



# Making ammonia from nitrogen and water microdroplets

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Water (H<sub>2</sub>O) microdroplets are sprayed onto a magnetic iron oxide (Fe<sub>3</sub>O<sub>4</sub>) and Nafion-coated graphite mesh using compressed N<sub>2</sub> or air as the nebulizing gas. The resulting splash of microdroplets enters a mass spectrometer and is found to contain ammonia (NH<sub>3</sub>). This gas–liquid–solid heterogeneous catalytic system synthesizes ammonia in 0.2 ms. The conversion rate reaches  $32.9 \pm 1.38 \text{ nmol s}^{-1} \text{ cm}^{-2}$  at room temperature without application of an external electric potential and without irradiation. Water microdroplets are the hydrogen source for N<sub>2</sub> in contact with Fe<sub>3</sub>O<sub>4</sub>. Hydrazine (H<sub>2</sub>NNH<sub>2</sub>) is also observed as a by-product and is suspected to be an intermediate in the formation of ammonia. This one-step nitrogen-fixation strategy to produce ammonia is eco-friendly and low cost, which converts widely available starting materials into a value-added product.

ammonia formation | water microdroplets | heterogeneous catalysis

Ammonia (NH<sub>3</sub>) is the simplest stable compound of hydrogen and nitrogen. It is the starting material for making many nitrogen-containing compounds, but its primary use is as a fertilizer. Ammonium nitrate, ammonium sulfate, and urea are also alternative fertilizers that are converted from ammonia (1). Large-scale ammonia production is achieved by the Haber–Bosch process in which nitrogen (N<sub>2</sub>) and hydrogen (H<sub>2</sub>) react at high pressure (80 to 300 atm) and high temperature (300 to 500 °C) in the presence of a catalyst (usually magnetic iron oxide, Fe<sub>3</sub>O<sub>4</sub>) to form ammonia: N<sub>2</sub> + 3H<sub>2</sub> → 2NH<sub>3</sub> (2). The hydrogen source is usually methane (natural gas), which is reacted with steam at 700 to 1,000 °C and 3 to 25 atm pressure. Hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide are formed: CH<sub>4</sub> + H<sub>2</sub>O → CO + 3H<sub>2</sub> (+ small amount of CO<sub>2</sub>). Subsequently, the carbon monoxide and steam are reacted using nickel as a catalyst to produce carbon dioxide and more hydrogen: CO + H<sub>2</sub>O → CO<sub>2</sub> + H<sub>2</sub>. Between 1.8 and 2.1 tons of CO<sub>2</sub> are emitted for every ton of NH<sub>3</sub> synthesized from H<sub>2</sub> by the Haber–Bosch process (3). In 2021, the amount of NH<sub>3</sub> produced exceeded 150 million metric tons, corresponding to producing roughly 300 million metric tons of CO<sub>2</sub> associated with H<sub>2</sub> from the steaming of methane. It is estimated that ammonia synthesis accounts for more than 2% of global energy consumption (4) and about 1% of atmospheric CO<sub>2</sub>. Consequently, there is much interest in developing a method for making ammonia on a large scale with substantially less damage to the environment. We describe a method for forming ammonia from water and nitrogen at room temperature and atmospheric pressure without using photochemistry or electrochemistry. This chemistry utilizes the highly reactive characteristics of water microdroplets (5). Much additional work is in progress to determine whether this process can be scaled up, the ammonia can be concentrated, and the ammonia yield made sufficiently high to make this process feasible on a large scale. This report represents a step in realizing an eco-friendly way to produce substantial amounts of ammonia.

