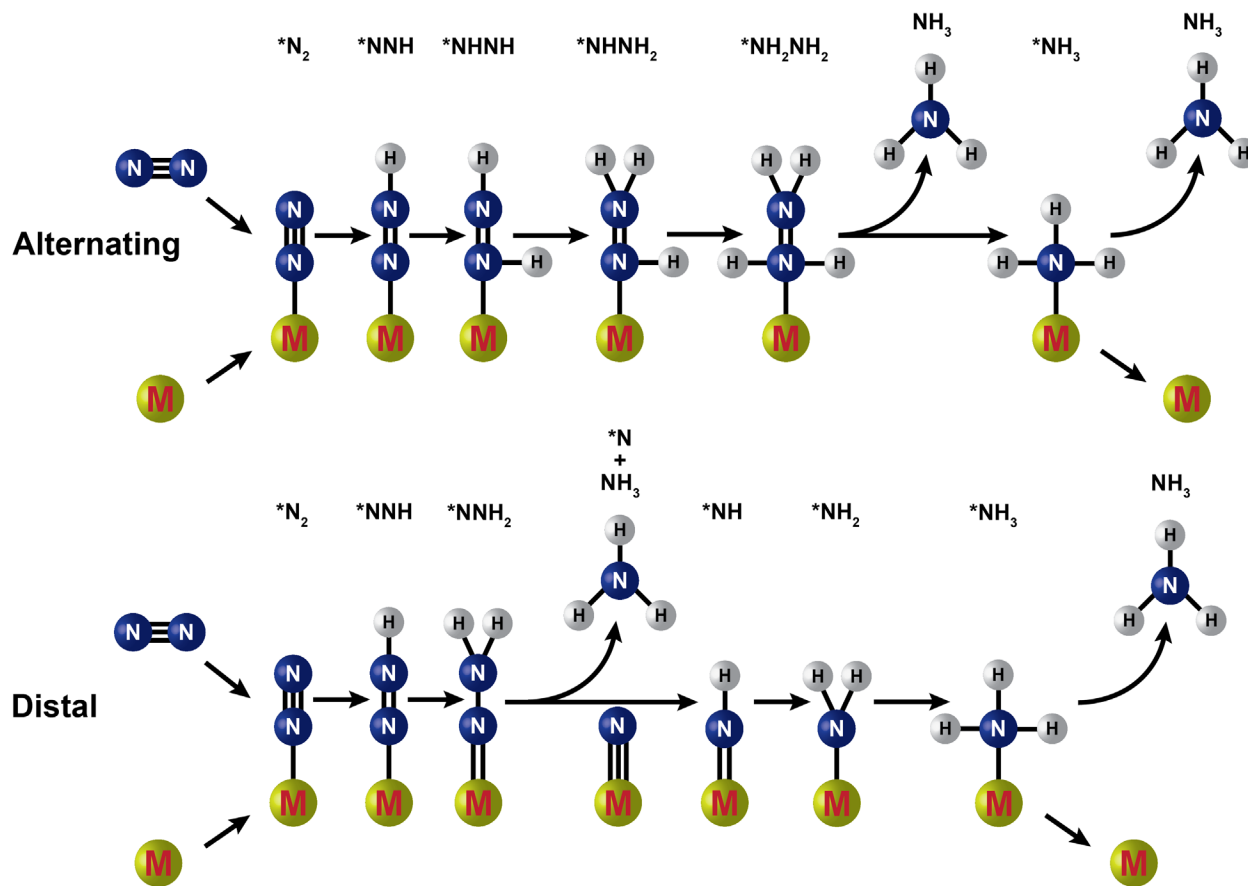


Figure 3. Associative nitrogen reduction pathways Chatt-type pathway for nitrogen fixation for symmetric or alternating addition of hydrogen versus asymmetric or distal addition of hydrogen.^{50,53}

