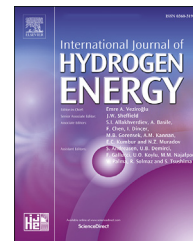


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Reversible ammonia-based and liquid organic hydrogen carriers for high-density hydrogen storage: Recent progress

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ABSTRACT

Liquid hydrogen carriers are considered to be attractive hydrogen storage options because of their ease of integration into existing chemical transportation infrastructures when compared with liquid or compressed hydrogen. The development of such carriers forms part of the work of the International Energy Agency Task 32: Hydrogen-Based Energy Storage. Here, we report the state-of-the-art for ammonia-based and liquid organic hydrogen carriers, with a particular focus on the challenge of ensuring easily regenerable, high-density hydrogen storage.

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Introduction

Hydrogen and hydrogen-based fuels remain a key part of the portfolio of energy storage methods which are needed to

ensure a transition to a renewable electricity-based energy sector. The hydrogen energy cycle is based on the interconversion of water and hydrogen as a way of storing and releasing energy from renewable electricity. The technical

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challenges associated with the implementation of a large-scale hydrogen energy system have been divided into four main areas: hydrogen production, distribution, storage and utilisation [1]. In hydrogen storage, a wide range of hydrogen carriers, particularly solid materials, have been explored as alternatives to the compression or liquefaction of pure hydrogen in the context of hydrogen fuel cell vehicles [2–8]. However, most of the explored materials only achieve reversible, high-density hydrogen storage under reaction conditions far from the operating parameters of a vehicle-based system [9,10]. As a result, hydrogen storage in current and prototype hydrogen fuel cell vehicles is almost exclusively based on compression: 70 MPa hydrogen gas in the GM HydroGen3 [11], Toyota Mirai [12], Honda Clarity [13], Hyundai ix35 [14], Audi h-tron quattro [15], and Mercedes-Benz GLC-F-CELL [16], and 35 MPa hydrogen gas in the Riversimple Rasa [17].

Although the development of hydrogen storage technology that meets the demanding requirements of on-board hydrogen delivery [18] remains a key goal, it is not the only use to which hydrogen storage can be applied. This diversity of applications was recognised in the framing of International Energy Agency Task 32 to include stationary energy storage applications. In this article, we will articulate the potential for liquid hydrogen carriers to be used as stationary energy stores and in the distribution of hydrogen alongside their development for vehicular use. In these other scenarios, the 70 MPa compressed hydrogen storage option is prohibitively expensive [19,20], and therefore alternative hydrogen storage approaches will be needed.

Some key characteristics of a selection of liquid hydrogen carriers are shown in Table 1, alongside those of 70 MPa compressed hydrogen gas and liquid hydrogen, for comparison. A survey of these properties quickly reveals some of the key advantages of liquid carriers over the compression/liquefaction of pure hydrogen. The volumetric hydrogen densities (considering the material only) of these carriers reach as high as 150% of the value for liquid hydrogen in the case of liquid ammonia. Critically, these high hydrogen densities are achieved under ambient or near-ambient storage conditions. This is in contrast to the high pressures or low temperatures required to achieve practically useful

volumetric hydrogen density with pure hydrogen. From a safety perspective, the liquid carriers listed in Table 1 all have narrower explosive limits in air than pure hydrogen, though have toxicity issues which must be addressed to ensure safe use.

A working energy network system requires energy storage technologies at many different scales of energy, power and storage duration. High volumetric energy density, under modest storage conditions, makes liquid hydrogen carriers attractive options for large-scale and longer-duration energy storage. In these cases, the lower round-trip efficiency of hydrogen production and storage relative to other energy-storage technologies is compensated by its high energy density, transportability and low self-discharge rate [23,24]. This type of energy storage may be required for the inter-seasonal balancing of energy demand in areas with large seasonal variations in energy use. For example, primary energy use in the United Kingdom between the winter and summer has varied on average by over 200 TWh over the past 20 years [25]. The synthesis and storage of hydrogen during times of excess electricity could then displace much of the large natural gas consumption during the UK winter, which accounts for most of this seasonal variation [25]. In this example, 10–20 Mt of hydrogen would need to be stored across the winter, depending on the efficiency of the energy release technology. Although geological hydrogen storage may be cheapest in locations where it is available [19,20,26], in other cases, conversion to a liquid carrier is likely to be the most effective means of storing of hydrogen at large scale [19]. Chemical energy storage is also considered to be a viable model for storing renewable energy from “stranded” renewable power generation, where grid connections are not economically viable [27–29].

The uses of hydrogen storage in stationary energy storage outlined above are in addition to the well-documented potential for hydrogen to contribute to the decarbonisation of transport, which currently constitutes around 35% of all energy end use [30]. Infrastructure for the distribution of hydrogen for transport is a key limiting step for the roll-out of fuel cell vehicles, and requires significant capital investment [31,32]. Liquid hydrogen stores have the potential to significantly alleviate cost associated with the distribution of

Table 1 – Comparison of some key properties of a range of reversible liquid hydrogen carriers with compressed and liquid hydrogen.

Storage method	Storage conditions	Hydrogen density (kgH ₂ /m ³)	H ₂ release conditions	Explosive limits (%vol in air)	PEL ^a (ppmv)	Vapor pressure (MPa @ 298 K)
Compressed H ₂	70 MPa	42	Pressure release	4–75	N/A	–
Liquid H ₂	20.28 K	70	Evaporation	4–75	N/A	–
Liquid NH ₃	239.81 K @ 0.1 MPa 1 MPa @ 298 K	121	Catalytic T > 400 °C	15–28	50	1.1
Methylcyclohexane (MCH)	Ambient	107	Catalytic T > 300 °C	1.2–6.7 (MCH) 1.2–7.1 (Toluene)	500 200	0.006
Methanol	Ambient	100	Catalytic T > 200 °C	6.7–36	200	0.017
Formic acid	Ambient	53	Catalytic T > 50 °C	18–34	5	0.006

^a Permitted Exposure Limit, Occupational Safety and Health Administration, U.S. Department of Labor. Given as 8-h time weighted average concentrations [21,22].

hydrogen because of their straightforward storage and applicability to existing fuel transport methods. This allows larger quantities of hydrogen to be transported in each truck/ship load. This is particularly important when considering supply models such as those in active development for Japan (Fig. 1), where it is envisaged that hydrogen will be produced in regions with low-cost renewable electricity (e.g. Australia and the Middle East) and shipped to Japan for use as a fuel. The hydrogen storage methods under active consideration are liquid hydrogen, ammonia, methylcyclohexane and methane [33]. In this way, liquid hydrogen carriers have the potential to enable global hydrogen trade.

There are a number of different models for the involvement of liquid carriers in future hydrogen infrastructures:

- Large stocks of carrier transported by ship could be dehydrogenated at ports or in other centralised facilities and then distributed as pressurised or liquefied hydrogen.
- Dehydrogenation could be performed at hydrogen refuelling stations. It has been suggested that carriers could be tailored to deliver hydrogen at elevated pressure [34–36], reducing the reliance on compressors, which dominate the capital cost of refuelling stations [37]. Metal hydrides are also being explored for the production of compressed hydrogen [38].
- Liquid hydrogen carriers could be used for on-board delivery of hydrogen to a fuel cell, as has been the focus for solid-state hydrogen stores. This application is currently furthest from technical deployment due to the difficulties associated with on-board dehydrogenation and the safety issues associated with the carriers themselves.

In each of these applications, the requirements for hydrogen storage and release in a liquid carrier may vary. However, it is reasonable to state that achieving reversible hydrogen storage under moderate conditions is a key goal in the development of all liquid hydrogen carriers. Here, we will focus on recent research highlights in realising the potential of ammonia-based and liquid organic hydrogen carriers. The review does not consider carriers where hydrogen release is also accompanied by carbon dioxide release, of which formic acid and methanol have been most widely discussed. The reader is directed to several recent reviews in those areas [36,39–41]. Likewise, the hydrolysis of sodium borohydride and solution-based dehydrogenation of ammonia borane are not considered here. While aqueous solutions of these materials have comparable hydrogen storage density to methylcyclohexane [42], their hydrolysis results in the formation of a heterogeneous mixture of products containing strong B–O

bonds which require harsh conditions to regenerate the starting materials [41,43,44]. Water must also be evaporated from the hydrolysed product before regeneration, making use of these solutions energy intensive and costly [45]. While much research has focussed on catalyst development for hydrogen release [46], relatively little work is published on the issues of regeneration [45].

Ammonia

Ammonia is among the most important synthetic chemicals; its industrial-scale production is credited with growing the food required to feed roughly half the current human population [47]. However, despite its very high volumetric hydrogen density (see Table 1) and mature synthesis and distribution infrastructure, ammonia has not featured prominently among the discussion of likely hydrogen carriers in recent decades. This partly relates to a U.S. Department of Energy decision in 2006 not to fund research into on-board hydrogen delivery from ammonia due to stated concerns over the high temperature of ammonia decomposition, the size and cost of catalytic reactors, poisoning of Polymer Electrolyte Membrane (PEM) fuel cells by residual ammonia, and safety issues [48].

Despite these concerns, the potential for ammonia to contribute significantly to a hydrogen-based energy system has been highlighted in a number of perspective articles in the literature [49–53]. In recent years, interest in its use in energy applications has become more widespread – some of this interest is likely to be as a result of the aforementioned effort by the Japanese government to establish a hydrogen trade sector based on the synthesis of reversible liquid hydrogen carriers in locations with abundant renewable power [33]. Indeed, the construction of two pilot ‘green’ ammonia production facilities is planned in Australia over the next few years, representing the first steps in the development of this hydrogen export model [54,55].