## Results and Discussion

An ultrasonic spray setup is used for ammonia production (Fig. 1A). Gas-phase N<sub>2</sub> and liquid-phase H<sub>2</sub>O, as starting materials, are sprayed through a graphite mesh that is coated with ferrous ferric oxide (Fe<sub>3</sub>O<sub>4</sub>) and Nafion. After passing through the catalyst mesh, reaction products in microdroplets are analyzed with a mass spectrometer (MS). It is found that an ammonia-associated adduct peak appears in the mass spectrum at *m/z* 36, [NH<sub>4</sub>OH+H]<sup>+</sup> (Fig. 1B). Additionally, hydrazine, *m/z* 55, [N<sub>2</sub>H<sub>4</sub>+Na]<sup>+</sup>, is also found. This is presumed to be an intermediate in the formation of NH<sub>3</sub>, indicating successive hydrogenation of the N<sub>2</sub> bound to Fe<sub>3</sub>O<sub>4</sub> (6). When we replaced the compressed N<sub>2</sub> by compressed air (78% N<sub>2</sub>) as the nebulizing gas, the intensity of the ammonia peak is not seriously reduced (Fig. 1C). When water is directly sprayed from the syringe by N<sub>2</sub> gas with no catalyst mesh positioned in the middle, the peak at *m/z* 36 became much weaker and was speculated to be the hydroxyl radical adduct with a

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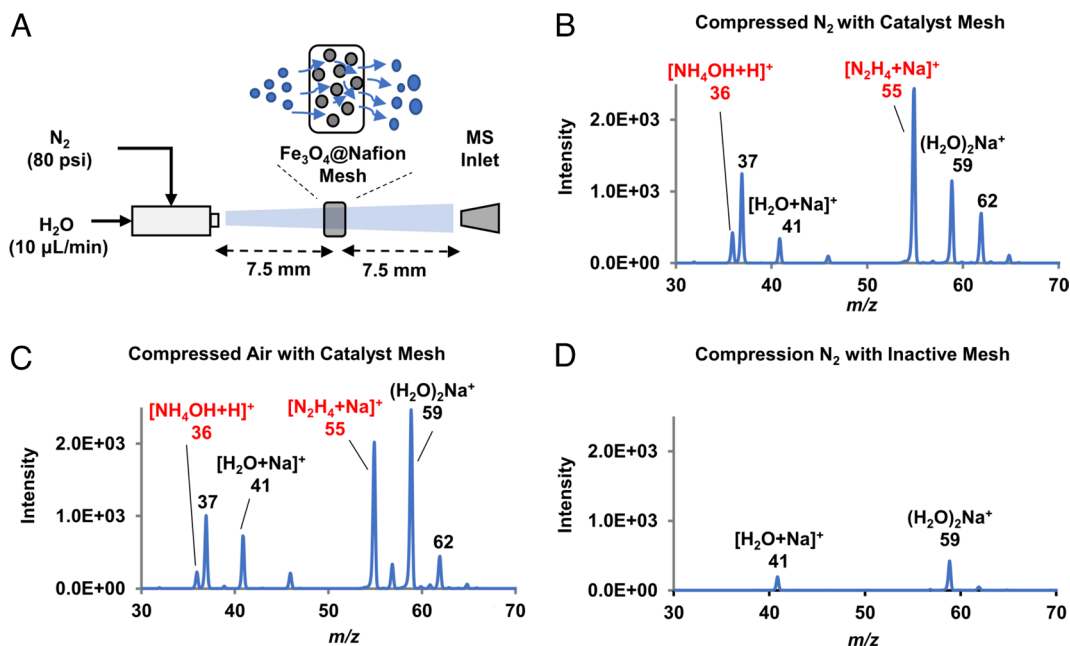
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**Fig. 1.** Diagram of the (A) ultrasonic spray setup combined with a MS for the online monitoring of the ammonia formation process. (B–D) Representative mass spectra under different conditions for the ammonia formation. (B) compressed nitrogen with catalyst; (C) compressed air with catalyst; and (D) compressed nitrogen with no catalyst coated on the mesh.

hydronium cation  $[\text{HO}\cdot+\text{H}_3\text{O}]^+$  that we have previously identified (7). Hydrogen–deuterium exchange (HDX) mass spectrometry experiments were conducted to differentiate these two isobaric ions (8). It was revealed that the HDX pattern of  $[\text{NH}_4\text{OH}+\text{H}]^+$  generated from the heterogenous catalysis is different from that of the  $[\text{HO}\cdot+\text{H}_3\text{O}]^+$ . As another negative control, when the mesh having no catalyst coating was positioned between the sprayer and the MS inlet, the peaks at  $m/z$  36 and 55 disappeared (Fig. 1D), which excluded false positive interference from the  $[\text{HO}\cdot+\text{H}_3\text{O}]^+$  ( $m/z$  36) and  $[\text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2]$  ( $m/z$  55). These negative controls illustrate the roles water microdroplets play in providing hydrogen to  $\text{N}_2$  bound to the  $\text{Fe}_3\text{O}_4$  surface for ammonia generation.

