

Ammonia as a Carbon-Free Energy Carrier: NH₃ Cracking to H₂

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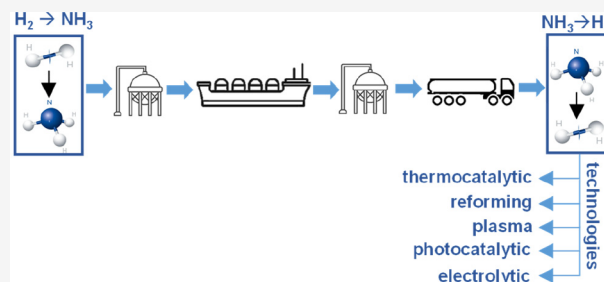
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ABSTRACT: In the energy transition from fossil fuels to renewables, hydrogen is a realistic alternative to achieving the decarbonization target. However, its chemical and physical properties make its storage and transport expensive. To ensure the cost-effective H₂ usage as an energy vector, other chemicals are getting attention as H₂ carriers. Among them, ammonia is the most promising candidate. The value chain of NH₃ as a H₂ carrier, considering the long-distance ship transport, includes NH₃ synthesis and storage at the loading terminal, NH₃ storage at the unloading terminal, and its cracking to release H₂. NH₃ synthesis and cracking are the cost drivers of the value chain. Also, the NH₃ cracking at large scale is not a mature technology, and a significant effort has to be made in intensifying the process as much as possible. In this respect, this work reviews the available technologies for NH₃ cracking, critically analyzing them in view of the scale up to the industrial level.



1. INTRODUCTION

In the energy transition era from fossil fuels to renewables, a radical change is happening in the energy system to achieve the decarbonisation target. In this framework, hydrogen plays a leading role as an energy vector for the generation of clean and sustainable energy.^{1,2}

Nowadays, almost all the hydrogen is produced and used on-site in industry, through the catalytic steam reforming of methane, which is a well-established and cost-effective commercial technology for large-scale applications.² Nevertheless, a large amount of CO₂ is emitted during the steam reforming process, both directly and indirectly. The biggest issues related to hydrogen application are its storage and transport. Hydrogen has a very low energy density by volume (between 1 and 2 kWh/L if compressed in the range of 350–700 bar, as reported in Figure 1, which is much less than other fossil-based fuels) and, due to its small molecular size, it tends to diffuse through the materials, causing their embrittlement.

To overcome these problems, other chemicals are to be studied for large-scale efficient and economical H₂ storage and transportation,⁴ usually referred to as hydrogen carriers. Once arriving at the destination, the hydrogen carrier is converted to allow H₂ release and distribution. Among these H₂ carriers, ammonia is one of the most promising candidates. NH₃ has a high hydrogen content (17.8% by weight) and can be liquefied at a reasonable temperature (−33.34 °C) at atmospheric pressure. For this reason, its transport and storage are relatively easy, also taking into account that existing infrastructures can be exploited.⁵

Ammonia is a global commodity, and infrastructures for its storage and transportation already exist worldwide. This

evidence could enable the early accelerated adoption of large-scale application of NH₃ as an energy carrier.³ There are 38 and 88 ammonia import and export ports, respectively, including 6 ports that both export and import ammonia.⁶

Specifically, with regard to storage, two main types of storage tanks are available: isothermal tanks (up to 45000 t) and spherical pressure tanks (1000–2000 t).⁷

On the other hand, for transportation, pipelines or ships can be adopted. The United States has 3060 km of pipeline (from Texas to Iowa) and a pipeline from Russia to Ukraine is 2420 km long, transporting ammonia for use in fertilizer and chemical plants.⁸

Cargo tankers dedicated to ammonia marine transport are also quite common and similar to the ones for LPG products due to the similarities between the two carriers. Research efforts in this area are devoted to enable NH₃ fuelling for these cargos. A network of six Scandinavian companies is expected to start deliveries in 2024–2025.⁹ Fortescue, too, is planning to convert its existing fleet (eight 260 000 t iron ore carriers) to run on green ammonia.⁶

Figure 2 represents the NH₃ value chain as a hydrogen carrier in the case of a long-distance NH₃ transport via ship. First, ammonia must be synthesized cost-effectively at the loading terminal.

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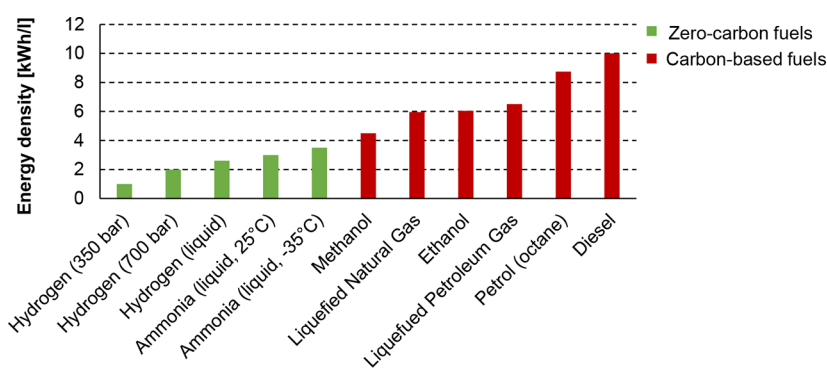


Figure 1. Volumetric energy density of a range of fuel options.³

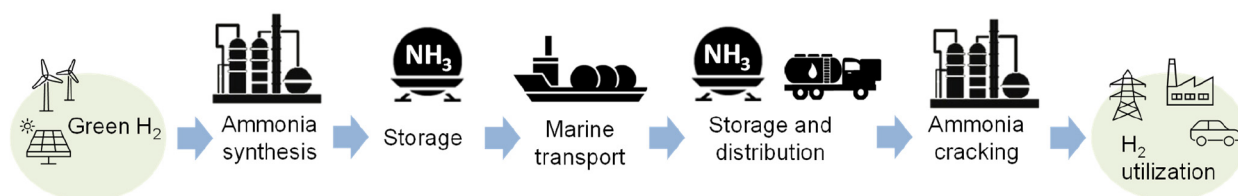


Figure 2. NH₃ value chain as a hydrogen carrier.

Ammonia is an essential global commodity, mainly used for the production of nitrogen-based fertilizers. As one of the building blocks of chemical engineering, it is produced in large-scale industrial plants through the well-known Haber–Bosch process. The Haber–Bosch technology involves the conversion of H₂, produced via steam methane reforming, and N₂ at high temperatures and pressures. As a result of H₂ production from fossil fuels, NH₃ is responsible for causing ~1% of total greenhouse gas emissions, according to the International Renewable Energy Agency (IRENA).¹⁰ A transition to renewable or low-carbon ammonia is therefore essential to bring CO₂ emissions closer to net zero by the midcentury.¹¹ Among the available alternatives, blue ammonia is obtained starting from hydrogen produced by steam reforming of methane with CO₂ capture and storage. On the other hand, green ammonia can also derive from green hydrogen obtained through electrolysis driven by renewable energy. The decarbonization of ammonia production is an integral part of the global transition to net-zero emissions by 2050.

Once produced, ammonia must be stored and then transported via ship, as in the case of Figure 2, or by pipeline, track, or train to the unloading terminal. If a H₂ network is present, NH₃ cracking can be performed at the arriving terminal so that H₂ can be distributed to the end users. Otherwise, NH₃ must be transported to a H₂ hub, where cracking takes place and the produced H₂ can be utilized or further transported to the end users. As can be easily inferred, the cost drivers of the overall ammonia value chain are the NH₃ synthesis and cracking.