Nitrogenase Mimics Although there have been a variety of “bio-inspired” molecular catalysts for nitrogen reduction, there has also been a wealth of research attempting to mimic the cofactor and ligand binding of the natural nitrogenases. Recently, it has been demonstrated for the first time by Peters and co-workers that a single Fe atom in a molecular complex is capable of binding⁴⁶ and reducing⁵⁴ dinitrogen to produce ammonia. These $[(EP^R)_3Fe-N_2]^-$ ($R = Ph$ and iPr) complexes are tetradentate ligands containing $E = Si$,⁴⁶ B , or C ,⁵⁴ and three phosphine ligands. P or N based ligands are electron rich, allowing the coordination of dinitrogen and

increasing π -back-bonding, which weakens the triple N_2 bond.^{42,46,54,55} These ligands are continuing to be advanced, including recent work on carbazole-based PNP-type pincer ligands.⁵⁶

Phosphorus-based ligand systems are generally a popular electron donor system used to stabilize various metals for ammonia synthesis. PNP ligands have been used to stabilize Co in various oxidation states, producing 4.2 ± 1 NH_3 equivalents.⁵⁷ Large amounts of both reducing agent and proton source increased the NH_3 production to 15.9 ± 0.2 NH_3 equivalents, along with 1.0 ± 0.4 NH_2NH_2 intermediate.⁵⁷ Using a boron containing pincer (PBP)-type ligand with similar molecular structure only catalyzed 0.4 NH_3 equivalents, indicating PNP is important to the production of NH_3 .⁵⁷ It was found that shorter Co- N_2 distances resulted in the best catalyst, and the ligand hardly affected $N\equiv N$ bond stretching.⁵⁷ A tris(phosphine)boron complex resulted in a 2.4 equivalents of ammonia per Co.⁵⁸ A triphosphine based ligand system was shown to produce up to 63 equivalents of NH_3 /Mo over a 20 hour experiment.⁵⁹ This result is the highest reported conversion using a transition metal catalyst and is believed to occur because of the ease of reduction for these complexes.⁵⁹

Ligand chemistry has been shown to change the coordination, charge, and spin state of an atom.⁴⁵ Seeking to mimic the nitrogenase structure, sulfur and carbon donors have been incorporated into the ligand inner-sphere, as they are similarly found in the FeMo-co structure. Recently, the first Fe complex containing FeMo-co analogue ligands (sulfur and carbon) was synthesized and demonstrated to bind N_2 .⁶⁰ The studies undertaken with this complex demonstrated that, upon reduction, an Fe-S bond is broken and an Fe- N_2 complex with a weakened N_2 is formed.^{40,60} Electropositive aryl compounds were also developed in a ligand system to offset negative charges formed on a carbon atom to produce a stable compound.⁵⁴ While the complex was shown to be catalytically active, over time, the reaction produced a

significant amount of catalytically inactive complexes, decreasing the overall viability of the complex.⁵⁴ It is believed that the flexibility of the Fe-C interaction greatly influences N₂ binding and reduction at a single Fe site.⁵⁴ A cyclic alkyl(amino) carbene (CAAC) type ligand was shown to produce ammonia in small amounts through an end-on binding of N₂ at a flexible two/three coordinate system at low temperatures.⁵⁵ However, attempts to utilize this complex at room temperature proved ineffective producing only 0.4 ± 0.2 NH₃ equivalents.⁵⁵

In a similar manner, hydrides have been incorporated into the ligand sphere to mimic the bridging hydrides of FeMo-co.³⁵ Bridging hydrides are strongly implicated as the key N₂ binding species, where low or intermediate spin Fe ions are formed. Hydrides have been demonstrated to act as a base or nucleophile in a di-iron sulfide complex, where reduction of the hydride led to N₂ binding.³⁹ Late transition metal hydride complexes display weakly activated dinitrogen binding, whereas early transition metal hydride complexes result in complete reduction of the triple bond of N₂ upon coordination.⁶¹ This trend shows the importance of the central metal for initial reduction, while later reactions are shown to be sensitive to steric and electronic characteristics provided by ligands.⁶¹

In a different approach, molecular complexes that differentiate from the FeMo-co have been developed. The ease of conversion of tris(trimethylsilyl)amine (N(SiMe₃)₃) into NH₃ upon hydrolysis presents an alternative approach to nitrogen fixation.⁶² Nishibayashi and co-workers were the first to produce NH₃ based on tris(trimethylsilyl)amine (N(SiMe₃)₃) through the use of an iron pentacarbonyl (Fe(CO)₅) complex under ambient conditions.⁶² This concept has also been applied to vanadium, chromium, molybdenum, and cobalt complexes.

