Beyond fossil fuel-driven nitrogen transformations


BACKGROUND: The invention of the Haber-Bosch (H-B) process in the early 1900s to produce ammonia industrially from nitrogen and hydrogen revolutionized the manufacture of fertilizer and led to fundamental changes in the way food is produced. Its impact is underscored by the fact that about 50% of the nitrogen atoms in humans today originate from this single industrial process. In the century after the H-B process was invented, the chemistry of carbon moved to center stage, resulting in remarkable discoveries and a vast array of products including plastics and pharmaceuticals. In contrast, little has changed in industrial nitrogen chemistry. This scenario reflects both the inherent efficiency of the H-B process and the particular challenge of breaking the strong dinitrogen bond. Nonetheless, the reliance of the H-B process on fossil fuels and its associated high CO2 emissions have spurred fundamental changes in the way people live and work. Major effort has been devoted to developing alternative and environmentally friendly processes that would allow NH3 production at distributed sources under more benign conditions, rather than through the large-scale centralized H-B process. Hydrocarbons (particularly methane) and water are the only two sources of hydrogen atoms that can sustain long-term, large-scale NH3 production. The use of water as the hydrogen source for NH3 production requires substantially more energy than using methane, but it is also more environmentally benign, does not contribute to the accumulation of greenhouse gases, and does not compete for valuable and limited hydrocarbon resources. Microbes living in all major ecosystems are able to reduce N2 to NH3 by using the enzyme nitrogenase. A deeper understanding of this enzyme could lead to more efficient catalysts for nitrogen reduction under ambient conditions. Model molecular catalysts have been designed that mimic some of the functions of the active site of nitrogenase. Some modest success has also been achieved in designing electrocatalysts for dinitrogen reduction. Electrochemistry avoids the expense and environmental damage of steam reforming of methane (which accounts for most of the cost of the H-B process), and it may provide a means for distributed production of ammonia. On the oxidative side, nitric acid is the principal commodity chemical containing oxidized nitrogen. Nearly all nitric acid is manufactured by oxidation of NH3 through the Ostwald process, but a more direct reaction of N2 with O2 might be practically feasible through further development of nonthermal plasma technology. Heterogeneous NH3 oxidation with O2 is at the heart of the Ostwald process and is practiced in a variety of environmental protection applications as well. Precious metals remain the workhorse catalysts, and opportunities therefore exist to develop lower-cost materials with equivalent or better activity and selectivity. Nitrogen oxides are also environmentally hazardous pollutants generated by industrial and transportation activities, and extensive research has gone into developing and applying reduction catalysts. Three-way catalytic converters are operating on hundreds of millions of vehicles worldwide. However, increasingly stringent emissions regulations, coupled with the low exhaust temperatures of high-efficiency engines, present challenges for future combustion emissions control. Bacterial denitrification is the natural analog of this chemistry and another source of study and inspiration for catalyst design.

ADVANCES: Major effort has been devoted to developing alternative and environmentally friendly processes that would allow NH3 production at distributed sources under more benign conditions, rather than through the large-scale centralized H-B process. Hydrocarbons (particularly methane) and water are the only two sources of hydrogen atoms that can sustain long-term, large-scale NH3 production. The use of water as the hydrogen source for NH3 production requires substantially more energy than using methane, but it is also more environmentally benign, does not contribute to the accumulation of greenhouse gases, and does not compete for valuable and limited hydrocarbon resources. Microbes living in all major ecosystems are able to reduce N2 to NH3 by using the enzyme nitrogenase. A deeper understanding of this enzyme could lead to more efficient catalysts for nitrogen reduction under ambient conditions. Model molecular catalysts have been designed that mimic some of the functions of the active site of nitrogenase. Some modest success has also been achieved in designing electrocatalysts for dinitrogen reduction. Electrochemistry avoids the expense and environmental damage of steam reforming of methane (which accounts for most of the cost of the H-B process), and it may provide a means for distributed production of ammonia. On the oxidative side, nitric acid is the principal commodity chemical containing oxidized nitrogen. Nearly all nitric acid is manufactured by oxidation of NH3 through the Ostwald process, but a more direct reaction of N2 with O2 might be practically feasible through further development of nonthermal plasma technology. Heterogeneous NH3 oxidation with O2 is at the heart of the Ostwald process and is practiced in a variety of environmental protection applications as well. Precious metals remain the workhorse catalysts, and opportunities therefore exist to develop lower-cost materials with equivalent or better activity and selectivity. Nitrogen oxides are also environmentally hazardous pollutants generated by industrial and transportation activities, and extensive research has gone into developing and applying reduction catalysts. Three-way catalytic converters are operating on hundreds of millions of vehicles worldwide. However, increasingly stringent emissions regulations, coupled with the low exhaust temperatures of high-efficiency engines, present challenges for future combustion emissions control. Bacterial denitrification is the natural analog of this chemistry and another source of study and inspiration for catalyst design.

