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Ammonia Synthesis by Mechanochemistry

Federico Cuccu,^[a] Duncan L. Browne,^{*,[b]} and Andrea Porcheddu^{*,[a]}

The design and use of organic, inorganic, and metal-based catalysts is critical to academic and industrial laboratories all around the world. In this framework, ammonia production

embodies the most iconic use of catalysis. This review aims to describe the most recent and exciting developments in the mechanocatalytic preparation of ammonia.

1. Introduction

Catalysis is one of the most fundamental concepts in chemistry, encompassing several branches and chemical processes geared towards time- and energy-saving. The choice of a catalyst nowadays lies on organic and inorganic materials having the feature of accelerating a reaction in the product's direction by lowering the system's activation energy.

Since its first description in 1836 by Berzelius,^[1,2] catalysis has impacted many chemical processes which would have been otherwise inaccessible. In more recent years, endeavors intensified in discovering new types of catalysts and optimizing parameters to help extend the selectivity of existing ones towards more reaction/substrate types. Indeed, academia and industry consistently use catalysis as a tool for obtaining products with high yields as well as reasonable reaction times. However, the rising concern of environmental pollution pushes the chemistry community to converge towards milder procedures, avoiding waste such as solvents and away from the use of precious-metal catalysts.

In such a scenario, emerging technologies have the potential to pave the way to support more sustainable chemical manufacture. Mechanochemistry is favored as a clean and green technique, allowing reactions to be performed either entirely solvent-free or requiring a significantly reduced amount of solvent through so-called liquid-assisted grinding (LAG).^[3] Its effectiveness has been demonstrated in several branches of chemistry, covering physical,^[4-6] inorganic,^[7-9] organic,^[10-13] and

pharmaceutical^[14,15] chemistry. Furthermore, a recent trend urges researchers to include examples of scale-up experiments in their manuscripts to demonstrate this technology's potential applicability.^[16,17] Accordingly, the focus is especially on wide-ranging procedures enabling the achievement of highly valuable chemicals.

In this framework, ammonia (NH₃) embodies a key role in chemistry. As part of several plants^[18] and animals^[19] biotransformation, it is an abundant inorganic compound in nature. This nitrogen-containing molecule is of particular interest as a precursor of almost 45% of the world's food^[20] and as a fertilizer,^[21] as well as playing a leading part in industrial companies for the synthesis of fine chemicals,^[22] including pharmaceuticals. It is present in its gaseous form at room temperature but may be obtained as a liquid if stored under controlled temperature and pressure.

Its synthesis has been discussed for centuries since Haber's protocol was established in 1909.^[23] It consists of nitrogen fixation with molecular hydrogen over an iron-based catalyst containing different amounts of iron, aluminum, potassium, calcium, molybdenum and magnesium oxides, and potassium hydroxide.^[24] The process itself is heterogeneous catalysis-promoted, meaning that solid and gaseous phases interact on the catalyst surface, giving rise to the reaction. Despite being exothermic, it requires harsh reaction conditions to activate the species (130 bar, 400/500 °C per 1800 tons of ammonia); molecular nitrogen is a very stable compound (triple bond energy of 945 kJ mol⁻¹ and bond constant force of 22.4 mdyne Å⁻¹).

Several additional strategies have been outlined since then, involving traditional and emerging technologies such as electrochemistry,^[25] photochemistry,^[26] thermochemistry,^[27] as well as alternative catalysts^[28] (Figure 1). Herein we provide a general overview of two examples amongst a flurry of recent and remarkable reports on the use of mechanochemistry for ammonia production.

2. Discussion

2.1. Mechanosynthesis of NH₃ via hydrogenation of molecular nitrogen

Very recently, some research groups faced the challenge of ammonia synthesis by mechanochemistry.^[29] For instance, Han's

[a] F. Cuccu, Prof. Dr. A. Porcheddu
 Dipartimento di Scienze Chimiche e Geologiche
 Università degli Studi di Cagliari
 Cittadella Universitaria
 Monserrato
 09042 Cagliari (Italy)
 E-mail: porcheddu@unica.it

[b] Dr. D. L. Browne
 Department of Pharmaceutical and Biological Chemistry
 UCL School of Pharmacy
 29-39 Brunswick Square
 Bloomsbury
 London, WC1N 1AX (UK)
 E-mail: duncan.browne@ucl.ac.uk

