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Hydrogen Revolution: Advances in Catalytic Ammonia Decomposition

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Abstract

The simple storage of ammonia combined with the tendency to liberate hydrogen without carbon dioxide emissions has made ammonia breakdown popular among the research community in recent years. This review article has discussed the current advances in ammonia breakdown technology for hydrogen generation, focusing on new materials and mechanical designs for catalysis. Moreover, it would help to update the knowledge about the catalytic reaction processes and emphasize the benefits and drawbacks of each strategy. Furthermore, the significance of discovering a cost-effective metal catalyst with better efficiency and higher reliability is also debated. This article may serve as a fundamental resource to scale up information about the catalytic production of hydrogen from ammonia.

Keywords: Ammonia; Hydrogen; Catalysis; Metallic Catalyst; Clean Energy

1. Introduction

In the contemporary world, sustainability and renewable energy are some of the hottest topics for the research community. Researchers and scientists are heavily focused on slowing the rate of climate change by introducing environment-friendly energy sources [1, 2]. Hydrogen (H2) production has drawn much interest and gained a leading position as a source of clean energy due to its extraordinary gravimetric energy density, for industrial applications, auxiliary power units, and zero-emission vehicles[3, 4]. Nevertheless, there are still significant obstacles in making the technology of hydrogen-based products like fuel cells commercially available including energy-intensive H2 storage plus delivery system[5]. Therefore, cheaper, efficient, and sustainable methods for H2 production, transportation and storage remain exceedingly required on an urgent basis[6, 7]. The ammonia cracking reaction, also known as the thermal ammonia (NH3) breakdown process, has emerged as a potentially viable source of clean energy because it contains a high content of hydrogen (17.8%) and it is easy to liquefy at a lower pressure of 8.6 bar and temperature of 20 0C [8-10]. Catalysts with high durability and efficiency are essential for the ammonia decomposition reaction at lower temperatures and full conversion of the NH3 in the gaseous form [11]. Historically, ruthenium (Ru) has been a common metal catalyst for the ammonia decomposition reaction; however, practical uses for Ru are hindered because of its high cost and unavailability [12]. Hydrogen is emerging as a key alternative energy source for transportation, particularly in vehicles. It is also used in stationary applications for both residential and industrial power generation, as well as for storing surplus electricity produced during off-peak times[13]. The primary method used in the current commercial hydrogen generation is catalytic steam methane reforming, a proven and cost-effective technique for producing large amounts of hydrogen. As an alternative, water electrolysis is a very energy-intensive process that produces hydrogen with excellent purity and cleanliness[14].

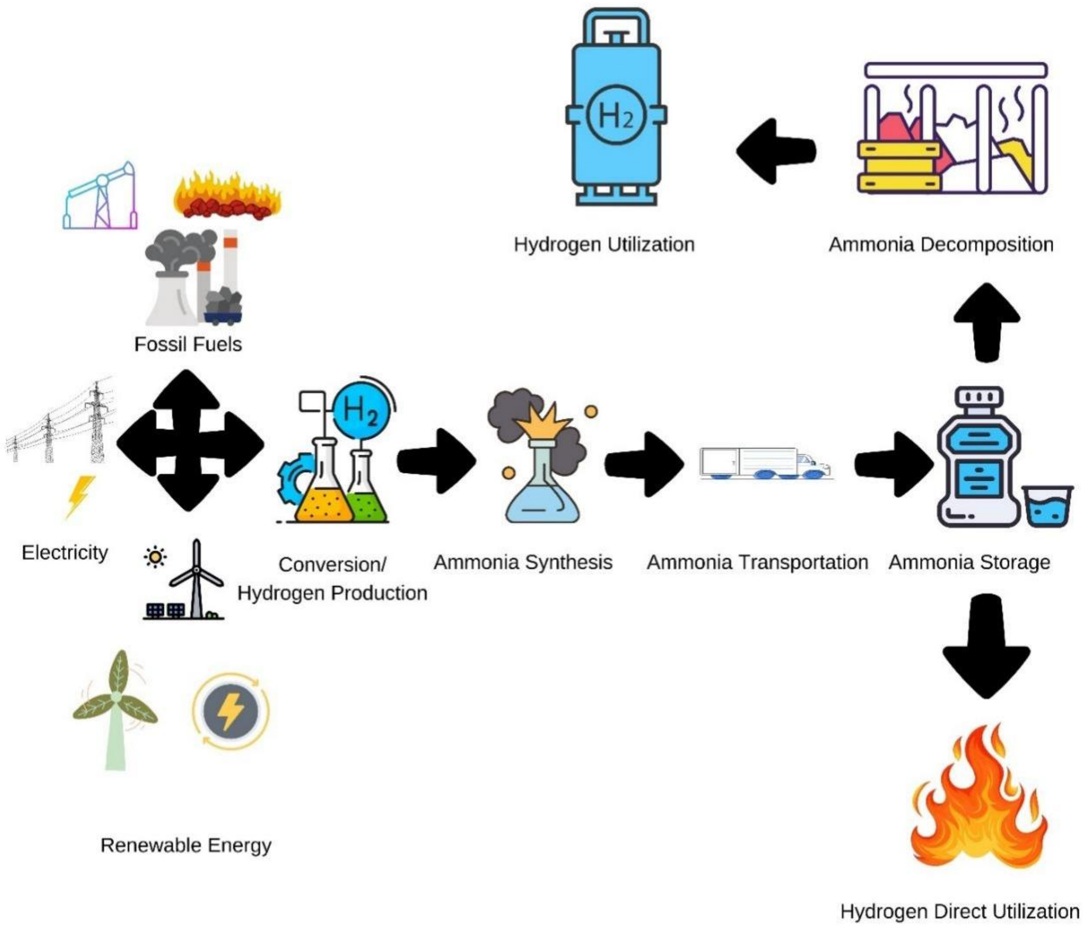


Fig. 1. The pivotal role of ammonia (NH_3) as an energy source in both contemporary and prospective energy frameworks.

Therefore, to compete with traditional energy sources, large-scale hydrogen generation from electrolysis requires decreasing the price of electricity derived from clean environment energy sources[15]. Due to fossil fuel's enormous carbon footprint, clean and efficient alternative fuels are needed. Fuel cells, which produce electricity using hydrogen and have little environmental impact, provide this. Furthermore, since fuel cells produce power continuously, they have an advantage over batteries. The problems with current hydrogen technologies are related to hydrogen storage and transportation. The storage material weakens and becomes embittered because of hydrogen's propensity to permeate through the components[16]. These days, storing hydrogen usually entails either keeping it in a cryogenically chilled liquid at minus 20 K at normal air pressure (1 atm) or compressing it into a gas at pressures as high as 691 atm at ambient temperature or around 298 K[17]. Using materials with high specific surface areas and having pore dimensions of appropriate size, for instance, metal hydrides, metal-organic frameworks (MOFs), and carbon-based materials, like covalent organic frameworks (COFs), as adsorbents for the gas is an alternate strategy for storing hydrogen[16, 18]. However, difficulties in material regeneration and large-scale hydrogen transport after adsorption necessitate using an alternative approach for hydrogen chemical storage[19]. Compounds like calcium hydride, potassium hydride, lithium tetra borohydride, sodium tetra borohydride, and LiAlH4 are examples of materials used as hydrogen storage media[20]. Numerous catalysts have been studied for ammonia's low-temperature breakdown[8, 21, 22]. Among these catalysts, which have been studied, ruthenium has been proven to be the most efficient metal catalyst.

Although catalysts based on ruthenium show better results in ammonia breakdown, their limited availability and high cost prevent them from being widely used in industry. Given these drawbacks, nickel has become an accessible and affordable substitute for ruthenium-based catalysts in the ammonia breakdown process[23, 24]. Recently, researchers have extensively explored metallic catalysts based on different transition metals like cobalt (Co), chromium (Cr), iron (Fe), molybdenum (Mo), nickel (Ni), palladium (Pd), platinum (Pt), and ruthenium (Ru), etc [25-29]. The main focus of these investigations has been to comprehend how the two metals' combined activity accelerates ammonia breakdown. The significance of novel techniques for synthesising catalysts and subsequent modification by selecting supports, adding promoters, and improving operating conditions have also received great attention. Recent literature has highlighted the functions of base and precious metal catalysts in this setting[30]. The breakdown of ammonia at low temperatures and its storage and purification has received much attention; nevertheless, it's crucial to remember that the bimetallic catalyst systems for ammonia decomposition were not mainly covered in any of these investigations. Highlighting and summarising the most recent developments and research findings on bimetallic catalysts for ammonia-to-hydrogen production is crucial. This involves considering ways to save costs, improve catalytic performance, and precisely modify the composition and structure of the catalyst. With an emphasis on studies published primarily after 2015, this article focuses on the catalytic activity, its durability, the effects of different metals, the roles of support materials and promoters, and, finally, mechanical and kinetic investigations of a variety of metallic catalysts for the hydrogen production by the decomposition of ammonia[31].