As an alternative, ammonia can be considered as an energy vector, being used directly as a fuel, avoiding cracking, or undergoing a partial cracking in order to improve its combustion characteristics. Although slightly beyond the scope of this work, the partial cracking process will be briefly discussed later in this paper, because, in the authors' opinion, it constitutes an interesting alternative.

Nowadays, NH₃ cracking finds industrial application at small scale with capacities from 1 to 1500 kg H₂/day (from 0.2 to 118 t H₂/yr)¹⁰ in the field of metallurgy to ensure the on-site

H₂ production for the bright hardening of metals. In these processes, operated at atmospheric pressure, liquid ammonia is heated up to a temperature of 800–1000 °C and it is then passed over a Ni-based catalyst, which is responsible for its dissociation into H₂ and N₂, with a ratio of H₂/N₂ in the produced gas of ~3:1. Very little ammonia traces in the product mixture can be eventually removed using molecular sieve-based technology.¹²

The process is driven by electric energy: its specific electricity consumption is reported to vary in the range of 2.3–3.125 kWh/Sm³ of gas produced.¹³ The produced gas, known as forming gas, finds applications in furnaces for annealing processes in a reducing atmosphere, such as brazing, sintering, deoxidation, and nitritization. On the other hand, larger ammonia crackers find application in heavy water production process, to be used as a moderator in nuclear reactors.¹⁴ The ammonia is used as an intermediary to produce deuterium in the gaseous phase. Examples of these NH₃ cracking plants can be found in Argentina (cracking capacity of over 1400 t/d) and India (cracking capacity of 800 t/d).⁶

The transition to large-scale hydrogen production will require milder operating conditions and improvement in the energy efficiency of cracking plants.

Recently, in 2020, Siemens et al.¹⁵ have proposed feasibility studies on large-scale ammonia crackers, while large-scale ammonia decomposition plants have been planned in northern Europe for hydrogen production. Proton Ventures BV¹⁶ reports that the consortium of the Transhydrogen Alliance, which includes also the Port of Rotterdam, has planned an ammonia decomposition plant of 3.7 Mt of NH₃ per year for the output of 500 kt H₂ per year (75% ammonia conversion to hydrogen on a mass basis), with a first deadline for the project completion in 2024.

In addition, Uniper¹⁷ announced an ammonia cracker with a hydrogen production of 295 kt per year, corresponding to 10% of the expected H₂ demand in Germany by 2030, at the port of Wilhelmshaven. Again, considering a 75% ammonia conversion to hydrogen on a mass basis, the ammonia feed to the cracker corresponds to 2.2 Mt per year.

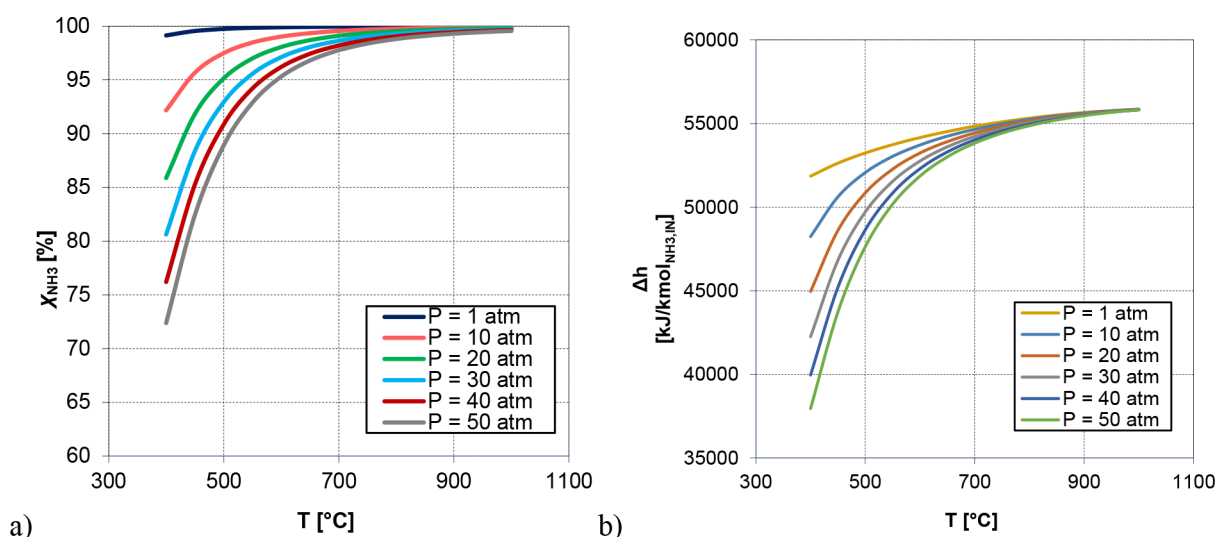


Figure 3. Thermodynamic analysis of NH₃ cracking. (a) NH₃ conversion as a function of temperature and at variable pressure; (b) enthalpy of reaction as a function of temperature and at variable pressure.

Furthermore, Cadent, Equinor, and Northern Gas Networks aim to convert the North of the United Kingdom to hydrogen by 2035 in the framework of the H21 North of England project. In this framework, ammonia is considered as one of the most promising hydrogen carriers.¹⁸

This outlines the potentiality of ammonia for long-term hydrogen supply to the heating market and as interseasonal hydrogen storage method. As a matter of fact, to allow the NH₃ application as an effective H₂ carrier, minimizing the specific H₂ transportation costs, research efforts must be focused at enabling efficient ammonia synthesis and cracking with low associated CO₂ emissions.

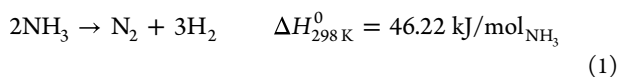
To this aim, in order to identify the weaknesses and discuss the potential of NH₃ application as a H₂ carrier, this Review reports the available technologies to perform H₂ production from NH₃.

Each alternative is critically analyzed in view of the process scale up to the industrial level. Most of the technologies described here are in the early stages of development and quite far from commercialization.

Active and fundamental research is still required to increase the technology readiness levels (TRLs).

2. AMMONIA DECOMPOSITION TECHNOLOGIES

NH₃ decomposition to H₂ is an endothermic process, as reported in reaction 1, that can occur with or without a catalyst.



Reaction 1 is favored at high temperatures and low pressures, considering that it is endothermic and occurs with an increase in the number of moles. The thermodynamic behavior of the reacting system is better shown in Figure 3.

Figure 3a displays the equilibrium ammonia conversion as a function of the temperature and at variable pressures. Values as high as 99.99% are reached at 400 °C and 1 atm. At these temperatures, the dissociation reaction is kinetically limited.¹⁹ The huge reaction heat needed to sustain the process, reported in Figure 3b, as a function of temperature and at variable

pressures, is one of the main concerns about the overall process economics.

