

Review

Recent Progress on Hydrogen Production from Ammonia Decomposition: Technical Roadmap and Catalytic Mechanism

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Abstract: Ammonia decomposition has attracted significant attention in recent years due to its ability to produce hydrogen without emitting carbon dioxide and the ease of ammonia storage. This paper reviews the recent developments in ammonia decomposition technologies for hydrogen production, focusing on the latest advances in catalytic materials and catalyst design, as well as the research progress in the catalytic reaction mechanism. Additionally, the paper discusses the advantages and disadvantages of each method and the importance of finding non-precious metals to reduce costs and improve efficiency. Overall, this paper provides a valuable reference for further research on ammonia decomposition for hydrogen production.

Keywords: ammonia decomposition; hydrogen production; thermocatalytic; non-thermal plasma-catalytic; electrocatalytic; photocatalytic



Citation: Huang, X.; Lei, K.; Mi, Y.; Fang, W.; Li, X. Recent Progress on Hydrogen Production from Ammonia Decomposition: Technical Roadmap and Catalytic Mechanism. *Molecules* **2023**, *28*, 5245. <https://doi.org/10.3390/molecules28135245>

Academic Editors: Dai Dang and Ning Yan

Received: 9 June 2023

Revised: 30 June 2023

Accepted: 2 July 2023

Published: 6 July 2023



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1. Introduction

Reducing carbon emissions is a pressing global challenge. The development of clean and renewable sources of energy, such as wind or solar, is an effective way. At the same time, efficient and reliable energy storage and carriers are indispensable due to the intermittency and variability of such natural energy sources. Hydrogen is considered an excellent energy carrier due to its carbon-free, renewable, and environmentally friendly features [1–4]. However, low volume energy density and serious safety issues concerning storage and transportation hinder its large-scale applications. A feasible approach is reversibly storing hydrogen in liquid or solid hydrides (hydrogen carriers) and then generating hydrogen through catalytic processes as required. Among potential hydrogen storage intermediates, ammonia (NH₃) is the most promising candidate due to its competitive advantages in terms of hydrogen storage capacity, zero carbon emissions, availability, cost, and safety [5–8].

Ammonia's hydrogen content is as high as 17.6 wt%, and the hydrogen volume density is about 123 kg-H₂/m³, much higher than other modern hydrogen storage systems [5]. Moreover, ammonia is readily liquefied at room temperature (25 °C) and a light pressure of ca. 10 atm, resulting in a higher volumetric energy density than pressurized H₂ [6,7]. In addition, ammonia is widely used as an important chemical material in modern industries, such as nitrogen fertilizers, refrigerants, and NO_x-reducing agents. Due to the strong, long-term demand, the infrastructure for its production, storage, and supply has been well developed. As such, compared to other zero-carbon fuels, ammonia is a widely available, practical, and affordable choice [8]. Furthermore, the extensive use of ammonia over the years has contributed to developing safety codes and standards. Thus, ammonia safety has been ensured.

Ammonia decomposition plays a crucial role in the renewable energy sources to hydrogen user's process, as outlined in Figure 1. The development of these technologies is not synchronized. The production capacity of hydrogen and ammonia is not a significant obstacle to meeting the high demand, while the current ammonia decomposition system

does not allow mass hydrogen production with adequate purity. Therefore, ammonia decomposition may become the bottleneck of the hydrogen chain, which is why it is getting dramatically increased attention [9–11].

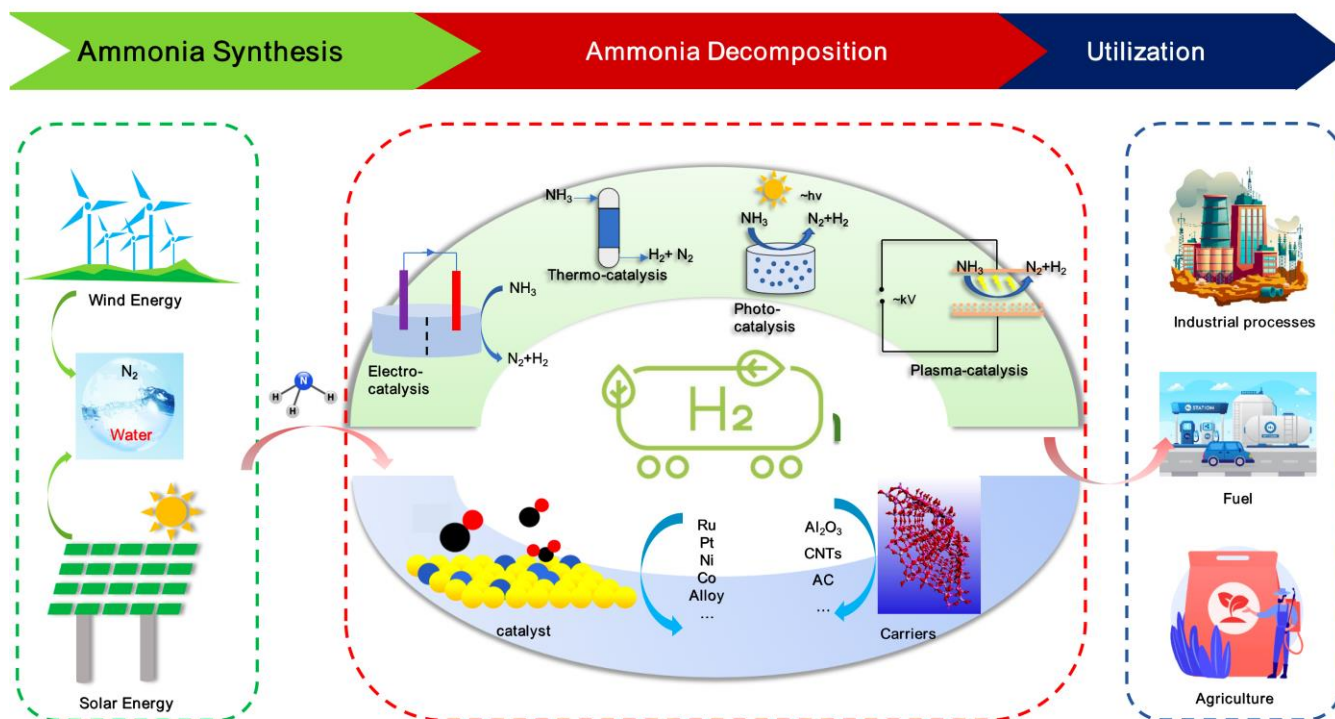
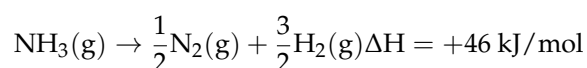


Figure 1. The status of hydrogen production from ammonia decomposition in ammonia economy.

In the past ten years, and especially in the past five, pioneering research and follow-up studies have resulted in new conceptions, methods, and materials for ammonia decomposition. These approaches and underlying mechanisms urgently need to be summarized and understood in detail and are reviewed herein. This paper first analyzes the benefits and drawbacks of various technologies and then describes their characteristics, principles, and mechanisms. Afterward, the composition, performance, and synthesis methods of a series of catalysts are covered.

2. Categories of NH₃ Decomposition

The utilization of NH₃ as a carrier for H₂ has become more widespread due to its beneficial properties and importance in industrial settings, as well as its ability to mitigate air pollution [2,12]. Compared to H₂, NH₃ is more easily liquefied and stored, making it a more feasible alternative.



To produce clean H₂, various technologies have been developed, such as thermo-catalytic NH₃ decomposition, photocatalytic NH₃ decomposition, plasma-catalytic NH₃ decomposition, and electrocatalytic NH₃ decomposition. Figure 2 shows the advantages and disadvantages of each method [10,11,13–18]. Understanding these methods is key to determining the current capabilities of the NH₃-to-H₂ conversion technologies. Figure 3 compares the performance of various technical methods for ammonia decomposition. The results were obtained under different conditions, enabling a thorough evaluation of the effectiveness of each approach [10,19–25]. Further discussion has been explored regarding the benefits and drawbacks of each approach below.

Ammonia Decomposition				
Technical targets: ✓ Clean production process ✓ Efficient and low-cost catalyst ✓ Reactors for safe production that can be applied on a large scale				
Methods	Thermocatalytic decomposition	Photocatalytic decomposition	Electrocatalytic decomposition	Non-Thermal Plasma-catalytic decomposition
Advantages	High conversion rate; Simple process; Technology mature.	Clean reaction process, no contamination; High conversion rate; Mild operating conditions; The catalyst is recyclable.	Less energy is consumed than hydrolysis to produce hydrogen; Mild operating conditions; More potential application prospects.	Quickly create high-temperature reaction conditions; The catalyst has higher dispersibility; Improve the internal energy of reactant molecules and accelerate the reaction; Strong synergy with the catalyst; The catalyst heating rate is high.
Challenges	Too high a temperature causes the catalyst to coke and reduce efficiency; Starting time can not meet the requirements of the engine; Time delay, inefficiency; High demand for external heating and high reaction cost.	The performance of the photocatalyst is too weak; The photocatalyst has the limitations of complex synthesis process, low surface area, insufficient activity, low stability and high band gap.	Slow speed and limited practical use; Poor performance associated with highly utilized precious metal loads; Expensive electrocatalysts; The use of monometallic catalysts is unstable.	The energy produced by the plasma is too much to consume; Relatively high heat loss due to conduction leads to low energy efficiency; Low catalyst target selectivity.
R&D focus	Construction of morphologically or nanostructure-controllable heterophase catalysts; Look for highly efficient, inexpensive, stable and reactive catalysts; Research and development of catalyst carriers with high dispersion and good stability; Introduce good catalyst additives.	Photocatalyst activity, stability and excellent selectivity; Fabrication of new Z-scheme heterostructures to minimize nitrogen oxide formation; Increase H ₂ production to control decomposition products; Development and utilization of semiconductor-based catalysts.	Good catalytic activity, good selectivity and long-term stability; Low-cost and efficient electrocatalyst; Design nano-catalysts that uniquely modify surface chemistry, electronic structure, electroactive sites, and conductivity.	A new type of reactor combined with a catalyst; The choice of catalyst with high efficiency, low cost, high selectivity and high stability; Optimization and design of reactor types.