Ammonia is attractive as a way of storing energy from renewables in part because of its flexibility. It can be used as a hydrogen carrier, a direct fuel for combustion and fuel cells [56–58], or sold in its current use as a fertiliser feedstock. Indeed, recent modelling suggests that ammonia produced from renewables is already cost-competitive with traditional production [29,59], with the added incentive of reducing the carbon footprint of an industry which is estimated to account for around 1.5% of global greenhouse gas emissions [60]. In considering here the use of ammonia as a hydrogen carrier, the areas of concern outlined in the 2006 U. S. DOE report are a

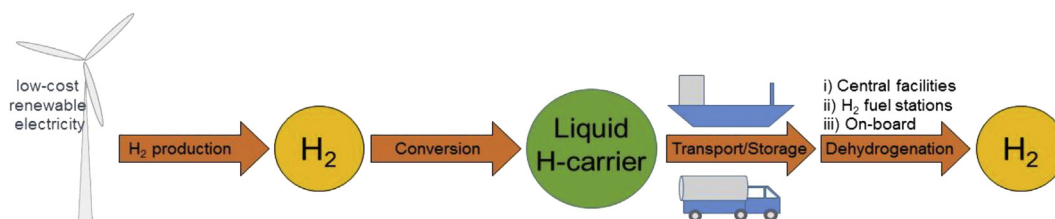


Fig. 1 – A schematic process diagram of the role of liquid hydrogen carriers in facilitating the use of hydrogen for energy storage.

useful way of structuring the discussion of recent research progress. We shall outline approaches to the development of catalysts for the synthesis and decomposition of ammonia under milder reaction conditions, efforts to address toxicity concerns through the storage of ammonia in the solid state and preventing the exposure of fuel cells to ammonia through absorbent and membrane approaches.

Ammonia synthesis

The industrial production of ammonia through the conventional Haber-Bosch process consumes 1–2% of the annual global energy demand and generates about 2.9 metric tons of CO₂ per metric ton of NH₃ produced [61]. While a majority of these emissions arise from the synthesis of hydrogen, ammonia production by the Haber-Bosch process requires high reaction temperatures (350–500 °C) and pressures (15–35 MPa of H₂ and N₂ with a ratio of 3:1) [62,63]. An improvement in the rate of this process (i.e., the development of ammonia synthesis catalysts), so that it could be operated at lower temperatures (or pressures), could have significant impact on both the economy and the environment. For example, calculations on an industrial ammonia synthesis process indicated that decreasing the equilibrium synthesis temperature from 440 °C to 360 °C would save around 1 GJ/MT of ammonia produced [64]. Enabling ammonia synthesis at milder conditions may also facilitate small-scale ammonia production linked to renewable power sources through more flexible operation. In this section, we highlight recent innovations in catalyst materials as well as advances in alternative production process to the Haber-Bosch process, specifically, electrochemical ammonia synthesis.

Thermal ammonia production

It has been reported that the activities of transition metals in catalyzing NH₃ synthesis exhibit a volcano-type dependence of the activity on the chemisorption energy of N (as shown in Fig. 2) [65]. This dependency can be explained by the Brønsted-Evans-Polanyi (BEP) and scaling relations, because a linear correlation between the N₂ dissociation energy and adsorption energy of N has been clearly demonstrated [65,66]. This linear relationship provides a theoretical guideline for the search for efficient catalysts within the volcano-type plot; efficient NH₃ synthesis requires a catalyst which strongly activates the reactants (N₂ and H₂), but also a relatively weak binding of the intermediate species and products [65,67]. Therefore major effort to achieve ammonia synthesis at low temperatures (i.e., 150–400 °C) has mainly focused on mitigating the N adsorption energy, boosting the electron donation effect, and more recently, new approaches to breaking the scaling relation. We highlight these recent advances in the following section.

Fe and Ru are the best single-metal catalysts because of their moderate adsorption energy for N₂ [65]. Combining a transition metal at the left side of the volcano-type plot with another one at the right side could be an effective way to approach the optimal N adsorption energy. In 2000, a report proposed ternary nitrides (Fe₃Mo₃N, Co₃Mo₃N and Ni₂Mo₃N) as a novel class of NH₃ synthesis catalysts [68]. Especially, Cs promoted Co₃Mo₃N gives higher activity than that of the industrial catalyst KM1 (Fe-based catalyst with promoters such

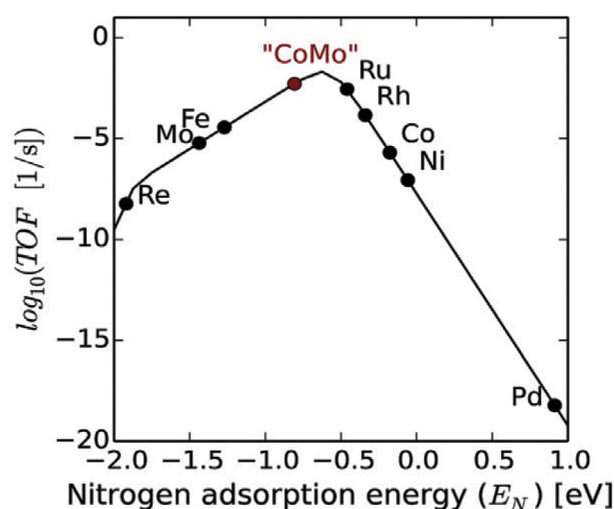


Fig. 2 – Volcano-type activity curve of ammonia synthesis. Rate shown as a function of the nitrogen adsorption energy on different transition metals, which implies there is an optimum for the nitrogen adsorption energy. Reproduced with permission from [65]. Copyright 2015 Elsevier.

as K₂O, CaO, Al₂O₃). Because Co adsorbs N₂ too weakly and Mo adsorbs N₂ too strongly, the outstanding performance of Co–Mo alloys is attributed to the moderate adsorption energy of N on Co–Mo. Recently, Hargreaves et al. examined the role of lattice nitrogen in Co₃Mo₃N using isotopic (¹⁴N/¹⁵N) experiments and computational modelling, demonstrating the lattice nitrogen (¹⁴N) in the ternary nitride exchanges with ¹⁵N in the gas phase, and that NH₃ synthesis using Co₃Mo₃N occurs via a Mars-van Krevelen type mechanism (as shown in Fig. 3a) [69–71]. Co₃Mo₃N was converted into Co₆Mo₆N under a hydrogen flow at ambient pressure to generate NH₃. Based on this concept, a series of ternary nitrides have been studied as nitrogen transfer agents to produce NH₃ by directly reacting with H₂. Co-doped tantalum nitride was found to be highly active, with 52% of the nitrogen in the nitride reacting with H₂ to yield NH₃ [72]. The addition of Co, Fe or K to manganese nitride only promotes the lattice nitrogen depletion to form N₂. However, adding a small amount of Li can improve the hydrogenation rate of lattice nitrogen in Mn₃N₂ at 300 °C [73].

Next to changing the strength of the N adsorption energy by using alloys that form nitride compounds, the addition of electronic promoters such as alkali or alkaline earth metal oxides can weaken the N≡N bond, and thus improve the activity of transition metals [74]. However, the promotion is still not sufficient to generate NH₃ under mild conditions. Hosono et al. employed an inorganic electride compound (C12A7:e[−]: a crystal of Ca₂₄Al₂₈O₆₄ with four cavity-trapped electrons serving as anions) as a catalyst support. Because the work function of C12A7:e[−] is 2.3 eV lower than that of Ru, this electride can act as an efficient electron donor for Ru [75]. The Ru/C12A7:e[−] catalyst with particle size of Ru around 8.5 nm shows an activity that is two orders of magnitude larger than that of the Cs promoted Ru/MgO catalyst. Kinetic analysis and infrared spectroscopy revealed that C12A7:e[−] enhances the electron back donation and N₂ dissociation. As a result, the

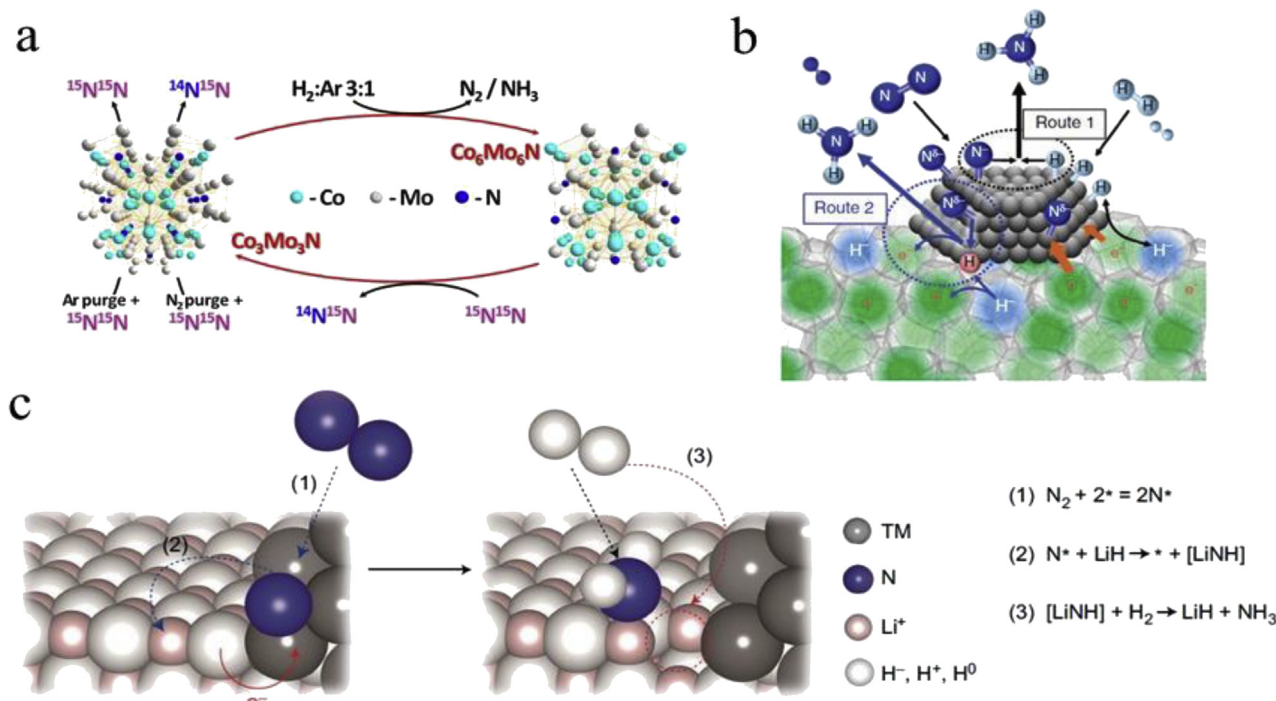


Fig. 3 – (a), Ammonia synthesis using $\text{Co}_3\text{Mo}_3\text{N}$ catalyst occurs via a Mars-van Krevelen type mechanism. Reproduced with permission from [71]. Copyright 2013 American Chemical Society; (b), Ammonia formation mechanism over $\text{Ru}/\text{C12A7:e}^-$ catalyst. Reproduced with permission from [76]. Copyright 2015 Nature Publishing Group; (c), Relayed ammonia synthesis mechanism for 3d-transition metal-LiH composite catalyst. Reproduced with permission from [67]. Copyright 2016 Nature Publishing Group.

