



Renaissance of ammonia synthesis for sustainable production of energy and fertilizers

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Green ammonia synthesis via the Haber–Bosch (HB) process has become a major field of research in the recent years for production of fertilizers and seasonal energy storage due to drastic drop in cost of renewable hydrogen. While the field of catalysis and engineering has worked on this subject for many years, the current process of ammonia synthesis remains essentially unaltered. As a result, current industrial developments on green ammonia are based on the HB process, which can only be economical at exceptionally large scales, limiting implementation on financially strained economies. For green ammonia to become an economic “equalizer” that supports the energy transition around the world, it is essential to facilitate the downscalability and operational robustness of the process. This contribution briefly discusses the main scientific and engineering findings that have paved the way of low-temperature and pressure ammonia synthesis using heterogeneous catalysts.

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Introduction

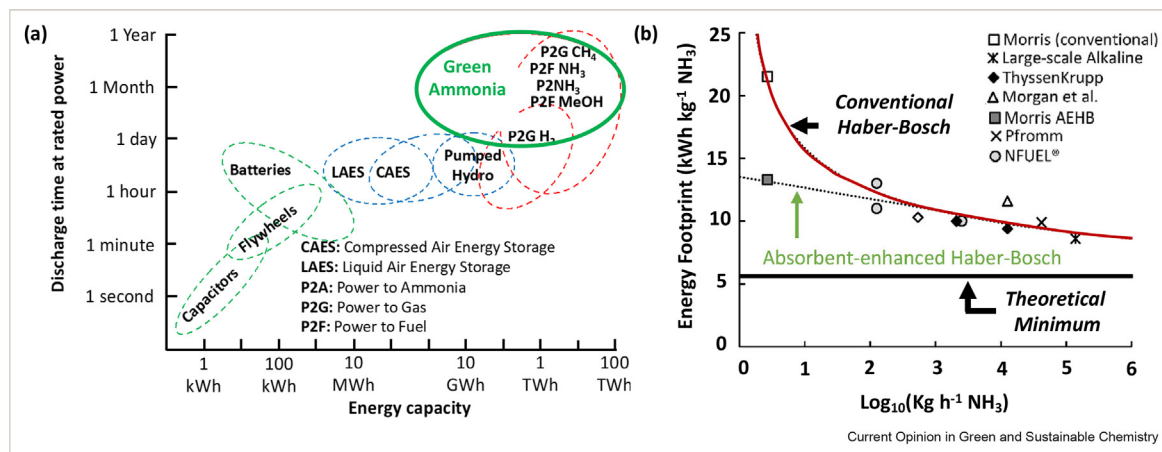
Ammonia (NH_3) is considered as the only carbon-free hydrogen storage compound that can overarch water, energy, and food value chains, while allowing long- and short-term energy storage at lower costs than that of pure hydrogen (Figure 1) [1–3]. Ammonia Haber–Bosch (HB) synthesis is undoubtedly one of the most important inventions in recent history as it allowed large-scale production of nitrogen-based fertilizers. Annual production of NH_3 is c.a. 160 million tons per year, which are primarily utilized in the production of fertilizers (c.a. 80%), helping to feed over 70% of the

world population [4,5]. As a result, nearly 50% of the nitrogen found in the human body has passed by the HB process [6].