Figure 2. Advantages and disadvantages of different NH₃ decomposition methods.

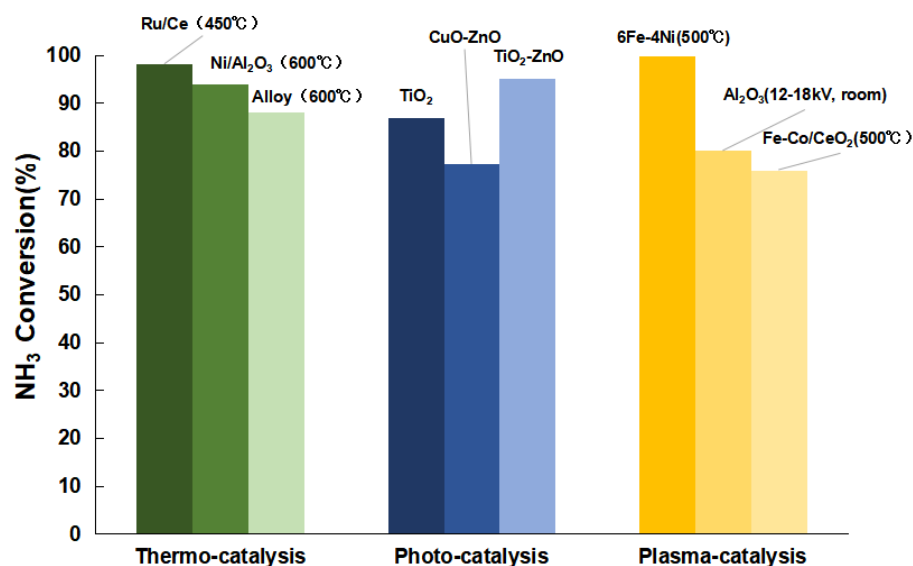


Figure 3. A comparison of various technical methods for ammonia decomposition. (As the evaluation of electrocatalytic NH₃ decomposition for H₂ production is mainly based on current density, no comparison is made here with other technical methods) [10,19–25].

2.1. Thermocatalytic NH₃ Decomposition

It should be noted that without a catalyst, the temperature needed for ammonia decomposition is quite high. This is due to the strong hydrogen bonds present within ammonia molecules, which demand a high level of energy to break apart. As a result, ammonia molecules break down into hydrogen and nitrogen [10,13,26,27]. Therefore, ammonia decomposition without a catalyst is not practical, as it necessitates high temperature

and energy consumption as well as having a low reaction rate. Consequently, catalysts have been created to hasten the sluggish kinetics of NH_3 decomposition and stimulate H_2 production, as shown in Figure 4.

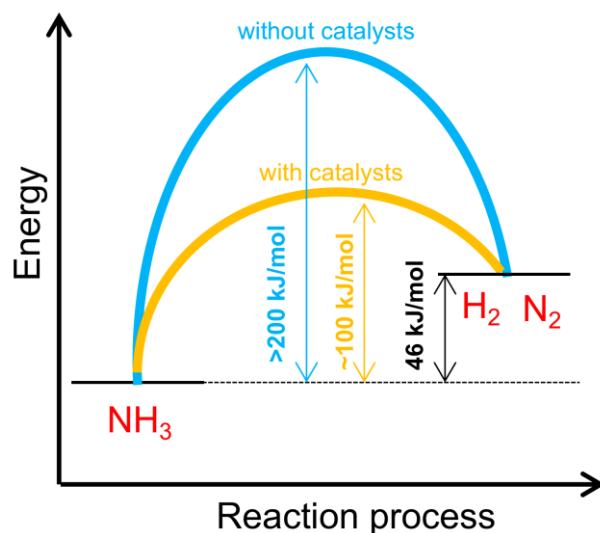
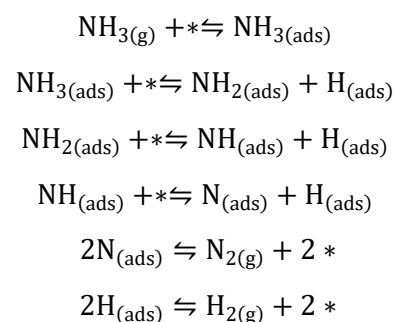


Figure 4. Energy profiles for ammonia decomposition without catalyst and with catalyst.

The catalytic dissociation of ammonia can be explained as a process where ammonia molecules are absorbed into the active site of the catalyst, leading to a sequence of reactions involving dehydrogenation and recombinative desorption [7,9,28]. The reaction is generally accepted to occur in several steps, as shown in Scheme 1. Firstly, there is a molecular adsorption of NH_3 that generates surface NH_3^* at the active sites of metal catalysts. Then, NH_3^* undergoes incremental dehydrogenation, resulting in the production of N^* and H^* atoms. Finally, N^* and H^* undergo recombinative desorption, leading to the release of N_2 and H_2 into the gas phase. These reactions culminate in the creation of di-nitrogen and di-hydrogen on the surface of the catalyst.



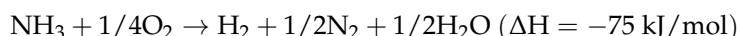
Scheme 1. Elementary kinetic steps for the ammonia decomposition reaction; (*) refers to an unoccupied adsorption site on the catalyst [29].

Regarding the ammonia synthesis reaction, dissociative nitrogen adsorption is typically viewed as the rate-determining step. Nevertheless, there's a possibility that recombinative nitrogen desorption could also impact the rate of the decomposition reaction. This matter requires further investigation and research to determine its actual impact on the reaction kinetics. Lucentini et al. conducted a survey and analysis of various catalytic systems. The technological status and challenges of ammonia decomposition were first presented in their paper. Then, state-of-the-art catalytic systems and related reaction mechanisms were described in detail. Finally, the structured reactors for the decomposition reaction of ammonia were explored [10]. In summary, the nitrogen desorption is the dominant

slow step, but the complexity of the reaction increases with the catalyst composition, active phase, and reaction conditions.

Regarding the catalysts, there has been a growing interest in using transition metal-based catalysts for NH_3 -to- H_2 conversion. Although Ru-based catalysts have demonstrated excellent performance, they are less practical for large-scale applications due to their high cost [30–32]. Therefore, Fe and Ni-based catalysts have emerged as promising alternatives due to their superior performance, but efforts are still underway to further reduce costs, optimize activity, and increase their operational lifespan [33–38]. One approach to improving the activity of these catalyst systems is to use rare earth element-based heteroatoms, such as La and Ce, for doping. This results in improving the surface properties, increasing the number of active sites, and enhancing the catalytic activity of Fe and Ni-based catalysts [39–43]. Another approach is to create multi-metal alloy-based structures, which can further enhance the catalytic activity by providing better dispersion of the metal atoms, improving the stability of the catalyst, and increasing the resistance to poisoning [28,44–49].

The conventional process of H_2 production through thermocatalytic NH_3 decomposition is slow. It requires external energy input to heat the catalyst to at least 400°C for a sufficient time, resulting in time delay and low energy efficiency. Therefore, a more suitable approach for the H_2 production process is needed that does not require external energy input. One such approach involves exposing a pretreated catalyst to a mixture of NH_3 and O_2 gases at a specific ratio at room temperature. This approach is known as low-temperature ammonia oxidation, and it removes the need for the high-temperature decomposition of NH_3 . The reaction proceeds as follows:



Katsutoshi Nagaoka et al. studied hydrogen production using an acidic $\text{RuO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst by exposing ammonia and O_2 at room temperature, as shown in Figure 5 [50]. The exothermic adsorption of ammonia on the catalyst causes the catalyst bed to rapidly heat up to the auto-ignition temperature of catalytic ammonia, resulting in the oxidative decomposition of ammonia to generate hydrogen. A differential calorimeter and a volumetric gas sorption analyzer were used in the study to measure the heat released by the physisorption of multiple ammonia molecules and the chemisorption of ammonia onto both the RuO_2 and acidic sites on the $\gamma\text{-Al}_2\text{O}_3$. The results showed a significant amount of heat evolved during both processes.

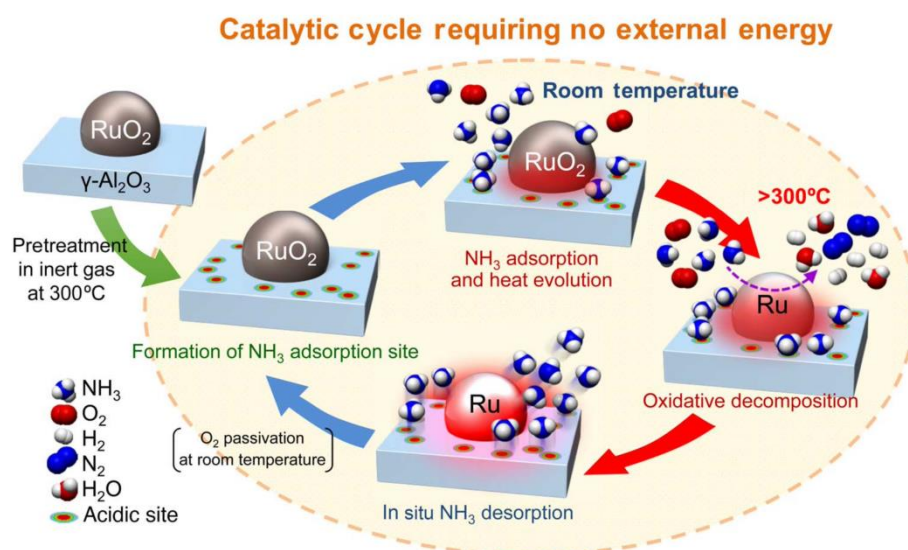


Figure 5. Schematic of the catalytic cycle developed for oxidative decomposition of ammonia (reproduced with permission from [50], Copyright Science, 2017).