hydrogenation of N atoms rather than the dissociative adsorption of N_2 over Ru is now the rate determining step [76]. Fig. 3b shows the proposed reaction mechanism over $\text{Ru}/\text{C12A7:e}^-$. NH_3 can be formed in two ways: via the Langmuir–Hinshelwood mechanism or by direct reaction of N adatoms with H radicals. Because the electride C12A7:e^- can reversibly store hydrogen in the form of H^- , poisoning of the Ru surface by adsorbed hydrogen atoms was suppressed. In a more recent work, a new electride Y_5Si_3 was also explored for ammonia synthesis by Hosono's group [77]. 7.8 wt% Ru loaded Y_5Si_3 catalyst exhibits an NH_3 formation rate of 1.9 mmol/g/h under the condition of 0.1 MPa and 400 °C, which is even higher than that of $\text{Ru}/\text{C12A7:e}^-$ (0.7 mmol $^{-1}\text{h}^{-1}$). As with C12A7:e^- , the strong electron-donating ability of Y_5Si_3 to Ru promotes N_2 dissociation and reduces activation energy of NH_3 synthesis. They showed that the performance of $\text{Ru}/\text{Y}_5\text{Si}_3$ did not degrade, even if the support Y_5Si_3 was submersed into water before use or if 3 vol% of water vapor pressure was introduced into the reaction gas. This is unlike other catalysts, such as nitride or hydride-based catalysts, where chemical stability against air and water is a major problem. These features may make $\text{Ru}/\text{Y}_5\text{Si}_3$ a promising candidate for practical application.

A relatively new class of NH_3 synthesis catalysts is aimed at breaking the scaling relationship by providing two different active sites. Chen et al. proposed LiH as a second active centre for N hydrogenation and subsequent NH_3 desorption, so that the NH_3 formation rate would no longer solely dependent on transition metals [67]. LiH can act as a strong reducing agent and remove activated nitrogen atoms from the transition metal or its nitride to form LiNH_2 . LiNH_2 further splits H_2 to

give off NH_3 and thereby regenerates LiH. This subsequent catalysis over two different active centers is depicted in Fig. 3c. At 300 °C, catalytic activities of 3d-transition metals (V, Cr, Mn, Fe, Co and Ni)–LiH composite catalysts are 1–4 orders of magnitude higher than those of single transition metal catalysts and some of the catalysts outperform the reference Cs–Ru/MgO catalyst. These composite catalysts have apparent activation energies that are very close to the E_a value (49 kJ mol $^{-1}$) of the hydrogenation of LiNH_2 , suggesting that the hydrogenation of LiNH_2 is now the rate determining step. A similar high activity was reported for CNTs supported BaH_2 –Co catalysts [78], and $\text{Ca}(\text{NH}_2)_2$ supported Ru catalysts [79]. The addition of barium-doped $\text{Ca}(\text{NH}_2)_2$ to Ru nanoparticles with a mean size 2.7 nm can improve the NH_3 synthesis activities significantly, which are 2 orders of magnitude higher than that of Cs–Ru/MgO below 300 °C [80]. Nano sized Ru–Ba core-shell structures were formed during catalytic reaction, which possibly account for the superior performance. A recent paper discussed that alkali or alkaline earth hydrides, including LiH, BaH_2 , KH, CaH_2 , and NaH, can increase the catalytic activity of manganese nitride by several orders of magnitude [81]. Alkali and alkaline earth metal imides can function as nitrogen carriers that mediate ammonia production via a two-step chemical looping process: Firstly, N_2 is fixed through the reduction of N_2 by alkali or alkaline earth metal hydrides to form imides; Secondly, the imides are hydrogenated to produce NH_3 and regenerate the metal hydrides. This chemical loop process mediated by BaNH and catalyzed by Ni produces NH_3 at 100 °C and atmospheric pressure [82]. These results demonstrate that the cooperation

of transition metals and alkali or alkaline earth hydrides creates an energy-efficient pathway that allows NH_3 synthesis at lower temperatures.

As discussed above, recent studies for ammonia synthesis catalysts are dedicated to modifying the electronic structures of transition metals under the governing of scaling relations or break the scaling relation by providing two different active sites. Ternary nitrides have a comparable activity with the industrial catalysts and can even produce NH_3 at ambient pressure. Electride-supported Ru catalysts boost the N_2 activation and surpass the H_2 poisoning (an obstacle for industrial Ru-based catalysts working under high H_2 pressures). Transition metal-hydride catalysts can separate the N_2 activation and hydrogenation or desorption steps to achieve low temperature catalysis. These encouraging results promote the search for practical low-temperature ammonia synthesis catalysts.

Electrochemical ammonia production

Electrochemical reduction of dinitrogen into ammonia at near ambient conditions represents a key enabling technology, which would accelerate the transition to an energy and chemical infrastructure based on electrical energy from renewable sources. Small-scale decentralized plants could accommodate the intermittency of, e.g., wind and solar energy, and produce ammonia for both fertiliser production and for energy storage purposes [50]. Such devices could easily be combined with safe storage solutions, where the produced ammonia can be stored safely and reversibly at high density in benign, low-cost metal halide salts [83,84], but until now, efficient and selective electrocatalysts for the nitrogen reduction reaction (NRR) have remained elusive.

It has been shown using density functional theory (DFT) calculations that certain metal nitrides, e.g. vanadium and zirconium nitride [85,86], can produce ammonia at potentials as low as -0.5 V vs. RHE, but the stability of the nitrides under reaction conditions and low Faradaic Efficiencies (FE) due to competing hydrogen evolution reaction (HER) remain a challenge [87]. DFT calculations have also shown that nanostructuring the nitride catalysts can lead to improve performance [88–90], which has recently been confirmed experimentally for VN [91] and Mo_2N [92] nanowires.

A large number of different materials and approaches for electrochemical nitrogen reduction have been proposed, see e.g. Ref. [93] and references therein, but common for all are the low FE and ppb/ppm yields of ammonia, which makes quantitative ammonia detection a substantial challenge and the need for ^{15}N labelled control experiments to confirm the origin of the nitrogen essential.

Two lithium-mediated approaches have recently been proposed; a lithium-ion conductor approach by Han et al. [94] and a lithium-nitride cycling scheme by Nørskov et al. [95], where the latter holds promise of economic viability; in particular, if suitable and less thermodynamically stable nitride species are identified. The use of aprotic electrolytes was also recently proposed by MacFarlane et al. to limit the availability of protons and suppress HER [96,97] and inspiration from secondary Zn-air batteries for suppression of HER by synergistic doping [98], may also hold promise.

To overcome the massive challenges involved, it is evident that a close coupling between theory and experiment is needed in order to identify more efficient NRR electrocatalysts [63].

Ammonia decomposition

The release of hydrogen from ammonia under modest reaction conditions is one of the key challenges of the implementation of ammonia-based hydrogen storage. This challenge requires a broadening of the traditional focus of ammonia catalyst development – the synthesis of ammonia at large scale in high-pressure reactors – towards the goal of hydrogen production at high rates and moderate (<500 °C) temperatures [99,100]. The precise application of ammonia decomposition (e.g. forecourt decomposition, on-board vehicular H_2 production) and the extent of ammonia decomposition required for the power generation technology (Fig. 4) will determine the precise activity characteristics required for the catalysts. This emphasises the requirement for the development of a wide range of catalyst materials.

Transition metal catalysts

The decomposition of ammonia over transition metal based catalysts has a history which goes back to the early times of ammonia synthesis. Several reviews have been published which cover all important aspects of catalyzed ammonia decomposition and highlight potential new research fields [100–103].

The discovery of the NH_3 synthesis (Haber-Bosch process) by Fritz Haber around one hundred years ago had a tremendous influence on the development of the chemical industry [104]. However, not only the synthesis but also the decomposition of NH_3 over iron and ruthenium based catalyst, which in fact are used for the ammonia synthesis, has been studied [105–108]. Most publications in the first decades focus more on kinetic aspects of iron and ruthenium

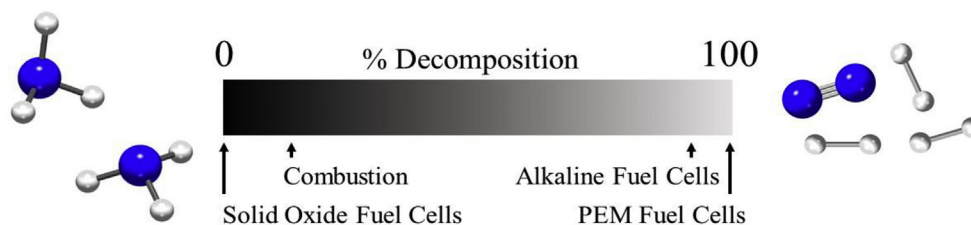


Fig. 4 – Indicative ammonia decomposition levels required for different power generation technologies.

catalysts than on a systematic scan of additional potential decomposition catalysts [109–114]. Later, the search for efficient decomposition catalysts was extended to other transition metals such as Ni, W, Mo, or Co, and also to supported precious metals [115,116].

Based on the excellent properties of Ru as an ammonia synthesis catalyst, the performance of transition metals in general for the decomposition reaction was evaluated. Several aspects were identified to be crucial for the activity of the decomposition catalysts: type of (a) active metal and (b) support, (c) surface area and particle size, (d) catalyst dispersion, and (e) the role of promoters. Choudhary et al. investigated supported metal catalysts in ammonia decomposition and observed a decrease of the ammonia conversion in the following order $\text{Ru} > \text{Ir} > \text{Ni}$ [117]. A comparison of the behavior of Ru, Rh, Pt, Pd, Ni, and Fe as active components identified Ru among other metals as most active catalyst [118]. Catalytic testing of Ru prepared on different supports (carbon nanotubes (CNT), activated carbon (AC), Al_2O_3 , MgO, ZrO_2 , and TiO_2) revealed that Ru on CNTs exhibits the highest conversion of ammonia.