The HB process utilizes magnetite iron catalyst to convert nitrogen and hydrogen, mixed in a 1:3 ratio, into ammonia at elevated temperatures (450–600 °C) and pressures (100–250 bar). These harsh reaction conditions are required to activate the rather stable triple bond in the dinitrogen molecule (bond dissociation energy of 941 kJ/mol). To achieve sufficient catalytic activity, the temperature is increased inside the reactor. However, this leads to lower equilibrium yields as the ammonia synthesis process is an exothermic reaction ($\Delta H^\circ = -91.8$ kJ/mol). To counteract this effect, further pressure is applied to achieve the same yields, which leads to higher energy consumption for pressurization, recirculation, and heating [7]. The hydrogen required for ammonia synthesis is typically generated from fossil-based hydrocarbons. In the 1920s, hydrogen was primarily generated by steam reforming of coal and lignite. However, the onset of low-cost and cleaner (lower chlorine and sulfur contents) natural gas shifted hydrogen production to steam methane reforming (SMR). Currently, the vast majority of large-scale ammonia synthesis plants are coupled to SMR, which drastically improved the energy efficiency. By coupling endothermic SMR with exothermic ammonia synthesis, it was possible to drive down the specific energy consumption (SEC) of the process to c.a. 7.2 kWh/kg of NH_3 (~ 26 GJ/ t_{NH_3}) [8]. Further energy efficiency gains can be achieved as the theoretical SEC of integrated ammonia synthesis with SMR is c.a. 5.6 kWh/kg of NH_3 (~ 20.9 GJ/ t_{NH_3}) [1]. This is expected to come from the additional improvements in the energy efficiency of compressors and reformers. However, regardless of the energy efficiency gains, the ammonia synthesis process is far from being sustainable. This single chemical process is responsible of 1%–2% of the world energy consumption, and its concomitant CO_2 footprint is the largest of any chemical product, accounting for 1.6% of the anthropogenic CO_2 emission worldwide [6]. Clearly, developing more efficient and sustainable strategies for producing this chemical can reduce our dependence on fossil fuels and mitigate the climate change.

The pursue of green ammonia has triggered the interest of academics for decades, which has led to important developments in the fundamental understanding of the catalytic cycle of ammonia synthesis on enzymes [9],

Figure 1



Storage of electricity for different technologies (adapted from Ref. [3]) (a) and energy footprint of electrolysis-based Haber–Bosch process (adapted from Ref. [1]) (b).

photo- [10], thermal- [11,12], plasma- [13], and electro-catalysts [14]. In this context, electrochemical reduction strategies have drawn significant attention in recent years, leading to a large number of reports on new materials, electrolyte media, and reactor configurations as a direct route for energy storage. Notably, Li-mediated electrochemical reduction strategies conducted in organic media are perhaps one of the few approaches where sufficient catalytic activity can be achieved to consider its practical application [15,16]. While these results seem promising, it is important to consider the difficulties in discriminating true activation of dinitrogen from activation of oxidized nitrogen impurities in the system. Broadly speaking, the approaches based on nonconventional activation of nitrogen (e.g., enzymes, photo-, plasma-, and electro-) suffer from low reaction rates. This leads often to so-called “false positive.” This issue was recently highlighted by Prof. D. R. MacFarlane and Prof. A. N. Simonov, who argue that the majority of nitrogen reduction reactions (NRRs) reported in the recent literature using aqueous electrolyte, and a significant fraction of those using organic media do not meet three key criteria for discriminating false positives, including; (1) sufficiently high yield rates of ammonia formation, (2) reliable and conclusive ¹⁵N₂ isotope experiments that support direct ammonia synthesis, and (3) rigorous control and quantification of oxidized forms of nitrogen in the experiments [17]. Thus, important research efforts are still needed to ensure the practical implementation of these routes in the future.

The required hydrogen can be potentially generated from biomass via gasification [18] and/or reforming processes [19–23], or water electrolysis using renewable electricity. However, it was not until recent years that the industry considered green ammonia as a

commercially attractive alternative thanks to the drastic decrease in the cost of green hydrogen [24,25]. The reduction in the cost of renewable electricity (wind and PV) has made possible the scaling-up of renewable power plants around the world, which in combination with improvements in cost and energy efficiency of electrolyzers has set the stage for green hydrogen [4]. The generation of hydrogen from water electrolysis using renewable electricity could potentially reduce the footprint of ammonia synthesis from 1.6 to 0.1 tCO₂/tNH₃, with the prospective to reduce it to nearly zero emissions in the future [8,26]. Direct storage of hydrogen becomes more expensive than NH₃ already after one day [26]. Thus, transforming hydrogen into ammonia has become a necessary step to reduce the final cost of highly fluctuating renewable electricity [4]. While there are many power-to-chemicals storing routes that could be utilized for this purpose, ammonia is the only carbon-free strategy that can be scaled up in economical manner from MWh to TWh using commercially available technologies (see Figure 1a) [3]. The advantage of this pathway is that NH₃ can be utilized both as a fertilizer precursor and as an energy carrier [27].