2.2. Non-Thermal Plasma-Catalytic NH_3 Decomposition

Thermocatalytic decomposition of NH_3 generally occurs at a temperature above 873 K, while traditional thermal reforming or decomposition of NH_3 typically requires a high temperature of about 1300 K. Despite the presence of a catalyst, the reaction temperature is still relatively high, restricting the reaction's useful applications. To start chemical reactions at lower temperatures, researchers have investigated the potential of alternate strategies involving electrical discharges or non-thermal plasmas [18,21,51]. Researchers have explored the potential of plasma-catalytic NH_3 decomposition. The results show that non-thermal plasma can effectively transform NH_3 into H_2 with less influence from the gas temperature [52–54]. The results of studies conducted on plasma-catalytic NH_3 decomposition suggest that it can be produced with lower energy consumption and higher efficiency [22,55–57].

Generally, the decomposition of ammonia induced through the direct application of plasma is restrained due to the following reasons: (1) Energy efficiency: Direct application of plasma does not now have any significant advantages in terms of energy use in contrast to catalytic decomposition [58–60]. This is because, beneath equilibrium conditions, ammonia can decompose at relatively low temperatures. (2) Plasma stabilization: When ammonia undergoes direct-discharge conditions, it decomposes to produce nitrogen and high concentrations of hydrogen [61]. This makes it challenging to stabilize the plasma, which similarly complicates the process of ammonia decomposition. However, one can still take advantage of the benefits of plasma, such as the speedy introduction of high-temperature reaction conditions. In the catalytic reaction system, plasma can function solely in the preliminary start-up stage segment till the catalyst bed is heated up to the reaction temperature [14]. In this case, hydrogen can be produced immediately at the beginning of the plasma system via the capability of a decomposition reaction. At the same time, the catalyst can be heated quickly via the warmth supplied via the plasma.

The mechanism for the plasma-assisted conversion of NH_3 can be divided into two parts. (1) Plasma mechanisms: These involve electron-induced chemistry, such as electron impact reactions, quenching of excited species, and ion reactions. The energetic electrons in the plasma interact with the NH_3 molecules, leading to various chemical reactions. (2) Thermal mechanisms: These involve conventional thermal mechanisms for thermally induced chemistry. The heat generated by the plasma contributes to the overall conversion of NH_3 . Thermal energy helps break and form chemical bonds, facilitating the conversion process. Bang et al. conducted an experimental and numerical study of the plasma-assisted conversion of NH_3 (Figure 6). They used a mixture of NH_3 (1 mol%) diluted in N_2 at atmospheric pressure. This allowed them to investigate the effects of plasma on NH_3 conversion under specific conditions [62]. They observed that the conversion of NH_3 took place even at room temperature during their study. They found a local peak in conversion at around 600 K. This finding suggests that the plasma-assisted cracking of NH_3 has the potential to be cost-effective by reducing the temperature range required for the cracking reaction. Lowering the temperature window for the cracking reaction can lead to energy savings and improved efficiency in the conversion process.

2.3. Electrocatalytic NH_3 Decomposition

The electrochemical process is also a promising alternative for onboard use, as hydrogen and nitrogen can be gained from the decomposition of ammonia at a moderate temperature [17,63,64]. Liquid ammonia has a theoretical electrolysis voltage of 0.077 V, significantly lower than water's electrolysis voltage of 1.23 V [16,63]. When ammonia is electrolyzed, hydrogen molecules are produced at the cathode, and amide ions are released. Amide ions are oxidized at the anode to form nitrogen molecules. The electrolysis reactor must be designed as a highly closed electrolytic cell under stringent experimental conditions to prevent the oxidation and hydration of metal amides [63]. However, the current efficiency is only 85% at a high cell voltage of 2 V due to the inevitable reverse reaction in

liquid ammonia. To make ammonia electrolysis practical, it is necessary to reduce the cell voltage as much as possible at a high current.

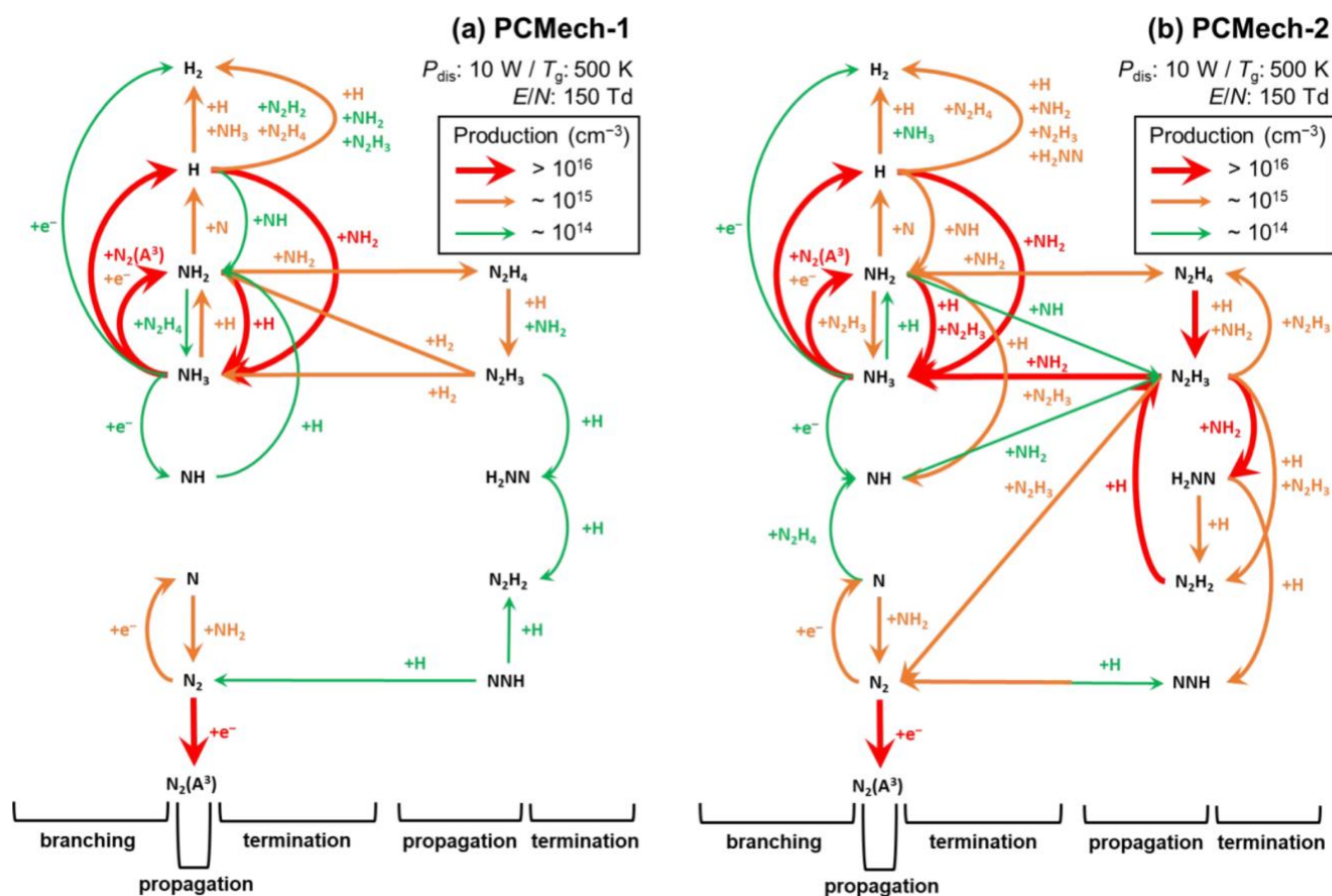
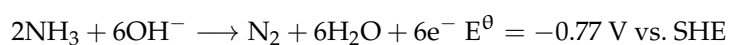


Figure 6. Schematic of the primary chain reactions for (a) PCMech^{-1} and (b) PCMech^{-2} for the NH_3/N_2 combination (1/99 mol%) with $T_g = 500 \text{ K}$, $E/N = 150 \text{ Td}$, and $P_{\text{dis}} = 10 \text{ W}$. (reproduced with permission from [62], Copyright American Chemical Society, 2023).

The electrocatalytic NH_3 decomposition can occur in an aqueous electrolyte under certain pH conditions, either through the NH_3 oxidation in an alkaline environment caused by OH^- ions after the adsorption of NH_3 onto the electrode or through NH_4^+ oxidation by the oxidants such as hypochlorous acid in low pH environments [65–67]. However, electro-corrosion and sluggish kinetics in acidic electrolytes can lead to low efficiency in the electrochemical process. Alternative approaches to address this issue involve using alkaline electrolytes for electrocatalytic NH_3 decomposition, which have been extensively studied and offer the potential to overcome undesirable problems related to acidic environments towards electrode materials. Ideally, in an NH_3 decomposition system, NH_3 is oxidized to N_2 at the anode, while H_2O is reduced to H_2 at the cathode, producing the gaseous H_2 and N_2 from an ammonia solution. However, it is well known that the side reaction of OER may be a competing process with the Electrocatalytic NH_3 decomposition at the anode.