2. Metal-based Catalytic Systems for Hydrogen Generation; An Energetic Overview

The current review article aims to provide a database for finding the metal combinations that will maximise the creation of hydrogen via ammonia breakdown. The metal combination has a significant effect on the process of catalysis. As described in Fig. 2, the activation energy depends on the catalyst, the active metal, alongside its support. The lowest activation energies are found in iron, ruthenium, nickel, and cobalt-based catalysts as evident from different literature reports. Their near-ideal nitrogen binding energies, (especially ruthenium's,) are the reason for their lower energies. On the other hand, the most significant activation energies are seen in tungsten and vanadium carbides and nitrides[32].

Bimetallic catalysts have emerged as trailblazing materials in heterogeneous catalysis to outperform their monometallic counterparts in areas like selectivity, activity, and durability. The fact that the metals in bimetallic catalysts interact synergistically is primarily responsible for their improved performance[33]. An essential consideration in the development and enhancement of bimetallic catalysts is the binding energy of nitrogen atoms, which indicates the intensity of their contact with the metal surface. Most of the active site composition is still unknown and must be well understood since it greatly impacts the catalyst's activity. Further exploration based on, density functional theory (DFT) in addition to scanning tunnelling microscopy (STM) have hinted that the presence of isolated metal atoms, flaws on the catalyst surface, and the microstructure of the surface may all have a substantial effect on the ammonia decomposition process[34]. The distribution of metals inside bimetallic complexes determines their classification into several categories. This affects the surface of the catalyst and its catalytic activity in the breakdown of ammonia. Bimetallic alloys and monolayer bimetallic are the two primary kinds discussed in this article. A single layer of a secondary metal (aditional-metal) is dispersed over the surface of the primary metal (host metal) in monolayer bimetallic structures, resulting in a configuration that may be used to depict the exterior of core-shell bimetallic nanoparticles or the surface of an alloy. These monolayer structures may have an ad-metal positioned just below the surface of the host metal in a subsurface arrangement or above the host metal in a surface arrangement. Computational investigations demonstrate that these arrangements have unique characteristics not seen in systems that merely include the host metal or the ad-metal[35].

Regardless of the intrinsic binding energies of the metals, the binding energies of the bimetallic complexes may be greater or lower than those of the parent metals. Therefore, it is a difficult task to build these specialized monolayer bimetallic catalysts clearly and rationally [36]. Both metals are present in the bulk and surface in their pure phase composition throughout the alloy production process. This entails a uniform distribution of atoms across the core and surface. An illustration of the structure of a bimetallic alloy helps to clarify this. In contrast to the monolayer bimetallic structure, the alloy's surface features are shaped by combining the parent or fundamental metals' surface qualities. The periodic interpolation approach is used to forecast the structure of active catalysts. It creates a bimetallic alloy with an intermediate binding energy by combining metals with low binding energy for nitrogen with those with high binding energy[37]. Much work has recently gone into creating effective and affordable bimetallic catalysts for ammonia catalytic cracking and degradation. As a result, the following sections will emphasize the significance of bimetallic catalysts, which combine base and noble metals to produce hydrogen from ammonia.

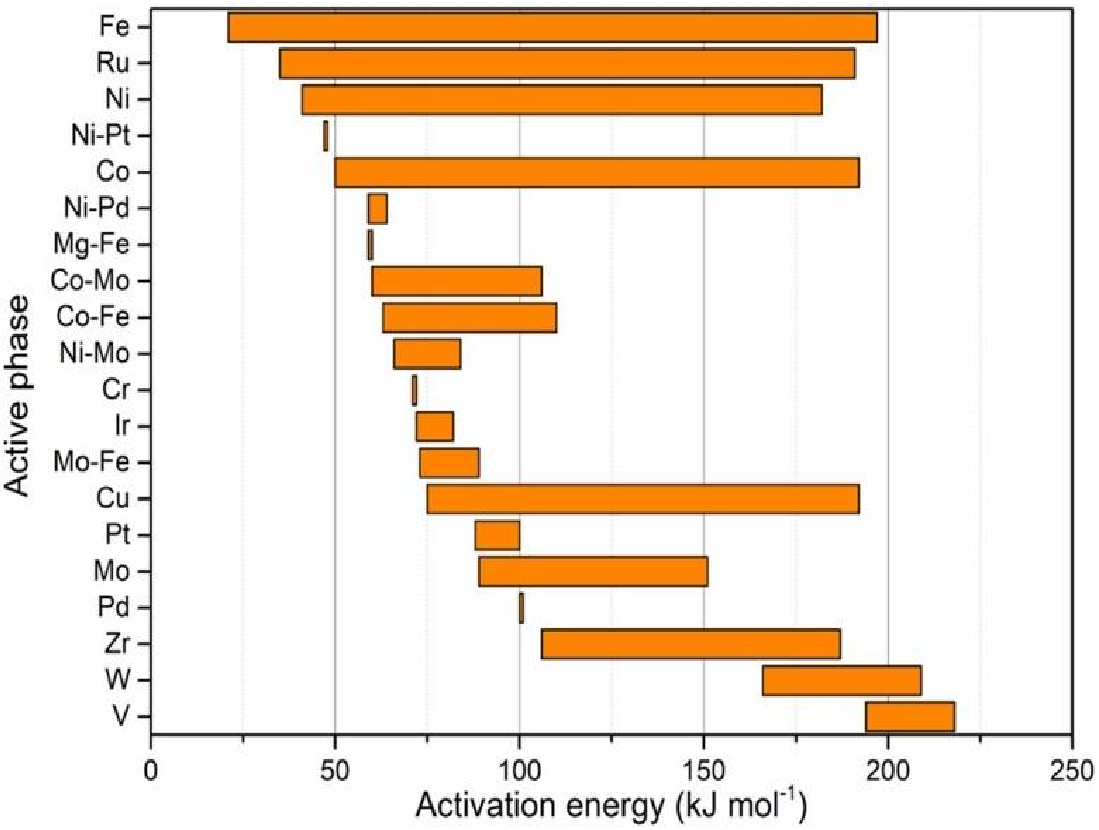


Figure 2. Activation energies of metal-based catalysts for ammonia decomposition. Reproduced with permission from ref.(32). Copyright © 2021, ACS.

3. Materials and Approaches for Decomposition of Ammonia

Ammonia (NH3) is a stable substance with high hydrogen density, easy storage, and well-developed infrastructure and technology for its production. Therefore, it is a very promising chemical. Because of ammonia's advantageous qualities, significance in industrial settings, and capacity to reduce air pollution, its use as a carrier for H2 has expanded[38]. Since NH3 is easier to liquefy and store than H2, it is considered as a more practical substitute.

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g) \quad \Delta H = +46 \text{ kJ/mol}$$

Several approaches, including thermocatalytic, photocatalytic, and electrocatalytic NH_3 breakdown, have been developed to produce clean H_2. Table 1 lists each method's benefits and drawbacks[32, 39]. To determine the present efficiencies of the ammonia to hydrogen conversion technologies, it is required to understand these techniques in detail. The performance of several technical approaches for ammonia decomposition is shown in Figure 1. As the outcomes were collected under various circumstances, each approach's efficacy should be thoroughly assessed[40].

3.1 Thermocatalytic NH3 Decomposition

Thermal breakdown or catalytic cracking is the most frequently used method to produce hydrogen from ammonia. It is possible to perform the process with or without a catalyst because the presence of a catalyst lowers the temperature required for the breakdown. To reduce the energy input (heat) into the system, it is crucial to investigate the energetics of the whole process at various reactor layouts. It should be known that ammonia breakdown requires a reasonably high temperature without a catalyst. This is because ammonia molecules contain strong hydrogen bonds that need a lot of energy to break. Consequently, ammonia molecules require a catalyst to disintegrate into nitrogen and hydrogen at lower temperatures. Different catalysts have been developed by researchers (as given in Figure-2) to accelerate the slow kinetics of NH_3 decomposition and promote H_2 generation[41].

Table-1. Advantages and disadvantages of different methods for ammonia decomposition.

<table>
<tr><th colspan="4">Catalytic Ammonia Decomposition</th></tr>
<tr><td colspan="4">Technical targets:
✓ Clean production process
✓ Low-cost catalyst and efficient
✓ Safe production reactors that can be applied on a large scale</td></tr>
<tr><th>Methods</th><th>Thermocatalytic</th><th>Photocatalytic</th><th>Electrocatalytic</th></tr>
<tr><td>Advantages</td><td>• Simple process
• High conversion rate
• Matured Technology</td><td>• Clean reaction process.
• High conversion rate.
• Mild operating conditions.
• Recyclable catalyst.</td><td>• Hydrolysis to produced hydrogen than less energy consumed.
• Mild operating conditions.
• More potential applications.</td></tr>
<tr><td>Challenges</td><td>• High temperature causes the catalyst to coke.
• Time delays, inefficiency.
• Starting time cannot meet the requirement of the engine.
• High reaction cost.</td><td>• Performance of photocatalyst is too weak.
• Photocatalytic has the limitations of complex synthesis process.
• Low surface area, insufficient activity, low stability and high band gap.</td><td>• Performance of photocatalyst is too weak.
• Photocatalytic has the limitations of complex synthesis process.
• Low surface area, insufficient activity, low stability and high band gap.</td></tr>
<tr><td>R & Focus</td><td>• Look for highly efficient, inexpensive, stable, reactive catalysts.
• Research and development of catalyst carriers with high dispersion and good stability.
• Introduced good catalyst additives.</td><td>• Increase H_2 production to control decomposition products.
• Development and utilization of semiconductor-based catalysts.
• Photocatalytic activity, stability and excellent selectivity.</td><td>• Good catalytic activity, good selectivity and long-term stability.
• Efficient and low cost catalyst.
• Design nano-catalysts that unique modify surface chemistry, electronic structure, electroactive sites and</td></tr>
</table>

			conductivity.