When thinking about the application of cracking at a large scale, alternatives must be identified to provide the reaction heat. One possible solution is to burn a suitable fuel gas. However, cracking of ammonia as a H₂ carrier to achieve the decarbonization target does not make sense environmentally if traditional fossil fuels are exploited to cope the reaction endothermicity, as their combustion is associated with a significant amount of CO₂ emissions. For this reason, it is proposed in the literature to burn part of the ammonia entering the process battery limits for the reaction to occur. Despite this solution can help in achieving the decarbonization target, a huge amount of NH₃ is needed as a fuel in the reaction furnace, with the consequent reduction of the net H₂ produced. Basing on the ammonia lower heating value, roughly 20% of the inlet NH₃, together with the 2% of the produced H₂, must be burned. As a result, research efforts in this field are twofold: on the one hand, novel catalysts are studied, possibly as active as Ni-based ones but at lower temperatures, and on the other hand, alternatives for low temperature NH₃ dissociation are being developed, which include the application of plasma, solar energy, or electrolysis for H₂ production. Each of these options is detailed in the following sections.

As a general remark, since the process is thermodynamically favored at low pressures, most of the experimental tests for novel catalytic systems are performed at atmospheric pressure. However, more recently, the effect of operating at higher pressures was also examined, considering that the hydrogen produced must be compressed for its supply. Still considering the reaction thermodynamics, ad-hoc reaction equipment is under evaluation, provided with a selective membrane, to remove H₂ after being generated.¹¹ In this way, the thermodynamic equilibrium for the cracking reaction is pushed to the right, thus allowing an increase in the H₂ yield.

2.1. Thermocatalytic Ammonia Cracking. NH₃ thermocatalytic decomposition occurs at moderate to high temperatures in the presence of a suitable catalyst.

Frequently, these catalysts contain a transition metal as active phase (Ni or Ru) supported on an inorganic oxide and modified by different types of promoters, usually alkaline.¹¹

Haldor Topsøe offers a number of solutions for NH₃ cracking catalysts. Ni-based catalysts are proven to be effective at high temperatures and show a high TRL. On the other hand, Co–Fe based or Fe-based catalysts can work at medium temperatures. Ru-based catalysts offer the advantage of working at low temperatures.²⁰

Nevertheless, the application of a Ru-based catalyst is not economically viable for the process scale up to the industrial level due to the prohibitive costs. As a result, research is devoted to finding the most suitable formulation of non-noble metal catalysts, also in combination with the noble active phase. The active phase, the promoters, and the support are all fundamental for the NH₃ cracking catalysts, the last presenting a high basicity and conductivity, as well as high thermal stability and surface area. Tables 1 and 2 report the list of the most studied catalytic systems in recent research papers, with the aim of offering an effective close-up of thermocatalytic NH₃ cracking. Due to the increasing interest in ammonia decomposition of the last years, many recent publications are available, aimed at reviewing the formulation and activity of NH₃ cracking catalysts. In 2021, Lucentini and colleagues

Table 1. List of the Most Studied Monometallic Catalysts Reported in Literature, Classified According to Their Active Phase^a

active phase	support	loading [wt %]	temp, T [°C]	conversion [-]	ref
Ru	γ-Al ₂ O ₃	0.5–5	350–580	74	27
Ru	K-γ-Al ₂ O ₃	4	350	70	28
Ru	SiO ₂	10	400	14	29
Ru	ZrO ₂	0.5–5	500–550	76–84	30
Ru	Ba-ZrO ₂	3	500	38	31
Ru	MgO	0.8–5	400–450	53–60	30
Ru	K-La ₂ O ₃	4–5	350	70	32
Ru	La ₂ O ₃ –ZrO ₂	3	450	63–81	33
Ru	CeO ₂	7	400	77	34
Ru	Cr ₂ O ₃	5	600	99.9	35
Ru	CNT	0.5–7	400–600	~100	36–38
Ni	γ-Al ₂ O ₃	5–70	450–600	9–93	39–46
Ni	Ce–Al ₂ O ₃	21.7	550	90	45
Ni	SiO ₂ /Al ₂ O ₃	65	450	9–34	47
Ni	ZrO ₂ –Al ₂ O ₃	20	500	42	48, 49
Ni	CeO ₂	10–30	400–600	3–60	40
Ni	La ₂ O ₃	10–30	450–500	12–50	41, 50, 51
Ni	SiO ₂	10	450–550	4–50	47
Ni	ZrO ₂	10–40	450–550	4–31	51
Ni	MgO	6–30	450–650	12–88	43, 52, 53
Ni	CNT	5	500	9–25	30
Fe	γ-Al ₂ O ₃	1–90	580–600	86	54–56
Fe	MgAl ₂ O ₅	4.6	500		57
Fe	SiO ₂		400	61	58–60
Co	Al ₂ O ₃	5–90	500–600	21–100	55, 61, 62
Co	CNT	5–7	450–500	8–61	63–66
Co	MgO	20	400	25	67–72

^aData taken from refs 11,22–24.

Table 2. List of the Most Studied Bimetallic Catalysts Reported in the Literature, Classified According to Their Active Phase^a

active phase	support	loading [wt %]	temp, T [°C]	conversion [-]	ref
Co–Ni	Al ₂ O ₃		650	90	73
Co–Ni	SiO ₂				74
Co–Ni	Ce _{0.6} Zr _{0.3} Y _{0.1} O ₂	1–9	350	10	75
Fe–Ni	Al ₂ O ₃	8 Fe–2 Ni	500	98	73
Co–Mo	Al ₂ O ₃	2.5–5	500–600	60–99.5	76
Ni–Ru	CeO ₂	2.5 Ni–0.5 Ru	450	>99	40
		0.29 Ru	400		
Ru–Fe	Al ₂ O ₃	0.97–3 Ru	400–600	44–97.5	77
La–Ni	Al ₂ O ₃	10	550	92	

^aData taken from refs 11 and 26.

published an extensive work about the state-of-the-art of catalytic systems and their kinetics aspects.¹¹ Rizi and Shin, in 2022,²¹ along with Peters and coauthors (2023),¹⁹ Sun and others, (2022)²² and Lamb and colleagues (2019)²³ have recently reviewed catalysts characterization, activity, and performances. Chen and others (2021) focused on Ru-based catalysts,²⁴ while Bell and Torrente-Murciano (2016) reported the ammonia decomposition using non-noble metal catalysts.²⁵ Bimetallic catalysts for hydrogen production from ammonia have been investigated by Khan and others (2022).²⁶

The reaction mechanism for ammonia cracking is detailed in the following, where the asterisk symbol (*) stands for the catalyst active site.



As a general remark, the rate-determining step (RDS) of NH₃ decomposition is the cleavage of N–H bond for noble metals and the desorption of N₂ for non-noble metals.²² However, it is not easy to draw general statements. The support and promoter also play crucial roles in determining the reaction rate.

The decomposition rate of ammonia can be described as from expression 8, with the reaction orders α and β being, respectively, $\alpha > 0$ and $\beta < 0$.^{22,25}

$$r = k_0 e^{-E_a/RT} P_{\text{NH}_3}^\alpha P_{\text{H}_2}^\beta \quad (8)$$

The range for values of the parameters in eq 8 is summarized in Table 3. Exact values of these parameters must be retrieved from a detailed mechanistic study on the reacting system under consideration.

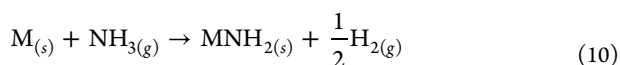
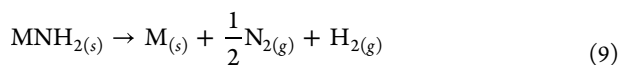
Table 3. Values of Reaction Rate Parameters of eq 8 Reported in the Literature^a

catalyst	E_{app} [kJ/mol]	α	β
Ru-based	75–130	-	-
Ni-based	70–290	0.3÷1	-0.4÷-0.8
Fe-based	90–190	0.5	-0.7
Co-based	110–180	-	-
Co–Ni	54	-	-
Co–Mo	60–110	-	-

^aData taken from refs 11, 25, and 78.

