

Green ammonia synthesis

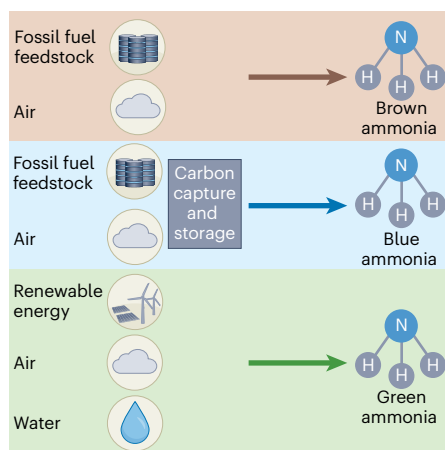


The Haber–Bosch process revolutionized ammonia production on a global scale. In this Focus issue, we examine the new era of green ammonia synthesis.

The Haber–Bosch process to synthesize ammonia enabled an increase in food production over the past century and, therefore, an increase in global population. Each year, around 170 million metric tonnes of ammonia are produced globally with approximately 80% used in fertilizers^{1,2}. However, the Haber–Bosch process consumes 1–2% of the total global energy production, 3–5% of the world’s natural gas production and produces 1–3% of our CO₂ emissions^{3–5}. A sustainable, or green, revolution is essential in the way we synthesize this important chemical.

In 1908, Fritz Haber combined nitrogen from the air with hydrogen from natural gas, over a metal catalyst at high pressure and temperature, to produce (brown) ammonia⁶. Carl Bosch scaled the process and, in 1913, the first commercial Haber–Bosch plant opened⁷. Since, the Haber–Bosch process has been modified to make ammonia synthesis cleaner. For example, the inclusion of a carbon capture unit negates emissions from the conventional Haber–Bosch process, producing blue rather than brown ammonia – an important stopgap as we transition to greener methods. The use of hydrogen from water electrolysis rather than methane, in combination with the use of renewable energy, produces green ammonia. Also, the development of catalysts permitting milder conditions is an active research goal. Flexibility in the plant is also being targeted by redesigning key reactor components to allow for the intermittency that comes hand-in-hand with the use of renewable energy. A [Comment](#) by Torrente-Murciano and Smith, and a [Review](#) by Ye and Tsang discuss these developments.

Moving away from the Haber–Bosch process, electro- or photocatalytic reduction of nitrogen is gaining popularity as an alternative, direct method to produce green ammonia. Nitrogen from the air is reduced to ammonia directly in the presence of water, under ambient conditions. Activation of nitrogen and water by excited electrons is



necessary, and these can be generated electro- or photochemically. Taking electrocatalytic ammonia synthesis as an example, slightly less energy is needed to produce ammonia than for the Haber–Bosch synthesis⁸. However, most catalysts show low efficiencies and therefore cannot compete. Electrocatalytic nitrate reduction is gaining in popularity, as it does not involve the activation of the strong N≡N bond and nitrate is a pollutant in many water sources. An [Article](#) in this issue describes the synthesis of Cu/CuAu core/shell nanocrystals with single-atom alloy layers for the electrocatalytic reduction of nitrate to ammonia. An 85.5% Faradaic efficiency of nitrate to ammonia with a yield rate of 8.47 mol h⁻¹ g⁻¹ is achieved.

Green ammonia can be produced through a lithium-mediated process. In a [Q&A](#), Suzanne Zamany Andersen describes the process as a hybrid of lithium-ion batteries and electrocatalysis. Lithium spontaneously reacts with nitrogen to form lithium nitride which, if protonated, can form ammonia. Organometallic complexes can also be used as homogeneous catalysts to produce ammonia under mild conditions. In an [Article](#) in this issue, Yoshizawa, Nishibayashi and co-workers discuss the use of molybdenum complexes with PCP-type pincer ligands for the synthesis of ammonia from N₂ at room temperature and atmospheric pressure, requiring far less energy input than the Haber–Bosch process. In a [Q&A](#), Paul Chirik discusses how organometallic catalysis can be used to form weak chemical bonds, such as N–H in ammonia. The use of well-defined

complexes allows for precise tuning of properties and therefore the ability to tune N–H bond strength.

Before the Haber–Bosch process, fertilizers were mainly produced by mining niter deposits and guano. Access to these resources caused conflict in the 19th and 20th centuries⁹ and restrictions and changes in global supply of ammonia still cause market instabilities today. As both COVID-19 and the war in Ukraine have shown, global production of key chemicals or energy can lead to increases in the market price (the long-term average ammonia price is approximately US\$300 per tonne, but this rose to as high as US\$1,350 per tonne at the start of 2022¹⁰), which the buyer is forced to pay if no domestic supply is available. In a [Perspective](#), Salmon and Bañares-Alcántara advocate that the production of ammonia using renewable energy, for use in fertilizers and as energy storage, should be carried out on the ocean. This frees up land space for domestic renewable electricity production, providing a safety net against energy market shocks, and allows the use of abundant resources at sea to produce ammonia, which can be shipped to shore. The [Q&A](#) with Suzanne Zamany Andersen also touches on this, as if ammonia can be produced via a lithium-mediated process, in a modular way, on farms, farmers are protected from global uncertainties in the fertilizer market.

It is estimated that 48% of the global population are fed with crops grown with synthetic fertilizers¹¹. Additionally, as we start looking to carbon-free fuels, ammonia is attractive as a green energy vector because the energy density of ammonia is higher than that of liquid hydrogen (12.7 MJ L⁻¹ compared to 8.5 MJ L⁻¹) and it can be stored at much higher temperatures (–33 °C compared with –253 °C)¹². From the articles in this issue, it is clear that the synthesis of ammonia requires input from many disciplines across chemistry, materials science, and chemical engineering. In addition, policy changes and radical thinking about resource allocation will be needed for the large-scale production of green ammonia. The last commercial revolution in ammonia synthesis was over 100 years ago – watch this space!

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