Whether a support has a positive effect on the ammonia decomposition is strongly dependent on the nature and structure of the support materials. CNTs and activated carbon (AC) facilitate a high dispersion of Ru on the surface and prevent particle growth of the active catalyst [118,119]. High dispersion has a positive influence on the stability of the catalyst and therewith on the catalytic activity. Nevertheless, even though high catalyst dispersion is beneficial, several studies showed that for very small Ru particles the turn-over-frequency (TOF) is significantly lower than for larger Ru particles [120,121]. Over-dispersed catalysts may result in too small catalyst particles, which do not provide enough space for the recombination of N atoms to N_2 molecules [122]. Furthermore, Li et al. investigated the importance of the structure of different carbon supports such as CNTs, AC, mesoporous carbon (CMK-3), graphitic carbon (GC), and carbon black (CB). The catalytic activity decreases from $\text{Ru/GC} > \text{Ru/CNTs} > \text{Ru/CB} > \text{Ru/CMK-3} > \text{Ru/AC}$ [122]. Within this order the degree of graphitization is decreasing. Conductive supports facilitate the electron transfer from promoter or support to the active metal catalysts which explains changes in catalytic activity. Yin et al. also related improved activities of Ru catalysts to an increased basicity of the support material [118]. The recombinative desorption of nitrogen from the surface appears to be the rate-limiting step in ammonia decomposition [122] but stronger basicity seems to support N_2 desorption [118]. The combination of basicity with good electronic conductivity of the support appears to be essential for the development of efficient catalysts for ammonia decomposition.

Alkali, alkaline earth, or rare-earth ions added as promoters can further enhance the decomposition of ammonia. Among all studied promoters K, Cs, and Ba are the most beneficial and therefore also the most studied ones [123–127]. Promoters may prohibit sintering of the active metal catalysts as known for ammonia synthesis and the modification of CNTs with KOH was reported to decrease of the N_2 desorption temperatures [118]. Decomposition of ammonia on metals occurs in a stepwise sequence starting with the adsorption of

ammonia on the metal followed by stepwise dehydrogenation of NH_3 and recombinative desorption of H_2 and N_2 [103]. On precious metals, N–H cleavage is discussed as the rate-determining step, while for non-precious metals, N_2 desorption is the rate-limiting step. All modifications of the support or the presence of additives may alter the desorption step of N_2 and change therewith the catalytic properties of the catalyst system.

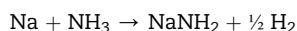
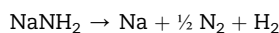
However, even though Ru-based catalysts are most promising for ammonia decomposition, high costs and limited resources of precious metals require the development of more economical alternatives as catalysts. As alternative catalysts mainly Fe, Ni [128,129], Co, or Mo have been investigated, either as pure phases or supported on carbon materials or porous/non-porous oxides. Depending on reaction temperatures, Fe and Mo form different types of nitrides during decomposition, while Co reduces to metallic state which was evidenced by *in situ* diffraction studies [130–133]. Recently, reaction pathways of Mn catalysts (Mn nitrides) were studied by *in situ* neutron diffraction [134].

Iron nanoparticles encapsulated into shells of porous silica are considerably more active in ammonia decomposition than unsupported nanoparticles. The encapsulated catalyst is much more stable since mainly sintering of particles is prevented even at higher temperatures [135,136]. Core-shell nanostructures with SiO_2 , Al_2O_3 , MgO as porous shell materials and encapsulated catalysts, such as Fe, Co, Ni, and Ru, are interesting but complicated model systems. They may assist with understanding fundamental processes, but compared to pure metals or simple supported catalysts their reaction temperatures are not significantly lower and such systems may not be feasible for large scale industrial applications/production.

In addition to transition metal nitrides, carbides could also be interesting catalysts. The activity of WC and VC for hydrogen generation was investigated by several groups and some interesting properties were reported [137–139].

Metal amide/imide catalysts

Group I and II metal salts have rarely been considered as candidates for ammonia decomposition catalysts outside of their established use as promoters in transition metal systems. However, the catalytic activity of a Group I metal amide was first reported in 1894 by Titherley, who observed continuous decomposition of ammonia by sodium amide (NaNH_2) heated to “dull redness” [140]. Titherley proposed that the decomposition was as a result of the concurrent decomposition and synthesis of sodium amide, two reactions which had been observed in isolation:



Despite this observation and the extensive recent interest in light metal amides for solid state hydrogen storage applications [2,141–143], no further investigations of the ammonia decomposition activity of sodium amide were reported until 2014, when a more detailed study found that it showed similar performance to 5% Ru on Al_2O_3 above 425 °C

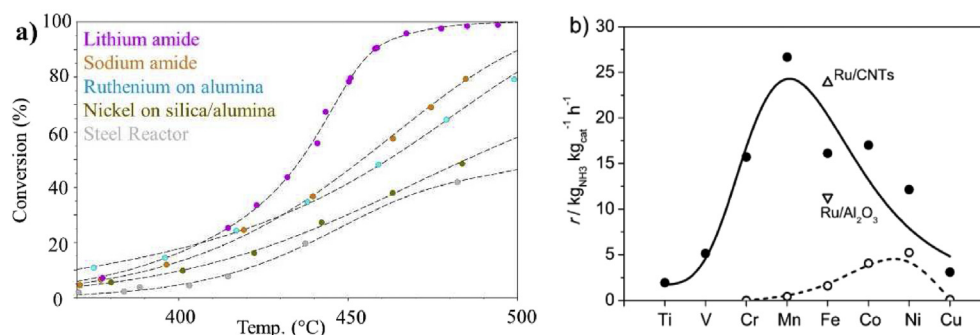


Fig. 5 – Variable-temperature ammonia decomposition performance of a) lithium and sodium amide compared with supported nickel and ruthenium catalysts, measured in a 46.9 cm³ cylindrical stainless steel reactor (0.5 g catalyst, 60 sccm NH₃ flow), modified with permission from [146]. Copyright 2015 Royal Society of Chemistry; b) lithium imide-transition metal (nitride) composites (filled points) compared with transition metal nitrides (Cr, Mn, Fe) and carbon nanotube supported transition metals (Co, Ni, Cu) (open points), along with selected Ru-based catalysts, reproduced with permission from [145]. Copyright 2015 Wiley-VCH.

[144]. Parallel investigations focused on the synergy of lithium imide (Li₂NH) and 3d transition metals were published later by Chen et al., in 2015 [145].

These results, together with the limitations on the practical use of sodium amide due to its high volatility under operating conditions [140,144], prompted a wider survey of light metal amides and imides for active catalysts. Publications to date have included lithium amide/imide (LiNH₂/Li₂NH) [146], lithium imide-3d transition metal composites [145,147], sodium/potassium amide (Na/KNH₂)-manganese nitride [148], lithium-calcium imide (Li₂Ca(NH)₂) [149], ruthenium-magnesium/calcium/barium amide (M(NH₂)₂, M = Mg, Ca, Ba) [150] and potassium/rubidium-manganese amide (M₂[Mn(NH₂)₄], M = K, Rb) [151]. Of the systems studied thus far, lithium amide/imide-containing materials appear to be the most active, showing significantly superior catalytic activity to 5% Ru on Al₂O₃ [145,146] (Fig. 5a), and superior performance to carbon nanotube-supported ruthenium [145,147], which is widely seen as one of the most active ammonia decomposition catalyst formulations. These results, shown in Fig. 5b, contrast with the accepted promoter activity trends for other alkali metal salts [152], which places lithium as the least active promoter [101].

This activity trend for metal amides points to a different function compared with catalyst promoters. There have been

a number of hypotheses as to the precise role of the metal amide/imide in the reaction (Fig. 6). Of particular interest is whether the amide/imide alone can catalyze the decomposition of ammonia. Many of the published studies report the activity of composites of metal amides/imides with transition metals and transition metal nitrides [145,147,148,150,153,154]. In these cases, it is proposed that the catalytic activity results exclusively from the interaction of the amide/imide with the transition metal, either via the ammonia-mediated formation and decomposition of a ternary nitride (e.g. Li₇MnN₄, Li₃FeN₂, Ca₆MnN₅) if possible (Fig. 6iii) [145,147,155], or else by electronic interaction between the metal and NH_x species in the metal amide/imide promoting the cleavage of N–H bonds (Fig. 6ii) [150,153].

Catalytic activity has also been reported for metal amides/imides without the formation of transition metal composites [144,146,149]. For lithium amide-imide, the onset of ammonia decomposition activity was correlated with destabilization of lithium amide to form lithium imide [146]. Isotope studies of the reaction were used to suggest an ammonia decomposition pathway based on the cyclic formation and decomposition of a lithium-rich material such as lithium nitride-hydride (Li₄NH, Fig. 6i) [146]. *In situ* powder diffraction studies have identified solid solutions of lithium amide and imide (Li_{1+x}NH_{2-x}),

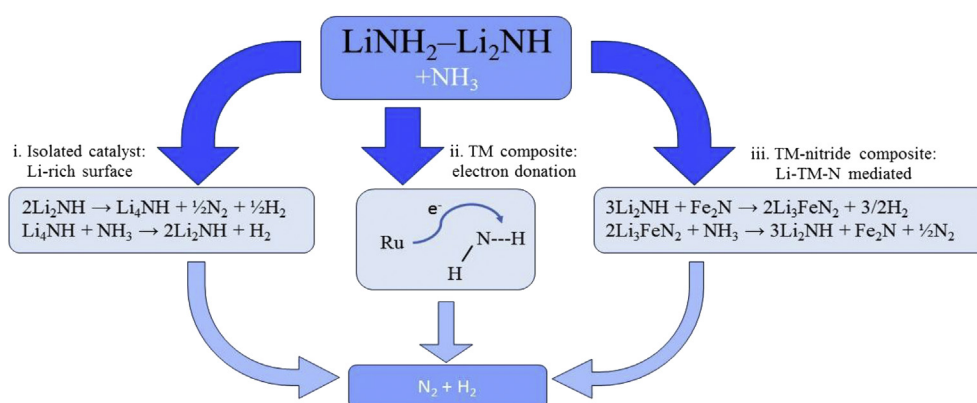


Fig. 6 – Proposed mechanisms for ammonia decomposition reactions involving lithium amide-lithium imide.

$0 < x < 1$) as a bulk phase present under ammonia decomposition conditions ($>500^\circ\text{C}$ under low flow of ammonia) for a number of lithium imide-based catalyst formulations [146,149]. Both lithium nitride-hydride [156] and many ternary lithium nitrides [157,158] are expected to be unstable under ammonia/hydrogen, so it is more likely these species may be observed on the surface or interfaces of catalysts than in the bulk structure.