The long history of industrial ammonia synthesis (+100 years) has led to well-established and safe protocols for production, storage, and transportation. Thus, it is not surprising that its large-scale deployment as energy carrier and transportation fuel for maritime applications has been accelerated in the last few years [4]. Alkaline water electrolysis for ammonia synthesis was operated at large-scale 300 tNH₃ d⁻¹ in the past (1990s) [28,29]. Nowadays, countries such as Japan [30], Spain [31], Australia [32], Germany [33], the Netherlands [3], and the United Kingdom [34] have drafted clear plans to use

“green” ammonia as energy storage material for renewable electricity surplus in the next 10 years. As shown in Figure 1b, the electrochemical HB ammonia synthesis process can lead to energy footprint as low as c.a. 8 kWh/kg_{NH₃} at scales of c.a. 10⁵ kg_{NH₃}/h. At the small scales (e.g., 0.5 kg_{NH₃}/h), however, heat losses increase the energy consumption of the HB process up to 22 kWh/kg_{NH₃}, which leads to downscalability issues [4,13]. This is particularly relevant if one considers that in the future, decentralized electricity generation will play an essential role in decarbonizing the electricity mix in developing countries [35]. Furthermore, one can anticipate that the large investment costs associated with GWh-scale systems for green ammonia production, typically in the order of billions of euros, will make difficult the adoption of this technology in the developing world where the access to financing is limited [36]. As a result, extrapolating this to remote regions in economically constrained countries is not straightforward.

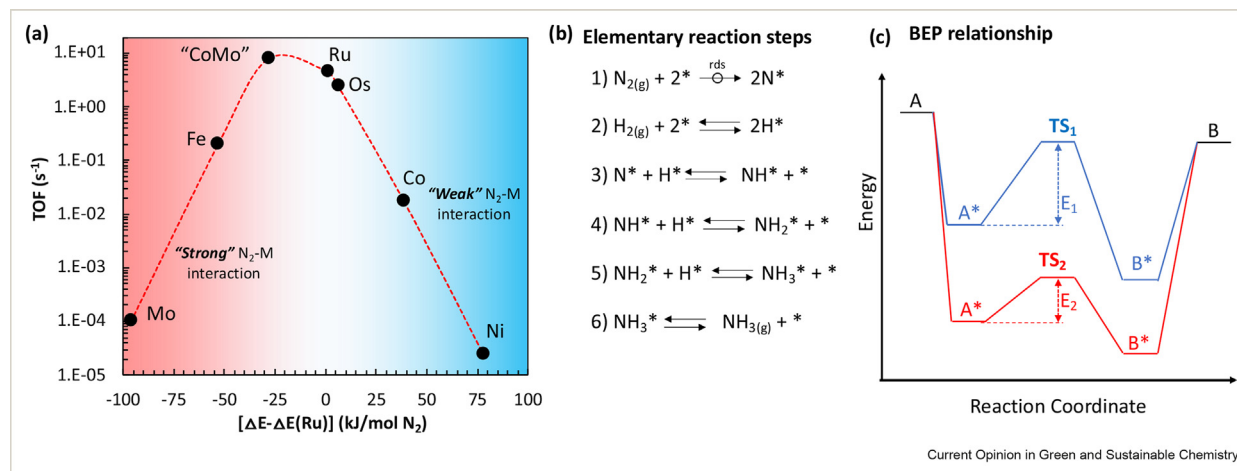
To cope with this issue, a group of researchers at the University of Minnesota developed a process that used an absorbent that selectively removes ammonia from the product mixture, allowing fast and nearly isothermal separation of ammonia [37–39]. The so-called “absorbent-enhanced Haber–Bosch or AEHB” can be operated at pressures 10 times smaller than those used in the conventional HB, allowing the utilization of cheaper alloys in the construction of the reactor and avoiding the utilization of expensive compressors [1,39–41]. Such an AEHB process may limit the energy consumption of the synthesis loop to below 3 kWh/kg [1]. Supported metal halides can be used for ammonia absorption and storage (6–8 mol of NH₃ per mole of MgCl₂ and CaCl₂) [29,37,42–48]. Unfortunately, when the absorption materials are used at the temperatures required for this process (300–450 °C), for Fe-based catalysts [37], the metal halide surface area significantly decreases. This leads to an excessive drop in absorption capacity [29]. In this context, developing inexpensive, stable, and active catalysts for dinitrogen reduction at low temperature holds the key for widespread deployment of green ammonia technology in small and medium scales for long-term energy storage and fertilizers production. This contribution summarizes the most recent advancements in low-temperature activation of nitrogen using heterogeneous catalysts and the future research and technological challenges in the implementation of these new materials for the production of green ammonia.