Some critical sonic spray conditions were systematically varied to optimize the nebulizing gas pressure (80 psi), external high voltage (0 kV) on the sprayer, the extra potential (0 V) and heating temperature (30 °C) applied to the catalyst mesh, and the internal diameter of the spraying capillary. The best capillary diameter is found to be 50  $\mu\text{m}$  in diameter, which can generate microdroplets with the median size at 10  $\mu\text{m}$ . It is worth noting that the ammonia production process reaches an optimum value when neither external potential nor extra heat is applied to the catalyst mesh or to the spray source, avoiding electric or thermal power consumption.

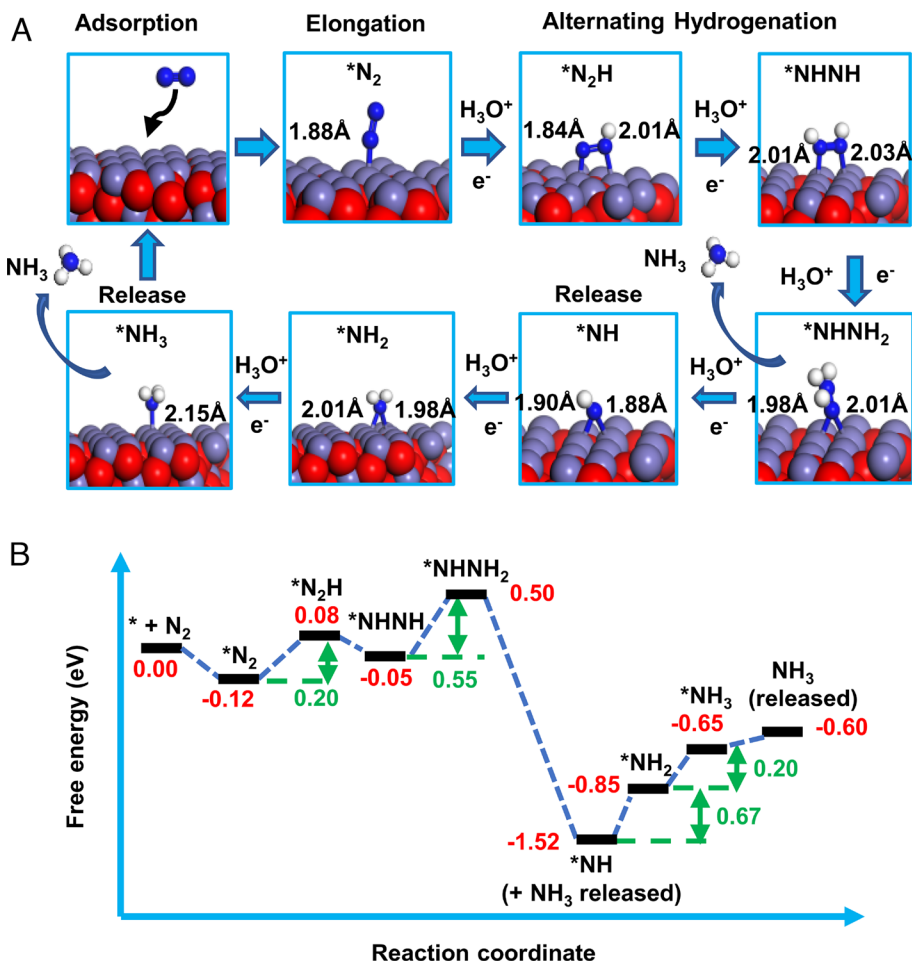
The concentration of the produced ammonia was quantitatively estimated under the optimum sonic spray conditions. A series of diluted ammonium hydroxide standard solutions ( $n = 3$ ) were first sprayed through the mesh without any catalyst coating and then into the MS to create a quantitation curve. The maximum concentration of the ammonia generated under optimal conditions was around  $61.9 \pm 2.2 \mu\text{M}$ . Assuming that the spray-catalyst contact area is  $3.1 \times 10^{-4} \text{ cm}^2$  and the total reaction time is 50 min, the ammonia yield rate is estimated to be  $32.9 \pm 1.3 \text{ nmol s}^{-1} \text{ cm}^{-2}$ .