Recently, functionalization of dinitrogen to afford nitrogen-containing compounds has been surveyed for almost all of the transition metal complexes, including: hafnium and

rhodium,⁶³⁻⁶⁵ as well as ruthenium and osmium complexes.⁶⁶ Although these are not considered “bio-inspired”, they have started inspiring new classes of molecular catalysts for nitrogen reduction. The future of molecular catalysts will focus on improved performance, but also immobilization of the molecular catalyst on the electrode surface. There are a variety of strategies being investigated, including encapsulation in polymeric coatings (i.e. Nafion), covalent binding to electrode surfaces, and non-covalent immobilization with pyrene tethers that pi-pi stack to carbon electrodes.

Heterogeneous Catalyst Mimics In general, alkali metals have been used as promoters in the iron-catalyzed HBP, but a mechanistic understanding of these promoters has evolved from work on molecular catalysts. Holland and co-workers developed the first iron potassium complex capable of cleaving N₂ and producing NH₃ through the formation of two nitrides (N³⁻).⁴² Alkali metals are shown to provide easier reduction for the overall complex,⁶⁷ allowing N-N breaking to occur as long as there are three iron atoms in the complex.⁴⁴ The size of the alkali metal can influence the shape of trimetallic clusters, but the primary influence of the alkali metal on the overall complex is to provide stability to the supporting ligands.⁶⁸ It was shown that oxygen bridges between Fe and potassium, which have been observed on the HBP catalyst, hold these components in place to provide N₂ binding locations.⁴⁹

Computational studies suggest alkali metals such as potassium enable dinitrogen reduction through arrangement of the Fe atoms,⁴⁹ stabilization of the N³⁻ species,⁴⁸ and/or increases in the π -back-bonding of the Fe.^{41,68} Thermodynamically, the positively charged alkali metal helps stabilize highly reduced complexes, pulls electron density away from the N₂, and produces stable reduced products.⁶⁷ Kinetically, the alkali metal cation- π bonding arranges

multiple iron atoms close together and with sufficient flexibility to allow multi-step and multi-electron reactions.⁶⁷ It has been suggested that the environment provided by the alkali metal cations is analogous to that provided by the positively charged histidine (His) and arginine (Arg) residues found near the Fe-S face in the nitrogenase.⁶⁷

Table 3. Summary of key molecular catalyst complexes. Ammonia production amounts are normalized to one metal used for the core reactive center.

Metal Core	Complex	Temperature [°C]	Pressure [atm]	NH ₃ equivalent
Single Fe	(TPB)Fe(N ₂)[Na(12-crown-4) ₂]	-78	1	59-88.1 ^{69,70}
	(CAAC) ₂ Fe	-95	1	3.3±1.1 ⁵⁵
	(CAAC) ₂ Fe[BAr ^f ₂]	-95	1	3.4±1.0 ⁵⁵
	C-atom anchor	-78	1	36 ⁵⁴
	Boron substituted complexes	-78	1	3.8 ⁶⁹
	Anionic boron substituted complexes	-78	1	84 ⁷¹
	PNP	-78	1	14.3-22.7 ^{72,73}
	PPP	-78	1	66.7 ⁷⁰
	[Fe(N ₂)(dppe) ₂]	-78	1	0.95 ⁷⁴
Single Co	PNP	-78	1	15.9 ⁵⁷
	[(TPB)Co(N ₂)[Na(12-crown-4) ₂]	-78	1	2.4 ⁵⁸
Single Ru/Os	Tris(phosphine)silyl ligands	-78	1	4.3 Ru/120 Os ⁶⁶
Single Mo	[HIPTN ₃ N]Mo(N ₂)	25	1	7.56±0.11 ²⁸
	PPP	25	1	63 ⁵⁹
	Pyridine-based diamide	22	1	10.8 ³¹
	PCP	25	1	115 ³²
Two Mo	PNP	25	1	26 ⁷⁵
	Metallocene-substituted PNP	25	1	22 ⁷⁶
	PNP	25	1	415 ³⁰