Activation of N₂ on metal-supported catalysts

The search for metal-supported catalysts for dinitrogen reduction has been a topic of exhaustive research for over a century. Albeit the important scientific advances

made over the years, the industrial catalysts currently used for ammonia synthesis are remarkably similar to those developed in the early to mid 1900s [49]. Currently, Fe- and Ru-based catalysts are typically found in industrial ammonia synthesis processes. The vast majority of all the ammonia plants in the world use Fe catalysts promoted by metal oxides (e.g., Al₂O₃ and K₂O), which improve the thermal stability of iron towards sintering during reaction, while increasing the surface area and activity of the catalyst. Although ruthenium catalysts are 10-fold more active than iron at low pressures, their commercial implementation was not possible until 1992 when the first ammonia synthesis plant was commissioned in Canada [7]. As of 2010, only sixteen ammonia plants were operating using Ru catalysts promoted by barium and cesium on activated carbon at low pressure using the Kellogg Brown and Root (KBR) advanced ammonia process (KAAP) [50]. The main reason for this despair implementation between the two catalysts is related to the higher cost of Ru compared with Fe, and the low stability of the Ru-based catalysts as the carbon support can undergo methanation in the presence of hydrogen. The catalytic activity of metal surfaces towards nitrogen dissociation was not fully understood until the onset of theoretical calculations of transition states of key reaction intermediates using density functional theory in the 21st century [11]. The mechanistic picture of this process on nonferrous catalysts was initially developed by Ozaki et al., who proposed that the rate of ammonia synthesis, limited by nitrogen dissociation (step 1 in Figure 2b), is related to the energetics of the nitrogen species on the surface of the catalyst [51]. This led to the derivation of volcano plots in which the catalytic activity of the metal surface is related to the strength of the interaction between the N₂ molecule and the surface, i.e., the Sabatier principle. As it can be noted from Figure 2a, when the interaction of the metal with nitrogen (e.g., Mo) is too strong or weak (e.g., Ni or Co), the observed turnover frequency is too low as the reaction is limited by either desorption or adsorption steps, respectively [52]. Therefore, for the reaction to proceed, the interaction of the reactive species must be moderate (e.g., Ru and Os) to obtain sufficient catalytic activity. This realization led to the development of descriptors based on theoretical predictions of metal surfaces and nitrogen species that allowed the development of more sophisticated catalysts. An example of these are the bimetallic catalysts [53] and metal nitrides [54] (Co₃Mo₃N), which have faster rates than commercial Fe catalysts for ammonia synthesis at low temperatures. Because on these catalysts the dinitrogen dissociation takes place on very similar sites, the energetics of the transition state, which is equivalent to the apparent activation barrier, for the dinitrogen triple bond scission, is coupled to the surface-adsorbed species following the Brønsted–Evans–Polanyi or linear energy scaling relationship (Figure 2c) [49]. As a result, it is not possible to independently vary the

