**REVIEW**

# Hydrogen Revolution: Advances in Catalytic Ammonia Decomposition

*Muhammad Anis Aslam [1], Muhammad Mustaqeem [2], Muhammad Sohail Abbas [3,4]\*, Rashid Ahmad [3]\**

[1]*Shanghai Key Laboratory of Hydrogen Science & Center of Hydrogen Science, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*

[2]*Institute of Chemistry, University of Sargodha, Sargodha 40162, Pakistan*

[3]*Department of Chemistry, University of Malakand, Chakdara, Dir-L 18800, Pakistan*

[4]*CAS Key Laboratory of Nanosystems and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China*

## 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. It has evolved as a promising method for hydrogen ($H_2$) production. The discussion highlights the critical role of catalyst composition, support materials, and promoters in enhancing activity, stability, and scalability. By comparing the advantages and limitations of each method, this work provides a roadmap for future research aimed at optimising $NH_3$-to-$H_2$ conversion for sustainable energy applications. This review article has discussed the current advances in ammonia breakdown technology for hydrogen generation, focusing on new materials and mechanical designs for catalysis especially emphasising thermocatalytic, photocatalytic, and electrocatalytic methods. Importance is given to exploring the recent developments of efficient and cost-effective catalysts, including monometallic (e.g., Ru, Ni) and bimetallic systems (e.g., Ru-Ni, Ni-Co), as well as metal hydrides. The Challenges, like high reaction temperatures, slow kinetics, and catalyst deactivation, are explored, and prospective solutions, such as low-tem-

*CORRESPONDING AUTHOR:*

Muhammad Sohail Abbas, Department of Chemistry, University of Malakand, Chakdara, Dir-L 18800, Pakistan; CAS Key Laboratory of Nanosystems and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China; Email: gul.rao85@gmail.com; Rashid Ahmad, Department of Chemistry, University of Malakand, Chakdara, Dir-L 18800, Pakistan, Email: rashmad@gmail.com

perature oxidative cleavage and plasma-assisted methods. The review also explores the mechanistic insights into $NH_3$ decomposition pathways and the synergistic effects of bimetallic catalysts. Moreover, it would help to update the knowledge about the catalytic reaction processes and emphasise 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 ($H_2$) 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 $H_2$ storage plus delivery systems [5]. Therefore, cheaper, efficient, and sustainable methods for $H_2$ production, transportation and storage remain exceedingly required on an urgent basis [6,7]. The ammonia cracking reaction, also known as the thermal ammonia ($NH_3$) breakdown process, has emerged as a potentially viable source of clean energy (**Figure 1**) 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 $^0$C [8–10]. Catalysts with high durability and efficiency are essential for the ammonia decomposition reaction at lower temperatures and full conversion of the $NH_3$ 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].

Therefore, to compete with traditional energy sources, large-scale hydrogen generation from electrolysis requires decreasing the price of electricity derived from clean environmental 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 $LiAlH_4$ are examples of materials used as hydrogen storage media. Numerous