OUTLOOK: Demands for greater energy efficiency, smaller-scale and more flexible processes, and environmental protection provide growing impetus for expanding the scope of nitrogen chemistry. Nitrogenase, as well as nitrifying and denitrifying enzymes, will eventually be understood in sufficient detail that robust molecular catalytic mimics will emerge. Electrochemical and photochemical methods also demand more study. Other intriguing areas of research that have provided tantalizing results include chemical looping and plasma-driven processes. The grand challenge in the field of nitrogen chemistry is the development of catalysts and processes that provide simple, low-energy routes to the manipulation of the redox states of nitrogen.
INORGANIC CHEMISTRY

Beyond fossil fuel-driven nitrogen transformations


Nitrogen is fundamental to all of life and many industrial processes. The interchange of nitrogen oxidation states in the industrial production of ammonia, nitric acid, and other commodity chemicals is largely powered by fossil fuels. A key goal of contemporary research in the field of nitrogen chemistry is to minimize the use of fossil fuels by developing more efficient heterogeneous, homogeneous, photo-, and electrocatalytic processes or by adapting the enzymatic processes underlying the natural nitrogen cycle. These approaches, as well as the challenges involved, are discussed in this Review.

Reduced forms of nitrogen, particularly ammonia (NH₃), are vital to life. Before the early 1900s, all reduced N came from biological nitrogen fixation by microbes. This landscape changed in the early 1900s with the invention by Haber and Bosch of an industrial process to reduce N₂ to NH₃ (N₂ + 3 H₂ → 2NH₃). The Haber-Bosch (H-B) process has led to fundamental changes in the way food is produced, and its impact is underscored by the fact that about 50% of the N atoms in humans today originate from it. For these reasons and others, the H-B process has been called the most impactful invention of the 20th century. However, it is energy-intensive, consuming 1 to 2% of the world's annual energy output. The main energy requirements arise from the high reaction temperatures (~700 K) and pressures (~100 atm) and, most importantly, from the need for large quantities of H₂. Nevertheless, at scale, the H-B process is surprisingly energy-efficient. In addition to the high energy demand, however, there is a second problem with the process that is potentially more serious. Specifically, the source of H₂ is usually natural gas (4), and, consequently, the H-B process generates about 1.9 metric tons of CO₂ per metric ton of NH₃ produced (3 CO₂ per 8 NH₃) (5).

Nitrogen in its more oxidized forms is also industrially, biologically, and environmentally important. Oxidation of N₂ to nitric oxide (NO) and nitrogen dioxide (NO₂), which are collectively referred to as NOₓ (the representation of neutral forms of oxidized nitrogen), occurs naturally in lightning and also during combustion of fuels in air. In fact, plasma-driven oxidation of NO to NO₂ (the Birkeland-Eyde, or B-E, process) preceded the H-B process as the first commercial approach to nitrogen fixation. However, the B-E process is not economically competitive with the H-B process and, as a result, the demand for oxidized nitrogen, primarily in the form of nitric acid (HNO₃), is satisfied by catalytic oxidation of H₂ and nitric oxide (NO) generated NH₃ at elevated temperatures through the Ostwald process. Nitrogen oxides (NOₓ, which represents both neutral and anionic forms of oxidized nitrogen) are also produced on a large scale by bacteria. These processes include oxidation of NH₃ to nitrate (NO₃⁻) by nitrifying bacteria and reduction of NO₂⁻ to nitrite (NO₂⁻), NO, nitrous oxide (N₂O), and ultimately N₂ by denitrifying bacteria. The conversion of NH₃ and NOₓ to N₂ by the action of these bacteria is used in wastewater treatment and is the primary pathway for loss of applied fertilizers in agriculture. Nitrogen oxides are common environmental pollutants, and thus catalysts to reduce these oxides to N₂ are also of considerable practical importance. For example, NOₓ generated during combustion is a primary component of photochemical smog (9). The development of active catalysts for reducing NOₓ to N₂ (three-way catalytic converters, or TWCs) led to considerable improvements in air quality in the late 1970s (10), and TWCs now operate on hundreds of millions of vehicles worldwide. However, increasing stringent emissions regulations, coupled with the low exhaust temperatures from high-efficiency engines, present challenges for the future control of combustion emissions (11). The soluble forms of the nitrogen oxides, primarily NO₂ and NO₃⁻, are similarly hazardous to human health and contribute to the eutrophication of waterways (12). Sustainable approaches for catalytically converting these pollutants to N₂ remain an unmet challenge (13).

In this Review, we report on the results of a U.S. Department of Energy workshop held in October 2016 that focused on the challenges and opportunities associated with fundamental aspects of nitrogen chemistry. We begin by discussing the thermochemistry of nitrogen transformations; we then focus on the reduced forms of nitrogen, primarily NH₃, followed by the oxidized forms.