The studies of isolated metal amides and imides were performed in stainless steel reactors because of concerns over the reactivity of strong basic NH_2^- and NH^{2-} anions with conventional quartz or glass reactors [140,159]. However, the use of stainless steel makes it difficult to rule out the effect of the reactor walls on the catalysis in these studies. Strong evidence exists for the integral involvement of the metal amide/imide in the ammonia decomposition reaction (particularly given the activity observed in combination with otherwise inactive metals such as V and Cr [145]), and for the enhanced ammonia decomposition activity of metal amides and imides combined with transition metals and their nitrides; whether this combination is necessary for catalysis to occur remains an ongoing subject of investigation. In either case, it is clear that there is scope for significant development of this new family of ammonia decomposition catalysts, which use abundant materials to produce hydrogen from ammonia with very high catalytic activity.

Across all ammonia decomposition catalyst systems, further systematic investigations are required to ensure comparable experimental conditions for all materials. This is mandatory to guarantee comparable and sound results. Furthermore, *in situ/operando* studies have shown great potential for a better understanding of catalytic ammonia decomposition and future research will benefit substantially from further experiments in these areas.

Solid-state ammonia storage

Although it is less flammable than hydrogen, ammonia does have significant toxicity concerns, both to humans and, particularly, to marine organisms. While some studies have suggested that ammonia would pose similar risks to existing transportation fuels [160,161], it is clear that advanced controls may be necessary for the use of ammonia in energy infrastructure, both for stationary storage solutions and for applications in the transportation sector, e.g., for automotive deNO_x in diesel exhaust. In both cases, cost and safety aspects are essential, while the density of accessible ammonia which can be stored and released close to the operating temperatures is crucial in the latter case.

Storage of ammonia in solids has been considered as a means for safely storing ammonia, offering significantly reduced ammonia vapor pressure [83,91,162]. While this adds a requirement to thermally desorb ammonia from these materials, many such compounds achieve very high volumetric ammonia density (Fig. 7) when compacted into solid tablets [83], and so do not significantly compromise the storage advantages of ammonia. Much of the research on these systems has focused on the relationship between structure, the identity of the metal cation/s and the resultant thermal stability of the ammoniate. Some of the recent work in this area is summarized below.

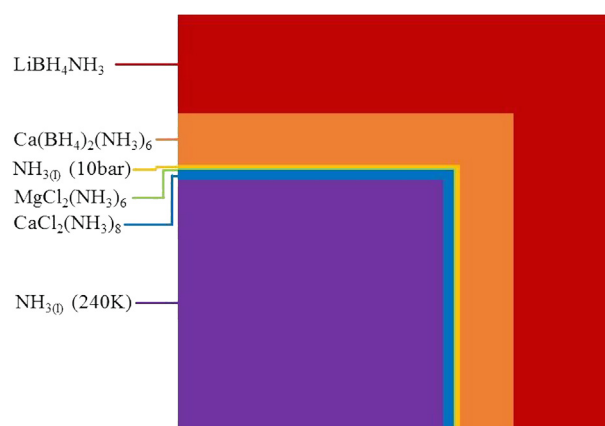


Fig. 7 – Storage volume for a range of different ammonia storage methods, with a constant mass of ammonia. Solids are assumed to be able to be pelletised to 95% of their crystal structure volume [83].

Metal halide ammines

One class of materials which offer a potential solution are metal halide salts such as MgCl_2 , which can reversibly store 9.1 wt% hydrogen (material-only) in the form of ammonia in $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ [162]; albeit the ab-/desorption temperature for automotive applications can be better matched with other metal halide salts [83,163].

Through combined use of DFT calculations and evolutionary algorithms, it has been possible to computationally design novel metal halide ammines to exactly match a set of required operating conditions and improvements in the accessible storage capacity by $>10\%$ have been achieved using a ternary metal halide [84,164]. These accelerated design strategies are now implemented in the open source Atomic Simulation Environment (ASE) [165] and can be used to design mixed metal halide salts for specific storage solutions by adapting the fitness function of the genetic algorithm to match a specific constrain on, e.g., cost or energy density, yielding excellent agreement with experimental observations [166].

In the design of new metal halide ammines for practical application of the storage materials, both the surface [167] and bulk [168] ab-/desorption kinetics of ammonia should be taken into consideration, as should changes in the crystal structures during ammonia ab-/desorption [169,170], as these may lead to large stresses on the storage containers.

Ammine metal borohydrides

One recently-explored alternative to metal halide ammoniates are ammine metal borohydrides. More than 45 ammonia metal borohydrides have been synthesised and characterised in the past few years and they represent a range of different structure types [171,172]. Metal borohydrides, which themselves have been extensively investigated as hydrogen storage materials [6,8,172] often form 3D framework structures where BH_4^- complexes bridge two metal atoms by edge sharing (η^2), e.g. the structures of magnesium, calcium, strontium, manganese and yttrium borohydride where the metals form tetrahedra, $[\text{M}(\text{BH}_4)_4]$, or octahedra, $[\text{M}(\text{BH}_4)_6]$ [173]. Introduction of NH_3

molecules interrupts these frameworks; the ammine yttrium borohydrides, $Y(BH_4)_3 \cdot nNH_3$ are an illustrative example [174]. With one ammonia molecule in the formula unit, $n = 1$, the structure consists of two-dimensional layers, while with $n = 2$, the structure is chain-like, 1D. With $n = 4$ and 5 the structure is built from neutral molecular complexes, and with $n = 6$ and 7 from complex cations, $[Y(NH_3)_n]^{3+}$ with BH_4^- complexes as counter ion in the solids [174].

In these compounds the BH_4^- complex contributes significantly to the structural diversity of ammine metal borohydrides. The BH_4^- tetrahedra coordinate to a metal in a flexible manner with a range of $M - B$ distances and varying hapticities from η^0 to η^3 , i.e. BH_4^- can be either terminal or bridging ligand or act as a counter ion in the solid state [171,173]. This contrasts the ammonia molecule that coordinates more strongly with less flexibility, always via the electron pair donated by nitrogen, and acts as a terminal ligand [172].

Comparison of ammine metal borohydrides and ammine metal halides. Structural analogies between ammine metal borohydrides and chlorides/bromides exist, considering only heavier atoms, i.e. neglecting hydrogen atoms. For example, $M(BH_4)_2 \cdot 6NH_3$ ($M = Mg, Mn$ and Ca) and $MgX_2 \cdot 6NH_3$ ($X = Cl$ and Br) are isostructural [175,176], and $Sr(BH_4)_2 \cdot 2NH_3$ and $MCl_2 \cdot 2NH_3$ ($M = Ca$ and Sr) are structurally similar [177]. The borohydride complex, BH_4^- , is a non-spherical anion in contrast to the halide anions; therefore crystal structures of ammine metal borohydrides often have lower symmetry than their halide analogues, as usually observed when comparing metal borohydrides and metal halides [171]. The structural similarities are most pronounced for compounds with higher number of coordinated ammonia molecules (n), where both BH_4^- and the halides X^- , anions act as counter ions in the solid-state with a predominantly ionic bonding, η^0 . Significant structural differences of $MgX_2 \cdot nNH_3$, $X = BH_4^-$ or halides, are observed for smaller number of NH_3 ligands (low n) due to the presence of di-hydrogen bonds and the non-spherical shape of BH_4^- .

Despite minor differences, the thermal stability for ammine metal borohydrides and chlorides are similar when comparing the peak temperature of NH_3 release, e.g. $Y(BH_4)_3 \cdot 7NH_3$ ($\sim 80^\circ C$) and $YCl_3 \cdot 7NH_3$ ($\sim 100^\circ C$), and $Mg(BH_4)_2 \cdot 6NH_3$ and $MgCl_2 \cdot 6NH_3$ have similar stability ($\sim 150^\circ C$), whereas $Mn(BH_4)_2 \cdot 6NH_3$ ($\sim 130^\circ C$) is slightly more stable than $MnCl_2 \cdot 6NH_3$ ($\sim 105^\circ C$).

Di-hydrogen bonds in the structures. All ammine metal borohydride structures contain di-hydrogen $H^{\delta-} \dots H^{\delta+}$ contacts between partly positively charged hydrogen, $H^{\delta+}$ bonded to N in NH_3 and partly negatively charged hydrogen, $H^{\delta-}$ bonded to B in BH_4^- . For $Y(BH_4)_3 \cdot nNH_3$ and $Sr(BH_4)_2 \cdot 4NH_3$ the shortest di-hydrogen contacts are in the range 1.850–2.035 Å and are intermolecular, either connecting layers, chains, molecular clusters or connecting complex ions, while it is intramolecular for $Sr(BH_4)_2 \cdot nNH_3$ ($n = 1$ and 2) within a 2D layer [174,177]. In comparison, the intramolecular hydrogen contacts between $H^{\delta-} \dots H^{\delta-}$ in a BH_4^- complexes and $H^{\delta+} \dots H^{\delta+}$ in NH_3 molecules are ~ 2.00 Å and 1.63 Å, respectively, while the shortest di-hydrogen contact in NH_3BH_3 is 2.02 Å.

Trends in thermal decomposition. The thermal decomposition of a large number of ammine metal borohydrides has been investigated and revealed that ammonia absorption results in the destabilization of metal borohydrides with low electronegativity metals ($\chi_p < 1.6$), while metal borohydrides with high electronegativity metals ($\chi_p > 1.6$) are stabilized by NH_3 . The stabilization is possibly due to shielding of metals with high electronegativity by complex formation.

A characteristic of the ammine metal borohydrides which does not occur for metal halides is the potential for gas release either as hydrogen or ammonia. Tailoring which gas is released could be useful in employing ammine metal borohydrides in particular applications, especially as ammonia must often be decomposed before use. The mechanism for decomposition of ammine metal borohydrides remains not fully understood. Strong di-hydrogen bonds have been hypothesised to cause H_2 elimination in the solid-state. However, detailed analysis of experimental data disagree with this hypothesis. For example, ammonia release is observed for $Y(BH_4)_3 \cdot nNH_3$ ($n = 7$ and 6), which has the strongest di-hydrogen bonds (~ 1.85 Å) among the series of compounds, $Y(BH_4)_3 \cdot nNH_3$ ($n = 7, 6, 5, 4, 2$ and 1) [174]. Similarly, $NaBH_4 \cdot 2H_2O$ does not directly release H_2 , but decomposes into $NaBH_4$ dissolved in the crystal water, despite the presence of strong di-hydrogen bonds (1.77–1.95 Å) [178].