catalysts have been studied for ammonia's low-temperature breakdown [8,20–22]. Among these catalysts that 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 synthesizing catalysts and subsequent modification by selecting supports, adding promoters, and improving operating conditions has 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].
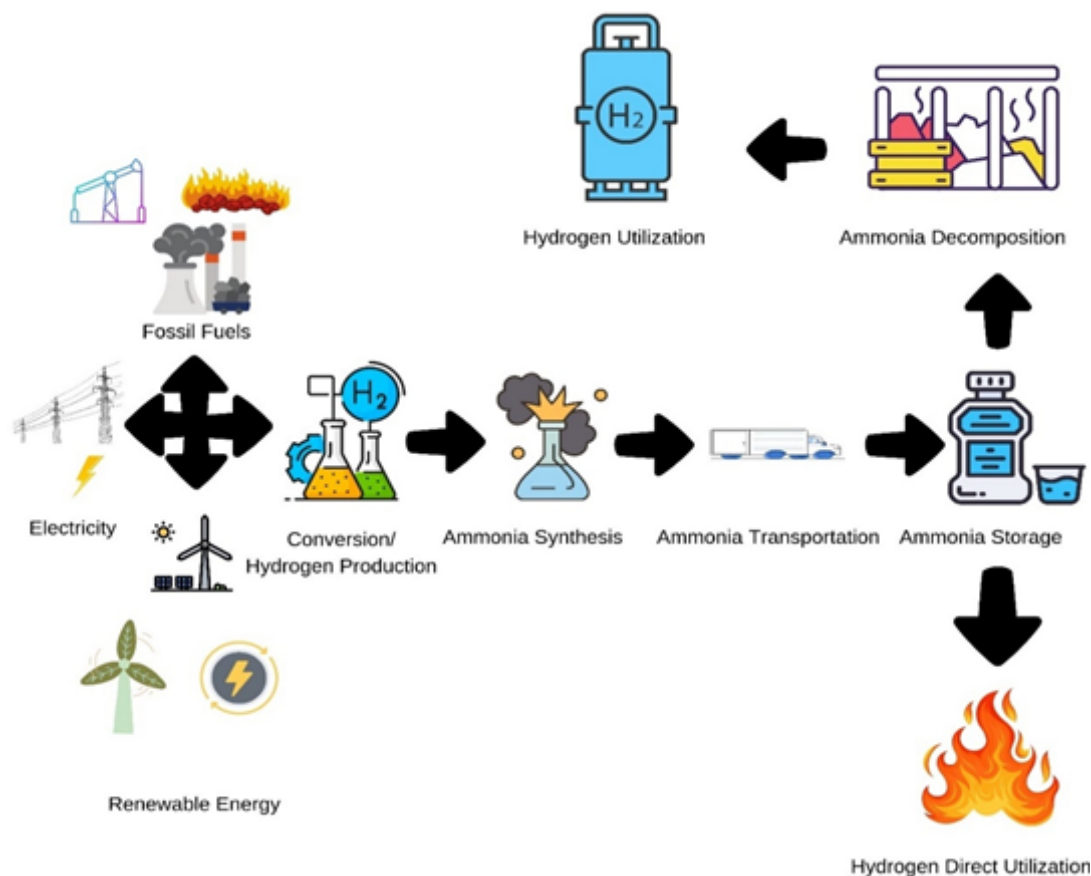


**Figure 1**. The Pivotal Role of Ammonia ($NH_3$) as an Energy Source in Both Contemporary and Prospective Energy Frameworks.

## 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 **Figure 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].
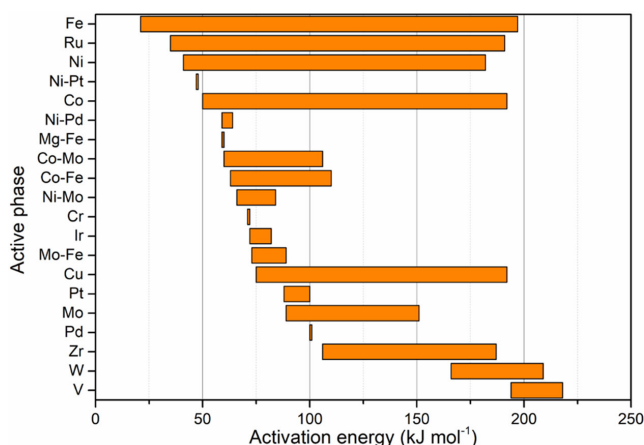


**Figure 2**. Activation Energies of Metal-Based Catalysts for Ammonia Decomposition. Reproduced with Permission from Ref. [32]. Copyright © 2021, ACS.

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 under-stood since it greatly impacts the catalyst's activity. Further exploration based on density functional theory (DFT), in addition to scanning tunneling microscopy (STM), has hinted that the presence of isolated metal atoms, flaws on the catalyst surface, and the micro-structure 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 (additional-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 specialised 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.

# 3. Materials and Approaches for Decomposition of Ammonia

Ammonia ($NH_3$) 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 $H_2$ has expanded [38]. Since $NH_3$ is easier

to liquefy and store than $H_2$, it is considered as a more practical substitute.