Thermochemistry of nitrogen fixation

The energy expenditures for various reductive and oxidative N₂ fixation pathways are compared in Fig. 1 (14–16). Hydrocarbons, including biomass and fossil fuels (particularly methane), and water are the only two sources of hydrogen atoms that can sustain long-term, large-scale NH₃ production. The use of water as the hydrogen source for NH₃ production requires substantially more energy than using methane (by 613.4 kJ/mol N₂), but it is also more environmentally benign, does not contribute to the accumulation of greenhouse gases, and does not compete for valuable and limited hydrocarbon resources. However, these advantages can be fully realized only if the energy comes from a clean, renewable source such as the Sun or wind.

When water is used as the feedstock, there is only a small (32.9 kJ/mol N₂) thermodynamic advantage for the direct synthesis of NH₃, compared with a two-stage synthesis involving water splitting followed by the H-B process. The overall energy saving may, however, become more substantial if the H-B process is avoided altogether and direct reductive N₂ fixation is conducted under milder conditions.

The two most important N-containing commodity chemicals are NH₃ and HNO₃. In 2017, their worldwide production was estimated to be 150 (17) and 50 (18) million metric tons, respectively. Presently, nearly all HNO₃ is manufactured using a three-stage approach—steam reforming of methane, the H-B process, and then the Ostwald process (Fig. 1)—but this approach is energetically wasteful compared with direct oxidative N₂ fixation.

An attractive alternative route to HNO₃, which avoids the NH₃ intermediate, is direct N₂ oxidation to aqueous HNO₃ (Eq. 1).
\[
N_2(\text{g}) + 2.5O_2(\text{g}) + H_2O(\text{liq}) \rightleftharpoons 2H^+ (\text{aq}) + 2NO_3^- (\text{aq}) \quad (1)
\]

The equilibrium constant for this reaction is \(\sim 2.7 \times 10^{-3} \text{ M}^1/\text{bar}^{3.5}\) (standard Gibbs free energy \(\Delta G^\circ = 14.6 \text{ kJ/mol N}_2\) (14–16, 19), which is large enough to drive spontaneous formation of \~90% of atmospheric O2 in any pool of water on the surface of Earth. Moreover, if equilibrium were to be achieved between Earth’s atmosphere and oceans, the oceans would contain \~0.02 M HNO3, and \~90% of atmospheric O2 would be consumed. Fortunately for life on Earth, under ordinary conditions and in the absence of a catalyst, Eq. 1 is unmeasurably slow in both directions.

**Reduction of N2 to NH3**

**Overview**

As discussed in the previous two sections, the most important N2 reduction reaction is NH3 synthesis, specifically \(N_2 + 3H_2 \rightleftharpoons 2NH_3\). Given that this reaction is slightly thermodynamically favorable under ambient conditions, major effort has been devoted to developing alternative and environmentally friendly processes that would allow \(NH_3\) to be produced at distributed sources under more benign conditions, rather than through the large-scale centralized H-B process. This goal is particularly important in developing countries where the population, and hence the need for food, is increasing rapidly. In these countries, access to fertilizer is hampered by poor transportation infrastructure and insufficient capital to build large chemical plants. For example, there are no large-scale \(NH_3\) production facilities anywhere in East Africa. To address this need, substantial effort has been expended to understand N2 reduction using a variety of catalysts, including heterogeneous, enzymatic, and homogeneous catalysts, as well as electro- and photocatalysts.

**Heterogeneous catalysis**

The commercial H-B process is carried out using a heterogeneous catalyst based on iron and promoted with \(Al_2O_3\) and potassium. It is now well accepted that the relative activity of metallic catalysts can be correlated to their binding energies with N-containing species in terms of a volcano-shaped relationship. Metals that bind nitrogen too strongly or too weakly are on either side of the volcano (20). For metals that have low binding energies, N2 dissociation is rate-limiting. For metals with high binding energies, N2 dissociation occurs, but desorption of the resulting atomic N (and other N-containing intermediates) is slow, limiting the number of available binding sites and thereby slowing the catalytic rate (21).

Recent calculations suggest that the energies of all intermediates and transition states involved in a conventional NH3 synthesis reaction network scale with the N-binding energy. As shown in Fig. 2, these correlations limit the rate of NH3 synthesis on transition metals to much lower values than would be possible on a material with both a low N2 dissociation barrier and more moderate binding energies (22). An important challenge is to break this type of scaling relationship, which should lead to the development of catalysts yielding reaction rates that are potentially orders of magnitude higher than the current state of the art.

Advances in the synthesis, characterization, and modeling of nontraditional heterogeneous catalysts—such as intermetallics, alloys containing a single heteroelement, and shape-controlled materials—offer the promise for more active catalysts. These combined efforts should lead to catalysts that could potentially operate at lower temperatures and thus reduce the operating pressures of the H-B process. Another opportunity to reduce the CO2 footprint of the H-B process is to replace the methane reformer with a water electrolyzer to provide CO2-free H2, but this would require cost-effective, large-scale electrolyzers.