The NH_3/BH_4^- ratio (n/m) has also been suggested as an important factor in determining the composition of the released gas. The ratio (n/m) has been adjusted for the series of $M(BH_4)_m \cdot nNH_3$ ($M = Mg, Mn$ and Y), leading to increased H_2 content for lower n/m ratios. However, despite low n/m ratios, $LiBH_4 \cdot NH_3$, $Ca(BH_4)_2 \cdot NH_3$ and $Sr(BH_4)_2 \cdot NH_3$ release NH_3 , and not H_2 .

Alternatively, two other factors have also been suggested that the composition of the released gasses [177]:

(i) The stability of the metal borohydride (Fig. 8). Ammine metal borohydrides of relatively stable metal borohydrides ($\chi_p < \sim 1.0$), e.g. $LiBH_4 \cdot NH_3$, $Ca(BH_4)_2 \cdot nNH_3$ and $Sr(BH_4)_2 \cdot nNH_3$ [177], release NH_3 (with no H_2) by thermolysis in open systems and/or in a flow of an inert gas, i.e. $p(NH_3) \sim 0$, even when the NH_3/BH_4^- ratios (n/m) are low, ≤ 1 . This may be due to the significantly higher thermal stability of the respective metal borohydrides [177].

Ammine metal borohydrides of less stable metal borohydrides, Al , Zn , or Zr release NH_3/H_2 gas mixtures, which may be due to the lower decomposition temperature of the respective metal borohydrides. Thus, the less stable metal borohydrides react with NH_3 upon decomposition and release H_2 (and in some cases also some NH_3). As an example, $Al(BH_4)_3 \cdot 6NH_3$ releases H_2 and small amount of NH_3 at $\sim 165^\circ C$, and $Al(BH_4)_3$ decompose at significantly lower temperatures, $T_{dec}(Al(BH_4)_3) \sim 25^\circ C$ [10]. $Zn(BH_4)_2 \cdot 2NH_3$ releases 8.9 wt% H_2 at $T < 115^\circ C$ in contrast to $LiZn_2(BH_4)_5$, which releases a mixture of diborane and hydrogen via reduction of Zn^{2+} to Zn [179,180].

(ii) The partial pressure of ammonia during decomposition. In a closed system, the partial pressure of ammonia is increasing upon ammonia release, $p(NH_3) > 0$. Then, $LiBH_4 \cdot NH_3$, $Ca(BH_4)_2 \cdot nNH_3$ and $Sr(BH_4)_2 \cdot nNH_3$ first release some ammonia but release hydrogen exothermically at higher

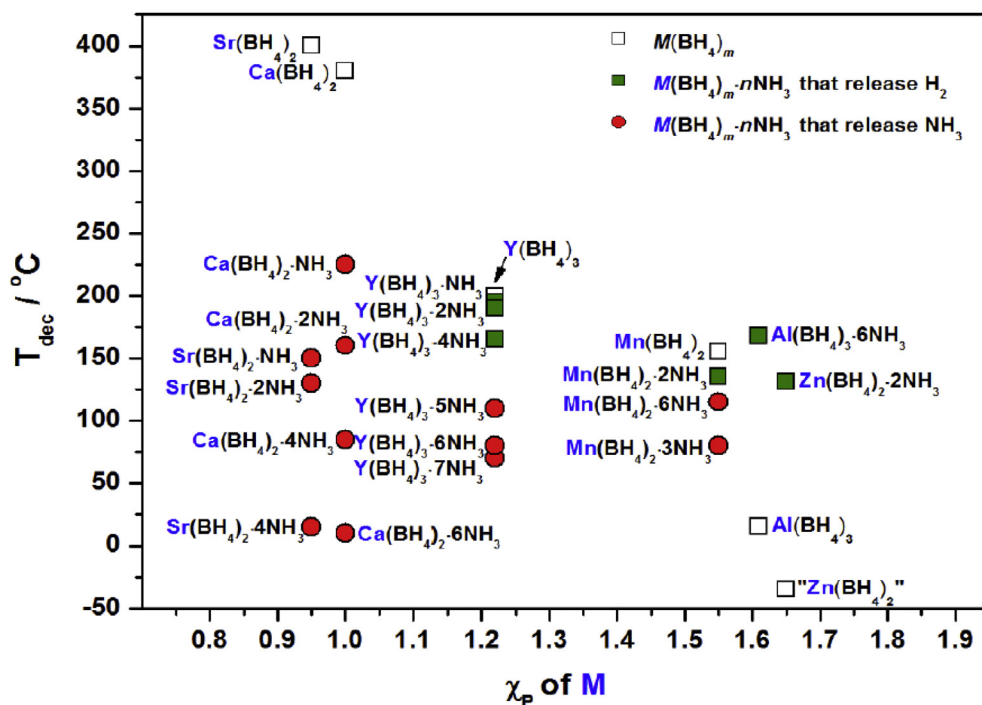


Fig. 8 – Decomposition temperatures, T_{dec} , for selected ammine metal borohydrides and the corresponding metal borohydrides. $\text{Zn}(\text{BH}_4)_2$ is not experimentally observed and is considered unstable. Reprinted with permission from [177]. Copyright 2015 Wiley-VCH.

temperatures, possibly via a solid-gas hydrogen elimination reaction between solid metal borohydrides and ammonia gas. Thus, when the ammonia release temperature of ammine metal borohydrides is significantly lower than the decomposition temperature of the corresponding metal borohydride, then initially ammonia is released, which react with the metal borohydride at higher temperatures via solid-gas reactions, when confined in a closed systems [177].

Using these characteristics governing the desorbed gas composition from ammine metal borohydrides as design rules may help develop systems with tailored gas compositions, generating the various levels of ammonia decomposition needed for different applications (Fig. 4).

Sorbent and membrane approaches to ammonia removal

Ammonia has been demonstrated to be irreversibly damaging to PEM fuel cells at low-ppm concentration levels [181,182]. While advances in ammonia decomposition catalysts will significantly assist in producing high-purity ammonia, reaching the <0.1 ppm benchmark for PEM fuel cells is beyond the thermodynamic limit for temperatures less than 725 °C, as shown in Fig. 9. Ammonia emissions must also be avoided even in the case of ammonia-tolerant power generation systems (e.g. alkaline fuel cells [183]) because of the toxicity of ammonia. As such, if ammonia is to be used as a hydrogen carrier, approaches to remove residual ammonia from the hydrogen gas stream are required.

Sorbent materials have been proposed as a means to achieve ultra-low concentrations of ammonia in dynamic hydrogen gas streams. Recently, lithium exchange type X zeolite was used in a flow of simulated cracked ammonia

(1000 ppm inlet concentration) to give 0.01–0.02 ppm ammonia in the purified hydrogen/nitrogen stream, up to a maximum storage capacity of 5.7 wt% [185]. Similar studies have also been reported for a number of metal halide sorbent systems, reaching storage capacities in excess of 10 wt% [186].

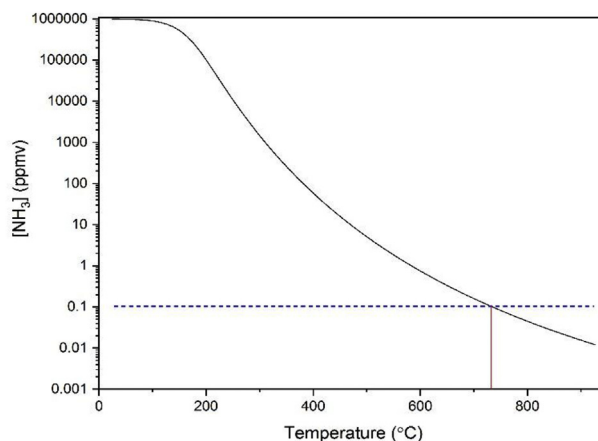


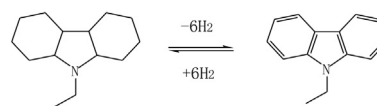
Fig. 9 – Variable-temperature equilibrium ammonia concentration at 0.1 MPa. The acceptable level for PEM fuel cells is shown as a dashed blue line, with the corresponding equilibrium temperature indicated with a red line. Thermodynamic data calculated from variable-temperature heat capacity data from Ref. [184]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Sorbent-based approaches such as these would function on the use of a cartridge of sorbent which could be regenerated by the application of heat to drive off the adsorbed ammonia.

There have also been recent advances in the use of membranes to purify hydrogen from cracked ammonia. A recently developed layered palladium-vanadium membrane offers significant cost benefit over pure palladium membranes [187,188]; while fragile membranes may not yet be suitable for on-board hydrogen purification, they are strong candidates for use in the production of pure hydrogen from cracked ammonia at the forecourt or in centralised facilities. A key advantage of membrane-based approaches is the simultaneous removal of nitrogen from the gas stream, avoiding the need for the use of pressure-swing adsorption or other secondary purification techniques.

Reversible liquid organic hydrogen carriers (LOHCs)

In the present review, formic acid and methanol as organic hydrogen carriers are not included. Therefore, in the LOHCs part, we only discuss cycloalkanes and their derivatives, such as N-heterocycles, substituted alkanes and fused ring compounds etc. LOHCs with hydrogen content of ~5–8 wt%, reversibility, moderate dehydrogenation temperature, commercial availability, production of CO_x-free hydrogen and more importantly, the compatibility with existing gasoline infrastructure, hold the promises as hydrogen carriers for both onboard application and large-scale, long-distance H₂ transportation [41,189–191]. However, the cycloalkanes, such as cyclohexane, methylcyclohexane and decalin, usually suffer from their high dehydrogenation enthalpy changes, requiring high dehydrogenation temperature [192]. Therefore, the development of new materials with favorable dehydrogenation enthalpy change (ΔH_d) is needed. On the other hand, kinetic barriers exist in both dehydrogenation and hydrogenation processes, which need optimization on catalysts. Therefore, the recent advances in these two aspects (thermodynamic and kinetic optimizations) will be summarized and discussed in the present review.



Scheme 1 – Dehydrogenation and hydrogenation of 12H-NEC and NEC pair.