Heterogeneous Catalysts

Over the years, the HBP has been improved and optimized, but the industrial catalyst used today is surprisingly similar to the original catalyst developed in the early to mid-1900's.⁷⁷ Studies on single crystal iron catalysts have shown that ammonia synthesis is a structurally sensitive reaction with the Fe(111) crystal face proving to be the most reactive.⁷⁸ The reactivity is theorized to result from the highly coordinated Fe sites (C7 within the Fe(111)), which experience the largest electronic fluctuations.⁷⁹ The presence of promoter species has been shown to greatly impact the catalyst structure and performance in the high temperature, high pressure environment of HBP.^{78,80} Promoter oxides (e.g., Al₂O₃ and K₂O) in operational industrial HBP catalysts are not fully reduced.^{78,80} The addition of non-reducible oxides prevents the sintering of the iron, increases the reaction rate,⁷⁸ and increases the Brunauer Emmett Teller (BET) surface area.⁸⁰

Non-ferrous catalysts did not receive notoriety until Ozaki et al. proposed that the energetics of chemical adsorption and desorption of nitrogen species on the surface could be associated, leading to so-called “volcano” plots.⁸¹ Iron, osmium, and ruthenium were at the optimum energy, or peak, of these volcano graphs, which shifted catalysis research toward ruthenium-based catalysts.⁸¹ Ruthenium catalysts promoted with Al₂O₃,⁸² MgO,⁸²⁻⁸⁴ MgAl₂O₄,⁸⁵ and a mixture of barium with cesium⁸⁶ proved to be effective for ammonia synthesis, leading to commercialization in the Kellogg Brown & Root (KBR) Advanced Ammonia Process (KAAP).⁸⁷ The KAAP was implemented in Canada in 1992 with a Ba/Cs-promoted Ru catalyst supported on graphitized carbon, which is 10 times more active than the HBP iron catalyst at low pressure.⁸⁷ As of 2010, only 16 ammonia plants used Ru catalysts.⁸⁸ In addition to the higher cost

of Ru over Fe, the catalyst suffers from loss of support and shorter catalyst life.^{88,89} Therefore, research for Ru catalysts and potential catalyst supports, like boron nitride,⁹⁰ non-thermal plasma,⁹¹ BaCeO₃ nanocrystals,⁹² lanthanide oxides (MgO,^{93,94} CeO₂,^{93,94} Sm₂O₃⁹³), graphitic nanofilaments,⁹⁵ and zeolites⁹⁶ continues. In recent work, Hara et al.⁹⁷ demonstrated that a calcium-aluminum-oxide-based electride ($[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} (\text{e}^-)_4$) acts as an electron-donating support for an Ru catalyst, resulting in ammonia production rates as high as 2120 $\mu\text{mol g}^{-1} \text{hr}^{-1}$ (gas inlet of H₂/N₂ (3:1), 1 atm, 673 K), in comparison to traditional alumina- or calcium oxide-supported Ru catalysts with ammonia production rates of 50 – 160 $\mu\text{mol g}^{-1} \text{hr}^{-1}$.

Sabatier's Principle limits heterogeneous catalysis of N₂ reduction The N₂ reduction reaction, whether the reductant is H₂ gas or proton/electron pairs, must break the N≡N triple bond and form three N-H bonds for ammonia formation. On a heterogeneous catalyst, N₂ will initially bind to the surface and may then dissociate to two adsorbed N atoms, or first partially reduce by forming an N₂-H bond and subsequently dissociating into two molecules. According to Sabatier's Principle, the optimal catalyst will have an intermediate binding energy of a key reaction intermediate, which in the case of N₂ reduction, would either be NH_x* or N₂H_x* species (x=0-2) (where "*" denotes a surface bound species).