Anode reaction:



Cathode reaction:



Overall reaction:



The use of electrocatalytic NH_3 decomposition to produce H_2 has many benefits, including simplicity and cost-effectiveness. However, problems remain, such as slow kinetics and poor selectivity. To increase the electrocatalytic NH_3 decomposition efficiency, various types of electrocatalysts have been studied, but their performance still cannot satisfy the requirements of industrial applicability. Therefore, it is important to develop new high-efficiency ammonia electrolysis electrodes for hydrogen production, as shown in Figure 7. Although platinum and other precious metal-based catalysts are effective for the process of electrocatalytic NH_3 decomposition (alkaline water electrolysis), their high cost and limited availability are significant drawbacks [16,17,68–70]. Recently, catalysts based on transition metals have shown promise for electrocatalytic NH_3 decomposition through various structural and morphological engineering techniques, including alloyed/core-shell formation, shape control, heteroatom doping, and self-supporting materials [40,66,71–73]. However, the current density of oxidation and selectivity achieved by these catalysts is still lower than what is required for practical application. Therefore, further research and development in this area is necessary.

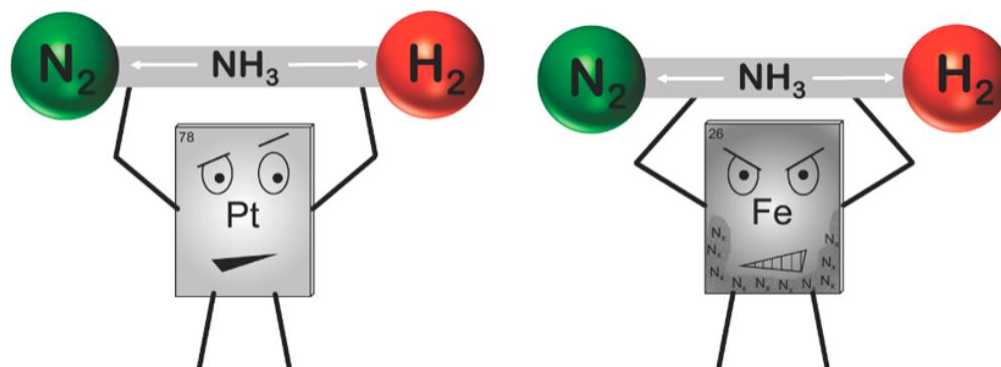
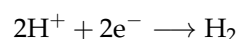
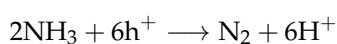
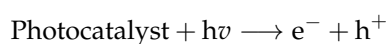


Figure 7. Pt and Fe catalysts decompose ammonia (reproduced with permission from [70], Copyright American Chemical Society, 2017).

2.4. Photocatalytic NH_3 Decomposition

The photocatalytic method of splitting NH_3 into N_2 and H_2 is also a promising approach, as it can be carried out using recyclable catalysts at room temperature and can easily control light exposure with a switch. Using sunlight to decompose ammonia through photocatalysis is an artificial photosynthetic reaction that occurs in alkaline conditions [15]. As shown in Figure 8, when the energy of the irradiating light exceeds the band gap of the photocatalyst it creates electron-hole pairs. The resulting holes act as strong oxidants, while the electrons in the conduction band can reduce O_2 to form hydroxyl radicals. To achieve the photocatalytic degradation of ammonia, the electrons and holes generated on the surface of a semiconductor must have appropriate reduction and oxidation abilities to interact with the adsorbed species on the catalyst surface and produce free radicals or other products.



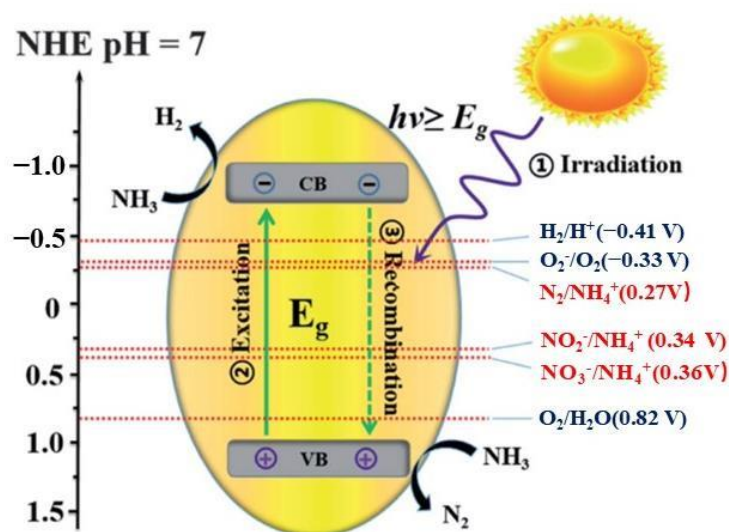


Figure 8. Illustration of the process of photocatalytic ammonia decomposition (reproduced with permission from [15], Copyright Royal Soc Chemistry, 2020).

So far, only a limited number of photocatalysts have been found to be effective in the decomposition of an aqueous ammonia solution. These include common photocatalysts, such as TiO_2 , ZnO , ZnS , Mo_2N , and graphene, as well as their hybrid materials that are loaded with metals [15,74–83]. Utsunomiya et al. studied the photocatalytic activity of TiO_2 loaded with different metals on the decomposition of ammonia and explored the NH_3 decomposition mechanism by proposing three reaction pathways [83]. As shown in Figure 9, route 1 involves the formation of NH radicals by removing one hydrogen atom from each of the two NH_2 radicals, while route 2 involves the coupling of adjacent NH_2 radicals to form $\text{NH}_2\text{-NH}_2$. Route 2' involves the formation of $\text{NH}_2\text{-NH}_2$ through the formation of $\text{H}_2\text{N-NH}_3$. The activation energies for routes 1 and 2 calculated by density functional theory (DFT) are 236 kcal/mol and 74.8 kcal/mol, respectively. Of these pathways, route 2 is considered energetically more favorable than route 1. Possible reaction pathways for the formation of N_2 and H_2 through $\text{NH}_2\text{-NH}_2$ coupling were further divided into two routes: route 2, which involves the coupling of NH_2 radicals to form $\text{H}_2\text{N-NH}_2$, and route 2', which involves the interaction of NH_2 with one NH_3 molecule in the gas phase. The activation energies of the two routes were estimated to be 74.4 kcal/mol and 59.2 kcal/mol, respectively. Therefore, it is plausible that NH_3 decomposition occurs via the formation of $\text{NH}_2\text{-NH}_2$ through routes 2 and 2'. Razak et al. reported the linear generation of H_2 from NH_3 over Pd/TiO_2 catalyst. They suggest that the production of H_2 from NH_3 was initiated by the interaction of N atoms on the Pd surface. This interaction led to the dissociation of N-H bonds under the catalysis of photogenerated electrons [84].

Recently, Yuan et al. have discovered that Cu-Fe-AR, which is not an effective thermocatalyst, can function as an excellent photocatalyst for NH_3 decomposition when exposed to short-pulse laser illumination [85]. The formation of adsorbate–metal excited states by hot carriers leads to the lowering of activation barriers, active site cleaning, and product desorption, resulting in enhanced reactivity and stability of Cu-Fe-AR compared to traditional thermocatalysts. Under continuous-wave LED illumination, Cu-Fe-AR manifests a high efficiency comparable to Cu-Ru-AR. Although Cu-Ru-AR exhibits slightly greater reactivity due to photothermal heating, the study demonstrates that photocatalysis can be efficiently performed with inexpensive LED photon sources, as shown in Figure 10. The results suggested that abundantly available metals might serve as productive and cost-effective catalyst substrates for plasmonic antenna-reactor photocatalysis.

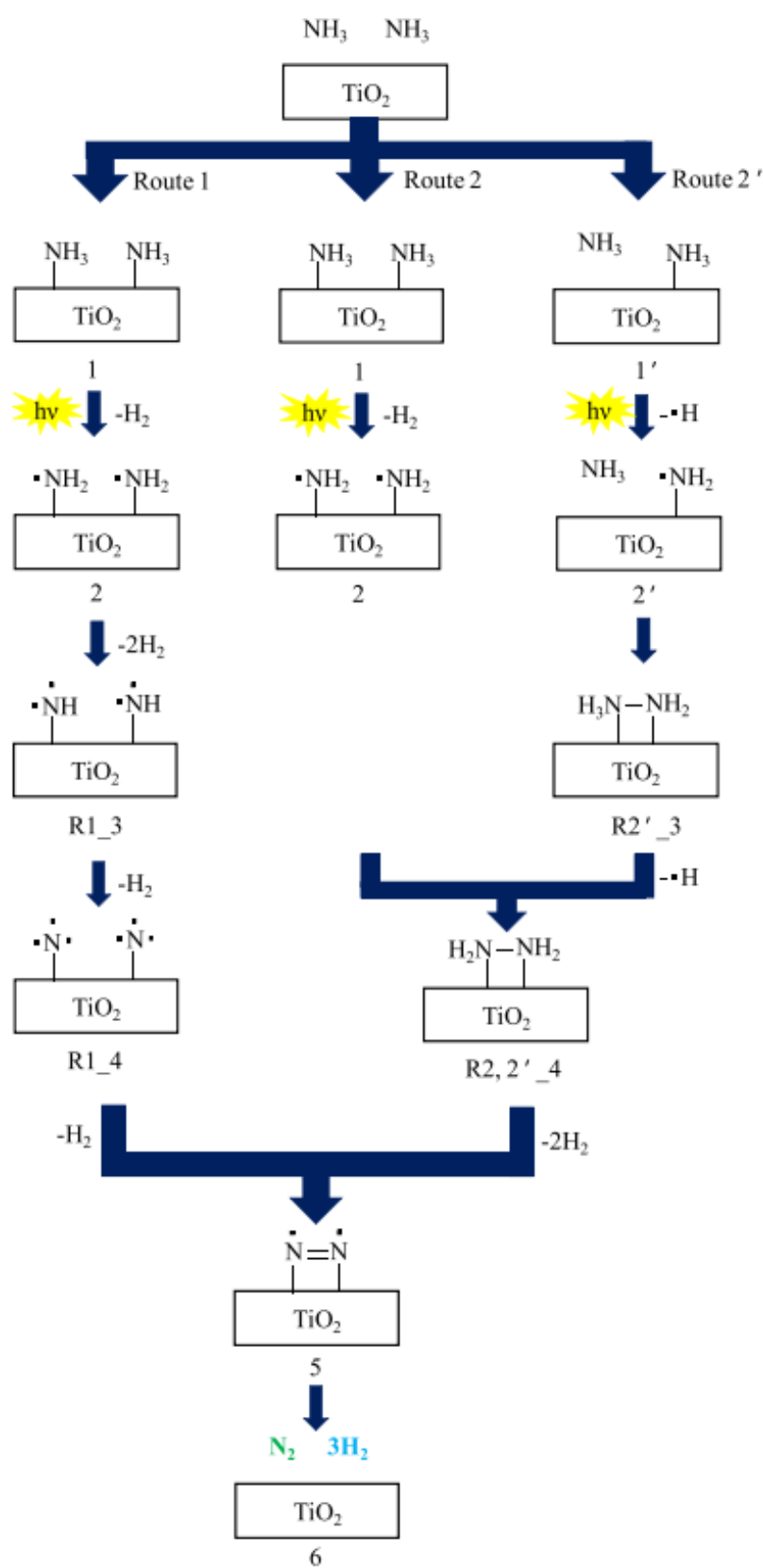


Figure 9. Reaction mechanism of NH_3 decomposition to N_2 and H_2 over TiO_2 photocatalyst (reproduced with permission from [83], Copyright Elsevier, 2017).