This reaction unfolds in several stages, as depicted in Scheme 1. Ammonia (NH3) initially undergoes molecular adsorption at the metal catalyst's active sites, forming surface-bound NH3*. Then this NH3* is converted by the stepwise dehydrogenation of NH3*, creating N* and H* atoms. Finally, the recombination and release of N* and H* through desorption processes yield nitrogen (N2) and hydrogen (H2) gases. These reactions collectively facilitate the production of N2 and H2 on the catalyst's surface.

$$2NH_3 \leftrightarrow N_2 + 3H_2 (\Delta H = +46.2 kJ/mol)$$

$$NH_3 + * \leftrightarrow NH_3 *$$

$$NH_3 * + * \leftrightarrow NH_2 * + H *$$

$$NH_2 + * \leftrightarrow N H * + H *$$

$$N H * + * \leftrightarrow H * + N *$$

$$[2H* \leftrightarrow H_2]$$

$$[2 N * \leftrightarrow N_2]$$

Scheme 1. Basic kinetic stages of the ammonia decomposition reaction; (*) denotes a vacant adsorption site on the catalyst[42]

Studies have shown that alkali, alkaline and rare earth metals are helpful boosters for ammonia production. To enhance the capability of NH3 decomposition, it is essential to identify the promoter's active component and optimize its interaction with the active site. For example, it has been observed that directly adding Cs metal vapour to Ru-based catalysts increases their activity for ammonia decomposition by order of magnitude compared to conventional catalysts. The distinct stimulation of ammonia decomposition by metallic Cs, as opposed to Cs-O or Cs-OH molecules, is responsible for this rise in activity[43]. Even at temperatures below room temperature, the reaction of liquid NH3 with LiH starts the process of producing compressed hydrogen with no heat needed from an outside heat source. This reaction produces more than

12 MPa of H2 in one hour. Other alkali metal hydrides mixed with NH3 might also be viable choices for producing compressed hydrogen, following the example given by the NH3-LiH combination. The metal amides produced as reaction byproducts may be effectively converted back to hydrides at temperatures lower than 300°C when exposed to a hydrogen flow condition of 0.5 MPa[44]. There has been an increasing interest Concerning the catalysts, in using catalysts based on d-block metals to convert NH3 to H2. Ru-based catalysts have shown good performance, but because of their high cost, they are not as much desirable for large-scale industrial applications[45]. The greater efficacy of catalysts based on iron and nickel has made them viable substitutes. However, ongoing initiatives focus on cutting expenses, improving functionality, and prolonging their service life[46].

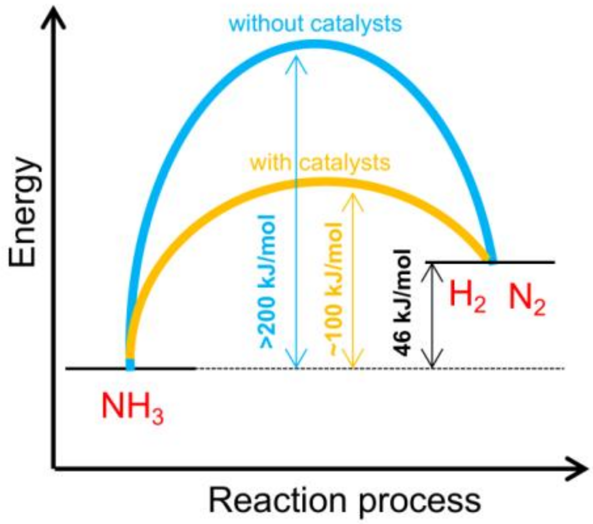


Figure 4. Energetic overview of ammonia decomposition with and without catalyst.

There are various parameters which influence the catalytic decomposition of NH3 like electrochemical properties, electronic energy state configurations, redox potential, including the catalyst morphology, and the number of active sites on it. In addition to being essential for breaking NH3 into nitrogen and hydrogen, the transfer of charges between the adsorption sites on the catalyst surface and its support may also be important for stabilizing transitory intermediate species like N* or H*. The metal catalyst's active sites and the support materials interact in this way. According to published data, the catalytic activity of various metals for the dehydrogenation of ammonia is ranked as follows: > Pt > Cr > Pd > Cu; Ru > Ni > Rh > Co > Ir > Fe. The de-linkage of the N-H bond is often the rate-limiting step for catalysts comprising metals like Pt, Pd, Ru, Ir, and Cu. In contrast, the desorption of nitrogen may have an impact on the rate-limiting step for many d-block metal-based catalysts, including Co, Fe, and Ni. As a result, depending on the catalyst, the rate-limiting steps in the NH3 decomposition process differ, making it difficult to characterize the reaction using just one parameter[47].

3.1 Ru-based catalysts for ammonia decomposition

Ruthenium (Ru), a transition metal, is well-known for its catalytic qualities. It is regarded as the most efficient metal catalyst for the breakdown of NH3. The capacity of a metal catalyst to break the strong N-H bonds in ammonia and enable it to break down into nitrogen (N_2) and hydrogen (H_2) gases is often used to evaluate a catalyst's efficacy in ammonia breakdown. When the ruthenium catalyst is said to possess a "moderate dissociative N_2 adsorption energy," the energy involved in dissociating molecular nitrogen (N_2) into individual nitrogen atoms after adhering to the catalyst's surface is being discussed, this process is essential to the production and breakdown of ammonia. The nitrogen molecules are assumed to attach to the ruthenium surface neither too strongly nor too weakly when they have "moderate" adsorption energy. The nitrogen molecules would stick to the catalyst surface too firmly if the adsorption energy were too high, making it impossible for them to be liberated as individual atoms required for the reaction. It would not be possible for the nitrogen molecules to split into atoms if the adsorption energy was too low. Consequently, ruthenium seems to provide a balance advantageous for catalysis based on its mild dissociative N_2 adsorption energy. It is both weak and strong enough to enable nitrogen atoms to react with hydrogen to generate ammonia (or, in the event of decomposition, to allow the nitrogen atoms formed from the breaking of NH_3 to recombine and desorb as N_3 gas). Strong enough to allow the nitrogen molecules to split into atoms. Because of this equilibrium, ruthenium functions as an effective catalyst in the breakdown of ammonia[48-50]. The traditional method of producing H2 via thermocatalytic NH3 breakdown is laborious. The catalyst must be heated to at least 400 °C for a considerable amount of time, which causes a delay in reaction time and poor energy efficiency. Consequently, a more appropriate method that doesn't use outside energy input is required for the H2 manufacturing process. One such method is to subject a catalyst prepared for a combination of NH3 and O2 gases at a specific ratio at room temperature. This method, called “low-temperature ammonia oxidation”, eliminates the requirement of high-temperature for ammonia breakdown. The reaction proceeds as follows:

$$NH_3 + 1/4O_2 \rightarrow H_2 + 1/2N_2 + 1/2H_2O \ (\Delta H = -75 \text{ kJ/mol})$$

An acidic RuO2/γ-Al2O3 catalyst was reported by Katsutoshi Nagaoka et al. to produce hydrogen utilizing ammonia and O2 at room temperature, as shown in Figure 5[51]. They used an acidic RuO2/γ-Al2O3 catalyst for the reaction of O2 and ammonia at room temperature. The temperature within the catalyst bed rises quickly to the auto-ignition point of ammonia. It happens because the adsorption of ammonia on the catalyst is exothermic in nature. This causes ammonia to break down oxidatively, producing hydrogen in the process. Utilizing a differential calorimeter and a volumetric gas sorption analyser, this investigation quantified the energy in the form of heat generated by the chemical and physical adsorption of ammonia onto the RuO2 and acidic sites of γ-Al2O3. The findings demonstrated that both stages produced a considerable quantity of heat.