Density functional theory calculations and microkinetic analysis have helped to illustrate how this trade-off results in iron and ruthenium catalysts being the optimal materials for the HBP. For dissociative N₂ reduction, it was shown that the binding energies of NH_x (x=0-2) species correlate with each other on late transition metals.⁹⁸ This correlation thus relates the binding energy of all reaction intermediates on various surfaces using a single descriptor - the

binding energy of N^* to the surface. Bronsted-Evans-Polanyi (BEP) relationships have been shown to hold for elementary N-N dissociation and N-H bond formation steps, linearly correlating the elementary activation barriers with the reaction energies.⁹⁹ This leaves the metal- N^* binding energy as a single descriptor that dictates all elementary reaction energies and activation barriers, and therefore, the overall rate of the ammonia synthesis reaction on late transition metal surfaces.

The consequences of Sabatier's Principle on the rate of N_2 reduction results in a volcano curve when activity is plotted against N^* binding energy (Fig. 4a). Metals to the left (strong N^* binding) result in lower ammonia synthesis rates due to slow N-H formation and metals to the right (weak N^* binding) are limited by N_2 activation. Fig. 4b shows the BEP linear correlation between the N_2 dissociation transition state stability and the N^* binding energy. No metal exists with a combination of intermediate N^* binding and a low energy N_2 dissociation transition state (bottom middle of plot) As the optimal material at the top of the "volcano" still displays a significant activation barrier for both N_2 dissociation and N-H bond formation, the Haber-Bosch reaction must be performed at elevated temperature (400-500 °C) to reach an acceptable rate. As higher temperature limits equilibrium conversion for the overall reaction, high pressure must be used to reach reasonable conversions, as described earlier.

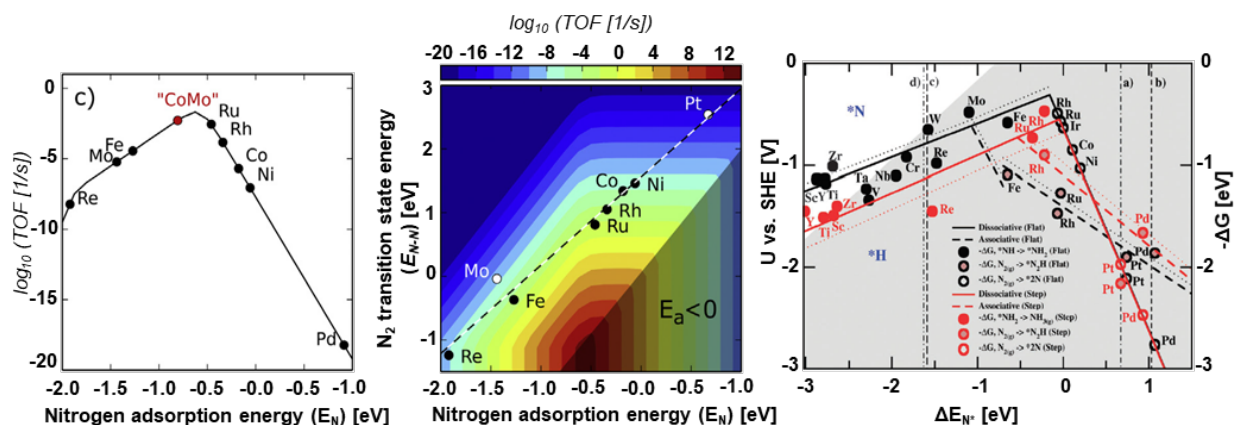


Figure 4. Computational predictions and theory-based limitations for heterogeneous (electro)catalysts (a) Volcano plot for ammonia synthesis on late transition metals.¹⁰⁰ (b) Scaling relationship for N₂ dissociation transition state intermediate on late transition state metals.¹⁰⁰ (c) Proposed volcano plot for electro-chemical nitrogen reduction on late transition metals.⁹⁸

Though N₂ electrochemical reduction may first form a N₂H* species before breaking the N-N bond, Norskov et al. suggested that similar scaling and BEP relationships will lead to an equivalent “volcano” relationship that would limit the ability of late transition metals to reduce N₂ electrochemically (Fig 4c). Analysis from their DFT data suggest that all late transition metals will have a significant overpotential for N₂ reduction regardless of the “associative” or “dissociative” paths.⁹⁸ As the hydrogen evolution reaction will have lower overpotentials, N₂ electrochemical reduction will also suffer from a selectivity challenge. This result is consistent with the experimental observation that no late transition metal is highly active or selective to N₂ electrochemical reduction at low temperature.