**Enzyme catalysis**

A range of microbes (bacteria and archaea) living in all major ecosystems are able to reduce N2 to \(NH_3\) using the enzyme nitrogenase. Nitrogen fixation by these microbes contributes to the global supply of \(NH_3\), but it is insufficient to support modern intensive agriculture. Exciting frontier areas for the application of microbial \(N_2\) fixation include engineering nitrogen fixation genes into eukaryotes (23), such as plants, and using nitrogen-fixing microbes in electrocatalysis cells that permit sustained \(N_2\) reduction to \(NH_3\) (24). Such systems offer the promise of providing...
localized solutions to N₂ reduction but are not likely to displace the need for large-scale N₂ reduction in the near term.

One important lesson to learn from biological nitrogen fixation is how the enzyme nitrogenase accomplishes reduction of N₂ to NH₃ at ambient temperatures and pressures and without H₂. The first nitrogenase to be purified (and the most widely distributed) is molybdenum-dependent and, as shown in Fig. 3, has a metal-cluster active site containing Mo, Fe, S, C, and homocitrate (FeMo cofactor).

An important step toward a mechanistic understanding of nitrogenase emerged from trapping an intermediate with 4H⁺ and 4e⁻ accumulated immediately before binding N₂. Characterization of this intermediate (25) (termed the E₅ state) has revealed the presence of bridging hydrides (Fe-H-Fe). The E₅ state undergoes reductive elimination of the two hydrides with release of H₂ with concomitant activation of the metal core by 2e⁻ for binding and reduction of N₂ to a metal-bound diazenido species (HN≡N–Fe). Although these studies have provided insights into the central catalytic step, which is the cleavage of these bonds, many challenges remain before the entire mechanism can be elucidated. These include a molecular-level understanding of both the early and late stages of the N₂ reduction pathways, an understanding of the roles of adenosine triphosphate (ATP) hydrolysis in driving electron transfer, and then reconciliation of the empirical mechanism with computational studies.

These foregoing challenges primarily involve substrate moieties bound as catalytic intermediates. In parallel, important questions remain about the FeMo cofactor active site of Mo-dependent nitrogenase. For example, what changes in redox and spin states of the seven Fe centers and the Mo center accompany the stepwise transformations of substrates? Additionally, the FeMo cofactor contains the first known example of a carbide (C⁺) in biology. The importance and function of this carbide with respect to mechanism are unknown. Understanding the structure of FeMo cofactor intermediates and synthetic analogs could provide important clues to guide the design of new homogeneous and heterogeneous catalysts for N₂ reduction (26).

Bioelectrochemical techniques offer a powerful alternative method of delivering electrons to nitrogenase. For example, it has been recently demonstrated that a CdS nanorod–nitrogenase MoFe protein hybrid achieves light-dependent N₂ reduction to NH₃ by using a sacrificial electron donor (31). Such systems offer a means to use light as the exclusive energy source to drive N₂ reduction.

Homogeneous catalysis

Synthetic homogeneous catalysts designed for N₂ reduction provide well-defined molecular precatalysts and intermediates, which can be thoroughly characterized by diverse spectroscopic techniques and thereby provide excellent opportunities for determining mechanistic information about N₂ reduction to NH₃. The reactivity of synthetic inorganic complexes offers insights into molecular reactivity and individual bond-making processes that occur in nitrogenases. The discovery of nitrogenase, along with a transition metal compound that contains N₂ bound to ruthenium (32), initiated a race to prepare NH₃ catalytically under mild conditions using a transition metal complex. Entire institutes were created in England and Russia in the late 1960s for this purpose. The stoichiometric N₂-to-NH₃ conversion using H₂SO₄ was demonstrated with low-valent Mo-N₂ and W-N₂ complexes in the 1970s (33); typically, the electrons required came from the metal complex. In 1983, Pickett and Talarmin accomplished the synthesis of NH₃ by using an electrochemical route starting from the tungsten complex [W(N₂)₂(PMe₃Ph)₃]; Me, methyl; Ph, phenyl, with the electrons supplied by the electrode and protons from an added acid (34). The catalytic reduction of N₂ to NH₃ by H⁺ and e⁻ was reported in subsequent studies, using, for example, a well-defined Mo-containing catalyst (35). Up to eight equivalents of NH₃ per Mo were formed, along with H₂. Experiments and calculations both support a mechanism involving the addition of 6H⁺ and 6e⁻ to the N₂ initially bound to a Mo⁷⁺ center. Altogether, eight of these proposed intermediates were prepared and characterized.