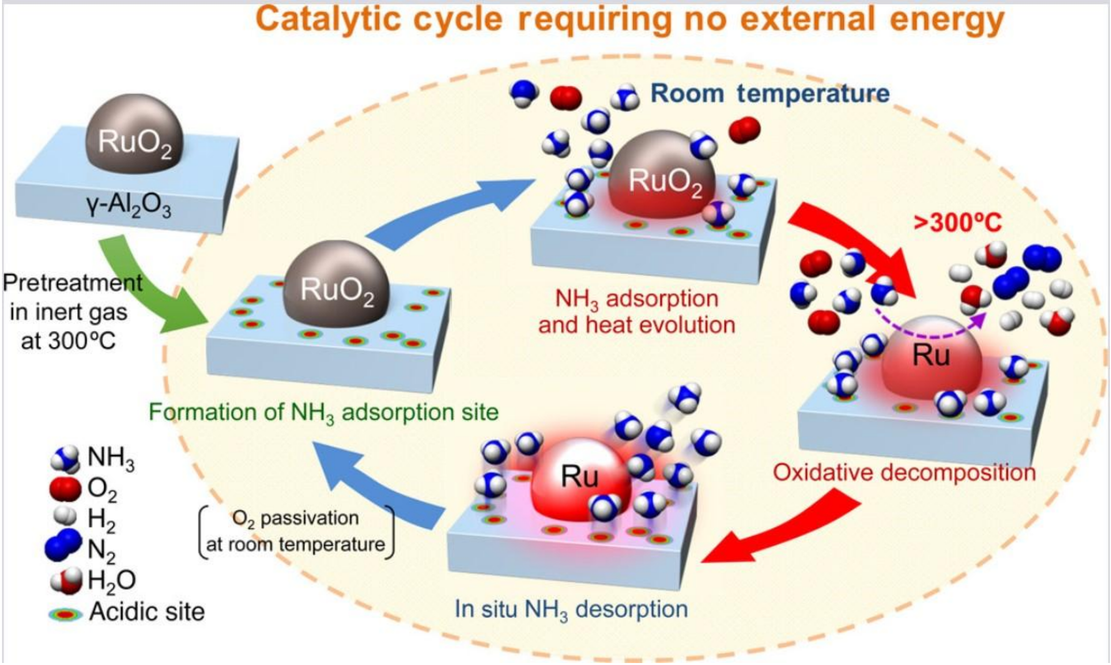


Figure 5: A cyclic representation of Ru-catalysed oxidative cleavage of ammonia. Reproduced with permission from ref.[32]. Copyright © 2021, RSC.

3.2 Ni-based catalysts for ammonia decomposition

The Ru-based catalysts are renowned for their outstanding stability without producing Ru nitrides and unique activity in ammonia decomposition processes. It is also known to be exceedingly stable. But Ru's high price and scarcity, linked to its noble metal status, are drawbacks [32]. As a result, creating commercially feasible catalysts that use transition metal elements rather than noble metals is receiving more attention. Since ammonia decomposes in an exothermic reaction, utilizing a catalyst that operates at a low temperature is preferable to save energy in contrast to noble metal catalysts, d-block metal catalysts exhibited reduced activity at low temperatures since their NH3 decomposition performance is equivalent to that of Ru catalysts, which is thought to be the best among non-precious metal catalysts. Ni-based catalysts are being explored as Ru catalyst substitutes[30].

In Ni-based catalysts, the size of the particles has a significant impact on their catalytic activity. Catalytic performance is significantly improved by particle sizes less than 5 nm; however, at temperatures higher than 400 °C, there might be a chance of particle coagulation, which may lead to the formation of particles of a bit larger size, which is considered more significant [30]. Inokawa and colleagues studied Ni's catalytic activity by controlling its particle size. By adsorbing and breaking down Ni(C5H5)2, on zeolite-Y, they created a CH zeolite catalyst. Following reduction at 400°C in an H2 environment, the TEM Fguire-6 demonstrated that the Ni nanoparticles in the catalyst, which was created using this wet impregnation process, had a larger and more significant size (10–15 nm) than the catalyst particles (2–5 nm) that were previously created.

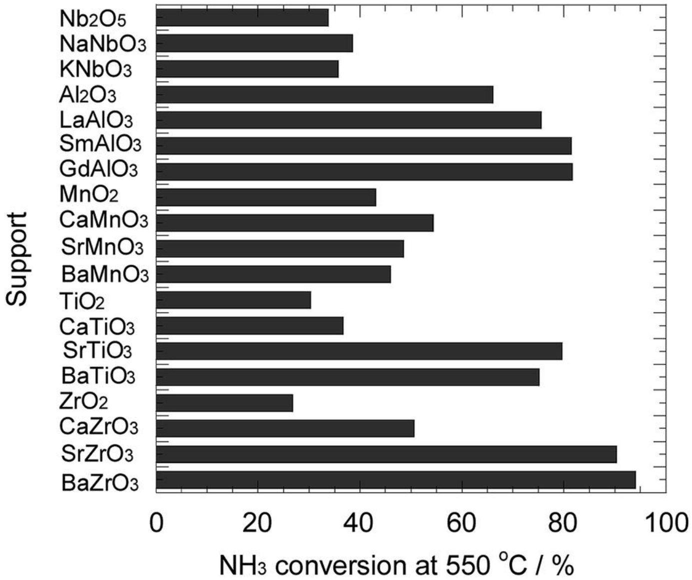
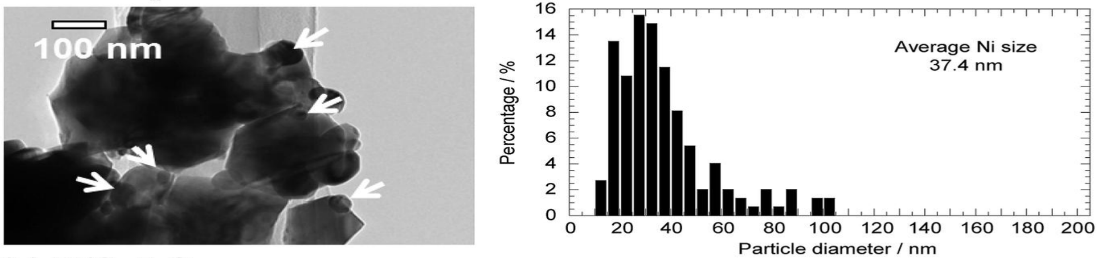
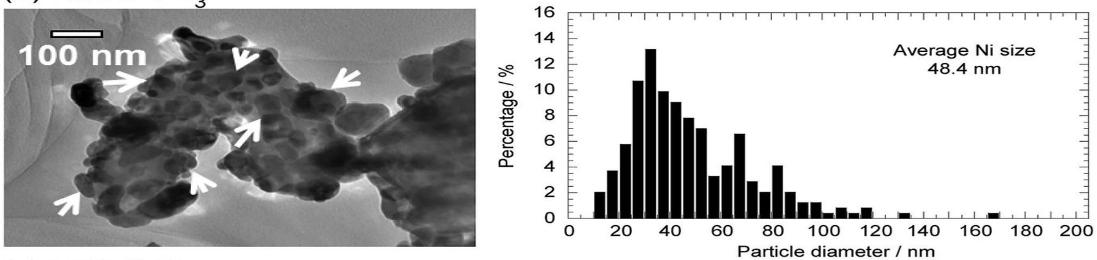


Figure 6 (A): Catalytic NH_3 decomposition using Ni-based catalysts supported on different oxides. Reproduced with permission from ref.[21]. Copyright © 2018, RSC.

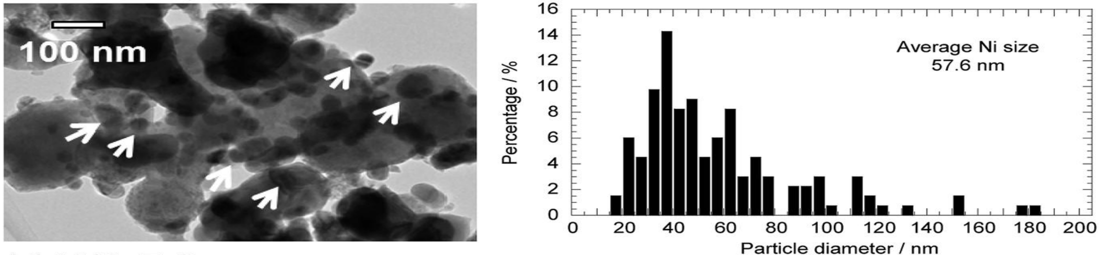
(a) Ni/ZrO_2



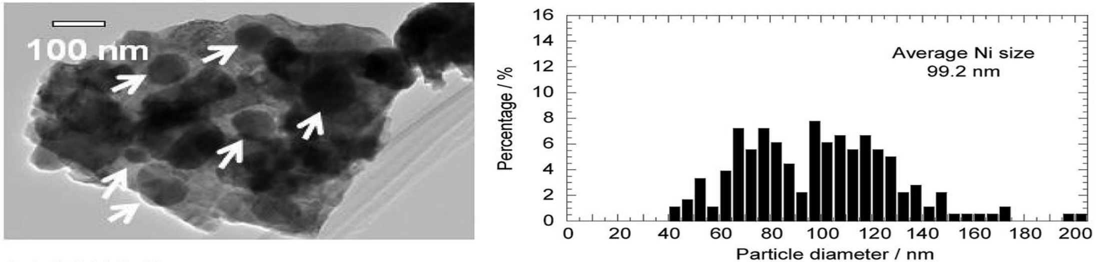
(b) $Ni/CaZrO_3$



(c) $Ni/SrZrO_3$



(d) $Ni/BaZrO_3$



(e) Ni/Al_2O_3

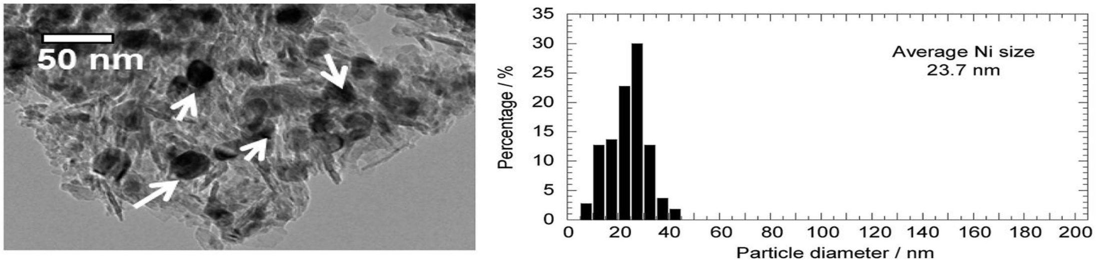


Figure 6 (B): TEM images and Ni particle size distribution histograms of 40 wt% (a) Ni/ZrO_2, (b) $Ni/CaZrO_3$, (c) $Ni/SrZrO_3$, (d) $Ni/BaZrO_3$, and (e) Ni/Al_2O_3. Reproduced with permission from

ref.[21]. Copyright © 2018, RSC.