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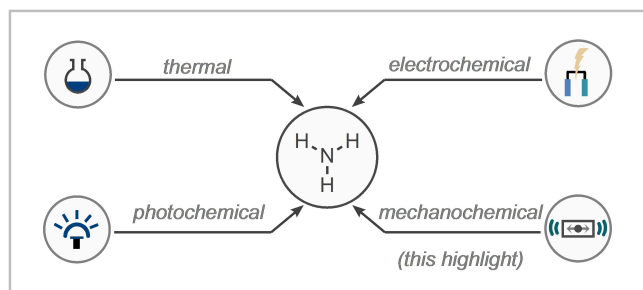


Figure 1. Several different technologies have been explored for the production of ammonia.

synthesis^[30] focused on the classical hydrogenation of nitrogen using an iron-based catalyst in a planetary ball mill. This stepwise synthesis is very effective, producing high-energy mechanical collisions between iron and nitrogen molecules. This procedure overcame several aspects of conventional ammonia synthesis, such as the required high temperature and pressure. The mechanochemical conditions were monitored as not exceeding 45 °C and 1 bar.

The procedure itself works smoothly at 250 r.p.m. in a planetary mill, achieving ammonia in higher yields calculated on the volume of the gas released (82.5% vol.) with an overall energy demand of 4.5×10^{12} J, less than 8 times the overall energy demand required for a laboratory scale Haber-Bosch process (39×10^{12} J).^[31]

Comparing all the methods, the authors were able to outline mechanochemistry as the most environmentally friendly technique, having almost removed any energy demand from the purification process. Indeed, the total energy demand for the mechanochemical procedure is set at 4.5×10^{12} J, in contrast with the electrochemical (228×10^{12} J) and the photochemical (38×10^{12} J) processes.

At the same time, a mechanistic study was conducted to understand the outstanding performance of this process. It was found that during the iron catalyst grinding, the high energy of impacts imparted on the powder surface active sites can trigger nitrogen dissociation, thereby giving rise to highly reactive Fe(N*) species (Figure 2a). These data were supported by XRD analysis showing a high nitrogen bulk Fe(N*) concentration, implying a thermodynamic non-equilibrium state favoring the subsequent hydrogenation step. XPS analysis, used to analyze the catalyst's surface, revealed a nitrogen concentration approximately 20 times higher than the commercially supplied Fe_xN (x=2,4). Interestingly, the catalyst was also found to behave somewhat smartly by modulating its size and shape to obtain a better system for hosting and releasing the nitrogen species. A latency period was also observed, attributable to the activation of the Fe catalyst by milling – likely representing the time required for increasing the surface area and augmenting the active sites.^[32]

Following the iron catalyst's activation and nitrogen dissociation, the milling jar is then pressurized with hydrogen. The high energy collisions and the rise in temperature inside the jar^[33] create suitable conditions for nitrogen desorption from