Additional Mo precatalysts for reduction of N₂ using chemical reductants and an acid—a dimolybdenum–dinitrogen complex (36) and a molybdenum nitride (37)—were subsequently reported in 2011 and 2015, respectively. In 2013, Fe complexes were reported that catalyze reduction of N₂ to NH₃ using a strong reducing agent (K₂C₇) and a strong acid at 200 K (38); improvements to the Fe system recently produced as many as 84 equivalents of NH₃ per Fe (39). These Fe complexes were designed to reflect the trigonal symmetry of the Fe in the catalytic face of the FeMo cofactor (Fig. 3) and to allow variation of an axial ligand, so as to explore tuning of N₂ binding and reduction by the unusual carbide at the center of the FeMo cofactor.

In all these cases, it appears that catalytic N₂ reduction is a six-electron process, involving many intermediate chemical species (M-NHY₃), but, unlike nitrogenase, without a mechanistic requirement for production of H₂. Nonetheless, in all cases, N₂ reduction is accompanied by production of H₂, and at least with the Fe complexes, this has been shown to involve a catalytic process, with H⁻ reduction competing with N₂ reduction.

Much work remains to move this field forward. For example, rational design of potential catalysts will be guided by accurate determination of the bond dissociation free energies (BDFEs) of N–H bonds, including likely intermediates such as M–N–NH, M–N–H₂, and M–N=N–NH₂. Initial experimental and theoretical estimates have shown that N–H BDFEs of coordinated NH₃ can vary considerably, and they demonstrate the importance of metal identity, metal oxidation state, and the attached ligands, which together tune the stability of potential intermediates. In addition, determination of the energies of these bonds will allow evaluation of energetic requirements of the individual chemical steps that ultimately lead to NH₃. 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 N₂ binding and multiple reductions at the metal site.

**Electrocatalysis and photocatalysis**

The potential-pH predominance (Pourbaix) diagram for the N₂-H₂O system shown in Fig. 4 reveals that reduction of N₂ to NH₄⁺ or NH₃ (Eq. 2) and the N₂ reduction line in Fig. 4) is thermodynamically possible under moderately reducing conditions.

\[
N_2(aq) + 8H^+(aq) \text{ [or 6H}^+(aq)\text{]} + 6e^- \rightarrow 2NH_4^+(aq) \text{ [or 2NH}_3(aq)]
\] (2)

Moreover, with a sufficiently active electrocatalyst, the N₂ reduction reaction can, in principle, proceed in a narrow range of negative potentials without interference from water reduction (line a in Fig. 4) over the entire pH range. However, at potentials below line a, an extremely selective electrocatalyst would be required to suppress parasitic water reduction. The nitrogen reduction reaction could be paired with a water oxidation half-reaction to supply the H⁺ and e⁻ required for a complete electrolysers cell. Such a cell would essentially combine water splitting with NH₃ formation as depicted by the direct reductive fixation route in Fig. 1. Despite the inviting prospect of a scalable NH₃ electrolysers cell running on renewable electricity at or near room temperature, the difficulty of selectively catalyzing the nitrogen reduction reaction has prevented development of an efficient electrochemical system.

At present, only a few examples of pairing the nitrogen reduction reaction with water oxidation at ambient temperature and pressure have been reported, and in all cases, owing to competing H₂ evolution, the faradaic efficiencies for NH₃ are so low that even its reliable detection is challenging (40, 41). For example, an efficiency of 0.833% and a production rate of 9.4 x 10⁻⁸ mol H₂ per square centimeter per second were measured at 353 K at an applied cell voltage of 1.2 V using Pt electrodes and a Nafion electrolyte (42). Another electrochemical approach involved an electrochemical cycling process for producing NH₃ (43). The cycling included separate steps of LIOH electrolysis, Li nitridation, and Li₂N hydrolysis, thereby circumventing the parasitic H₂ evolution reaction and leading to higher faradaic efficiencies for NH₃.

Proton-conducting ceramic oxides have been explored as electrodes for nitrogen reduction, and when they operate at higher temperatures, both the rate and the faradaic efficiency increase (44). For example, efficiencies in excess of 50% and rates in the range of 10⁻⁸ to 10⁻⁹ mol NH₃ per square centimeter per second have been attained above 673 K by using oxide or molten chloride electrolytes and a variety of metal or metal oxide cathodes (44, 45). However, higher temperatures introduce an additional energy burden and hence compromise the advantage of this approach compared with the H-B process.

Photochemical reduction of N₂ to NH₃ has also been reported, and these studies may contain guidance relevant to electrochemistry (46, 47). Photoelectrocatalytic routes to NH₃ have been summarized recently (48). One of the biggest challenges for photoelectrocatalytic NH₃ synthesis is the discovery of active and stable photoelectrode materials that are responsive to visible light. Synthetic nitrogenase mimics in the form of chalcogens, composed of Mo- and Fe-containing biomimetic clusters, can potentially accomplish photoelectrocatalytic N₂ fixation and conversion to NH₃ at ambient temperature and pressure. Both Fe-S and Mo-Fe-S chalcogens have displayed promising activity toward N₂ reduction (49).