The above analysis provides guidance in considering the design of electro-catalysts for electrochemical N₂ reduction. The correlations used to establish the plots in Figure 4 do have

noise, and the existence of BEP relationships for elementary electrochemical reactions across late transition metals is yet to be established (Fig. 4c considered only elementary reaction energies with an assumption that BEP relationships would hold). Though the “noise” in scaling or BEP relationships provides some hope for late transition metal catalysis, other materials or mechanisms may be needed to provide significant N₂ electro-reduction. Catalytic systems/materials that either lower activation barriers relative to the late transition metal BEP relationships, or break scaling or BEP relationships altogether, are needed.

Though these limitations lead to difficulty in discovering active and selective N₂ reduction catalysts, the nitrogenase enzyme system demonstrates significant turnover rates, for what is effectively an electrochemical reduction process at atmospheric conditions. Homogeneous catalysts demonstrate the possibility to reduce N₂ through different elementary reaction mechanisms, and both enzymes and homogeneous systems demonstrate the potential to use complex active sites to further impact catalyst performance.

Heterogeneous Electrocatalysts Electrochemical systems provide an easily scalable system, alleviate dependence on fossil fuels, and decrease energy consumption by utilizing renewable electric energy, thereby increasing accessibility. However, existing catalysts are plagued by low Faradaic efficiencies due to the competing hydrogen evolution reaction (HER). Components such as the catalyst material and electrolyte type (solid polymer, liquid or molten salt),^{4,101-105} have been modified to increase the electrocatalytic performance. The wide variety of different experimental parameters tested thus far lead to challenges in attempting to directly compare results. However, it is clear that the primary challenge that must be solved to enable electrocatalytic ammonia synthesis is the design of the electrocatalyst itself to suppress HER while supporting an optimized nitrogen reduction reaction (NRR) to ammonia. Further,

experimental^{4,105-107} and theoretical^{1,98} results on traditional transition metal catalysts and catalysts designed with well-known strategies (e.g., monometallic or bimetallic composition, well-known transition metal catalyst materials such as platinum or iron, morphological control of size or shape) suggest that these traditional strategies, alone, will not achieve high Faradaic efficiencies for NRR. Alternative approaches must thus be explored for electrocatalyst design that strategically combine optimization of dinitrogen adsorption and proton addition thermodynamics with successful suppression of HER at the electrocatalyst surface. The successful experimental demonstration of potential strategies necessitates continued development of the theoretical understanding of NRR reaction mechanism thermodynamics and kinetics, as well as detailed and careful experimental work to identify, evaluate, and understand synthetic heterogeneous electrocatalysts.

For the majority of the electrochemical systems, despite catalyst type, Faradaic efficiencies are still typically below 1%. One exception, a nano-Fe₂O₃ catalyst dispersed in a molten hydroxide electrolyte solution, has far exceeded other catalysts with a Faradaic efficiency of 35% (2.4×10^{-9} mol NH₃ cm⁻² s⁻¹ at 200°C and atmospheric pressure).⁴ Interestingly, this study found that changing the electrolyte molar ratio and composition did not affect the ammonia evolution potential but did contribute to changes in production rate results.⁴ It is likely that the combination of higher temperature with a controlled amount of water molecules within the electrocatalytic system both contributed to the high reported Faradaic efficiencies. However, the complexity of system operations and restriction to higher temperatures for a molten hydroxide electrolyte decrease the economic feasibility. On the other hand, polymer electrolyte membranes (PEM) such as Nafion have promising prospects to be utilized in low temperature ammonia synthesis due to the high conductivity of the polymer at low temperature ranges. Recently,