2.1.1. Amide-Imide Catalysts for Ammonia Cracking. As an alternative to the traditional noble metal-based catalysts, alkali-metal amides have been proposed in the literature for the enhancement of NH₃ reaction.⁷⁹ At the beginning of 1900, it was observed that ammonia can be decomposed into N₂ and H₂ in the presence of sodium amide (NaNH₂) upon heating.

In 2014, David et al.⁸⁰ showed that NH₃ dissociation to H₂ can be performed through NaNH₂ in a simple flow reactor. The observed performances were superior to those of Ru-based catalysts at 530 °C. Thus, considering the inexpensive catalytic material, the NaNH₂-based catalysts were seen as promising candidates for NH₃ cracking. Also, in 2015, Makepeace and others performed a mechanistic study to evaluate the reaction mechanism. They confirmed that N₂ formation is not the rate-limiting step and the reaction mechanism can be represented by eqs 9 and 10.⁸¹



Nevertheless, sodium amide has a very low melting point ($T = 210$ °C) such that it cannot be kept in the solid phase at the typical reaction temperature. Following this concept, different amides with a higher melting point have been tested as catalysts to favor ammonia decomposition. Lithium imide melts at 360 °C; the corresponding imide is proven to be even more stable in solid phase, so that it could be easily applied for H₂ production from NH₃.

In 2015, Makepeace and coauthors⁸¹ also showed that nonstoichiometric Li imide is highly active in ammonia decomposition. The hydrogen was produced with superior performance to those observed for Ni- or Ru-based catalysts. Some years later, the same authors deepened the study

synthesizing a series of solid solutions of lithium amide and imide with different compositions, analyzed through X-ray and neutron powder diffraction.⁸² These kinds of Li-based catalytic systems were considered by Zhang and Hu in 2011,⁸³ which focused their research on the analysis of lithium amide and imide with and without an anion promoter. It was found that NH₃ decomposition in the presence of LiNH₂ proceeded via two steps: first, the stable intermediate Li_{1.5}NH_{1.5} is formed, and then Li₂NH is produced, enabling NH₃ cracking to N₂ and H₂. When promoted with Cl⁻, the Li₂NH decomposition temperature was decreased by ~110 °C.

Starting from these systems, research is devoted to finding species with a lower imide formation temperature such that ammonia cracking can be performed under milder conditions. In this respect, several studies are available in the literature: sodium/potassium amide/calcium imide–manganese nitride,^{84–86} ruthenium–magnesium/calcium/barium amide⁸⁷ and potassium/rubidium–manganese amide,⁸⁸ lithium–calcium imide.⁸⁹ These catalytic systems have been reviewed in the work published by Makepeace et al. in 2019.⁹⁰ Among the proposed alternatives, lithium amide/imide seems to be the most active at a moderate temperature. Also, lithium calcium amide decomposition activity was reported to be comparable with the combination amide-imide.

Improved catalytic results can be achieved through a ternary system combining lithium amide and magnesium hydride.

Despite the significant achievement in this area, research efforts must be devoted at pushing the catalyst stability, thus minimizing the losses of the catalytic material and clarifying the reaction mechanism before thinking about the process application at an industrial scale.

2.2. Plasma for Ammonia Cracking. Plasma-driven ammonia cracking is seen as a promising alternative for instantaneous ammonia decomposition, because of high-energy electrons and enough reactive species are produced in a short time scale (less than microseconds).

The moderate gas temperature of the plasma-assisted NH₃ decomposition is one of the technology's most appreciated advantages. On the other hand, low ammonia concentration feedstock, due to the need of a carrier gas (Ar or N₂), and, as a consequence, low H₂ productivity, are the main disadvantages of plasma ammonia decomposition.

In a typical plasma process, the feed gas flows into a discharge reactor, where the discharge electrons are responsible for gas dissociation and products generation. Different types of plasma discharges have been investigated in the literature, which can be roughly classified in thermal plasma,

Table 4. Plasma Methods for Ammonia Decomposition Investigated in the Literature

plasma method type	features	NH ₃ conversion [%]	energy efficiency [mol H ₂ /kWh] ^a	ref
radio frequency discharge, RF	high-frequency (tens to hundreds of MHz) electromagnetic field is applied at low pressures, to make gas molecules ionized, to become highly reactive	>99	2.2	91
dielectric barrier discharge, DBD	high-frequency, high-voltage electrical discharge is applied at low operating temperature (room to a few hundred °C) to a gas confined between two parallel electrodes, at least one of which covered with a dielectric material	>99	6.1	92, 93, 96
microhollow cathode discharge, MCHD	high voltage is applied between the cathode and the anode at low pressures, the anode usually being a metallic rod placed coaxially with the cathode	15–30	1.3	94, 95
nonthermal arc plasma, NTAP	high electric current is passed through a gas at low temperatures, typically below 1000 °C, to ionize the molecules	>99	12.5–16.4	97

^aValues have been taken from the 2014 work by Zhao et al.⁹⁷

warm plasma, and nonthermal plasma, summarized in Table 4. In thermal plasma, the thermal effect on ammonia decomposition is dominant. Thermal plasma systems such as electric arcs or high-pressure radio frequency (RF) discharges provide ammonia dissociation by a high-temperature shift of thermodynamic equilibrium toward product formation.⁹¹ Plasma can be interpreted as a heater in this case, whose main limitations are related to the effective product quenching, to prevent the reverse reactions from occurring, and the energy efficiency of discharge.

These problems can be partially solved by cold plasma. In cold plasma, ammonia is dissociated at modest temperature, exploiting the high-energy electrons, with a consequently low H₂ generation rate. Examples of cold plasma applications include dielectric barrier discharge (DBD)^{92,93} and micro-hollow cathode discharge (MHCD).^{94,95} A DBD reactor was used by Bang and coauthors with the aim of developing a plasma-chemical kinetic mechanism for the NH₃ decomposition.⁹⁶

Warm plasma can maintain a moderate gas temperature for ammonia decomposition, with nonthermal arc plasma (NTAP) as one of the fundamental methods for warm plasma generation. In 2014, Zhao et al.⁹⁷ designed a NTAP reactor using two tube electrodes driven by alternating current. Despite the high energy efficiency of the system (12.5–16.4 mol H₂/kWh), the gas flow rate in the plasma reactor was low, thus causing a low hydrogen production. The same authors discussed strategies to enhance the energy efficiency of ammonia to hydrogen dissociation through plasma. First, the electrodes must be placed in small gaps, and electrode tubes must have a small diameter. Second, the discharge frequency must be decreased as much as possible to enhance both the gas-phase plasma and the electrode-surface catalytic decomposition of NH₃. Third, the reactor must be thermally insulated, such that the electrode temperature increases as much as possible.⁹⁷

A few years later, to exploit the advantages of energy efficiency of nonthermal plasma and to solve the problem of low product rates at the same time, studies of catalysts combining plasma were proposed in the literature, which are discussed in the following section.