Mounting evidence shows that water microdroplets can not only facilitate the one-electron ( $e^-$ ) reduction due to its unique air–water interface redox environment (9–13) but also capture

reactive carbocation intermediates promoted and stabilized by its interfacial hydronium ions ( $\text{H}_3\text{O}^+$ ) (14, 15). Therefore, we suggest that the abundance of  $\text{H}_3\text{O}^+$  and  $e^-$  at the microdroplet interface also plays a role in the hydrogenation of  $\text{N}_2$  molecules bound to the  $\text{Fe}_3\text{O}_4$  surface when in contact with water microdroplets, forming  $\text{H}_2\text{NNH}_2$  and ultimately  $\text{NH}_3$ .

Fig. 2 shows a proposed mechanism for ammonia formation based on DFT calculations. The results presented are similar to a previous DFT calculation by MacFarlane and coworkers (16).  $\text{N}_2$  interaction on the  $\text{Fe}_3\text{O}_4$  surface is estimated to be slightly physisorbed with a binding Gibbs free energy of  $-0.12 \text{ eV}$ . As a result, adsorbed  $\text{N}_2$  ( $^*\text{N}_2$ ) experiences elongation of the  $\text{N}\equiv\text{N}$  triple bond. The first hydrogenation step is estimated to be  $0.20 \text{ eV}$  uphill. The second hydrogenation step has a Gibbs free energy change of  $-0.13 \text{ eV}$  relative to  $^*\text{NH}_2$ . The third hydrogenation step has a Gibbs free energy of  $0.55 \text{ eV}$  with respect to the adsorbed cis-diazene species. The fourth hydrogenation step is downhill by  $2.02 \text{ eV}$  and leads to a rearrangement that liberates the first  $\text{NH}_3$  molecule. The fifth hydrogenation step is again uphill by  $0.67 \text{ eV}$  to form  $^*\text{NH}_2$ . The sixth and last hydrogenation step liberates another  $\text{NH}_3$  molecule with an energy input of  $0.20 \text{ eV}$ .

Air (or nitrogen) and water are among the most widely available natural resources on earth for ammonia preparation. The results demonstrate the robustness of the proposed heterogeneous catalysis system regardless of the purity of the starting nitrogen source. In terms of water, physically spraying micron-sized water microdroplets can gain huge contacting area of the microdroplets with the catalyst. Therefore, water microdroplets can help to increase the chance and area for the physical contact between  $\text{N}_2$  and  $\text{Fe}_3\text{O}_4$ , thereby overcoming the low solubility of  $\text{N}_2$  in aqueous solution (20 mg/L, 20 °C, 100 kPa). Nafion, which consists of perfluorinated sulfonic acid polymers, is also known to be a good source for proton transfer (17). Its usage also serves the whole reaction by providing the reducing proton and a hydrophobic surface to well preserve the water microdroplet survival rate during the process of passing through the catalyst



**Fig. 2.** Catalytic mechanism for ammonia formation from  $N_2$  and water droplets striking  $Fe_3O_4$ . (A) Diagrams of the reaction steps and (B) corresponding free energy changes found from DFT calculations.

mesh. We confirmed that introducing Nafion into the catalyst system did markedly enhance the ammonia production by providing exchangeable protons.

## Materials and Methods

More details about the catalyst preparation, ultrasonic spray setup, ammonia quantitation, and DFT calculation can be accessed from *SI Appendix*.

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**Data, Materials, and Software Availability.** All study data are included in the article and/or *SI Appendix*.

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