In addition, the CH zeolite catalyst was found to have preserved nanoparticles for more than 100 hours without deactivating. It remained highly active even after being heated to 500 degrees Celsius and undergoing an ammonia breakdown process. These techniques were used to produce Ni nanoparticles that outperformed those produced by the traditional impregnation process in terms of improved dispersion and exceptional thermal stability[52]. Zhang's investigation [53] showed that adding lanthanum to alumina enhanced catalytic efficiency and that the ideal ton of frequency utilizing Ni/Al2O3 catalyst was reached with Ni particle sizes ranging from 1.8 to 2.9 nm.

The catalytic performance of nickel is thought to be enhanced by adding rare earth metal promoters. In Ni/Al2O3 catalysts, Okura et al.[54] The following hierarchy of promotional efficacy was found: Eu ≈ Gd > Ce > La > Pr ≈ Nd > Y > Sm. The research also investigated the catalytic effectiveness of metal oxide supports for nickel (Ni), such as perovskite-type mixed metal oxides (ABO3). As shown in Figure 6, a solid correlation was found involving the catalytic efficiency trends observed and the basicity of these supports [21]. Ni catalysts based on perovskite-type oxides showed better catalytic activity than those using traditional oxide materials; among the catalysts tested, Ni/BaZrO3 proved the most efficient for NH3 breakdown. Using catalysts based on CeO2 and Al2O3, Lucentini et al. tested the process of decomposition with Ru, Ni, and Ni-Ru alloy [25]. The standard compositions used in the catalysts' design were 10% Ni and 2% Ru by weight. Ru was shown to be more reactive than Ni during the ammonia decomposition studies, while CeO2 was a better support material in terms of activity than Al2O3. However, Ru surface area loss from metal sintering with Ru/Al2O3 and Ru volatilization with Ru/CeO2 quickly reduced the efficacy of Ru-based catalysts. Conversely, Ni-based catalysts demonstrated stability once activated; they would deactivate below 450°C and stay reduced at temperatures over 450°C. The research findings indicate that at the start, Ru/CeO2 exhibits better performance in ammonia decomposition, but Ni/CeO2 provides more benefits regarding catalyst lifespan and economic feasibility.

3.3 Photocatalytic Decomposition of NH_3

The photocatalytic method of disintegrating of ammonia into nitrogen and hydrogen is a potential technique that uses room-temperature, and recyclable catalysts. The benefit of this approach is that light exposure may be readily adjusted using a switch mechanism. Interestingly, this photocatalytic mechanism for ammonia breakdown uses sunlight, simulating an artificial photosynthetic reaction which takes place in an alkaline environment[55]. Figure 7 shows that electron-hole pairs are produced when the energy of incident radiation is equal or greater than the band gap of the photocatalyst.

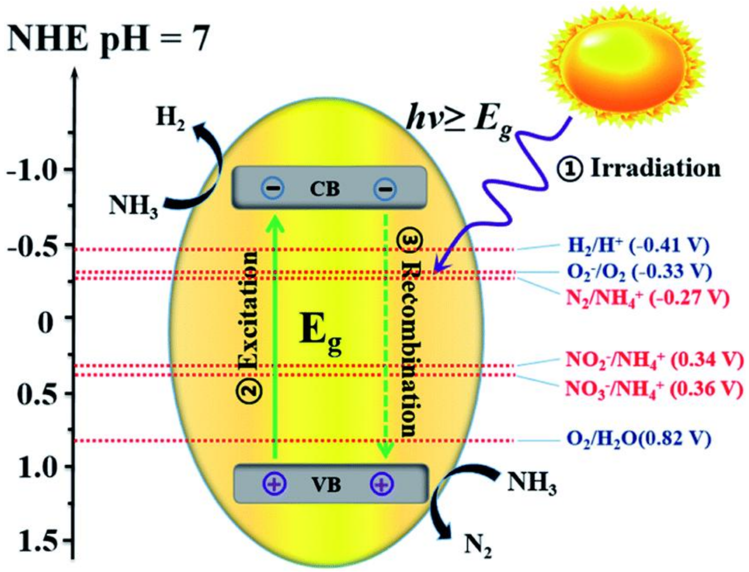


Figure 7. Photocatalytic decomposition of ammonia. Reproduced with permission from ref.[21].

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In the photocatalytic process, these holes function as solid oxidizers, and the electrons which move to conduction band as reducing agent. These electrons can effectively reduce O2 to produce hydroxyl radicals. Adequate reduction and oxidation potentials of electrons and holes on the semiconductor surface are essential for the efficient photocatalytic degradation of ammonia. This guarantees that they will interact with species that have been adsorbed on the catalyst surface, generating free radicals.

$$\text{Photocatalyst} + hv \rightarrow e^- + h^+$$

$$2NH_3 + 6h^+ \rightarrow N_2 + 6H^+$$

$$2H+ + 2e^- \rightarrow H_2$$

Thus far, a small number of photocatalysts have demonstrated efficacy in decomposing aqueous ammonia solutions. These include commonly used photocatalysts like graphene, ZnO, ZnS, Mo2N, and TiO2, as well as hybrid forms with metal loadings[56, 57]. Utsunomiya et al. concentrated on the breakdown of ammonia in their investigation of the photocatalytic characteristics of TiO2 impregnated with different metals. They investigated the mechanism of NH3 breakdown and proposed three other lines of inquiry to clarify the procedure[58]. Figure 9 describes the several pathways that lead to the degradation of NH3. In route 2, neighbouring NH2 radicals are coupled to generate NH2-NH2, whereas, in route 1, NH radicals are created by eliminating one atom of hydrogen from each of the two NH2 radicals. Density functional theory (DFT) calculations show that routes 1 and 2 have activation energies of 236 kcal/mol and 74.8 kcal/mol, respectively, but energetically, route 2 is the most favourable option. The two approaches for N2 and H2 synthesis through NH2-NH2 coupling route 2, which involves combining NH2 radicals to generate H2N-NH2 and route 20 which involves NH2 interacting with a single NH3 molecule in the gas phase are the subject of further investigation. These pathways are expected to have activation energies of 74.4 kcal/mol and 59.2 kcal/mol, respectively. This implies that NH3 breakdown most likely occurs via pathways 2 and 20, where NH2-NH2 formation occurs.