2.2.1. Catalysts Combining Plasma. There is a very significant number of studies in the literature dedicated to the study of NH₃ decomposition combining plasma and catalysts.

In 2019, Yi and co-workers⁹⁸ tested four monometallic catalysts (Fe/SiO₂, Co/SiO₂, Ni/SiO₂, and Mo/SiO₂) and four bimetallic catalysts (Fe–Co/SiO₂, Fe–Ni/SiO₂, Ni–Mo/SiO₂, and Co–Mo/SiO₂) with 10 wt % loading for plasma NH₃ decomposition reaction at 460 °C. Co-based catalysts showed higher activity than the Ni- and Fe-based ones. However, the high reaction temperature is one of the drawbacks of the process, which can be overcome through nonthermal plasma. In this perspective, the 2021 work by Lin et al.⁹⁹ proposed a novel NTAP reactor with NiO/Al₂O₃ catalyst. The catalyst was placed at the nozzle exit of the reactor, in order to avoid the interference between catalyst and plasma, as occurred in the 2019 works by Yi et al. and Hayakawa et al.⁹² These authors both evaluated the alternative of DBD plasma with the catalyst placed in the discharge zone. Hayakawa et al.⁹² studied a plasma-membrane reactor leading to high-purity H₂ production, with 10% Ni/Al₂O₃ as a catalyst at 700 °C. Under all

conditions, the maximum energy efficiency was 28.5%, thus far from ensuring an effective scaleup to the industrial level.

Furthermore, this configuration may lead to spark discharge with consequent damage of the plasma reactor itself.

Plasma-catalytic ammonia decomposition in a packed-bed DBD reactor was examined in 2022 by Andersen et al. with various dielectric materials.¹⁰⁰ MgAl₂O₄ with Ni impregnation yielded the highest conversion, but further developments are needed for it to become an energy-efficient technology. Ru/Al₂O₃ and soda glass (SiO₂) catalytic materials at atmospheric pressure and ambient temperature were investigated in a dielectric barrier discharge plasma plate-type reactor by El-Shafie and coauthors.¹⁰¹ They concluded that the SiO₂ material can be utilized as a catalyst, in view of enabling lower costs compared to Ru materials. DBD reactor together with Fe₃O₄ catalysts was also studied by Chen et al. in 2022, who showed that the activity increased with increasing particle size.¹⁰²

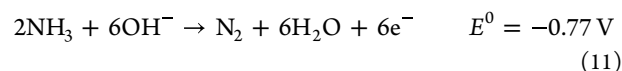
2.3. Electrolysis for Ammonia Cracking. In order to overcome concerns about the energy-effectiveness of hydrogen production, ammonia electrolysis has been proposed. Electrolytic ammonia decomposition has the advantage of generating hydrogen gas at room temperature. The electro-decomposition of ammonia can occur either in aqueous electrolytes, both acidic or alkaline, or nonaqueous electrolytes. The aqueous electrolysis is a pH-sensitive reaction that involves the NH₃ oxidation by OH[−] ions, when performed under alkaline conditions or by oxidants such as HOCl under acidic conditions.¹⁰³ A review on ammonia electro-oxidation reaction focused on the mechanistic understanding of the phenomena and electrocatalysts design has been published by Siddharth et al. in 2018.¹⁰⁴ Kim and colleagues recently reviewed Pt-based electrocatalysts for ammonia oxidation reaction.¹⁰⁵

The main drawbacks of the process are related to the low H₂ density achievable due to the limited NH₃ solubility in the aqueous phase, together with the highly corrosive environment generated because of the contact of NH₃ with the aqueous solution. This last issue can be faced through the nonaqueous electrolysis. All these alternatives are discussed in the following sections.

Critical points to be discussed for the process scale up are the identification of suitable materials active as electrocatalysts, the optimization of the process energy efficiency, and the competition between ammonia and water electrolysis in the same alkaline solution.¹⁰⁶

2.3.1. Aqueous Alkaline Electrolytes. Aqueous alkaline ammonia electrolysis proceeds via reactions 11 and 12 (see Figure 4, for the sake of clarity). At the beginning of the process, ammonia is oxidized to nitrogen at the anode. Water is produced as well as electrons, responsible for water reduction to hydrogen at the cathode. Overall, a low cell voltage of 0.06 (reaction 13) implies that the process is thermodynamically favored, much more than water electrolysis to generate hydrogen, and demonstrates the possible impact of ammonia electrolysis in the present hydrogen economy.¹⁰⁷ Despite the advantages, few studies have considered pure NH₃ electrolysis for H₂ production.¹⁰⁸

anode:



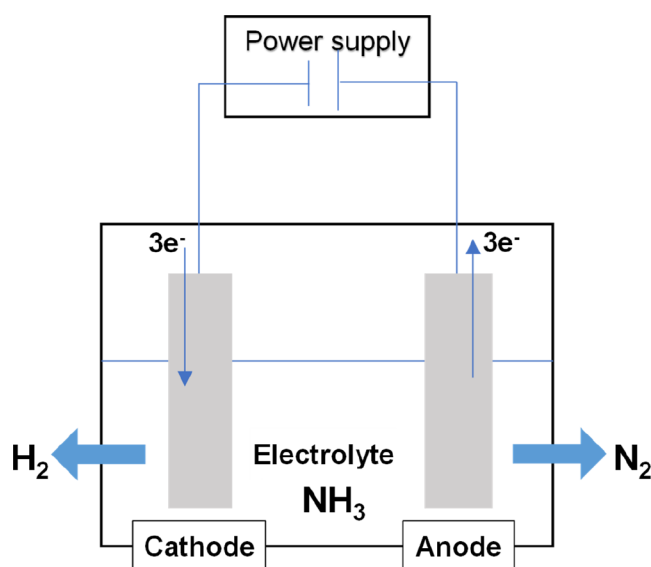
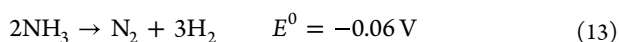


Figure 4. Schematic of the electrolytic cell for H₂ production.

cathode:



overall:



Electrodes play a crucial role in the overall efficiency of the process. In general, the anode is made of a material that can withstand the highly corrosive environment of the electrolyte and the oxidizing conditions needed to break down ammonia. Common anode materials include platinum, iridium, ruthenium, and nickel. On the other hand, the cathode material is typically chosen to promote the reduction of protons to hydrogen gas. Common cathode materials include nickel, stainless steel, and carbon-based materials, such as graphite. The choice of cathode material depends on factors such as cost, durability, and performance.

Extensive research has been carried out to develop electrocatalysts for electrolytic hydrogen through ammonia oxidation reactions (reaction 11) aiming to expedite kinetics and decrease overpotential, most of which are using noble metals like platinum,¹⁰⁹ iridium,¹¹⁰ silver¹¹¹ and ruthenium.¹¹² Pt and Pt-based bimetallics are known to be the most active electrocatalysts for NH₃ electro-oxidation,¹¹³ but they suffer of deactivation because of the adsorption of intermediates and they are too expensive to be applied at large scale. An attempt in improving the performances of traditional Pt-based electrocatalysts was performed by Hanada et al. in 2020.¹¹⁴ In their work, to increase as much as possible the surface area, Pt particles were supported on carbon nanotubes. As a result, the activation overvoltage decreased while the current density increased, leading to a more efficient system, compared to the Pt plate or Pt black electrodes.