**Plasma-driven transformations**

The feasibility of using plasmas consisting of ions, electrons, and excited molecular species to drive chemical reactions that are thermally inaccessible has been known for many years (7). For example, NH₃ was synthesized in laboratory-scale, nonthermal plasmas of N₂ and H₂ at temperatures and pressures lower than those used in the H-B process as early as the 1970s, and more recently, the synthesis has been demonstrated under much milder conditions (1 atm and 140°C) (50). The plasma synthesis of NH₃ has been carried out both homogeneously and in combination with heterogeneous catalysts (7, 50, 51).

Several mechanisms have been proposed to account for enhancements in catalytic activity in the presence of nonthermal plasmas (52-54). However, the fundamental science and practical engineering of plasma-driven NH₃ syntheses lag behind thermal and electrochemical routes and are therefore ripe for additional research. Further progress in this field will draw on the insights gained from traditional heterogeneous and electrochemical reductions.

**Chemical looping**

Chemical looping is perhaps most familiar from combustion, where two connected fluidized beds are used to cycle solid particles between an oxidized and a reduced state to combust a carbon-containing fuel with oxygen (55). Chemical looping can also be performed with two fixed beds instead of fluidized beds. Nitrogen can be used instead of oxygen for a similar looping approach in NH₃ synthesis (56). First, N₂ is contacted with a suitable solid-state transition metal to yield a nitride (activation). Second, NH₃ is harvested by contacting the nitride with steam or H₂ (57). Recently, lithium has been used as the parent metal for the nitride, but this approach requires liquid-phase electrolysis to recycle lithium, and this step is usually not present in chemical looping (43).

Potential advantages of chemical looping include the ability to independently control process conditions for N₂ activation and product harvest. In this sense, chemical looping can break the scaling relationship alluded to in Fig. 2. Operation at atmospheric pressure is another major advantage of chemical looping for nitrogen activation (58). On the basis of results from a pilot-scale plant, chemical looping for combustion, including CO₂ capture, is comparable to conventional combustion and appears to be economically attractive (59). This may be an indication of the possible economic feasibility of chemical looping for nitrogen activation.

**Oxidation of N₂**

**Overview**

The dominance of the H-B process in commercial N₂ fixation is arguably a direct consequence of the ready availability of H₂ from fossil hydrocarbons. As shown in Fig. 1, oxidative fixation of N₂ can, in principle, be achieved with a lower-energy input than reductive fixation if N₂, H₂O, and O₂ are used as reactants. Other nitrogen oxides are accessible at even lower free energies, especially when coupled with water to form the corresponding oxoacids.

Although H-B and natural processes have motivated substantial research into reductive N₂ fixation, direct N₂ oxidation remains largely unexplored despite its great practical value as a replacement for the Ostwald process. The fact that living organisms have not evolved to consume N₂ and O₂ produce aqueous HNO₃ suggests fundamental chemical challenges that merit investigation. As a result, there is very little literature on the homogeneous oxidative chemistry of N₂.

**Direct oxidation of N₂ with O₂**

NO₂ is unavoidably generated at the high temperatures that prevail during combustion in air. NO is the primary combustion-generated component of NO₂, and its formation can be viewed
in the context of its equilibrium with N₂ and O₂ (Eq. 3).

\[
N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \tag{3}
\]

The standard enthalpy of this reaction is 90.3 kJ/mol NO, and the entropy is 12.4 J/K per mol NO (14, 15), indicating that equilibrium is unfavorable for NO production under ambient conditions. Owing to the positive entropy, however, the equilibrium NO concentration rises rapidly with temperature, reaching 0.8% in air at 2000 K (60).

The direct bimolecular reaction of N₂ and O₂ to produce NO is symmetry-forbidden and has a negligible rate even at combustion temperatures. Rather, NO is produced during combustion via Eqs. 4 and 5, where O (and similarly OH) radicals attack N₂, as originally proposed by Zeldovich (67).

\[
O + N_2 \rightarrow NO + N \tag{4}
\]

\[
N + O_2 \rightarrow NO + O \tag{5}
\]

Analogous reactions are at play in high-temperature thermal plasma, as in the original B-E process. Thermal plasmas are unlikely to be energy-competitive with the H-B process, even if the latter uses a renewable H₂ source (62), because the overall energy efficiencies of N₂ activation are low, and rapid thermal quenching is required to suppress NO decomposition back to N₂ and O₂.

The aforementioned fundamental limitations can be mitigated using low-temperature, nonthermal plasmas generated by either a dielectric barrier discharge or microwave absorption at or below atmospheric pressure, potentially coupled with appropriate catalysts (7). According to current estimates, theoretical energy consumption for N₂ fixation via Eq. 3 in a nonthermal plasma (~400 kJ/mol N₂) is lower by more than a factor of 2.5 than that for the H-B process with methane-derived H₂ (62–64), and the energy efficiencies already attained in the laboratory (600 to 1200 kJ/mol N₂, assuming 100%-efficient plasma generation (63, 64)) are better than the H-B process using H₂ from water electrolysis (~3000 kJ/mol N₂ (62)), 40% of which would go to electrolysis (65). Experiments and kinetic models show that the primary effect of the nonthermal plasma is to accelerate Zeldovich-like reactions involving nonequilibrium, vibrationally excited N₂. Practical implementation of nonthermal plasmas is hampered by their relatively low power per unit reactant mass and thus low throughput.