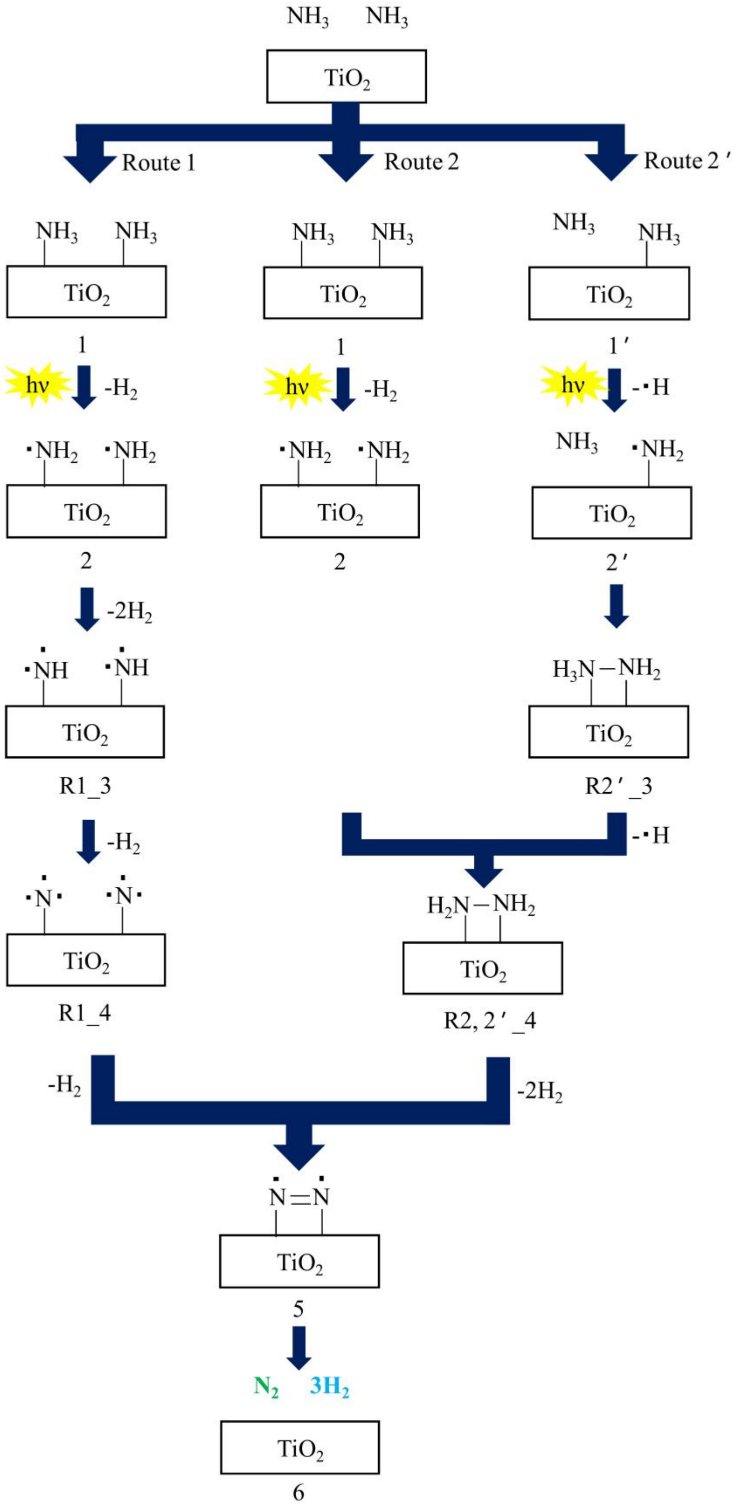
NH3 NH3
TiO2
Route 1
Route 2
Route 2′
1
1
1′
hν
-H2
-H2
-·H
2
2
2′
-2H2
H3N−NH2
R1_3
R2′_3
-H2
-·H
H2N−NH2
R1_4
R2, 2′_4
-H2
-2H2
N=N
5
N2 3H2
6

Figure 8. Mechanism of ammonia decomposition over TiO_2 photocatalyst. Reproduced with permission from ref.[58]. Copyright © 2017, Elsevier.

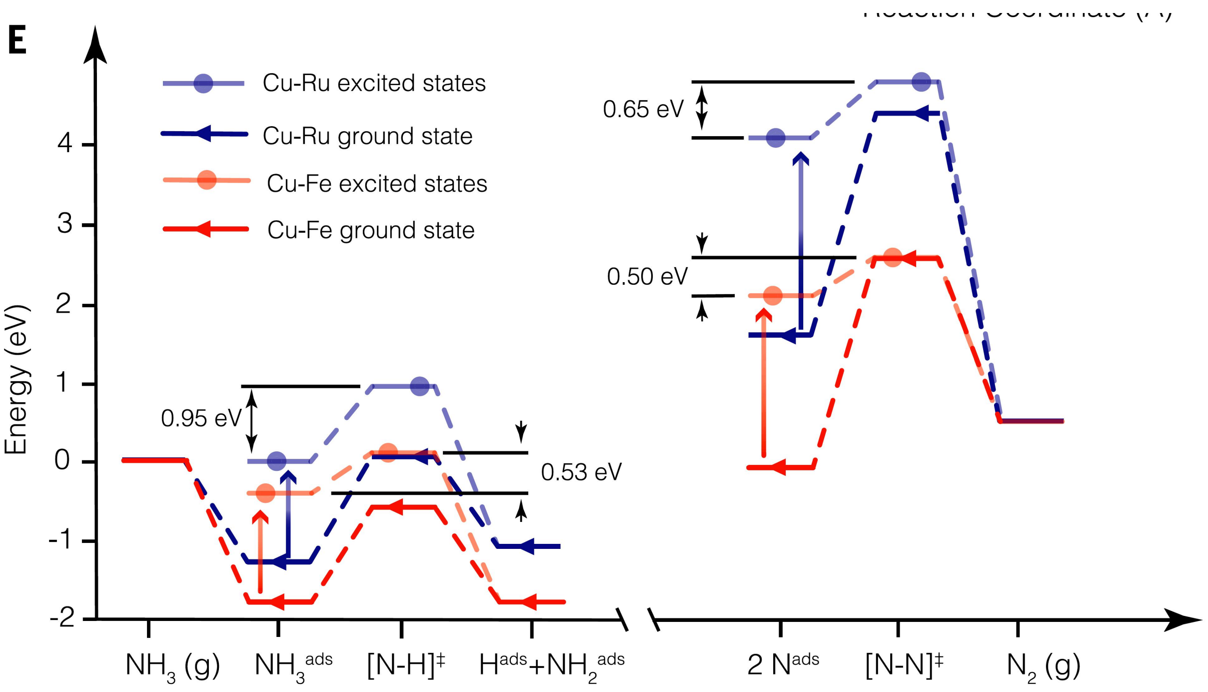

Figure 9. The energy diagrams for thermocatalysis (ground state) and photocatalysis (excited states) on Cu-Fe- and Cu-Ru-ARs are schematically compared. Blue arrows point to Ru-N, while red arrows point to electrical excitation on Fe-N. For simplicity, just the two feasible RDSs are provided; relocations of nitrogen atoms are not considered for this reason. Reproduced with permission from ref.[59]. Copyright © 2022, Science.

Razak et al. suggested that the interaction of nitrogen atoms on the palladium surface was the cause of the linear H2 synthesis from NH3 over a Pd/TiO2 catalyst. N-H bond dissolution was facilitated by this interaction when photogenerated electrons were present[57]. Yuan and coworkers. have recently found that Cu-Fe-AR, although not a very good thermos-catalyst, it may work as a photocatalyst for the breakdown of NH3 when subjected to short-pulse laser light[59]. Cu-Fe-AR has higher reactivity and stability than conventional thermal catalysts because heated carriers generate adsorbate–metal excited states. Lower activation energy barriers, clean, active sites, and effective desorption of reaction products are all made possible by these excited states. When continuous-wave LED lighting is used, Cu-Fe-AR reaches efficiency values similar to Cu-Ru-AR. Cu-Ru-AR shows much higher reactivity because of photothermal effects. However, the work emphasizes how effective it is to use inexpensive LED light sources for effective photocatalysis, as Figure 8 illustrates. The results show that easily obtained metals may be used as affordable and efficient substrates for photocatalysis using plasmonic antenna-reactor technology.

3.4 Electrocatalytic NH_3 Decomposition

The electrochemical method presents a viable alternative for onboard utilisation since it yields hydrogen and nitrogen via the breakdown of ammonia at a mild heat [60, 61]. The theoretical electrolysis voltage of liquid ammonia is 0.077 V, which is far less than water's 1.23 V electrolysis voltage. Amide ions are released, and hydrogen gas is generated at the cathode during the electrolysis of ammonia. At the anode, these amide ions are oxidized and nitrogen gas is produced. It is essential to build the electrolysis reactor as a securely sealed electrolytic cell working under exact experimental conditions to avoid oxidation and hydration of metal amides [62]. However, even at an elevated voltage of 2 V, the current efficiency stays at only 85% because of the reversible nature of the process in liquid ammonia. Ammonia electrolysis requires a high current and a significant decrease in the maximum cell voltage.

When NH3 is adsorbed onto an electrode, OH- ions can cause NH3 oxidation in an alkaline environment, or a low pH environment, oxidants like hypochlorous acid can cause NH4+ oxidation. These two processes can lead to electrocatalytic NH3 decomposition in an aqueous electrolyte[63-65]. On the other hand, slow reaction rates in acidic electrolytes and electro-corrosion are the causes of poor electrochemical process efficiency. These problems may be overcome by using alkaline electrolytes in the electrocatalytic breakdown of NH3. These materials have thoroughly been studied and are likely to mitigate the disadvantages concerned to acidic environments and electrode compositions.