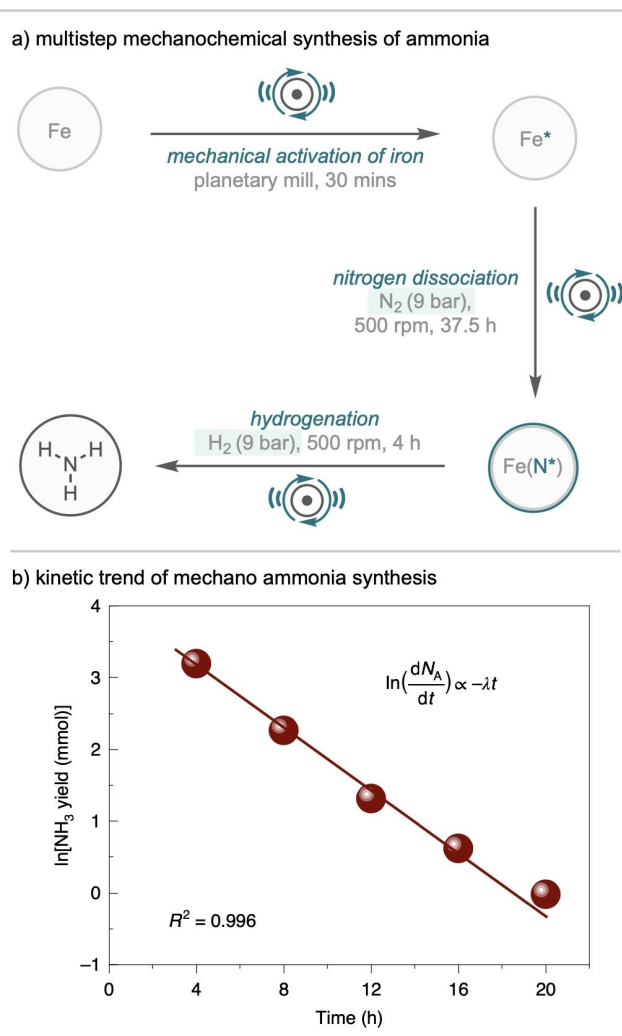


Figure 2. Representative scheme for a) the entire mechanochemical process of nitrogen fixation and b) linear decrease in the kinetic trend of the ammonia synthesis. Adapted from ref. [30]. Copyright (2021), with permission from Springer Nature.

the iron catalyst due to a growth in the entropy of the system. Then, the Fe(N*) species makes its way to the newly formed NH_x*. Kinetically, the hydrogenation takes place with a logarithmic, linear decay over time, revealing a fast progression that slows down reaching the steady state (Figure 2b). This is why the entire hydrogenation process requires over 4 h to reach completion.

Even though this protocol was extremely valuable in elucidating mechanistic insights and in proving the feasibility of a milder pathway, it still suffered from a few limitations, such as long reaction times. One of the main concerns about hydrogen lies in its production, which still necessitates the production of high amounts of carbon monoxide.^[34] In addition to environmental apprehension, the handling of hydrogen gas is operationally intense due to flammability and explosion risks.

2.2. Mechanochemistry of NH_3 through nitrogen fixation of water

Cui and Chen's mechanochemical approach to ammonia synthesis^[35] is an exciting alternative to the work of Han and coworkers. A thorough and detailed analysis of the state of the art, highlights the main issues with conventional and innovative protocols towards ammonia synthesis. In this regard, they pointed out mechanochemistry's relevance in this field, with inherent characteristics of solvent-free or solvent-minimized and reduced energy consumption.

Several elements of their procedure are worth to be highlighting. As previously stated, ammonia production is often achieved by means of different catalysts, relying on the well-established nitrogen reduction protocol.^[36] However, hydrogen production and handling drawbacks prompted them to evaluate a process featuring an alternative "proton" source. Water was found extremely useful in these terms, being a benign and environmentally friendly chemical. Using water, the authors outlined a conceptually novel procedure while simultaneously managing to decrease the operational, environmental, and cost implications of nitrogen fixation (Figure 3a).

Existing nitrogen reduction and fixation processes rely on very selective catalysts with different degrees of purity and very specific mixtures of metals.^[37] On this theme, the authors propose employing the iron metal present in the stainless-steel reaction vessel and balls as the catalyst,^[38] allowing a further reduction in costs^[39] and the pollution deriving from its uses.^[40]

The nitrogen fixation with water was then evaluated through three different control experiments. A planetary ball mill was set at an operational frequency of 650 r.p.m. at room pressure and temperature. Two of the three reactions were performed inside a 250 mL stainless steel jar, one filled with nitrogen and water while the other with argon and water (Figure 3b). This was useful to rule out any nitrogen contamination by air creating a false positive on the reaction outcome. The remaining control experiment was carried out inside a zirconia vessel with zirconia balls, with water and ammonia as inputs. This experiment demonstrated that the stainless steel components are required to deliver ammonia product. For each of the three reactions, several packages of balls (2–6 packages having 140 grinding balls of different diameters) and 50 mL of H_2O were used, and after 10 h of grinding, the ammonia content (calculated as NH_4^+ species) was evaluated. As predicted, the NH_4^+ ions were only detected in the stainless-steel vessel containing a nitrogen atmosphere, signaling the importance of the catalyst and nitrogen gas together (Figure 3b).