Figure 2



Calculated turnover frequencies (a) for ammonia synthesis as a function of the adsorption energy of nitrogen at 400 °C, 50 bar, gas composition H₂:N₂ 3:1, containing 5% NH₃ (adapted from Ref. [53] with permission of the American Chemical Society), (b) the reaction mechanism and (c) Brønsted–Evans–Polanyi relationship between the transition state energy and the binding of the adsorption species.

activation barrier and adsorbate–metal interaction. Furthermore, in these catalysts, nitrogen and hydrogen dissociation takes place on the same sites, leading to coverage dependence rates of reaction. In this system, Langmuir–Hinshelwood mechanism dictates that the rate of reaction decreases as a function of the hydrogen and ammonia partial pressures [51,55,56]. Thus, an optimal combination of reaction operating conditions and catalyst formulation is required to achieve sufficient catalytic activity.

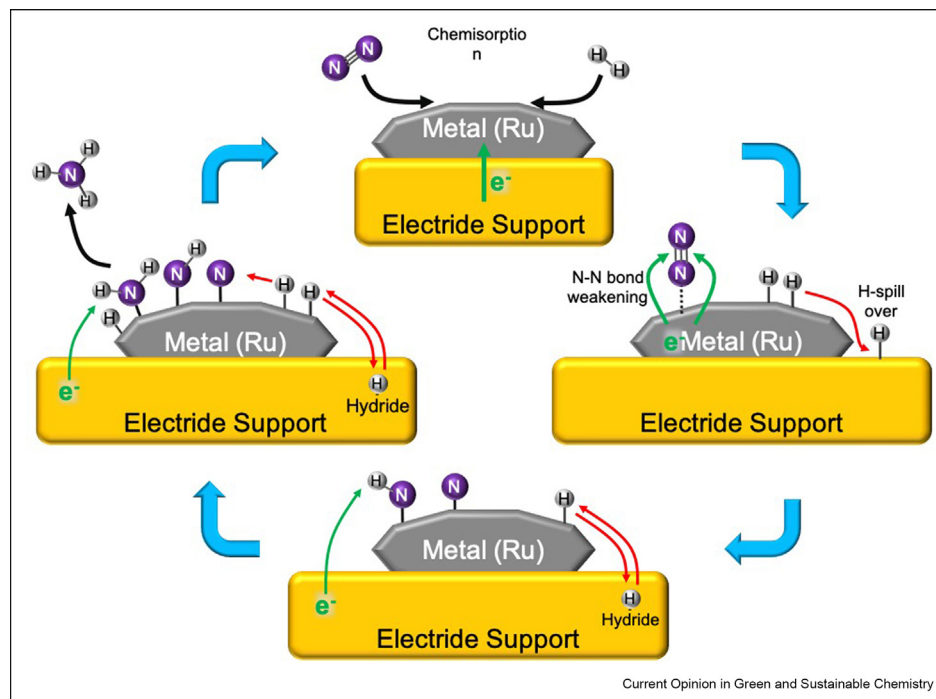
Transition metal–supported electrides

Breaking the scaling relationship between the transition state energy and the bonding strength of adsorbed species requires decoupling of the adsorption of nitrogen and hydrogen species with the energy required to break and/or form new bonds. To achieve this, it is necessary to increase the density of occupied states near the Fermi level on the metal; thus, the d-band electrons can weaken the triple bond of the nitrogen molecule via back-donation to the π^* antibonding states of the adsorbate. From the chemistry point of view, however, this is not an easy task. The nitrogen bond is extremely inert with an ionization potential of 15.841 eV and a gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of 10.82 eV. As a result, to effectively destabilize the bond, it is necessary to use a metal center that also has low work function, i.e., a metal that can donate electrons easily (e.g., metallic Na and K have 2.75 and 2.30 eV, respectively) [57]. However, these metals are unstable under reaction conditions relevant for ammonia synthesis and are only used as catalyst promoters [58].