In the same year, Sun et al.¹¹⁵ also demonstrated the electrocatalytic performances of Pt nanocubes (Pt-NCs) as electrocatalysts. Foamed Ag₃Cu₂ is claimed to be a low-cost and stable electrocatalyst for both aqueous and liquid ammonia oxidation by Zhang and colleagues.¹¹¹ Despite the encouraging results, still a lot of effort has to be performed to ensure the process application at a different scale from the laboratory one.

Non-noble metal electrocatalysts are based mainly on transition metals (Ni-based,^{116,117} Cu-based,¹¹⁸ or bimetallic Ni–Cu^{119,120}).

Ni foam electrodes, Pt-loaded Ni foam electrodes and Pt–Ir loaded Ni foam electrodes were tested by Jiang and co-workers in 2014.¹⁰⁶ High concentration and temperature of the electrolyte solution enhanced hydrogen production. However, for practical application, the current density must be further increased to allow a lower cell overvoltage.

Zhang and others (2017)¹²¹ proposed a NiCu/C anode catalyst and found that its activity depended on the ratio of Ni and Cu of the catalyst itself. The advantage of this alternative is related to the moderate catalyst cost, compared to the Pt- or Pd-based choices.

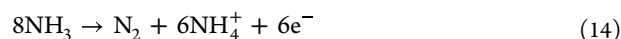
Aqueous alkaline electrolytes have the advantages of high ionic conductivity, due to the high concentration of hydroxide ions, but corrosivity, limited stability, and limited applicability pH range are their main drawbacks, which can be overcome, in part, by nonaqueous ammonia electrolytes.

2.3.2. Nonaqueous Liquid Ammonia Electrolytes. Nonaqueous liquid electrolytes refer to the use of liquid ammonia as the solvent for the electrolyte system, together with an ammonium-based salt, typically an alkali-metal amide such as sodium amide (NaNH₂) or potassium amide (KNH₂).

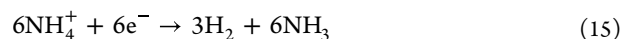
Liquid ammonia has the advantage of dissolving a wide range of salts, leading to high concentrations of mobile ions and a high ionic conductivity. Other key features are high stability and low viscosity. The corrosion issue registered by using aqueous ammonia electrolytes can be solved by the use of liquid ammonia electrolytes. Also, the application of these kinds of electrolytes eliminates the problem of possible subsequent undesired water oxidation and generation of unwanted nitrogen-based byproducts. However, limitations associated with the use of nonaqueous liquid ammonia electrolytes include the need for specialized equipment to handle and store liquid ammonia safely, as well as potential issues with the formation of solid electrolyte interfaces (SEIs) that can limit the performance and durability of the electrolyte.

Nonaqueous liquid ammonia electrolysis proceeds via reactions 14 and 15.¹²²

anode:



cathode:



overall:



Anode catalysts for liquid ammonia electrolysis have been reviewed by Akagi and coauthors in 2022.¹²³

Different kinds of nonaqueous electrolytes have been proposed in the literature, also considering the alternative of ionic liquids and ammonium salts to increase as much as possible the ammonia solubility in liquid phase. In 2010, Hanada and colleagues¹²⁴ used KNH₂ as electrolyte with high current efficiency. The same electrolyte was studied by Dong et al. in 2011.¹²⁵ In both cases, however, results showed a cell voltage that was too high. In 2011, Peng et al.¹²⁶ proposed the organic solvent *N,N*-dimethylformamide (DMF) and acetonitrile as reaction media. In these cases, the Pd presence promoted the NH₃ electrolysis, opposite to the aqueous

electrolysis. Later on, the application of ammonium salts was proposed as effective nonaqueous electrolytes.^{127,128} In the 2022 work of Jiang et al., different Ni-based metal combinations were tested and Ni–Co bimetallic materials were found to exhibit an impressive electrochemical performance if compared to other Ni–X (X = Ce, Fe, Mo) bimetallics in ammonia alkaline electrolytes.¹¹²

Still, the high cell overvoltage hindered the process applicability on a large scale.¹²⁸

2.4. Photocatalysis for Ammonia Cracking. To overcome the high endothermicity of conventional catalytic ammonia cracking, photocatalysis has gained attention because of its potential to promote the NH₃ dissociation reaction at room temperature. The process exploits the photoenergy for production of photoexcited electrons (e⁻) and holes (h⁺), involving the use of a photocatalyst, typically a semiconductor material (see Figure 5, for the sake of clarity).

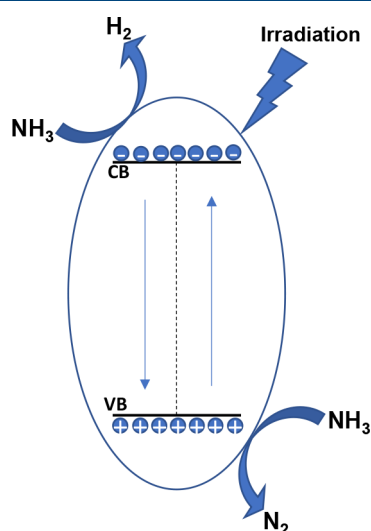


Figure 5. Schematic of photocatalytic ammonia decomposition.

Very few works are available in the literature regarding the photocatalytic decomposition of NH₃ to H₂. Recently, Zhang et al.¹²⁹ reviewed all the heterogeneous nanostructures for the photocatalytic NH₃ decomposition. However, to date, only some metal-loaded titanium oxides are proved to be effective photocatalysts for ammonia conversion.¹³⁰ In 2015, Reli et al.¹³¹ evaluated the photocatalytic activity of TiO₂ and cerium-doped TiO₂ photocatalysts, proving that the Ce ions were responsible for an increase in the catalysts surface area. TiO₂ as photocatalytic material was also studied by Razak and coauthors in 2023,¹³² Chen and colleagues in 2020,¹³³ and Shirashi et al. in 2020.¹³⁴

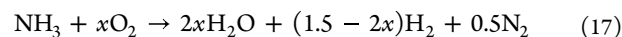
Razak and coauthors proved that Pd/TiO₂ has a high hydrogen production activity from ammonia, while Cu/TiO₂ showed no H₂ production in the investigated time range. In the authors' opinion, this is because Cu has a weaker ability to trap electrons from the conduction band of TiO₂. According to Chen and colleagues, TiO₂, N-TiO₂, and Ag₃PO₄ showed considerable NH₃ conversion in the case of simulated sunlight irradiation, while no activity under visible-light irradiation was observed for anatase TiO₂. They concluded that an effective visible-light-sensitive photocatalyst requires both a suitable band gap for visible-light response and a low-enough valence band edge for NH₃ activation to •NH₂. The approach followed

by Shirashi et al. in 2020 was different: they used TiO₂ as a catalyst, together with Pt and Au in aqueous NH₃ under UV light. A high photocatalytic activity was observed for this alloy catalyst, even if the noble-based metals is never seen as promising for the technology scaleup.

Photoelectrocatalytic processes were studied by Elizabeth et al. in 2020¹³⁵ in the presence of CuO nanoparticles into titania nanotube arrays (TiNTAs). The maximum ammonia removal was achieved at 50.1%, while 235.7 μmol of hydrogen were generated over 120 min under Hg lamp illumination.

NH₃ photocatalytic decomposition suffers from undesired nitrogen oxide production, which is detrimental for the process H₂ yield. Much work has to be done to identify a suitable photocatalyst with good activity and stability, high surface area, and simple synthesis approach.¹³⁰ Also, the photocatalytic efficiency is still too low for practical industrial applications.