Intriguingly, a powder was formed during the grinding process, which suggested a partial erosion of the vessel surface and balls. XRD of this powder showed a peak at 44.5° , suggesting the presence of (110) crystal plane of Fe (JCPDS 06-0696, particle size of 12.2 nm). ICP-OES analysis provided the accurate metal composition of the stainless-steel composing vessel and balls, consisting mainly of iron, chromium, nickel, manganese (around 69%, 18%, 9% and 2%, respectively), and

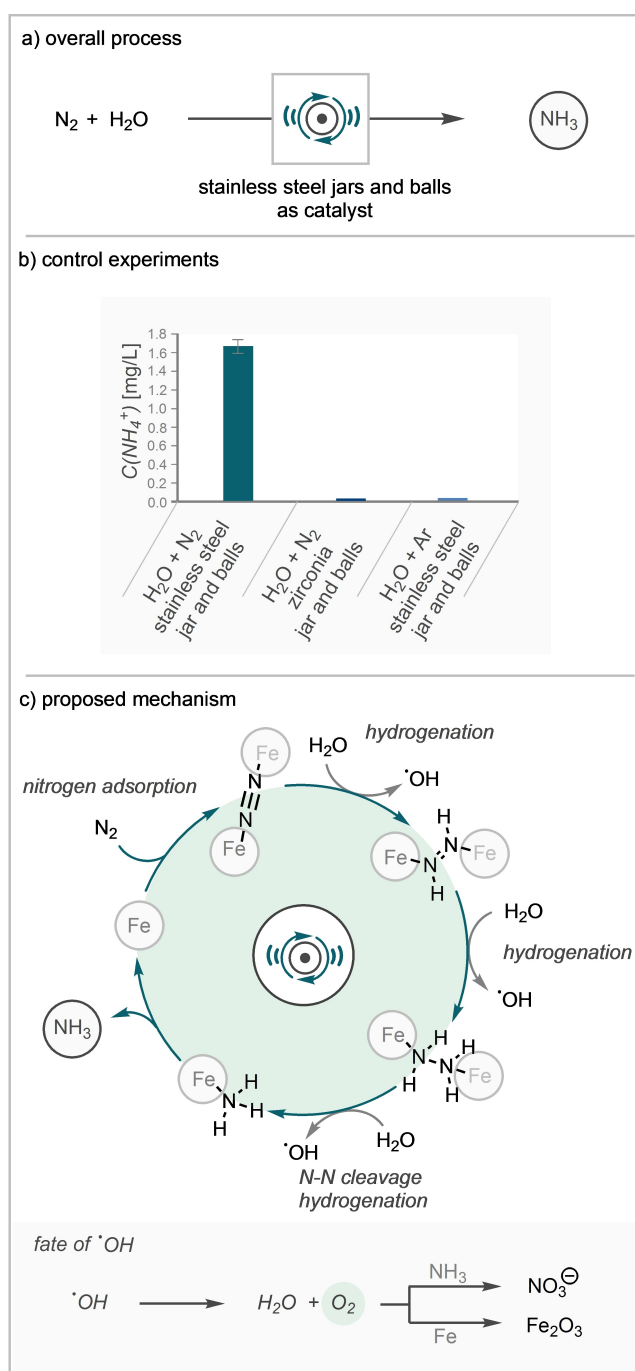
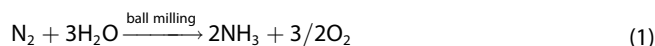


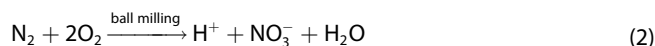
Figure 3. Nitrogen fixation experiments. a) General approach b) Plot describing the yield of ammonia in control experiments, c) proposed mechanism and fate of hydroxide radical. Reproduced with permission from ref. [35].

variable amounts of other metals (the remaining 2% is composed of many metals e.g., Cu, Ca, Co, Ti, Zr).

A deeper insight uncovered the presence of iron oxides, likely deriving from oxidation during the grinding process. The presence of free reactive oxygen can be attributed to water reacting with nitrogen by the following equations (eq. 1):



The formation of NO_3^- species, detected in trace amounts, supports this hypothesis, suggesting that a competitive reaction occurs during nitrogen fixation (eq. 2):



The nitrogen fixation mechanism was also confirmed by FT-IR experiments, confirming the hypothesized intermediate of the reaction. A clear peak at 3445 cm^{-1} was assigned to N–H and O–H stretching frequencies, while N–H and NH–NH bending frequencies were observed at 1640 and 1100, respectively. Furthermore, the product was detected by three characteristic signals: two are attributable to the NH_4^+ species (1454 and 2848 cm^{-1}), while the peak at 2925 cm^{-1} is ascribable to ammonia itself. Finally, Raman spectroscopy detected more precisely the presence of Fe_2O_3 with specific peaks at 213, 281, 392, and 1306 cm^{-1} , deriving a partial oxidation occurring on the iron surface. With this evidence, the authors proposed the mechanism depicted in Figure 3c. The reaction itself proceeds rapidly and cleanly on ammonia production. However, the competitive mechanism producing nitric acid must be considered a potential limitation of this technique, even if present in trace amounts, especially when assessing an industrial application. Moreover, the jar's wall erosion is something to bear in mind for jars' upkeep and replacement costs, even if water worked well as a lubricant by lowering the erosion rate.