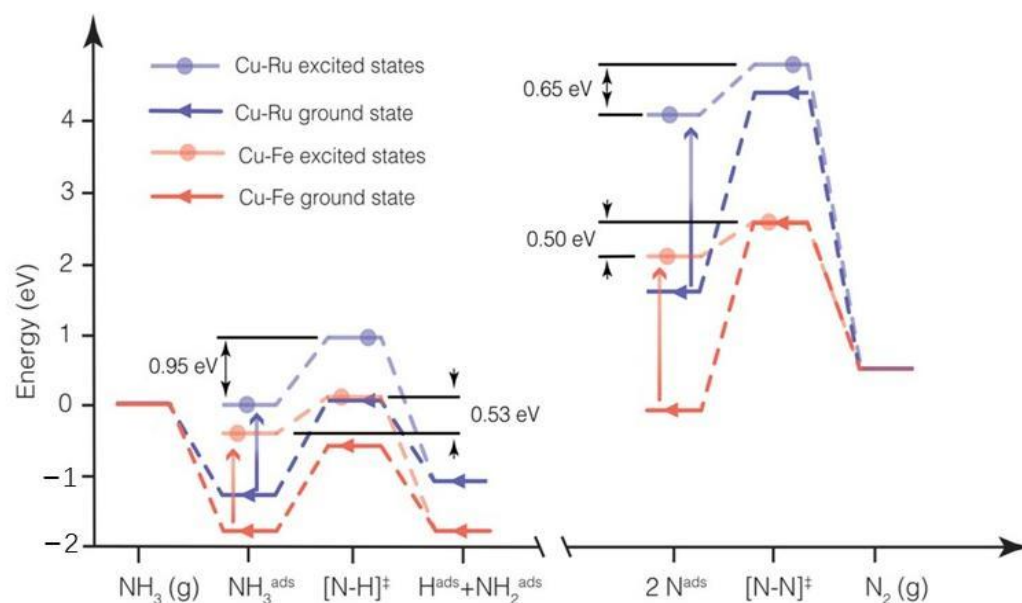


Figure 10. Schematic comparison of the energy diagram for photocatalysis (excited states) and thermocatalysis (ground state) on Cu-Fe- and Cu-Ru-ARs. Red arrows refer to electronic excitation on Fe-N, and blue to Ru-N. Only the two possible RDSs are included for simplicity; migrations of nitrogen species are not considered for the same reason (reproduced with permission from [85], Copyright Science, 2022).

3. Catalysts for NH_3 Decomposition

The choice of catalyst is critical for the efficient decomposition of ammonia to produce hydrogen at low temperatures, and different technologies require different catalysts. For example, the Ru group of catalysts is commonly used in thermocatalytic NH_3 decomposition, while the Pt group is suitable for both electrocatalytic and photocatalytic NH_3 decomposition. In addition to co-catalysts, such as Ru and Pt, photocatalysts are also required in photocatalytic NH_3 decomposition [9,26,72,73]. In non-thermal plasma-catalytic NH_3 decomposition, Fe-based catalysts have been the most studied [48,51,54]. Furthermore, for the industrialization of hydrogen production from ammonia decomposition, catalyst support is vital as it has a synergistic effect on the catalyst's performance. Therefore, this review will focus on precious metal catalysts, non-precious metal catalysts, multi-alloy catalysts, and other aspects, emphasizing the research emphasis on various catalysts in different NH_3 decomposition techniques. By understanding the unique roles catalysts play in different technologies, researchers can optimize performance and improve the overall efficiency of the ammonia decomposition process.

3.1. Precious Metal Catalysts

Precious metals are a significant type of catalyst material, with Ru-based materials being particularly noteworthy for their exceptional performance in NH_3 decomposition [7,9,10,31]. As a result, they have been extensively studied. The catalysis of NH_3 decomposition on Ru-based catalysts is primarily attributed to B5 active sites [31,86–88]. The B5-type site comprises a configuration of three Ru atoms in one layer and two additional Ru atoms in the layer directly above it at a monoatomic step on a Ru(0001) terrace [89], as shown in Figure 11. Thus, the number of B5 active sites is frequently linked to the size and shape of Ru nanoparticles on the catalyst surface [90,91].

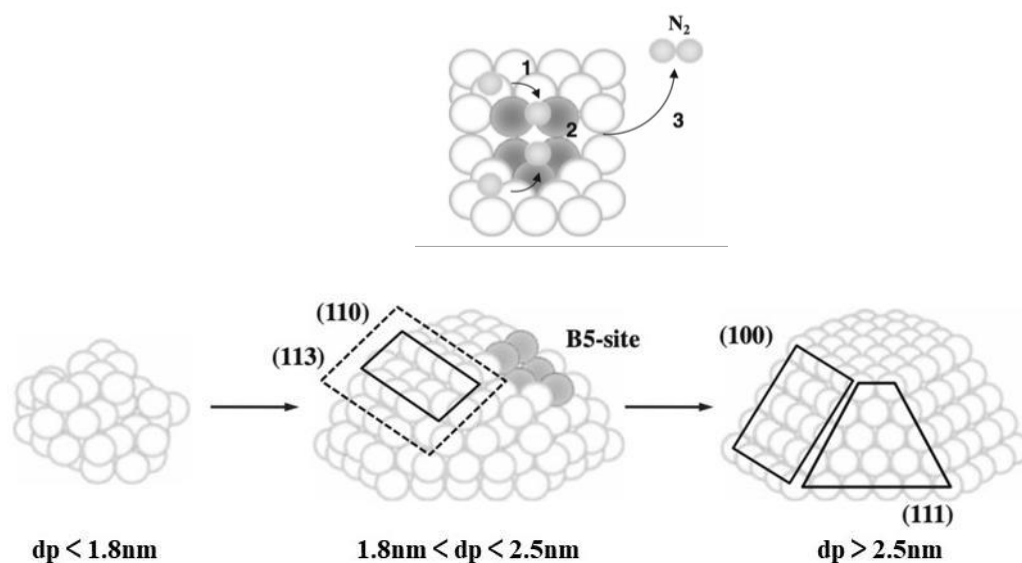


Figure 11. Scheme of associative adsorption of the two N atoms to form an N_2 molecule in a B5-type site: (1) N atoms diffusion to the B5-type site, (2) association of N atoms to form an N_2 molecule, and (3) desorption of the N_2 molecule ('three stages of the growth of an Ru particle' reproduced with permission from [91], Copyright Springer, 2009).

Kim et al. investigated the influence of the crystalline phase of alumina on the decomposition of NH_3 over Ru catalysts supported on alumina [87]. The results show that the dispersion and morphology of Ru are key factors for H_2 production from NH_3 decomposition over Ru/ Al_2O_3 catalysts and can be regulated by the support and calcination temperature. Among the Ru/ Al_2O_3 catalysts calcined at various temperatures and reduced at 573 K, Ru/ γ - Al_2O_3 with Ru particle sizes of 7–8 nm displayed the highest rate of ammonia decomposition. Feng et al. have demonstrated that Yttrium oxide (Y_2O_3) can effectively disperse and stabilize Ru nanoparticles as a functional support for catalysts [92]. Highly dispersed Ru nanoparticles on Y_2O_3 (Ru/ Y_2O_3) were prepared, and the catalytic activity of ammonia decomposition was evaluated. The results showed that at a relatively high weight gas hourly space velocity of $30,000 \text{ mLg}^{-1}\text{h}^{-1}$, the 5 wt.% Ru/ Y_2O_3 catalyst exhibited excellent catalytic activity, achieving near-complete NH_3 conversion at 475°C , superior to many Ru catalysts supported by typical oxides. Cha et al. reported the successful loading of highly monodisperse Ru particles onto alkali-exchanged zeolite Y support using an ion-exchange method coupled with a vacuum calcination treatment [93]. As shown in Figure 12, the resulting Ru/M-Y catalysts exhibit an average particle size of approximately 1 nm and contain both nanometer- and sub-nanometer-sized Ru particles. Hu et al. reported the successful synthesis of stable ruthenium (Ru) clusters with a size of about 1.5 nm by reduction of single Ru atoms under an ammonia atmosphere at 550°C [94]. These Ru clusters are uniformly dispersed on the surface of the ceria. The obtained supported ruthenium cluster catalysts exhibit exceptional activity for ammonia decomposition with an extremely high hydrogen production rate. Ru-based materials have potential applications in Photocatalytic NH_3 decomposition and Plasma-catalytic NH_3 decomposition. Iwase et al. have reported that a Ru-loaded ZnS photocatalyst demonstrated remarkable activity in decomposing an aqueous ammonia solution into H_2 and N_2 with a stoichiometric amount under simulated solar radiation [79]. In this reaction, the Ru co-catalyst was crucial in promoting ammonia oxidation to N_2 .