2.5. Ammonia Reforming. To provide NH₃ dissociation reaction heat, one possible solution is ammonia reforming. In this case, part of the NH₃ is oxidized to provide the energy needed by the NH₃ decomposition, such that the endothermic NH₃ cracking can be self-sustained through the heat generated in the oxidation phase.¹³⁶ The process proceeds as reported in reaction 17, where *x* is the stoichiometric coefficient of oxygen, which must be lower than 0.75 to ensure H₂ production.



The effective ammonia reforming for H₂ production involves the study of different aspects related to the process operability: the design of a suitable catalyst, the identification of an ad-hoc reactor capable of ensuring a proper heat management, and the exhaust gas treatment and disposal.

Regarding the catalyst, there are many important considerations to take into account in the catalyst design phase: the active phase composition and the support material together with the eventual promoters. As for the thermocatalytic ammonia dissociation, noble-metal-based catalysts are highly effective for the NH₃ reforming. One key aspect in synthesizing the best possible reforming catalysts is to avoid the H₂O adsorption on the active sites, which may compete with NH₃ and O₂, thus hindering the hydrogen production.¹³⁷ In 2017, Nagaoka et al.¹³⁸ successfully demonstrated the application of Ru oxide nanoparticles supported on Al₂O₃ and La₂O₃ for laboratory-scale ammonia reforming. The Ru-based catalytic system was also proved by Matsunaga et al. in 2020,¹³⁹ which considered a Ce_{0.5}Zr_{0.5}O_{2-x} catalyst support. Together with ruthenium, iridium was also selected as a catalyst candidate. However, its main drawback is related, as ruthenium, to its high cost.¹⁴⁰

While catalyst synthesis and formulation are not commonly perceived as a critical issue, the main concerns regarding the process scalability are related to the process heat management. Heat generated in the combustion section must be effectively transferred to the reforming section to enable NH₃ conversion to H₂ and N₂. Kim et al., in 2012,¹⁴¹ adopted a heat recirculating microcombustor configuration already developed for C₃H₈ air mixtures. Various conditions were tested to identify the combination of parameters that ensures the best possible operation. They found that fuel-rich mixtures (equivalence ratio = 1.25) have the advantages of reducing NO_x, but the operation around the stoichiometric ratio still provided acceptable nitrogen oxides production ensuring a satisfactory H₂ productivity at the same time. For the optimized operating condition, the authors reported a H₂

Table 5. Summary of the Analyzed Technologies with Related Pros/Cons^a

technology	TRL	pros	cons	T [°C]	P [bar]	H ₂ yield
Thermocatalytic (Ru-based catalysts)	3–4	<ul style="list-style-type: none"> Most studied active species Highly active even at low temperatures (lowest activation energy) Cheaper than Ru-based catalysts 	<ul style="list-style-type: none"> Very expensive → research efforts devoted to reducing the noble metal loading High GWP, directly proportional to the noble metal scarcity 	400–500	atmospheric	high
Thermocatalytic (Non-Ru-based catalysts)	8–9 (for Ni-based)	<ul style="list-style-type: none"> Ni-based catalysts very mature technology on small scale Good heat resistance and stability 	<ul style="list-style-type: none"> Higher reaction temperature needed than Ru-based catalysts 	>500	atmospheric	high
Amide-imide catalysts	3–4	<ul style="list-style-type: none"> Can favor the low temperature NH₃ decomposition (T < 450 °C) Conversion comparable to Ru-based catalysts 	<ul style="list-style-type: none"> Difficulty to keep the catalyst in solid phase at the reaction condition → loss of catalytic material. This problem can be solved considering a combination of 2 transition metals The catalyst reacts with the support 	<500	atmospheric	high
Reforming	3–4	<ul style="list-style-type: none"> Can sustain the endothermicity of the NH₃ dissociation reaction 	<ul style="list-style-type: none"> Not clear reaction mechanism → effect of the reactor wall DeNO_x system needed for NO_x abatement 	>500	atmospheric	high
Plasma	3–4	<ul style="list-style-type: none"> Room temperature operations in the case of non-thermal plasma High energy efficiency in the case of non-thermal plasma 	<ul style="list-style-type: none"> Proper reactor design necessary to maximize heat transfer High residence time → low gas flow rate Low NH₃ concentration → Ar separation downstream the plasma reactor 	ambient or slightly higher	atmospheric/subatmospheric	low
Catalyst combining plasma (DBD, NTAP)	3–4	<ul style="list-style-type: none"> High energy utilization efficiency → no need of cooling system. Heat is exploited for the catalyst heating 	<ul style="list-style-type: none"> Proper reactor design needed 	ambient or slightly higher	atmospheric/subatmospheric	low
Electrolysis	3	<ul style="list-style-type: none"> Green process → can be driven by renewable energy No direct CO₂ emissions associated Low reaction temperature 	<ul style="list-style-type: none"> Prohibitive cost of ammonia electrocatalysts due to the noble metal nature Electrode's corrosion for aqueous ammonia oxidation → can be solved using non aqueous liquid NH₃ electrolytes Applied current density must be further increased to sustain the low cell voltage and the durability of the electrolytic cell High over potential in the case of non-noble metal catalysts which leads to unwanted side reactions 	ambient	atmospheric	low
Photocatalysis	3	<ul style="list-style-type: none"> High faradaic efficiency with less energy needed than that for water electrolysis Green process → can be driven by solar energy Low temperature (T ambient) No direct CO₂ emissions associated 	<ul style="list-style-type: none"> Most of the available photocatalyst suffer from poor activity, low stability, low surface area, complicated synthesis approach NO_x generated that lower the yield in hydrogen Low NH₃ concentration 	ambient	atmospheric	low

^aThe TRL of the technologies has been defined by the authors considering what has been reported in the literature and by following the NASA guidelines.¹⁶⁴

production rate of 5.4 W (based on the lower heating value of H_2) with an ammonia conversion close to 97% and a NO_x concentration in the exhaust gas of 158 ppm.¹⁴¹ More recently, in 2018, Chiuta and Bessarabov¹⁴² studied an autothermal microreactor for NH_3 decomposition with counter current catalytic plate channels where the NH_3 oxidation occurred. The best operating conditions were proved to be NH_3 flow rate of 0.4 NLPM, fuel gas flow rate of 0.8 NLPM, corresponding to fuel-rich operation. The achieved NH_3 conversion was higher than 99%.

None of the considered alternatives were demonstrated at a scale different from the laboratory one, thus opening issues related to the process scalability, mostly regarding effective heat transfer on a larger scale. In this respect, microchannel reactor technology is supposed to be easily scaled up and convenient for modularized plants.¹⁴³

Nevertheless, the thermal efficiency, which can reach values as high as 98% in the case of limited NH_3 flow rate,¹⁴⁴ must be increased further on a large scale, thus reducing heat losses.

3. FURTHER INSIGHTS INTO AMMONIA CRACKING

Side aspects of ammonia cracking are discussed in the following, in particular, partial cracking (section 3.1) and downstream processes for ammonia purification (section 3.2).