Thermodynamic optimization

Early research on liquid organic hydrides for hydrogen storage focused on cyclohexane-benzene pair, methylcyclohexane-toluene pair, and decalin-naphthalene pair [192]. However, the dehydrogenation of these cycloalkanes occurs at relatively high temperature (usually higher than 300 °C) due to their high dehydrogenation enthalpy changes. Taking methylcyclohexane as an example, the calculated dehydrogenation enthalpy change is around 73.6 kJ mol⁻¹ H₂, leading to a dehydrogenation temperature of ca. 326 °C [193]. The strategies for optimization of ΔH_d from literature, including fused ring compound, heteroatom replacement and electron-donating substitution, are summarized in Fig. 10. It is shown that the decalin-naphthalene pair exhibits lower enthalpy change during dehydrogenation, hinting that the fused ring strategy is an optional method to optimize the thermodynamic properties [41]. Pez. et al. from Air Products and Chemicals company had predicted theoretically and demonstrated experimentally in their patent that fused ring compounds possess lower dehydrogenation enthalpy changes [194], in which the hydrogen storage properties of several fused ring compounds including pyrene, coronene and hexabenzocoronene were tested, showing superb reversible hydrogen storage properties compared with that of mono-ring counterpart (benzene-cyclohexane pair).

In the following patent from Air Products and Chemicals [190], it was demonstrated that better reversible hydrogen storage properties can be obtained by using heteroatoms (such as N, O, P, or B etc.) substituted hydrocarbons. Particularly, the dehydrogenation enthalpy changes are effectively enhanced in the N-heterocycles (Fig. 10), among which the N-ethylcarbazole (NEC) and dodecahydro-N-ethylcarbazole

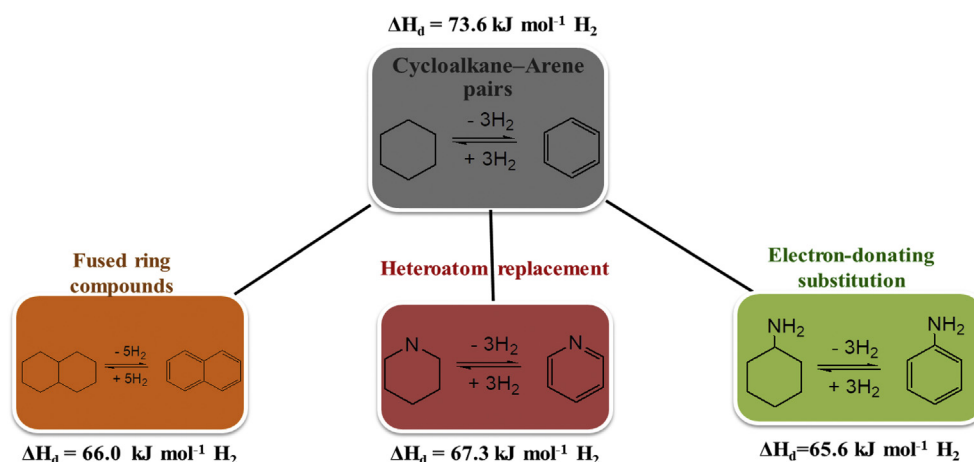


Fig. 10 – Strategies for optimization of dehydrogenation enthalpy change of cycloalkane in the literature.

(12H-NEC) pair with ΔH_d of $50.6 \text{ kJ mol}^{-1} \text{ H}_2$ exhibits superior reversible de/hydrogenation properties as shown in Scheme 1. 12H-NEC is liquid at room temperature and has a theoretical material gravimetric capacity of 5.8 wt%, exhibiting a potential candidate for liquid phase hydrogen storage application. As such, much attention has been given to the reversible NEC and 12H-NEC pair, especially in catalyst development which will be introduced in the following sections. Independently, Clot, Eisenstein and Crabtree et al. calculated the thermodynamic data and theoretical dehydrogenation temperature under 1 bar hydrogen of a series of N-heterocycles and found that the dehydrogenation enthalpy change can be effectively reduced by incorporation of N atoms into the rings [193], which may be due to that the N substituents can weaken α -CH bond in a saturated species. Actually, *in situ* XPS and *in situ* FTIR studies on the dehydrogenation of 12H-NEC indicated that the dehydrogenation started from the five-membered ring by weakening the C–H bond adjacent to N atom on Pd- and Pt-based model catalysts [195–197].

The calculation from Crabtree et al. also revealed that the substituted N outside the ring can be even more effective than a ring N in lowering ΔH_d through comparison of benzene-cyclohexane ($\Delta H_d = 17.6 \text{ kcal mol}^{-1} \text{ H}_2$), pyridine-piperidine ($\Delta H_d = 16.1 \text{ kcal mol}^{-1} \text{ H}_2$) and aniline-cyclohexylamine ($\Delta H_d = 15.7 \text{ kcal mol}^{-1} \text{ H}_2$) [193], which means the addition of electron donating groups would lower the temperature at which hydrogen can be easily released. Jessop and coworkers found a correlation between the dehydrogenation enthalpy of cycloalkane and Hammett parameter (σ) of substitute group as shown in Fig. 11 [198]. The Hammett parameter reflects electron donating ability of substitute group. Their work showed a linear correlation, i.e., the lower the Hammett parameter (or the more electron-donating substituent) the lower dehydrogenation enthalpy. Therefore, the electron-donating strategy would be a promising way to optimize the thermodynamic properties. However, the substituents outside the ring would have the chance to detach from the parent substance under harsh condition during dehydrogenation [198].

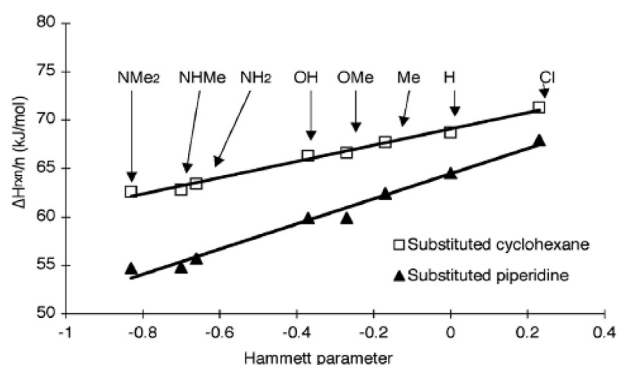


Fig. 11 – Calculated dehydrogenation enthalpies ($\Delta H_{\text{rxn}}/n$) of mono-substituted cyclohexane and para-substituted piperidine derivatives. Reprinted with permission from [198]. Copyright 2008 Royal Society of Chemistry.

Kinetic optimization

Heterogeneous catalysts

Since the N-heterocycles exhibit reduced dehydrogenation enthalpy changes, much attention has been given to these systems, especially on the development of catalysts. Crabtree and coworkers investigated several noble catalysts (Pd, Rh etc.) for the dehydrogenation of indoline and achieved 100% conversion using Pd/C catalyst only after half an hour in refluxing toluene [199]. For the heterogeneous catalyst, support is one of the key factors to the activity and stability. Sánchez-Delgado found that the hydrogenation rate of quinoline increased monotonically with the basicity of the support, i.e., $\text{MgO} < \text{CaO} < \text{SrO}$ [200,201]. Therefore, they proposed mechanism for catalytic hydrogenation, which involved the heterolytic hydrogen splitting and ionic hydrogenation on the metal/basic support interface due to the polarity of $\text{C}=\text{N}$ bond in quinoline [201,202]. By using this heterolytic hydrogen splitting function of the basic support, covalent triazine framework (CTF, a microporous support) supported Pd nanoparticles exhibited an improved activity in the hydrogenation of N-heterocycles in comparison with active carbon support [203]. Recently, Somorjai et al. used dendrimer-stabilized noble metal nanoparticles for the dehydrogenation/hydrogenation of N-heterocycles (tetrahydroquinoline and indoline) and achieved reversible hydrogen release and storage under mild condition, i.e., 130°C and 60°C for dehydrogenation and hydrogenation, respectively, which may be attributed to the basic property of the dendrimer support [204].

Unfortunately, only the N-heterocyclic parts participated in the dehydrogenation/hydrogenation in the above examples, meaning quite low usable hydrogen contents. As mentioned above, NEC and 12H-NEC pair with suitable thermodynamic properties and high hydrogen capacity (5.8 wt%) has drawn tremendous effort in the past decade. Table 2 summarizes the recent development of heterogeneous catalyst for this pair. The reversible NEC and 12H-NEC pair for hydrogen storage was firstly proposed by Air Products [190,194]. From the literature, it was found that Ru is the most active catalyst for hydrogenation [205,206]. Pd, on the other hand, appears to be highly active for dehydrogenation [207–209]. In the Air Products' patents, Ru and Pd on lithium aluminate were employed as hydrogenation and dehydrogenation catalysts, respectively [190], where ca. 5.6 wt% hydrogen can be reversibly stored and released. Smith and coworkers found around 100% conversion at 170°C over 5% Pd/SiO₂ catalyst for 12H-NEC dehydrogenation [205], showing outstanding catalytic capability. However, the partially dehydrogenated intermediates, such as octa- and tetrahydro-N-ethylcarbazole (8H-NEC and 4H-NEC), were found in the products. Similarly, Cheng et al. investigated the reversible hydrogen storage properties of NEC and 12H-NEC pair and found that the full hydrogenation of NEC was realized over a 5% Ru/Al₂O₃ catalyst at 180°C and 8.0 MPa hydrogen [210]. However, the dehydrogenation underwent a three stage process with a 5%Pd/Al₂O₃ catalyst, i.e., from 12H-NEC to 8H-NEC to 4H-NEC and further to NEC with the initial reaction temperatures of 128°C , 145°C , and 178°C , respectively. Smith and coworkers found the dehydrogenation activity and selectivity