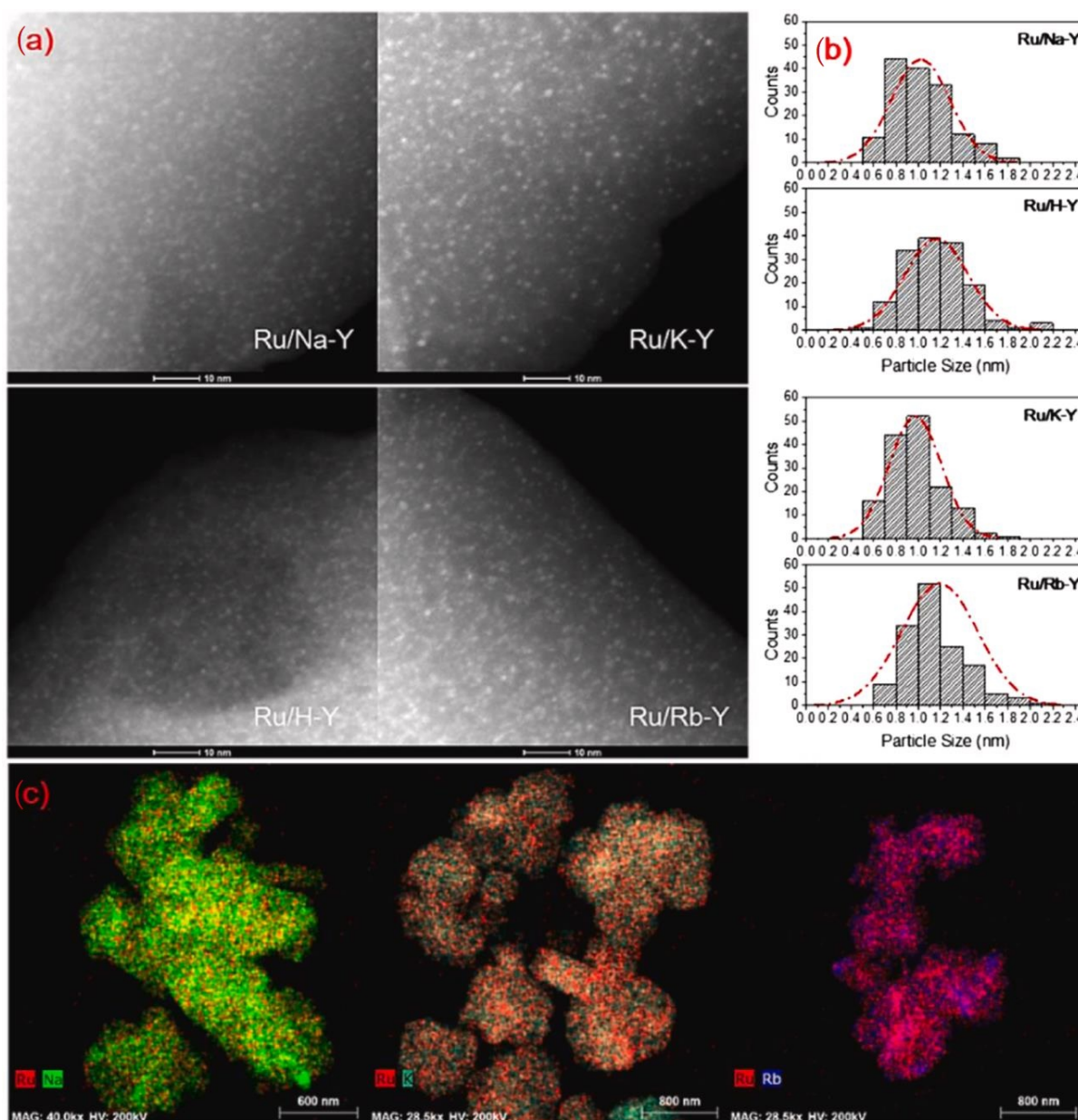


Figure 12. (a) HAADF-STEM images, (b) particle size distribution, and (c) EDS elemental mapping images of Ru/M-Y catalysts (M = H, Na, K, and Rb) (reproduced with permission from [93], Copyright Elsevier, 2021).

On the other hand, the support used also strongly affects the catalytic activity of Ru-based materials. Firstly, a support with a high specific surface area can enhance the dispersal of Ru nanoparticles, leading to improved NH_3 adsorption capacity [92–94]. Secondly, the characteristics of the support itself can have a synergistic effect with Ru nanoparticles, thereby enhancing catalytic activity [23,95–99]. For example, Jeon et al. synthesized a Y-doped BaCeO_3 perovskite and constructed a strong metal support interaction (SMSI) interface with Ru particles, as shown in Figure 13 [95]. The catalyst achieved 100% NH_3 decomposition efficiency at 500 °C and had a higher H_2 generation rate than most Ru-based catalysts. The improvement in catalytic performance can be attributed to the promotion of N_2 desorption by the SMSI interface. Yamazaki et al. studied Ru catalysts supported on $\text{CeO}_2\text{—PrO}_x$ composites (Ru/CP) prepared through coprecipitation [99]. The study found that the activity of the Ru/CP catalyst is higher than that of the Ru/ CeO_2 and Ru/ PrO_x catalysts, and the Pr content ($=\text{Pr}/(\text{Ce} + \text{Pr})$) reached the target value of 33–67%. It was

also revealed that increasing the Pr content in the catalysts enhanced the Ru dispersion but suppressed Ru metalation due to a strong “metal–support interaction”.

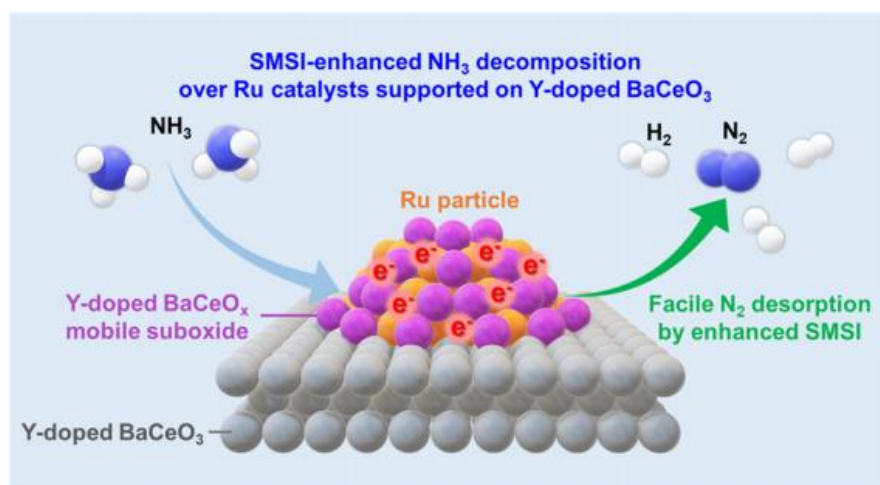


Figure 13. Schematic diagram of NH₃ decomposition of Ru/Y-doped BaCeO₃ catalyst (reproduced with permission from [95], Copyright American Chemical Society, 2022).

Apart from Ru-based materials, Pt-based materials are also extensively studied in the field of NH₃ decomposition. While Ru-based materials are mainly used for thermocatalytic NH₃ decomposition, Pt-based materials are typically employed for photocatalytic and electrocatalytic NH₃ decomposition [16,17,68,69,75,76,100]. In a study by Kominami et al., the photocatalytic NH₃ decomposition performance of metal-supported TiO₂ catalysts was investigated [76]. Pt/TiO₂ exhibited the best performance, with the amount of H₂ and N₂ reaching 90 and 28 μmol, respectively, after 4 h of light irradiation, as shown in Figure 14. The H₂/N₂ ratio was 3.2, consistent with the stoichiometric ratio of NH₃ decomposition. Dong et al. successfully electrolyzed liquid ammonia with metal amide as the supporting electrolyte using Pt electrodes [16]. In a subsequent study, they replaced the Pt electrode with a Pt/Rh/Ir alloy electrode, which tripled the current density [69].

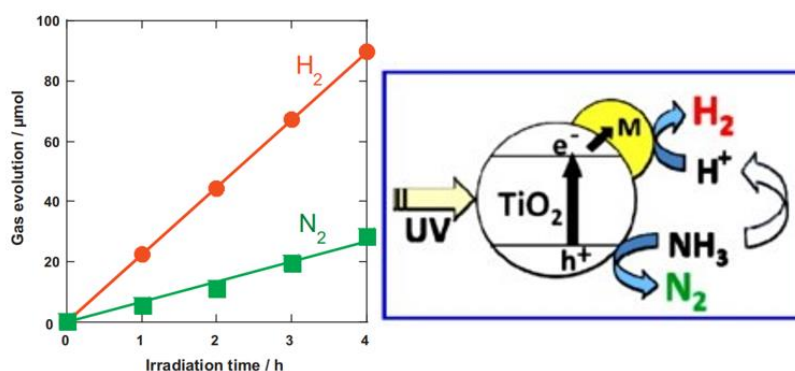


Figure 14. Schematic diagram of Pt/TiO₂ photocatalytic NH₃ decomposition performance and reaction mechanism (reproduced with permission from [76], Copyright Elsevier, 2012).

3.2. Non-Precious Metal Catalysts

Although precious metal materials have excellent NH₃ decomposition ability, their high cost as precious metals limits their potential for large-scale applications. Therefore, researchers are exploring the development of non-precious metal catalysts. Currently, non-precious metals such as Ni, Co, and Fe have demonstrated good NH₃ decomposition activity and are being investigated as potential alternatives [6,9,10,101].