A thermal, heterogeneous N₂ oxidation catalyst would have to activate N₂ and O₂ and be stable at the extreme temperatures at which NO production becomes thermodynamically favored. Because of these stringent demands, nonthermal electro-, photo-, or plasma-assisted oxidation routes likely offer the greatest opportunities for progress. The development of catalytic systems that can effectively couple with these external energy sources will be key to practical advances. Preliminary results with nonthermal plasmas, especially coupled to catalysts, are promising. There is a pressing need to uncover the fundamental mechanisms that unite plasma chemistry, surface chemistry, catalysts, and theory to guide optimization of plasma and rational development of appropriate catalytic materials.

**Electrochemical oxidation of N₂ to HNO₃**

The oxidation line in Fig. 4 shows that N₂ is electrochemically unstable toward NO₃⁻ under moderately oxidizing conditions (Eq. 6).

\[
N_{2(g)} + 6H_2O_{(aq)} \rightleftharpoons 2NO_3^{-}_{(aq)} + 12H^+_{(aq)} + 10e^- \tag{6}
\]

At pH > 13, this 10-electron reaction is more thermodynamically favorable than the parasitic four-electron water oxidation to O₂. Thus, it is possible for NO₃⁻ to be the only product of an anodic process, particularly in neutral and alkaline solutions, if a sufficiently active and selective electrocatalyst for Eq. 6 can be discovered. The corresponding cell-completing cathodic reaction can be either water reduction to H₂ or O₂ reduction to water. Little apparent progress has yet been made in developing such catalysts, but there is no reason to believe that they cannot eventually be discovered.

By coupling cathodic N₂ reduction (Eq. 2) with anodic N₂ oxidation (Eq. 6), an electrochemical cell consuming only atmospheric N₂ and water as feedstock to yield aqueous NH₄NO₃ (Eq. 7) can be envisioned.

\[
N_{2(g)} + 3H_2O_{(aq)} \rightleftharpoons NH_4^+_{(aq)} + NO_3^{-}_{(aq)} + H_2(g) \tag{7}
\]

The additional H₂ production is necessary for matching cathodic and anodic currents and maintaining the electrolyte pH constant. Such a cell would require a minimum of 1.08 V to operate in neutral or alkaline electrolyte, which is slightly lower than the minimum water electrolysis voltage of 1.23 V. Advances relating to a catalytic decomposition of water into H₂ and O₂ reduction to water. Little apparent progress has yet been made in developing such catalysts, but there is no reason to believe that they cannot eventually be discovered.

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\[
2NO + e^- \rightarrow N_2O_2^- \tag{8A}
\]

\[
N_2O_2^- + e^- \rightarrow N_2O_2^{2-} \tag{8B}
\]

\[
N_2O_2^{2-} + 2H^+ \rightarrow NO + H_2O \tag{8C}
\]

Coordination complexes of hyponitrites are not uncommon, and a tri-Cu hyponitrite coordination complex has been isolated as an intermediate in the catalytic decomposition of NO to N₂ (67). A Cu dimer has similarly been implicated as the active site in a Cu-exchanged zeolite catalyst for NO decomposition (68). NO₂ can be catalytically reduced to N₂ via several routes. Precious metals are active for NO₂ reduction by CO and hydrocarbons, but only under conditions in which O₂ concentrations are low (10). Vanadia/titania catalysts and metal-exchanged zeolites catalyze selective reduction of NO₂ by NH₃ (69). Nitrosamine appears to be the key N₂-forming intermediate in the catalytic pathway (Eq. 9).

\[
NH_3 + NO \rightarrow H_2NNO + H^+ + e^- \tag{9A}
\]

\[
H_2NNO \rightarrow N_2 + H_2O \tag{9B}
\]

This N₂-forming reaction is exothermic, implying substantial, but perhaps not insurmountable, kinetic challenges to reversing the chemistry. NO₂ can also be catalytically reduced with H₂ over Pd and Pt catalysts (13), and N₂ is typically the desired product (66). By suitable selection of promoters and control of the NO/NO₂ ratio, however, NH₃ can be produced over Pt catalysts (70). Likewise, NH₃ competes with N₂ as the product of the catalytic reduction of NO₂ and NO₃⁻ by H₂ over Pd catalysts (13).