3.1. Partial Cracking for NH_3 as an Energy Vector.

Ammonia has gained attention in recent years not only as a hydrogen vector but also as a fuel itself, due to its zero-carbon nature. However, there are two major limiting issues for the direct use of NH_3 in gas turbine and engine applications: its low combustion intensity¹⁴⁵ (much lower if compared to traditional carbon-based fuels, such as gasoline, diesel, or methane¹⁴⁶), resulting in a low burning velocity, and high associated NO_x emissions.¹⁴⁷

For these reasons, strategies for increasing the combustion intensity are of paramount importance for ammonia application as a fuel. Among them, partial NH_3 cracking leads to a NH_3 - H_2 mixture with very good combustion performances.^{148,149} However, the influence of the cracked gas composition on the combustion process must be understood. In 1967, Verkamp and co-workers proved that the minimum ignition energy, quenching distance, and flame-stability properties of 28% dissociated ammonia were equal to those of methane.¹⁵⁰ This result was confirmed by Valera-Medina and coauthors,^{151,152} according to which it is possible to stabilize ammonia-hydrogen flames with ~30% by volume of H_2 in the fuel blend. Blends with a significantly larger or smaller hydrogen proportion showed increased issues of flashback and blowout, respectively.¹⁵³ Mei and co-workers measured the laminar burning velocity in $NH_3/H_2/N_2$ /air mixtures at variable cracking ratios in the range of 10%–80%. For a cracking ratio of 40%, at atmospheric pressure, the system's behavior was proven to be close to that of methane/air mixtures at the same pressure, indicating that partial fuel cracking strategy can effectively enhance NH_3 combustion.¹⁴⁵

The behavior of the partially cracked NH_3 mixture is different from the NH_3 - H_2 mixture. The presence of N_2 in the cracked gas has a negative impact. The thermal effect of the cracked ammonia has a minor role in enhancing the flame speed, the laminar burning velocity showing a strong pressure dependency.¹⁵⁴ Khateeb and co-workers stated that the presence of nitrogen with a 3:1 $H_2:N_2$ volume ratio does not significantly alter flame stability limits.¹⁵³

Compared with cofiring H_2 , NH_3 partial cracking and the direct use of the produced mixture as a fuel can avoid the hydrogen separation from the cracked H_2 and N_2 , resulting in a cost-effective alternative worthy of consideration.

3.2. Ammonia Purification Section. Once produced, hydrogen must be separated from the unconverted ammonia as well as from the coproduced nitrogen. The most widespread technique for N_2 removal from H_2 is pressure swing adsorption (PSA), which has a claimed efficiency of hydrogen removal of ~80% according to the International Energy Agency G20 hydrogen report. A high degree of purification can be achieved,¹⁵⁵ both for H_2 valley or hydrogen refuelling station application.

As an alternative to pressure swing adsorption, H_2 permeable membranes can be exploited for hydrogen purification. H_2 separation membranes can be distinguished¹⁵⁶ in polymeric membranes (i.e., polysulfones, silicone rubbers, poly(vinyl chloride), natural rubbers, polycarbonates, and polystyrenes,¹⁵⁷ patented in most cases),²³ porous ceramic, and metal (porous and solid). Polymeric membranes suffer from contamination and have limitations in selectivity and permeability. Metal and ceramic membranes have good thermal stability and high H_2 permeability.^{158,159} Palladium-based membranes have been extensively studied because of the Pd catalytic activity for ammonia dissociation. These membranes are costly due to their noble nature. For this reason, various alternatives have been investigated such as Ni alloys,¹⁶⁰ Ni-Nb-Zr,¹⁶¹ ceramics,¹⁶² and porous stainless steel.¹⁶³

Frequently, these membranes are integrated with the reactor to favor the hydrogen separation *in situ*, thus shifting the equilibrium of the cracking reaction toward products. However, in this case, the challenge is to select operating conditions suitable for both hydrogen removal and hydrogen production.

4. CONCLUSIONS AND FUTURE PERSPECTIVES

Ammonia future demand depends on its two distinct utilizations: on the one hand, as a chemical feedstock and, on the other hand, as an energy vector and hydrogen carrier. As a matter of fact, among all the hydrogen vectors, NH_3 has the advantage of requiring the lowest total amount of capital for a fixed H_2 capacity,⁶ enabling hydrogen imports and energy transports at lower costs for long-distance trade.¹⁰ To make trade cost-effective, the cost of producing green hydrogen must be sufficiently less expensive in the exporting region than in the importing region to compensate for the transport cost. This cost differential will become larger as the scale of projects increases, and technology develops to reduce transport costs. This reflects the large impact that ammonia cracking has and the importance of decreasing the costs associated with cracking.⁶

However, unlike the ammonia synthesis, the technology is not as mature. Despite small-scale electrically driven ammonia crackers being already applied commercially in the context of the metallurgic industry, when thinking about the process application to larger scales, a cost-effective technology must be identified. In this respect, this work offers an overview of the available alternatives at the laboratory scale for NH_3 decomposition to H_2 . All of them are summarized in Table S, together with their advantages and disadvantages and their average TRL, assigned according to the NASA guidelines¹⁶⁴ and based on the information reported in the literature.

The traditional thermocatalytic ammonia cracking requires high temperatures and noble catalysts, such that research efforts must be devoted to finding less expensive catalysts possibly active under milder operating conditions. Addition of membranes to the reactor can be a useful approach to push the equilibrium of the reaction to the right, thus favoring H₂ production.

A reliable alternative for ammonia decomposition at lower temperatures consists of amide–imide catalytic systems. However, these kinds of catalysts are not revealed to be very stable. The reaction mechanism still must be understood, and strategies are needed to minimize the loss of the catalytic material. Also reforming of ammonia appears to be scalable for industrial application, if some issues related to the effective heat management will be solved.

Less mature technologies include nonthermal plasma, electrolysis, and photocatalysis for NH₃ decomposition. Among them, photocatalysis is the less ready to be applied at large scale, considering its scale up critical issues, even if it shows the big advantage of exploiting green energy.

Nonthermal plasma systems may have more potential than other NH₃ cracking processes, because of their lower energy consumption and operating temperature. Also, when a catalyst is combined with these kinds of reactors, H₂ production can be effectively increased. Despite the promising achievements, work must be performed to understand whether this equipment can be easily scaled up to the industrial level.

On the other hand, electrolysis offers the non-negligible advantages of performing the reaction at ambient temperatures and possibly exploiting renewable energy. However, the main drawbacks are associated with the prohibitive cost of noble-metal electrocatalysts, together with the energy intensity. The application of less-expensive catalysts leads to high metal overpotentials such that unwanted side reactions such as water oxidation can occur, causing the generation of unwanted products such as nitrates and nitrites. Possible improvements in this respect can be achieved through nonaqueous liquid ammonia electrolysis. In this way, corrosion issues, as well as water oxidation, can be overcome.

In conclusion, much research effort must be performed for NH₃ decomposition to H₂ industrial application. However, considering the NH₃ value chain of Figure 1 and bearing in mind that cracking is one of the cost drivers, together with synthesis, the development of novel technologies for NH₃ cracking should be parallel to the development of technologies for sustainable ammonia synthesis, to make NH₃ truly impactful as a H₂ carrier.

Ammonia production volume is expected to increase by a factor of 3–4 in the near future. The greening of the industrial sector, especially for retrofits of existing ammonia plants, should be the initial focal point. The main barriers to renewable ammonia are the cost of production and the absence of regulations on CO₂ emissions. A CO₂ penalty of ~USD 60–90 per tonne of CO₂ may be required to transition toward low-carbon ammonia.¹⁰

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Notes

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