Ni-based catalysts have received significant attention among numerous non-precious metal catalysts due to their lower cost and significant activity [7,102]. The activity of

Ni-based catalysts is primarily influenced by the size of Ni nanoparticles present on the catalyst surface [103–105]. Deng et al. obtained Ni nanoparticles with varying particle sizes through direct thermal reduction of nickel-containing Ca–Al layered double hydroxides (LDH) and tested them for NH_3 decomposition, as shown in Figure 15 [104]. Among these catalysts, the Ni/CaAlO_x catalyst with $\text{Ni}(\text{NO}_3)_2$ as the precursor exhibited the best NH_3 decomposition performance, with an NH_3 conversion rate of 99% at 550 °C. This is because the average particle size of the Ni nanoparticles, reduced with $\text{Ni}(\text{NO}_3)_2$ as the precursor, is the smallest (4.7 nm), allowing for better dispersion on the surface of CaAlO_x and, thus, more effective adsorption of NH_3 .



Figure 15. Schematic illustration of the synthesis of Ni nanoparticles derived from the thermal reduction of Ni-containing Ca–Al LDH (reproduced with permission from [104], Copyright Elsevier, 2021).

Besides the size of Ni nanoparticles, the support used in Ni-based catalysts also plays a crucial role in their catalytic activity. Currently, metal oxides such as CeO_2 [43,106–109], Y_2O_3 [110,111], Al_2O_3 [112–114], and La_2O_3 [115] are commonly used as supports for Ni-based catalysts used in NH_3 decomposition. The high activity of these metal oxide-supported Ni-based catalysts is typically due to the high dispersity of Ni nanoparticles, the strong interaction between the support and Ni nanoparticles, and the presence of oxygen vacancies on the support surface. Li et al. successfully used a Ni single-atom supported CeO_2 (SA Ni/ CeO_2) catalyst for NH_3 decomposition into H_2 under solar heating conditions [109]. The experimental results showed that at 300 °C, the rate of NH_3 decomposition to H_2 reached $3.544 \text{ mmol g}^{-1} \text{ min}^{-1}$, which was superior to all non-precious metal catalysts and most precious metal catalysts. Based on this, they combined their self-made solar heating system, and the H_2 generation rate of the catalyst under 1 sun reached $1.58 \text{ mmol g}^{-1} \text{ min}^{-1}$, which was 100 times higher than the previous record. Do et al. synthesized a series of Ni/ AlCeO_x composites using the cation-anion double hydrolysis method and used them as catalysts for NH_3 decomposition to H_2 production [114]. The experimental results showed that the catalyst exhibited excellent catalytic performance and could completely decompose NH_3 at around 550 °C. The improved catalytic performance can be attributed to the highly dispersed and reducible Ni atoms, the increased amount of surface oxygen vacancies, and the significantly enhanced NH_3 adsorption affinity.

Co-based materials have also been extensively studied as catalysts for NH_3 decomposition [116–118]. Many properties of Co-based catalysts are similar to those of Ni-based catalysts, and their catalytic activity is also influenced by the size of Co nanoparticles and the support structure [119–125]. Lei et al. successfully prepared small Co nanoparticles dispersed on N-doped carbon carriers (Co/NC-X) by pyrolyzing ZIF-67 in an N_2 atmosphere at different temperatures ($X = 500, 600, 700, 800$ °C). They used them as catalysts for NH_3 decomposition to H_2 , as shown in Figure 16 [125]. The Co NPs were evenly distributed and highly dispersed on NC, resulting in high catalytic activity. Among these catalysts, the NH_3 conversion rate of Co/NC-600 at 500 °C was 80%, and the H_2 production rate was $26.8 \text{ mmol g}^{-1} \text{ min}^{-1}$. Yu et al. investigated the effect of BaNH , CaNH , and Mg_2N_3 on the catalytic activity of Co in the NH_3 decomposition reaction [124]. In the

reaction temperature range of 300–550 °C, the formation rate of H_2 was in the order of $\text{Co-BaNH} > \text{Co-CaNH} > \text{Co-Mg}_2\text{N}_3$. Notably, the H_2 generation rate of Co-BaNH at 500 °C reached $20 \text{ mmol g}^{-1} \text{ min}^{-1}$, comparable to the active $\text{Ru/Al}_2\text{O}_3$. In-depth studies revealed that a $[\text{Co-N-Ba}]$ -like intermediate species was formed at the interface of Co metal and BaNH , which led to the higher catalytic activity of Co-BaNH .

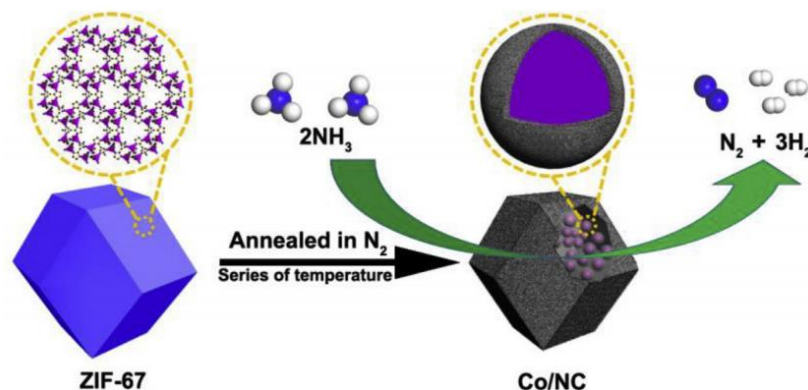


Figure 16. Schematic illustration of the synthesis of Co/NC-X (reproduced with permission from [125], Copyright Elsevier, 2022).

The NH_3 decomposition activity of Fe-based materials is generally lower than that of Ni-based materials and Co-based materials due to the higher bond energy of Fe-N compared to Ni-N and Co-N [9,101]. However, despite this, researchers still have great interest in Fe-based materials due to their low price [36–38,52,55,57,126,127]. Lu et al. found a hidden active phase in Fe-based catalysts for NH_3 decomposition, with the highest dehydrogenation rate corresponding to an evanescent $\text{Fe/Fe}_4\text{N}$ mixing phase [38]. However, the deposition of excess nitrogen atoms on the Fe-based catalyst can cause deactivation and a decrease in catalytic efficiency. Chen et al. observed a “particle size effect” in the activity of $\text{Fe}_3\text{O}_4/\text{Al}_2\text{O}_3$ catalyst in NH_3 decomposition, with TOFs increasing as the size of Fe_3O_4 nanoparticles increased [57]. As shown in Figure 17, this effect was also observed in plasma-catalyzed NH_3 decomposition.

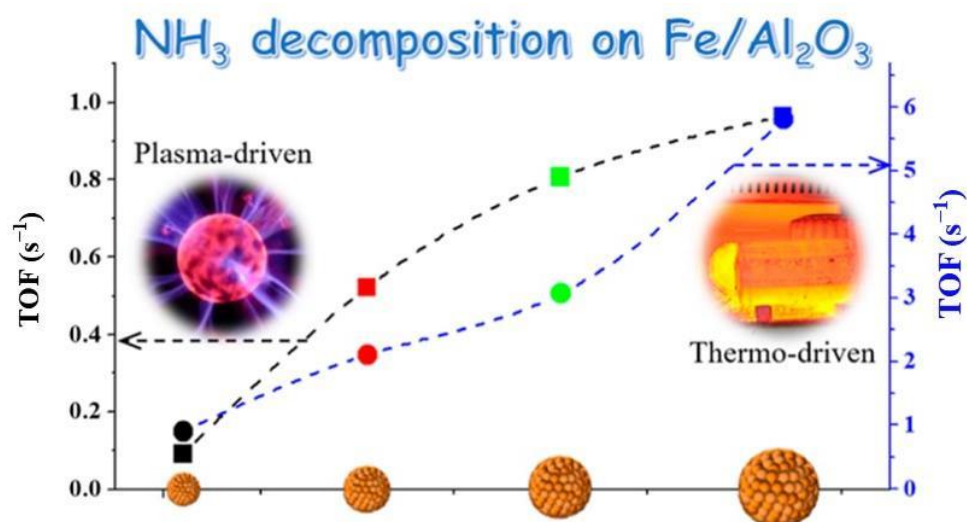


Figure 17. Schematic diagram of NH_3 decomposition ability of $\text{Fe/Al}_2\text{O}_3$ catalysts driven by plasma and thermo as the size of Fe_3O_4 nanoparticles increases (reproduced with permission from [57], Copyright American Chemical Society, 2022).

3.3. Multi-Metallic Catalysts

To overcome the limitations of single noble metal catalysts and single non-noble metal catalysts in the large-scale application of NH_3 decomposition, researchers are exploring the use of multi-metallic catalysts. These catalysts offer a balance between cost and performance, with low cost, good catalytic performance, and high stability. Additionally, the composition and morphology of different metals in the catalysts can be regulated, providing more possibilities for optimization.