In addition, such metal catalysts will be strongly inhibited by hydrogen dissociation as long as the nitrogen and hydrogen chemisorption occurs on the same active site [59]. Thus, to develop a highly effective catalyst for ammonia synthesis, it is necessary to use a metal that has (1) sufficient density of states near the Fermi level to back-donate electrons to the antibonding states of the nitrogen molecule, (2) sufficiently low work function to facilitate the electron donation process, (3) two different active sites for hydrogen and nitrogen chemisorption on the surface to avoid competitive chemisorption, and (4) low interaction with the product species to facilitate desorption.

The breakthrough arrived in 2011 when a group of researchers in Japan reported for the first time that electrons can be solvated inside a thermally stable electride [Ca₂₄Al₂₈O₆₄]⁴⁺•4e⁻ or (C12A7:e⁻) [60]. This metal oxide–based material results from treating in reducing environments the C12A7:O²⁻, which leads to the formation of trapped electrons inside the 0.4 nm cages of the material that are protected from oxidation by oxygen thanks to the 0.1 nm cage openings. At the time, this material was the first electride with room temperature stability; however, no particular application was developed for it in that work. A year later, the authors demonstrated that this material could potentially be used as an electron-donor and hydrogen storage material for ruthenium-based ammonia synthesis catalysts, in which it would be possible to enhance the activation of the nitrogen molecules on Ru surface thanks to the electron transfer from the C12A7:e⁻ electride to the metal, and the adsorption of hydrogen onto the support via spillover [61]. The authors proposed that in that

Figure 3



Proposed mechanism of reaction of ammonia synthesis on transition metal supported on electrides. Adapted from Ref. [61].

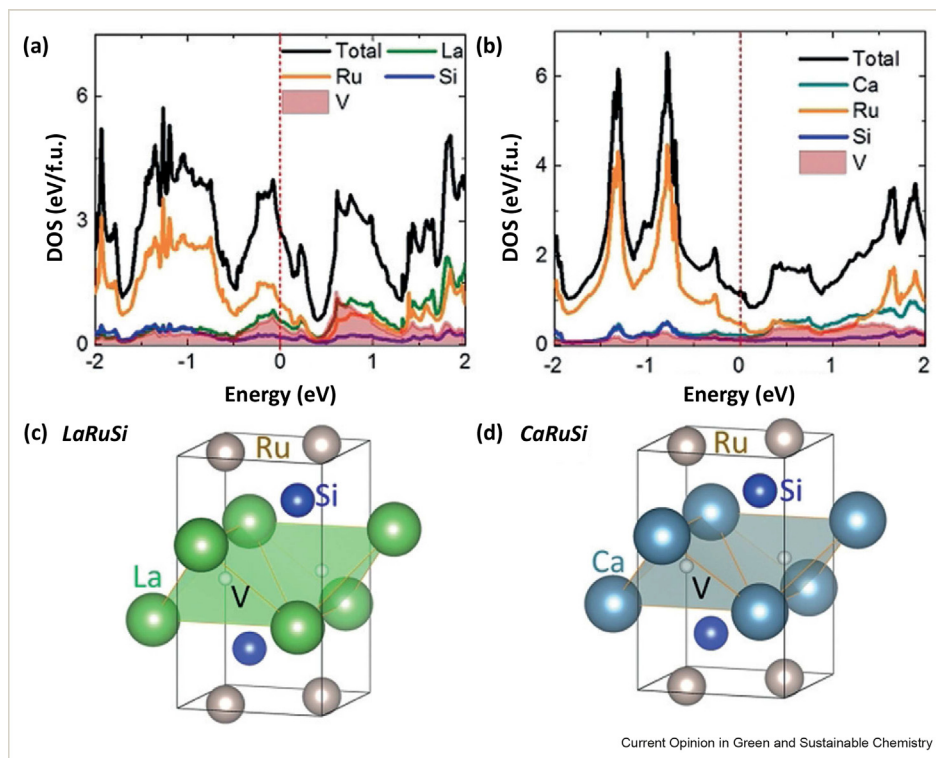
catalyst, the reaction mechanism was different from conventional Ru catalysts thanks to the (1) decoupling between the nitrogen and hydrogen chemisorption steps, (2) the increase in the electronic density of the occupied states of the d-band in the ruthenium catalyst near the Fermi level, and (3) the reduction of the work function of the metal.