several advances have suggested potential strategies in catalyst design that may overcome the challenge of low Faradaic efficiency. An Au-TiO₂ nanocomposite catalyst resulted in Faradaic efficiencies as high as 8.11 % ($3.5 \times 10^{-10} \text{ mol}_{\text{NH}_3} \text{ cm}^{-2} \text{ s}^{-1}$ at 20°C and atmospheric pressure, inlet gas as wet N₂),¹⁰³ suggesting a bimetallic catalyst comprised of elements from either side of the “volcano” plot (Fig. 4c)⁹⁸ may provide a more optimized surface. However, an increase in current density (i.e., increase in cell potential) leads to increased ammonia production along with a decrease in Faradaic efficiency,¹⁰³ which is a general trend seen with other electrochemical systems.^{106,107} The decrease in Faradaic efficiency occurs because the competing electrochemical reaction, hydrogen evolution, dominates at the catalyst surface, leaving no vacant sites for nitrogen reduction to occur. These results suggest that while the Ti-Au bimetallic combination seems to enhance NRR, the catalyst does not sufficiently suppress HER as the current density increases. Further research is needed to understand if these, and other, catalyst design strategies, such as the electrode-supported catalyst materials of Hara et al.,⁹⁷ will prove beneficial in electrochemical systems. Inherent in the need for further research on electrocatalyst design is the need for fundamental experimental studies to understand the NRR reaction mechanism and reaction dynamics at the catalyst surface, as well as to understand how material properties of catalysts directly impact reaction dynamics. The recent results from novel catalyst design suggest that, even though optimization of the overall electrochemical system is important, without a better understanding of how to control the adsorption and desorption of species on the catalyst surface, the Faradaic efficiencies of heterogeneous electrocatalyst will not improve. Further, due to ambient ammonia contamination, any evaluation of NH₃ electrocatalysts should report, at a minimum, a set of control experiments with argon to have an accurate measurement of Faradaic efficiency. Ideally, multiple approaches to experimentally verify ammonia production should be

used, including ion chromatography, ^{15}N isotope studies, and the common indophenol blue spectrophotometry method.

Outlook

The extensive research performed on delineating nitrogenase structure and developing molecular catalysts has resulted in an increasingly comprehensive view of the necessary structural environment for efficient N_2 reduction to NH_3 . In particular, nitrogenase research has used amino acid substitutions to control the enzyme catalytic environment, allowing study substrate and intermediates availability and ammonia production. Homogeneous catalysis research has developed successful ligand systems for N_2 reduction, as well as provided catalyst molecular structures that demonstrate necessary components for the N_2 reduction mechanism. Simple metal-based heterogeneous catalyst surfaces are highly unlikely to promote N_2 reduction to NH_3 at high Faradaic efficiency, and mechanistic insights from the nitrogenase and molecular catalyst research communities must be used to innovatively design successful heterogeneous catalysts.

DFT reports coupled with in-situ electrochemical observation of adsorption and desorption of nitrogen species will lead to a better understanding of surface interactions to reduce competing reactions on heterogeneous catalysts. DFT studies point researchers in an educated direction for selective catalyst design, but do not address the overall design of an electrochemical nitrogen fixation system. There is currently a lack of polymers to promote the transport of OH^- ions for a stable membrane separator, and proper experimental controls. Ammonia contamination in current research setups leads to the uncertainty of results and affects reproducibility of results. Ultimately, the problems facing the electrochemical ammonia synthesis industry require efforts

in both theory and experimental work from a broad array of researchers to achieve a low temperature, cost effective, and efficient system.

With future efforts identifying novel NH₃-evolving catalysts or novel approaches to further study known (bio)catalysts, the importance of product analysis must not be overlooked. This is important for determining substrate/product selectivity as well as confirming the production of NH₃. While NH₃ can be easily quantified by UV/Vis or fluorescence spectroscopy, such probes are susceptible to false-positive interference from other N-species (such as amino acids or creatine, a product of ATP regeneration in nitrogenase enzymatic assays) and an accompanying technique should also be employed, such as NMR spectroscopy of ¹H or ¹⁴N; the use of NMR also introduces the ability to easily confirm NH₃ production from ¹⁵N labeled nitrogen gas, which is important in eliminating contaminant sources of NH₃. Overall, there has been a wealth of materials and mechanistic research in nitrogen reduction catalysts for ammonia production over the last 5-7 years that is showing the ability to translate nitrogenase and molecular catalyst knowledge to heterogeneous catalysts is dramatically improving catalyst performance.

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The authors have no competing interests.

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