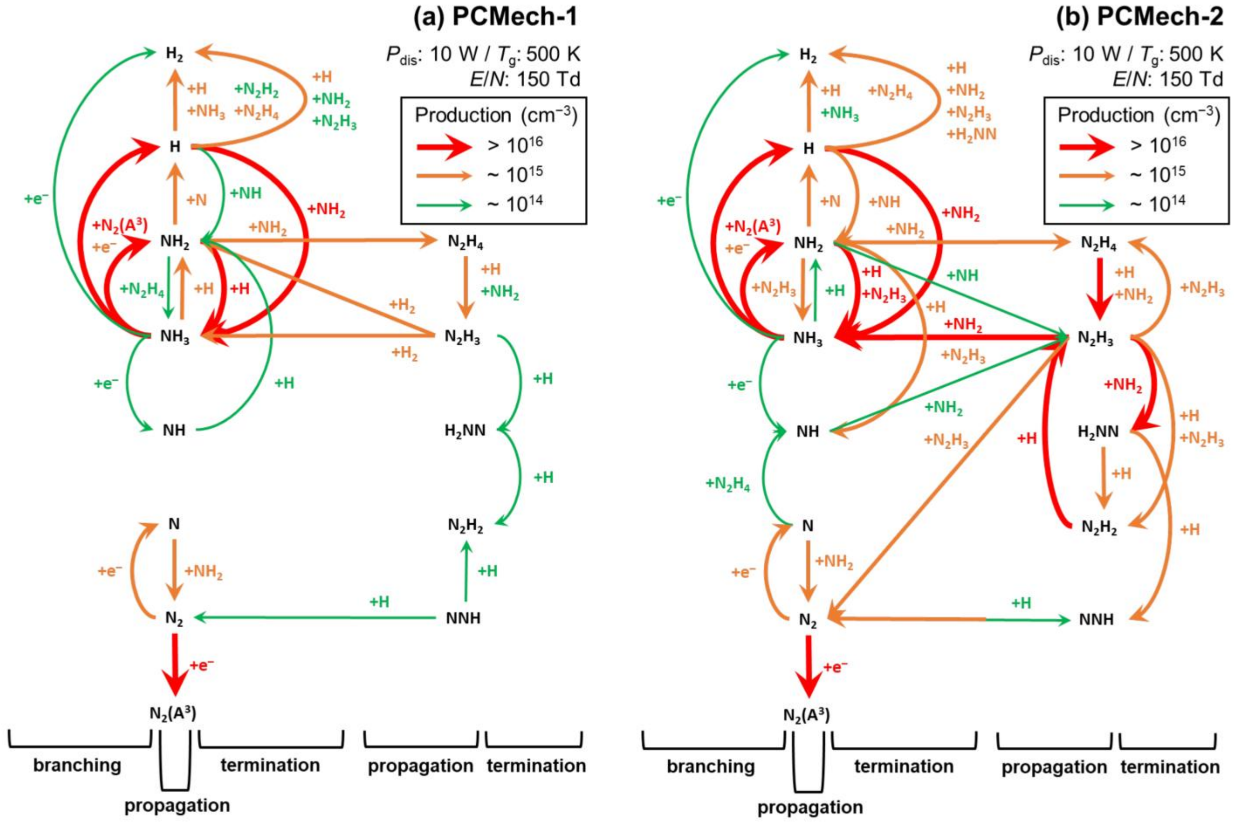

Figure 10. Schematic representation of the primary chain reactions for (a) PCMech-1 and (b) PCMech-2 for the NH3/N2 combination (1/99 mol%) with Tg = 500 K, E/N = 150 Td, and Pdis = 10 W. Reproduced with permission from ref.[63]. Copyright © 2023, ACS.

Ammonia solution is transformed into hydrogen and nitrogen gases in an ideal ammonia decomposition system, where ammonia is oxidized to nitrogen gas at the anode, and water is reduced to hydrogen gas at the cathode. As a result, the oxygen evolution reaction (OER) may compete with the electrocatalytic breakdown of NH3 at the anode as a side process.

Reaction at anode:

$$2NH_3 + 6OH^- \rightarrow N_2 + 6H_2O + 6e^- \quad E^\theta = -0.77 \text{ V vs. SHE}$$

Reaction at cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \ E^\theta = -0.829 \text{ V vs. SHE}$$

Overall reaction:

$$2NH_3 \rightarrow 3H_2 + N_2 \ E^\theta = -0.059 \text{ V}$$

Its simplicity and affordability are among the numerous advantages of electrocatalytic NH3 breakdown for H2 production. Still, issues like poor selectivity and delayed kinetics exist. Electrocatalysts of many kinds have been explored to improve the efficiency of electrocatalytic NH3 decomposition, but their performance is insufficient to meet industrial applicability standards till now. As shown in Figure 10, it is crucial to create new, highly effective ammonia electrolysis electrodes to produce hydrogen. For electrocatalytic NH3 breakdown (alkaline water electrolysis), platinum and other precious-metal-based catalysts work well (Figure 11), but they have significant disadvantages in the form of high cost and restricted supply(66-69). Recently, transition metal-based catalysts have shown potential for electrocatalytic NH3 degradation using a range of structural and morphological engineering methods, including shape control, heteroatom doping, alloyed/core-shell creation, and self-supporting materials(64, 70-73). Nevertheless, these catalysts' present selectivity and density of oxidation are still below what is needed for widespread use. Thus, further investigation and advancement in this field are required.

3.5 Ammonia Decomposition by Multi-Metallic Catalysts

In order to control the drawbacks of using mono metal atom-based catalysts and the broader application of ammonia decomposition, scientists are trying to explore the potential of catalysts with more than one metal atom. Such catalysts have a reasonable price, strong catalytic efficiency, and exceptional longevity. These traits provide a cost-performance balance. There are more optimization options since these catalysts' structure and content may be changed. Currently, most multi-metallic catalysts under investigation are bimetallic catalysts(74).

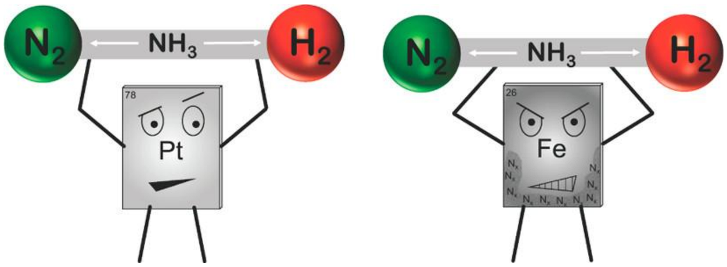

Figure 11. Ammonia decomposition by Pt and Fe catalysts. Reproduced with permission from ref.[32]. Copyright © 2023, ACS.

Commonly used bimetallic catalysts are Ru-Ni(26, 75), Ni-Co, Ni-Fe(2, 28, 76-78), etc. Hansgen and co-workers have demonstrated a computational framework that exploits nitrogen binding energies to find potential bimetallic catalysts(34). Using this approach, they predicted their catalytic behaviour based on their computer analyses. They found that Ni-Pt-Pt(111) may function as an even more potent bimetallic catalyst for NH3 breakdown than Ru. Tabassum and co-workers created a “K-CoNi alloy-MgO-CeO2-SrO” catalyst, as shown in Figure 12. They synthesized this catalyst by spreading CoNi alloy nanoparticles evenly over a mixed oxide support comprising of MgO–CeO2-SrO, boosted with potassium(2). With a remarkable 97.7% conversion rate for NH3, this catalyst performed exceptionally well at 450°C and 6000 mL per hour per gramme of catalyst. This investigation indicates that the presence of active sites at the metal/oxide interface enables the recombination of deposited nitrogen atoms, which results in the desorption of N2 and a significant decrease in the activation energy barriers.

Pt0.9Au0.1/TiO2, a bimetallic alloy nanoparticle-supported TiO2 photocatalyst with 90% Pt and 10% Au, was created by Shiraishi and associates(79). Compared to Pt/TiO2, this photocatalyst presented better catalytic activity, for converting ammonia into H2 and N2. The alloy's improved performance is partly due to the reduction of the Schottky barrier height at the metal/TiO2 interface caused by the presence of Au. This enhances the transport of electrons from the TiO2 conduction band to the metal particles.

In their investigation into the plasma-catalyzed breakdown of NH3, Yi et al. created and evaluated a variety of bimetallic catalysts, such as Fe-Co, Mo-Co, Fe-Ni, and Mo-Ni(80). According to the investigation, the performance of Fe-Ni catalyst was superior to the others in terms of catalytic activity. Subsequent analysis indicated that this catalyst has the largest capacity for the adsorption of ammonia, which is probably the main reason for its excellent catalytic performance. Jiang and coworkers investigated several forms of the NiCO2N compound, explicitly concentrating on nanoneedle formations on three-dimensional nickel foam. It was discovered that this arrangement has various benefits, such as a much larger surface area, more accessible active sites, better gas diffusion, as well as better charge transfer capabilities. Furthermore, the NiCO2N composite provided the best catalytic performance in the hydrogen evolution (HER) and ammonia electrolysis(81).

Development of multi-metal catalysts with three or more metal components is complex, yet, the potential is higher. A unique high-entropy alloy (HEA) CoMoFeNiCu nanoparticle was effectively used by Xie et al. for very effective NH3 breakdown. The miscibility limit of bimetallic CoMo alloys was overcome, as shown in Figure 13, by steadily adjusting the Co/Mo elemental ratio in CoMoFeNiCu HEA nanoparticles. The HEA catalyst performs better catalytically than Co-Mo catalysts and is less expensive than Ru-based catalysts. With this catalyst, the ideal NH3 conversion efficiency may approach 100% when reaction was carried out at 500 0C. Moreover, the HEA catalyst's alloy composition and surface adsorption characteristics can be precisely adjusted, showcasing its enormous potential for real-world uses(82).