Certain bacteria analogously reduce NO₃⁻ and NO₂⁻ through a series of gaseous intermediates, leading ultimately to N₂ in a process called...
denitrification (Eq. 10). In these bacteria, NO$_3^-$ acts as a terminal electron acceptor in an anaerobic respiration process. Electrons flowing through membrane-bound proteins produce a proton gradient that in turn is used to make ATP. Each step in the denitrification process is catalyzed by well-studied metalloenzymes that use unusual metal clusters to achieve their chemistry (73, 74). From a global nitrogen perspective, denitrification by these bacteria functions to convert fixed forms of N (NO$_3^-$) into N$_2$. In some cases, this process is beneficial, such as during wastewater treatment to remove nitrates. In other cases, such as in agriculture, denitrification results in loss of N that was applied to crops as fertilizer.

$$2\text{NO}_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O \quad (10)$$

**NH$_3$ oxidation**

Heterogeneous NH$_3$ oxidation with O$_2$ is at the heart of the Ostwald process and is practiced in a variety of environmental protection applications. Precious metals remain the workhorse catalysts, and therefore opportunities exist to develop lower-cost materials having equivalent or better activity and selectivity. The preferred NH$_3$ oxidations is carried out by NMOX, which is a mild, highly selective catalyst that is generalizable beyond N species—especially considering that enzymes related to AMO, such as particulate methane monooxygenase, effect similar transformations of unactivated alkanes (75).

Mechanistic understanding of NH$_3$- and NO$_3^-$-mediated oxidations offers insights into proton-coupled, multi-electron transformations that are crucial to redox catalysis. NH$_3$-oxidations are energetic, cytotoxic metabolite that AOA and AOBOX harness as a source of reducing equivalents. The absence of requisite e-heme biosynthesis pathways in AOBOX necessitates substitution of HAO for either a nonheme or a Cu-based enzyme for NH$_3$-oxidation (80). Thus, opportunities exist to fill in a missing link in the biogeochemical nitrogen cycle while expanding understanding of how transition metals can transduce energy from redox-active small molecules.

**Concluding outlook**

Since the beginning of the 20th century, both the ability to produce and the need to remEDIATE nitrogen-containing compounds have been coupled to fossil fuels. Demands for greater energy efficiency, smaller and more flexible distributed processes, and environmental protection provide growing impetus to expand the scope of proven pathways that are not driven by fossil fuels. Opportunities exist to identify new and radically improved pathways, but progress in this regard will require a molecular-level understanding of nitrogen transformation reactions, as well as the translation of these core insights to the discovery of new catalytic systems and alternative means of driving the energy content (11) of these reactions.

**REFERENCES AND NOTES**


For the full mechanistic understanding of this process and of the kinetic origins of selectivity is lacking. NH$_3$ and/or NO$_3^-$ are fuel for bacteria and archaea that use multi-electron oxidative reactions to generate reducing equivalents for cellular respiration and to establish a proton gradient for ATP synthesis (73, 74). Ammonia-oxidizing bacteria (AOB) and archaea (AOA) stoichiometrically convert NH$_3$ to NO$_2^-$, AOA and AOB first carry out the selective conversion of NH$_3$ to hydroxylamine (NH$_2$OH) by using an integral membrane Cu monooxygenase called ammonia monoxygenase (AMO) (Eq. 11). Active AMO has never been purified, and thus this challenging transformation awaits mechanistic elucidation.

$\text{NH}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{NH}_2\text{OH} \quad (11)$

The NH$_2$OH generated by AMO oxidizes to provide a net electron flow for cellular respiration. How AOA processes NH$_3$ is unknown (75). In AOB, this process is carried out by hydroxylamine oxidoreductase (HAO), which contains a rare, covalently modified c-heme, heme P460, to which NH$_2$OH binds at Fe and undergoes proton-coupled oxidation (76). Recent experiments strongly support NO as the enzymatic product of HAO reactivity, contrary to decades of dogma asserting NO$_2^-$ as the enzymatic product (76). Assuming a two-electron turnover of AMO, the three-electron oxidation of NH$_2$OH by HAO furnishes one net electron for cellular respiration. Stoichiometric production of NO$_2^-$ from NH$_3$ by AOB likely involves an additional, but as yet unidentified, third enzyme in the pathway. Cytotoxicity of both NO and NH$_2$OH may be managed by cytochrome P460, a monoheme enzyme...
Beyond fossil fuel–driven nitrogen transformations


*Science*, 360 (6391), eaar6611. • DOI: 10.1126/science.aar6611

**Transforming nitrogen without carbon**

How much carbon does it take to make nitric acid? The counterintuitive answer nowadays is quite a lot. Nitric acid is manufactured by ammonia oxidation, and all the hydrogen to make ammonia via the Haber-Bosch process comes from methane. That's without even accounting for the fossil fuels burned to power the process. Chen *et al.* review research prospects for more sustainable routes to nitrogen commodity chemicals, considering developments in enzymatic, homogeneous, and heterogeneous catalysis, as well as electrochemical, photochemical, and plasma-based approaches.

*Science*, this issue p. eaar6611

View the article online

https://www.science.org/doi/10.1126/science.aar6611

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