At present, bimetallic catalysts are the mainstream of multi-metallic catalysts [28]. Common bimetallic catalysts include Ru-Ni [128–130], Ni-Co [42,46,49,131,132], Ni-Fe [47,48,133], etc. Hansgen et al. developed a computational framework that utilizes nitrogen binding energies to identify potential monolayer bimetallic catalysts [134]. Through this framework, they were able to predict that Ni-Pt-Pt(111) would be an effective bimetallic catalyst for NH_3 decomposition, even exceeding the activity of Ru. Their calculations proved to be successful in identifying this high-performing catalyst. Tabassum et al. synthesized CoNi alloy nanoparticles that were well dispersed on mixed oxide support of $\text{MgO-CeO}_2\text{-SrO}$, with potassium promotion, resulting in the $\text{K-CoNi}_{\text{alloy}}\text{-MgO-CeO}_2\text{-SrO}$ catalyst, as shown in Figure 18 [49]. This catalyst exhibited high efficiency in converting NH_3 , with a conversion rate of 97.7% under reaction conditions of 450 °C and 6000 $\text{mLh}^{-1}\text{gcat}^{-1}$. The study suggests that the active sites located on the metal/oxide interface promote the recombination of adsorbed N atoms, leading to N_2 desorption and a significant reduction in activation energy barriers. Shiraishi et al. developed a bimetallic alloy nanoparticle-supported TiO_2 photocatalyst ($\text{Pt}_{0.9}\text{Au}_{0.1}/\text{TiO}_2$) with 90 mol% Pt and 10 mol% Au [20]. This photocatalyst demonstrated effective decomposition of NH_3 into H_2 and N_2 , with significantly higher catalytic activity than Pt/TiO_2 . The enhanced performance can be ascribed to the presence of Au in the alloy, which reduces the Schottky barrier height at the metal/ TiO_2 interface, leading to a more efficient transfer of conduction band electrons on TiO_2 to the metal particles. Yi et al. conducted a study where they prepared various bimetallic catalysts (Fe-Co, Mo-Co, Fe-Ni, and Mo-Ni) and utilized them for plasma-catalyzed NH_3 decomposition [22]. The results revealed that the Fe-Ni catalyst displayed the highest catalytic activity compared to the other catalysts. Further analysis indicated that the Fe-Ni catalyst had the highest NH_3 adsorption capacity, likely the primary reason for its superior catalytic activity. Jiang et al. investigated various morphologies of NiCo_2N compounds. They specifically focused on the structure of nanoneedles grown on 3D nickel foam. It was found that this particular structure exhibited several advantages, including a significantly increased surface area, more exposed active sites, enhanced charge transfer, and improved gas diffusion. Furthermore, the NiCo_2N composite demonstrated the most optimal catalytic activity in both the hydrogen evolution reaction (HER) and ammonia electrolysis [135].

Developing multi-metal catalysts containing three or more metal elements is a more challenging task, but it also holds greater potential. Xie et al. successfully utilized a novel high-entropy alloy (HEA) CoMoFeNiCu nanoparticles for highly efficient NH_3 decomposition [44]. As illustrated in Figure 19, they overcame the miscibility limit of bimetallic CoMo alloys by stably tuning the Co/Mo elemental ratio in CoMoFeNiCu HEA nanoparticles. The HEA catalyst has a lower cost than Ru-based catalysts and exhibits better catalytic performance than Co-Mo catalysts. At a reaction temperature of 500 °C, the optimal conversion efficiency of NH_3 using this catalyst can reach 100%. Furthermore, the alloy composition and surface adsorption properties of the HEA catalyst can be well-tuned, demonstrating its immense potential for practical applications.

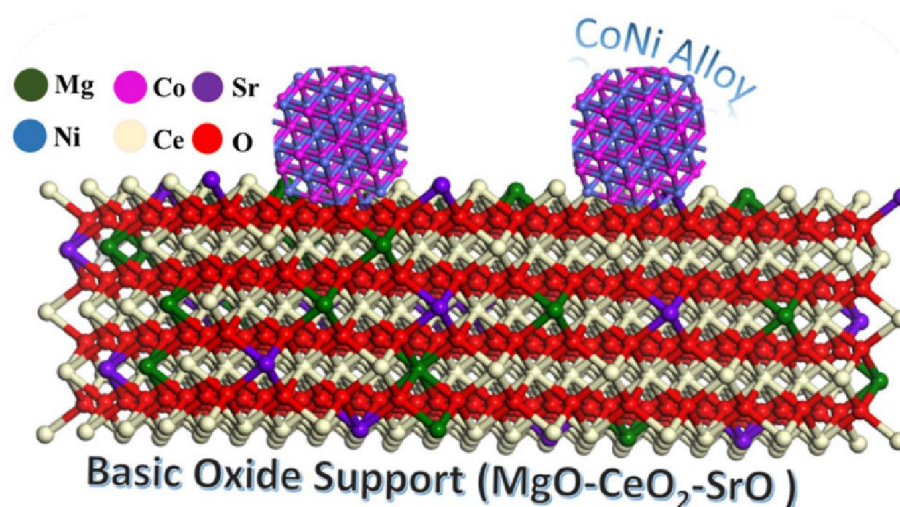


Figure 18. Schematic illustration for the decorated CoNi alloy on the oxide support of MgO-CeO₂-SrO (reproduced with permission from [49], Copyright Royal Society of Chemistry, 2022).

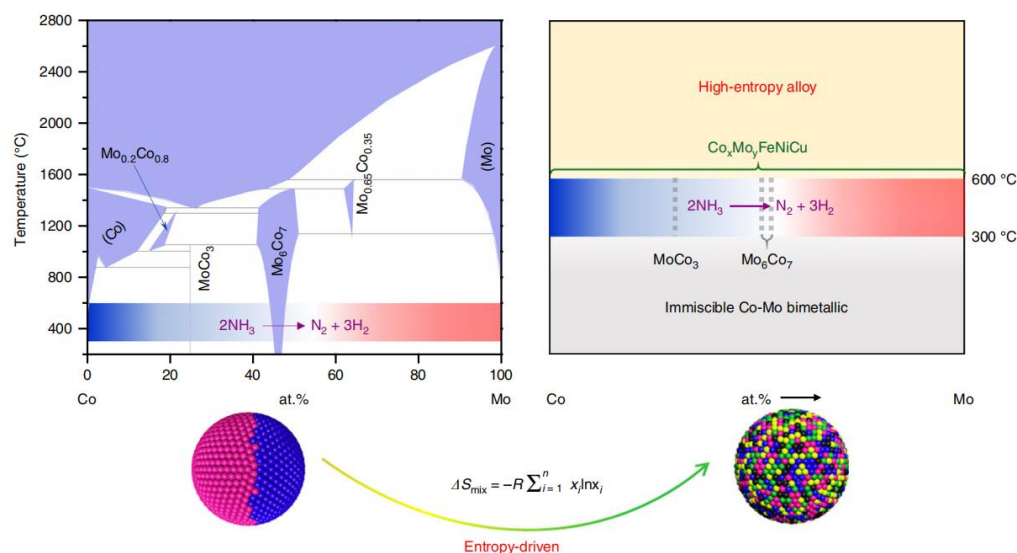


Figure 19. HEA catalysts breaking the miscibility limitation of conventional binary alloys (reproduced with permission from [44], Copyright Nature, 2019).

3.4. Other Catalysts

In addition to metal nanoparticles, some metal nitrides can also be used as NH₃ decomposition catalysts, such as Mo₂N [136–138], MnN [139], Co₃Mo₃N [140–142], etc. Huo et al. designed Mo₂N nanocrystals anchored on two-dimensional (2D) mesoporous silica/reduced graphene oxide (rGO) hybrid nanosheets (Mo₂N/SBA-15/rGO) as an NH₃ decomposition catalyst [136]. Benefiting from the highly dispersed Mo₂N nanocrystals and modest Mo-N band strength, the catalyst exhibits excellent catalytic performance with an ammonia decomposition rate as high as 30.58 mmol g^{−1} min^{−1}. Srifa et al. synthesized Mo₂N-based catalysts with Fe, Ni, and Co additives, as shown in Figure 20 [141]. The NH₃ decomposition activities of Co₃Mo₃N, Ni₃Mo₃N, and Fe₃Mo₃N catalysts were higher than Mo₂N catalysts. Among them, Co₃Mo₃N has the best catalytic performance, and the NH₃ conversion efficiency reaches 94% at 550 °C. The increase in catalytic activity can be attributed to adding Co, Ni, and Fe to increase the particle size and specific surface area of the catalyst and promote the recombination and desorption of N atoms.



Figure 20. Schematic diagram of Mo_2N catalysts with the addition of Co, Ni, and Fe for NH_3 decomposition (reproduced with permission from [141], Copyright Royal Society of Chemistry, 2016).

Researchers have also developed some NH_3 decomposition catalysts of sulfides and carbides, but the performance is average. Kraupner et al. synthesized mesoporous Fe_3C with high crystallinity [143]. The material has transmission pores with a diameter of 20 nm and a high specific surface area (about $415 \text{ m}^2 \text{ g}^{-1}$). At 700°C , the conversion rate of NH_3 is over 95%. Krishnan et al. successfully synthesized MoS_2 -supported acid, and alkaline functionalized (Al, Ti, and Zr)-Laponite catalysts [144]. The results show that the presence of heteroatoms (Al, Ti, and Zr) in the Laponite framework plays a key role in improving the reducibility, acid-base functional groups, and textural properties of MoS_2 . Among them, the MoS_2/Zr -Laponite catalyst has the best NH_3 decomposition performance, and its NH_3 conversion rate at 600°C degrees is 94%.

4. Conclusions

Ammonia decomposition is a highly efficient, environmentally friendly, and sustainable technology for hydrogen production that has attracted significant attention. This article explores the technical path and catalysts used for hydrogen production through ammonia decomposition. The article discusses various technologies and their catalytic mechanisms, highlighting their advantages and disadvantages and their potential for industrialization. The review also covers recent progress in catalyst research for ammonia decomposition, emphasizing the importance of finding non-precious metals to reduce costs and improve efficiency. Overall, this article provides valuable insights into the current state of NH_3 decomposition for H_2 production and the potential for future advancements in this field.

Author Contributions: Conceptualization, X.H. and W.F.; investigation, K.L. and X.L.; writing—original draft preparation, X.H. and Y.M.; writing—review and editing, W.F.; project administration, X.H.; funding acquisition, X.H. All authors have read and agreed to the published version of the manuscript.

Funding: The authors gratefully acknowledge the financial support from The University Synergy Innovation Program of Anhui Province (grant No. GXXT-2020-006 and grant No. GXXT-2022-025).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All necessary data of this review has been included in the paper and no further data is needed.

Conflicts of Interest: The authors declare no conflict of interest.

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