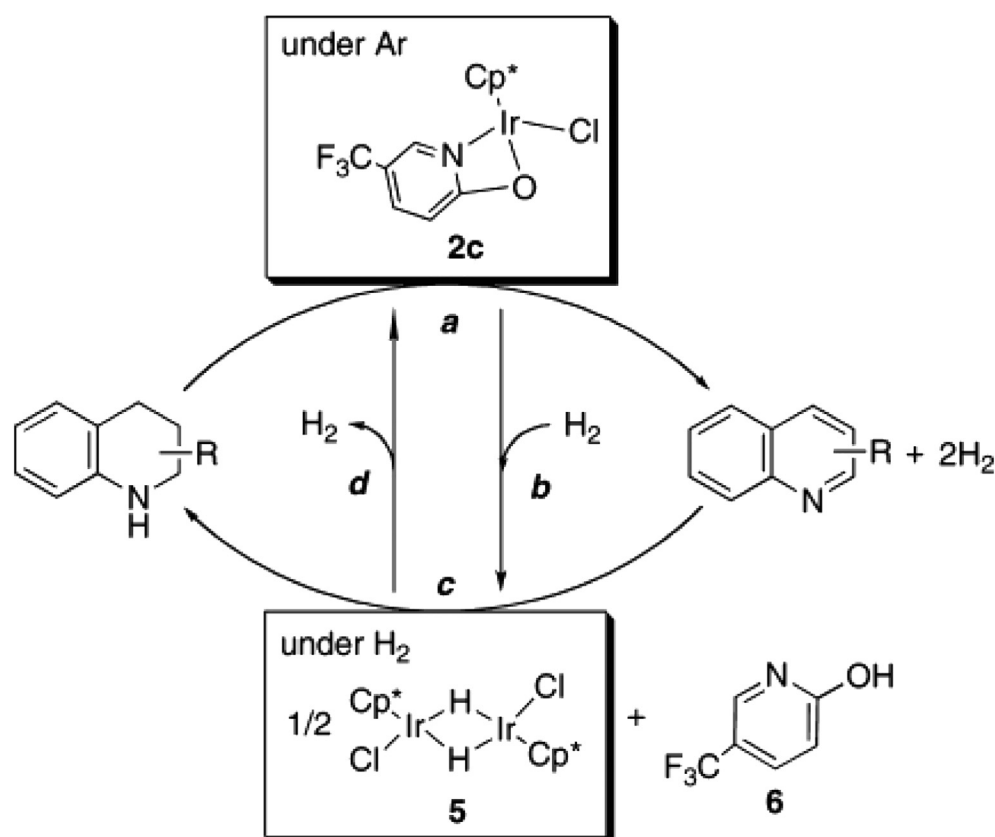
Table 2 – Heterogeneous catalysts for dehydrogenation/hydrogenation of NEC and 12H-NEC pair.

Catalysts	De/hydrogenation	Temperature /pressure	Products	Solvents	Refs.
5%Ru/lithium aluminate	Hydrogenation	160 °C/6.9 MPa	12-NEC	–	[190]
4%Pd/lithium aluminate	Dehydrogenation	197 °C/0.1 MPa	NEC	–	[190]
5%Ru/Al ₂ O ₃	Hydrogenation	130–150 °C/7 MPa	>95% 12-NEC	decalin	[205]
5% Pd/SiO ₂	Dehydrogenation	150–170 °C/-	NEC, 4H-NEC, 8H-NEC	decalin	[205]
5% Pd/C	Dehydrogenation	170 °C/-	NEC	decalin	[207]
4%Pd/SiO ₂ (9 nm)	Dehydrogenation	170 °C/-	NEC	decalin	[208,209]
Ru black	Hydrogenation	130 °C/7 MPa	12H-NEC, 8H-NEC, 4H-NEC	cyclohexane	[211]
Pd black	Hydrogenation	130 °C/7 MPa	12H-NEC, 4H-NEC	cyclohexane	[211]
Pt black	Hydrogenation	130 °C/7 MPa	12H-NEC, NEC	cyclohexane	[211]
65%Ni/SiO ₂ –Al ₂ O ₃	Hydrogenation	130 °C/7 MPa	12H-NEC, NEC	cyclohexane	[211]
5%Ru/Al ₂ O ₃	Hydrogenation	130 °C/7 MPa	98% 12H-NEC	molten reaction mixture	[212]
5% Ru/TiO ₂	Hydrogenation	130 °C/7 MPa	12H-NEC, 8H-NEC, 4H-NEC	cyclohexane	[213]
5t% Ru/Al ₂ O ₃	Hydrogenation	130 °C/7 MPa	12H-NEC, 8H-NEC, 4H-NEC	cyclohexane	[213]
Ru black	Hydrogenation	130 °C/7 MPa	12H-NEC, 8H-NEC, 4H-NEC	cyclohexane	[213]
Ru black	Hydrogenation	130 °C/7 MPa	12H-NEC, 8H-NEC, 4H-NEC	1,4-dioxane	[214]
Ru–, Rh–, Pd-based catalysts	Hydrogenation	130 °C/7 MPa	12H-NEC, 8H-NEC, 4H-NEC	cyclohexane	[206]
5%Ru/Al ₂ O ₃	Hydrogenation	180 °C/8 MPa	12H-NEC,	–	[210]
5%Pd/Al ₂ O ₃	Dehydrogenation	128 °C,145 °C,178 °C/-	8H-NEC, 4H-NEC, NEC	–	[210]

were strongly dependent upon the Pd size, i.e., the maxima in both activity and selectivity were obtained over a Pd/SiO₂ catalyst with an average particle size of 9 nm [208,209]. Although Ru catalyst showed the best activity for the hydrogenation of NEC, it suffered from lower selectivity to the desired product. Rh-based catalysts, on the other hand, exhibit a higher selectivity to 12H-NEC under comparable conditions [206].

Homogeneous catalysts

Catalytic dehydrogenation of 12H-NEC was also reported using homogeneous catalysts. In 2009, Jensen and coworkers found that an Ir-PCP pincer complex was an efficient catalyst for the dehydrogenation of 12H-NEC at 200 °C [215]. Meanwhile, they found that this Ir-based homogeneous catalyst was also active for the other organic hydrogen carriers, including perhydrodibenzofuran, perhydroindole, N-methyl perhydroindole,

**Fig. 12 – Over processes for the reversible catalytic dehydrogenation/hydrogenation of 2-MeTHQ.**

etc. [216] Fujita and Yamaguchi also developed a Cp^*Ir complex homogeneous catalyst bearing a 2-pyridonate ligand ($\text{Cp}^* = \text{pentamethylcyclopentadienyl}$) exhibited excellent activity in the reversible dehydrogenation/hydrogenation of 2-methyl-1, 2, 3, 4-tetrahydroquinoline (2Me-THQ) [217]. The author proposed a dehydrogenation/hydrogenation mechanism according to their experiment (Fig. 12). Under hydrogen pressure, the catalyst would convert to a hydride-bridged dinuclear Cp^*Ir complex (5 in Figure 12) that may catalyze the hydrogenation reaction by transfer hydrides to quinoline. However, the hydride would be liberated from the hydride-bridged dinuclear Cp^*Ir complex under Ar, forming 2c in Fig. 12, which would have the ability to catalyze the dehydrogenation of 2Me-THQ. However, only the N-heterocyclic part of the bicyclic quinoline system participates in both transformations and, consequently, the hydrogen gravimetric capacity of this system is quite low. Therefore, in the following investigation, they achieved efficient homogeneous perdehydrogenation of 2,6-dimethyldecahydro-1,5-naphthyridine with release and uptake of five molecules of H_2 catalyzed by Cp^*Ir complexes bearing functional bipyridonate ligands as a single precatalyst, which increased the hydrogen capacity dramatically [218]. Xiao and coworkers also reported a versatile cyclometalated $[\text{Cp}^*\text{Ir}^{\text{III}}]/\text{imino}$ complex for acceptorless dehydrogenation of N-heterocycles [219,220].

Despite the recent progress with Ir-based catalysts [215,217–221], the development of low-cost, non-noble metal catalyst for the dehydrogenation or hydrogenation of N-heterocycles is highly desirable. Jones and coworkers synthesised a $(^{\text{tPr}}\text{PNP})\text{Fe}(\text{CO})(\text{H})$ bifunctional catalyst ($^{\text{tPr}}\text{PNP} = ^{\text{tPr}}\text{PCH}_2\text{C}_6\text{H}_4\text{NCH}_2\text{CH}_2\text{P}^{\text{tPr}}_2$), which exhibited excellent performance in both dehydrogenation and hydrogenation of N-heterocycles [222]. Theoretical analyses on this Fe catalyst showed that the dehydrogenation mechanism of saturated N-heterocyclic substrates was highly dependent on the polarity of the C–N bond, i.e., the relatively unpolarized C–N bonds are dehydrogenated through a concerted proton/hydride transfer, whereas, the polarized C–N bonds entail stepwise (proton then hydride) bifunctional dehydrogenation [222,223]. Beside this Fe-based catalyst, Co- [224] and Ni-based [225] non-noble homogeneous catalysts were also reported by Jones' group and Crabtree's groups, respectively. Usually, these homogeneous catalysts require more than 20 h reaction time at high temperature. Li and coworker achieved acceptorless dehydrogenation of a series of N-heterocycles at ambient temperature by merging visible-light photoredox catalysis [226], where $\text{Co}(\text{dmgH})_2\text{Cl}_2$ and $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ were employed as catalyst and photosensitizer, respectively. In spite of advances were reported recently, the stability and reusability are main issues for the homogeneous catalysts, which needs further investigation in the future.

Conclusions and future opportunities

Hydrogen is likely to play a key role alongside electrification in decarbonising global energy systems. The high volumetric hydrogen density and ease of storage and transportation make liquid hydrogen-containing carriers attractive for reducing the infrastructure burden of implementing

hydrogen-based energy storage. Key opportunities exist already for the use of liquid carriers in facilitating hydrogen trade and inter-seasonal energy storage, with possible extensions towards on-board hydrogen storage for transportation. While much of the required technology to implement these carriers exists already, there are a number of areas where further improvements can be made. Designing lower cost, highly active catalysts which enable high round-trip efficiencies and dehydrogenation at moderate temperatures will always improve the economic viability of energy storage. There are particular opportunities to develop new catalysts which can integrate directly with intermittent renewable electricity generation. Therefore, continuing work in the development of electrocatalysts and catalysts which can operate under more moderate and variable reaction conditions, as well as thermochemical cycles for liquid carrier production, will be central to broadening the application liquid hydrogen carriers.

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Author contributions

All authors contributed to the design of the manuscript and commented on draft versions. JWM and WIFD coordinated the planning and writing of the manuscript. JWM and WIFD wrote section [Introduction](#). JWM wrote sections [Ammonia](#), [Metal amide/imide catalysts](#), and [Sorbent and membrane approaches to ammonia removal](#); TH and PC wrote section [Reversible liquid organic hydrogen carriers \(LOHCs\)](#); CW wrote section [Transition metal catalysts](#); PEDJ, FC and PN wrote section [Thermal ammonia production](#); TJ wrote section [Ammine metal borohydrides](#); TV wrote sections [Electrochemical ammonia production](#) and [Metal halide amines](#); YK contributed to section [Sorbent and membrane approaches to ammonia removal](#).

Appendix A. Supplementary data

The research materials supporting this publication can be accessed by contacting the relevant author/s for each of the papers cited in this review.

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.ijhydene.2019.01.144>.

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