2.3. Mechanochemistry for ammonia: what else?

In addition to the two reports highlighted, other laboratories worldwide have contributed to the emerging area of ammonia production by mechanochemical methods. In 2020, Sievers and coworkers reported a mechanochemical Ti-catalytic system operating at ambient temperatures.^[41] The synthetic route is composed of a sequence of transient microenvironment events at the catalyst surface by the action of milling, following what is proposed as a Mars-van Krevelen mechanism. A quite similar mechanism has been described above for the iron-catalyzed ammonia production, with titanium replacing iron in the formation of the metal-nitride species (TiN) inside the titanium lattice.

On the other hand, Schüth's group demonstrated how to perform a continuous catalytic synthesis of ammonia via mechanochemical and ambient conditions by means of a cesium-promoted iron catalyst.^[42] Contrary to the use of a planetary mill by other procedures, the authors use a mixer mill with specifically designed jars (reminiscent to an autoclave). This permitted the team to conduct a flow mechanocatalytic gas-phase reaction capable of producing ammonia.

Some exploration and improvements have been made in the synthesis of catalysts for mechanochemical ammonia production. Fan, Chen and coworkers, in 2022, developed a mechanochemical calcination of RuCo/MgTiO₃ catalyst for non-

thermal plasma-assisted ammonia production.^[43] The incorporation of the bimetallic RuCo species on the support matrix of MgTiO₃ was achieved by mechanical activation, whilst the catalyst was then used in the ammonia synthesis process under nonthermal plasma conditions, carrying it out inside a dielectric barrier discharge (DBD) plasma reactor. Lastly, in 2023, Cui and Chen furnished an alternative and miscellaneous procedure involving a mechanocatalytic N₂/H₂/H₂O system promoted by 304 stainless steel balls and jar.^[44] The presence of H₂ is beneficial for the inhibition of NO_3^- pathway shown in Figure 3, by likely consuming all the reactive oxygen species formed during the reaction mechanism.

3. Conclusions

In conclusion, two recent and innovative mechanocatalytic approaches toward ammonia synthesis have been briefly illustrated, along with some little insights into different mechanochemical approaches in the field. On the one hand, mechanochemistry proved to be at least comparable and, in many aspects, a better technology than alternative methods – including the industrial Haber-Bosch protocol. On the other hand, performing hydrogen fixation inside a ball mill enabled the use of inexpensive and very abundant iron as a catalyst, whereas a nitrogen fixation approach exploited the stainless steel of the reactor itself as a source of catalyst. Both cases drastically affected the reaction costs in a positive direction.

Despite this, these protocols are preliminary, and significant further development work is needed to understand if these processes can compete on a manufacturing scale appropriate for ammonia production. However, the promise and excitement of these discoveries as a prospect for green and sustainable alternatives are undeniable.

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Conflict of Interests

The authors declare no conflict of interest.

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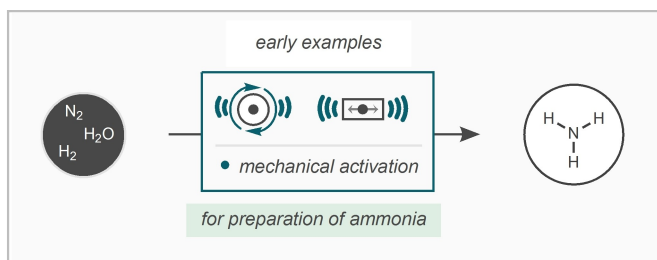
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CONCEPT



The manufacture of ammonia is a technologically well developed field. The application of mechanochemistry for the preparation of ammonia has

been realized over the past few years and may offer new opportunities for consideration. Here we highlight and describe some of those examples.

F. Cuccu, Dr. D. L. Browne, Prof. Dr. A. Porcheddu**

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