As shown in Figure 3, the mechanism started with the molecular chemisorption of nitrogen on the ruthenium surface, which is believed to occur atop mode, and the dissociative chemisorption of hydrogen. In this surface, the electron donor nature of the support (work function of 2.4 eV, similar to that of metallic K) led to an electron transfer to the d-band of the metal that enhanced the back-donation of electrons to the antibonding (π^*) molecular orbital of the dinitrogen molecule upon chemisorption. This facilitated the nitrogen dissociation at much lower temperature. In this system, the hydrogen is dissociated on Ru, followed by spillover to the electride support. In this material, the excess hydrogen would be encapsulated in the subnanometer cages of the C12A7:e⁻ in the form of hydrides (H⁻), leaving empty sites for nitrogen chemisorption. The nitrogen species on the surface progressively underwent sequential hydrogenation followed by desorption to form ammonia in a facile fashion. This resulted in an extremely active catalyst with TOF of 0.18 s⁻¹ and

apparent activation energies of c.a. 50 kJ/mol at 400 °C and 0.1 MPa, which are significantly better than those of the conventional Ru–Cs/MgO and Ru–Ba/AC catalysts (0.05–0.28 s⁻¹) at higher pressures (2.0–6.3 MPa) [62–65]. This mechanism was consistent with kinetic observations that showed that in the Ru/C12A7:e⁻, the reaction order was nearly one with respect to hydrogen, in stark contrast with conventional catalysts in which negative reaction orders on hydrogen are obtained. Furthermore, Fourier-transform infrared (FTIR) spectroscopic information of nitrogen chemisorbed on Ru/C12A7:e⁻ revealed a redshift of c.a. 72 cm⁻¹ in the broad peaks of N₂ end-on oriented on the surface with respect to Ru–Al₂O₃ and Ru/C12A7:O²⁻. This result indicated the weakening of the dinitrogen triple bond upon chemisorption on the Ru/C12A7:e⁻ to a much greater extent than in the conventional catalysts.

Conversely, the electride support C12A7:e⁻ had an extremely limited surface area (c.a. 1–2 m²/g) that rendered this catalyst with low practical value. As a result, the catalytic activity per unit of mass of this material (994–6089 $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$) was lower than that obtained on more traditional Ru–Cs/MgO catalysts (12,117 $\mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$) at 400 °C and 1.0 MPa. For this reason, the authors proposed the utilization of inter-metallic transition metal electrides as a platform for higher dispersion of expensive ruthenium catalysts for

Figure 4



Density of states (a–b) and lattice structures (c–d) of LaRuSi and CaRuSi, respectively. Adapted from Ref. [66] with permission of Wiley-VCH Verlag GmbH & Co.