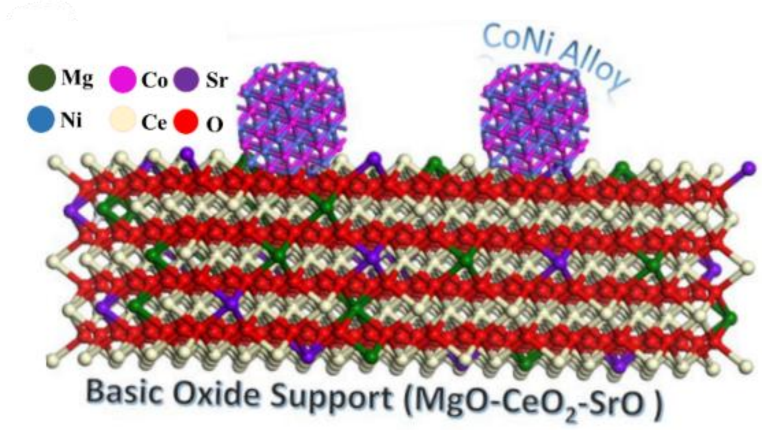

Figure 12. CoNi alloy supported on MgO–CeO$_2$–SrO. Reproduced with permission from ref.^{2}.

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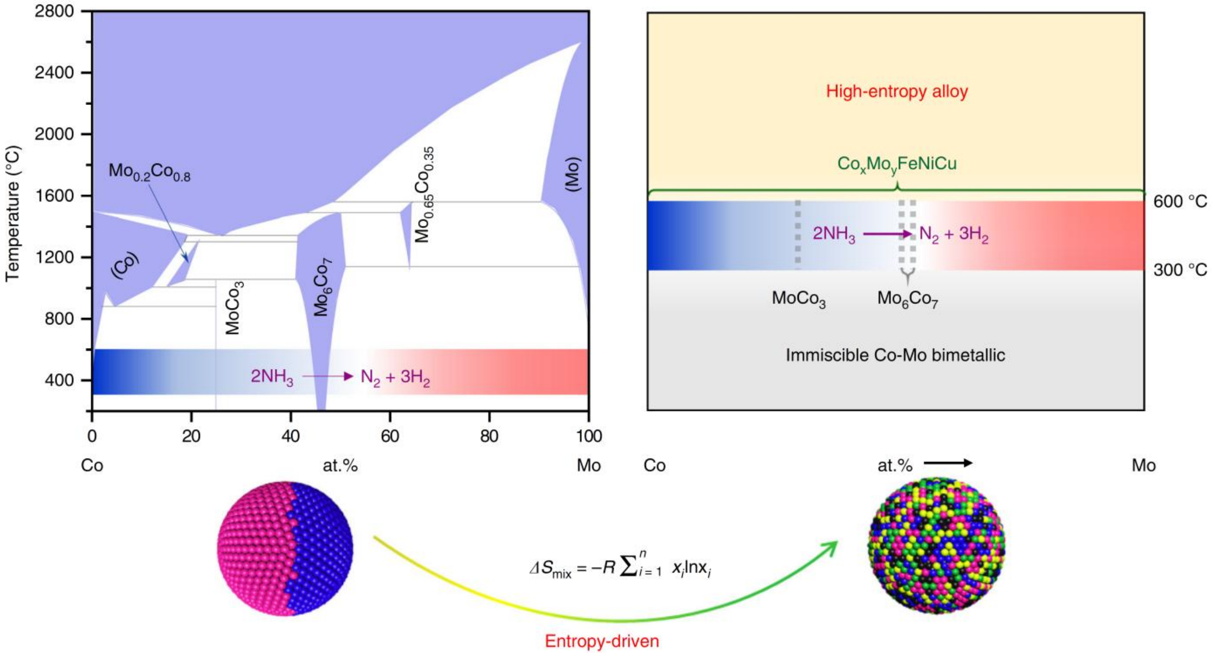

Figure 13. HEA catalysts breaking the miscibility limitation of conventional binary alloys. Reproduced with permission from ref.[2]. Copyright © 2019, Nature.

3.6 Metal Hydrides and Ammonia Decomposition

Certain elements, particularly those in groups I–IV, tend to create metallic hydrides. These hydrides readily undergo a chemical reaction with NH3 to produce a range of nitrides and amides(83). Bergstrom and Fernelius in 1933, comprehensively analyzed the interaction between alkali metals and ammonia to synthesize extended amides(84). These alkali amides have further been utilized in different industries to synthesize different organic chemicals. Sodium and potassium amides were first synthesized by Gay-Lussac and Thenard in 1807. Subsequently, lithium, rubidium, and caesium amides have been synthesized from the molten alkali metals and gaseous ammonia.LiNH2 was synthesized by Titherley in 1894 and has since been often used as a reagent in chemical synthesis(85).

Ammonia decomposition into hydrogen and nitrogen is limited due to the need for temperatures above 673 K, hindering its practical use. To use ammonia as a source of hydrogen, it is necessary to generate hydrogen from ammonia at or near room temperature. Subsequently, NH3 and hydrides of some alkali metals (Li, Na, and K) and alkaline earth metals

(Mg, and Ca) systems have been formulated to generate hydrogen, using the existing knowledge as a foundation. The response is articulated as follows.

$$MH + NH_3 \rightarrow MNH_2 + H_2$$

Leng et al. conducted the synthesis of LiNH2, NaNH2, KNH2, Mg(NH2)2, and Ca(NH2)2 by reacting ammonia gas with respective metal hydrides (MH). This process was carried out at ambient temperature, with a pressure of 0.5 MPa.(86). Simultaneously, Kojima and coworkers examined the potential for recycling metallic amides. They introduced LiNH2, NaNH2, and KNH2 into a hydrogen-rich environment with a pressure of 0.5 MPa. After a time interval of 4, 4, and 2 hours, respectively, 96%, 100%, and 92% of samples have been converted to LiH, NaH, and KH (87, 88). In LiNH2, two hydrogen atoms establish covalent bonds with a nitrogen atom, forming the amide ion [NH2]− and this amide ion forms an ionic bond with lithium-ion by. Therefore, the formation enthalpy of LiNH2 is relatively low compared to the hydrides (LiH) created by an ionic link. The LiNH2 decomposes at a higher temperature, forming the end product Li3N. Similarly, NaNH2 and KNH2 as exhibited the same behaviour. The breakdown tendencies of Mg(NH2)2 and Ca(NH2)2 are less than those of LiNH2 from a thermodynamic and kinetic perspective. This happens because the electronegativity of each atom is different which influences the bond strength. Therefore, the decomposition behaviour of each amide is different. As the Mg has a higher difference of electronegativity as compared to Li or Na, the strength of the ionic connection between Mg2+ and [NH2]− would be higher than that between Li+ and [NH2]−. This study effectively elucidates the accelerated synthesis of LiNH2 as compared to other amides examined. Furthermore, it can be concluded that the reactivity of alkali and alkaline earth metal hydrides with ammonia is enhanced when the electronegativity of the neutral cation decreases. Nevertheless, metal amides associated with a higher electronegativity value of the neutral atom of the cation can readily release ammonia.

$$NaNH_2 \rightarrow 1/2Na + N_2 + H_2$$

$$Na + NH_3 \rightarrow 1/2\ H_2 + NaNH_2$$

The researchers have successfully created NaNH2 as a highly efficient catalyst for breaking down ammonia. This catalyst facilitates the use of ammonia by incorporating the balanced breakdown and creation of NaNH2 from sodium metal(83). The decomposition efficiency of 99.2% at a temperature of 530 °C, using 0.5 g of NaNH2 and a flow rate of 60 cm3(STP) min−1 of NH3, demonstrates that the as-received NaNH2 performs just as well as a ruthenium catalyst in continuously decomposing NH3 in a stoichiometric manner. Yamaguchi et al. have proposed that the breakdown route of sodium amide is significantly influenced by the partial pressure of ammonia gas(89). A compound with imide-like characteristics might be produced during the breakdown process. Recently, an article has been published by our research group that describes the breakdown route of sodium amide. This is for the first time that mass spectroscopy and in situ transmission electron microscopy (TEM) have been used to study such a process(90). NH3 decomposition with additives of different metal hydrides was also reported. The following systems have been investigated as hydrogen storage materials with impressive volumetric and gravimetric hydrogen densities, such as Li−N−H, (91)Na−N−H, Li/Mg−N−H, and Ca−N−H etc.(90, 92, 93).

4. Conclusion

Ammonia breakdown is gaining much attention as a very practical, sustainable, and environmentally beneficial way to produce hydrogen. This paper explores the catalysts and technological methods used in ammonia breakdown to generate hydrogen. It looks at several technologies and their catalytic processes, describing the advantages and disadvantages of each, as well as the potential for industrialization. The paper also explores recent developments in ammonia decomposition catalyst research, stressing the vital role that non-precious metals play in reducing prices and improving efficiency. Metal hydrides have been investigated as a potential hydrogen transporter due to their many advantages. However, only a small number of effective instances have been put into practice so far. Most hydrides have insufficient absorption and desorption kinetics and are only practical at high temperatures. All things considered; this paper provides a perceptive review of the current state of NH3 breakdown for H2 generation as well as the potential for future improvement.

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