ammonia synthesis [66]. In this context, the group led by H. Hosono decided to use LaRuSi and CaRuSi directly as a catalyst for ammonia synthesis (see Figure 4c–d) [66]. The authors proposed that in this material, multivalent La and Ca cations in the XRuSi (X = La or Ca) can effectively donate electronic density to the metal center upon exposure to reducing atmospheres. As it is shown in Figure 4a–b, the density of states calculated for the two intermetallic structures indicates that in the case of LaRuSi, the density of occupied states (DOS) near the Fermi level increased substantially primarily due to the electron donation from the La to the Ru, while in the case of CaRuSi, the extent of the DOS near the edge is limited. This enhancement in the DOS near the Fermi level on the d-band of the metal center was the cause of to the high catalytic activity of the LaRuSi electride, which achieved apparent activation barriers of 35 kJ/mol and rates of $1760 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$. These were significantly higher than those of CaRuSi where only trace activity was detected (c.a. $60 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$) at 400 °C and 0.1 MPa. Comparable with the case of Ru/C12A7:e[−], this catalyst (LaRuSi) showed high resistance to

hydrogen poisoning, as indicated by positive reaction orders on hydrogen.

Since these seminal discoveries, this group has reported exciting new materials based on the same concept of transition metals supported on electron donor and hydrogen storage materials [67–72]. Recently, they reported a ruthenium-based catalysts (Ru/CaFH solid solutions) with measurable catalytic activities ($50 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$) at temperatures as low as 50 °C and 0.1 MPa of pressure (apparent activation barrier of 20 kJ/mol), which has paved the way for the application of these materials for low-temperature ammonia synthesis.

Future outlook and concluding remarks

Ammonia synthesis from renewable energies, either for fertilization or seasonal energy storage, is not any longer a futuristic concept discussed in the realms of academic circles. Instead, green ammonia is a reality as demonstrated by the number of large-scale commercial projects currently being developed around the world aimed at

decarbonization of the electricity grid and fertilizer production plants. While this exponential increase in green ammonia projects is exciting as it can bring us closer to the targets of the Paris Climate Change agreement [73], one can immediately realize that for the developing world, this technology will not be available in the short term simply due to the high thresholds for investment required in these large-scale energy projects. This calls for the development of technologies that can enable downscaling green ammonia production in an energy efficient and economic manner to facilitate market access to developing economies. In this scenario, reducing the pressures and temperatures required for ammonia synthesis becomes a major scientific and engineering challenge. Thus far, reducing the pressure can be achieved by using adsorption-enhanced HB process in which ammonia is selectively removed from the reaction mixture using metal halides, while temperature reduction can be accomplished by using transition metal catalysts supported on electron-donor supports with hydrogen storage capacity. The combination of these two approaches can potentially reduce operational and capital expenditures of the process even at small scales, thanks to the decreased SEC of the ammonia synthesis loop and the use of more conventional metal alloys for the construction of the reactor.

To bring these advancements in engineering and material science on ammonia synthesis closer to commercial implementation, it will be essential to develop (1) inexpensive versions of the catalysts using earth abundant transition metals without jeopardizing catalytic activity and stability and (2) support materials compatible with these catalysts with high surface area and thermal conductivity to enable efficient mass and heat transport inside the catalyst pellets. For this reason, one can anticipate that structured reactors with enhanced-mass/heat transport and low-pressure drops can potentially enable the development of compact high-performance ammonia synthesis reactors. Furthermore, decreasing the temperature in an exothermic reaction such as ammonia synthesis only makes sense up to a certain extent, as the autothermal operation of the unit becomes challenging if the heat losses are larger than the reaction heat. Therefore, it will be essential to consider the entire heat and mass balances of the process during the design of such ammonia synthesis reactor. Finally, regenerability and stability of the catalyst and adsorption materials should be carefully studied and demonstrated at industrially relevant operating conditions. This is particularly relevant if one considers that coupling this reactor unit to a renewable energy resource (PV or wind) will require important load variations. In conventional HB plants, the process is operated at nominal capacity for extended periods of time (typical life-span of a Fe-based catalyst is 10 years). Thus, load variability with minimum performance impact is a standing challenge

for engineers and material scientists working on green ammonia synthesis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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