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g) \ \Delta H = +46 \ kJ/mol \quad (1)$$
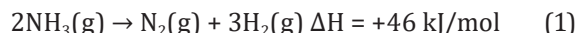
Several approaches, including thermocatalytic, photocatalytic, and electrocatalytic $NH_3$ breakdown, have been developed to produce clean $H_2$. **Table 1** lists each method's benefits and drawbacks [32,39]. To determine the present efficiencies of the ammonia to hydrogen conversion technologies, it 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].

**Table 1**. Advantages and Disadvantages of Different Methods for Ammonia Decomposition.

**Catalytic Ammonia Decomposition**

Technical targets:
- ✓ Clean production process
- ✓ Low-cost catalyst and efficient
- ✓ Safe production reactors that can be applied on a large scale

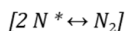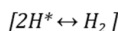| Methods | Thermocatalytic | Photocatalytic | Electrocatalytic |
|---|---|---|---|
| **Advantages** | <ul><li>Simple process</li><li>High conversion rate</li><li>Matured Technology</li></ul> | <ul><li>Clean reaction process.</li><li>High conversion rate.</li><li>Mild operating conditions.</li><li>Recyclable catalyst.</li></ul> | <ul><li>Hydrolysis to produced hydrogen than less energy consumed.</li><li>Mild operating conditions.</li><li>More potential applications.</li></ul> |
| **Challenges** | <ul><li>High temperature causes the catalyst to coke.</li><li>Time delays, inefficiency.</li><li>Starting time cannot meet the requirement of the engine.</li><li>High reaction cost.</li></ul> | <ul><li>Performance of photocatalyst is too weak.</li><li>Photocatalytic has the limitations of complex synthesis process.</li><li>Low surface area, insufficient activity, low stability and high band gap.</li></ul> | <ul><li>Performance of photocatalyst is too weak.</li><li>Photocatalytic has the limitations of complex synthesis process.</li><li>Low surface area, insufficient activity, low stability and high band gap.</li></ul> |
| **R & Focus** | <ul><li>Look for highly efficient, inexpensive, stable, reactive catalysts.</li><li>Research and development of catalyst carriers with high dispersion and good stability.</li><li>Introduced good catalyst additives.</li></ul> | <ul><li>Increase $H_2$ production to control decomposition products.</li><li>Development and utilization of semiconductor-based catalysts.</li><li>Photocatalytic activity, stability and excellent selectivity.</li></ul> | <ul><li>Good catalytic activity, good selectivity and long-term stability.</li><li>Efficient and low cost catalyst.</li><li>Design nano-catalysts that uniquely modify surface chemistry, electronic structure, electroactive sites and conductivity.</li></ul> |

## 3.1. Thermocatalytic $NH_3$ 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 with-

out 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].

This reaction unfolds in several stages, as depicted in **Scheme 1**. Ammonia ($NH_3$) initially undergoes molecular adsorption at the metal catalyst's active sites, forming surface-bound $NH_3$*. Then this $NH_3$* is converted by the stepwise dehydrogenation of $NH_3$*, creating N* and H* atoms. Finally, the recombination and release of N* and H* through desorption processes yield nitrogen ($N_2$) and hydrogen ($H_2$) gases. These reactions collectively facilitate the production of $N_2$ and $H_2$ on the catalyst's surface.

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

$$NH_3 + * \leftrightarrow NH_3 *$$

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

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

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

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

$$[2 N * \leftrightarrow N_2]$$
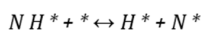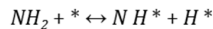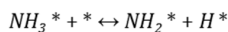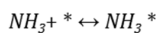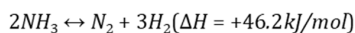
**Scheme 1.** Basic kinetic stages of the ammonia decomposition reaction; (*) denotes a vacant adsorption site on the catalyst [42].

Studies have shown that alkali, alkaline and rare earth metals are helpful boosters for ammonia production. To enhance the capability of $NH_3$ decomposition, it is essential to identify the promoter's active component and optimise 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 an 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 $NH_3$ 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 $H_2$ in one hour. Other alkali metal hydrides mixed with $NH_3$ might also be viable choices for producing compressed hydrogen, following the example given by the $NH_3$-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 $NH_3$ to $H_2$. 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].

There are various parameters that influence the catalytic decomposition of $NH_3$, such as electrochemical properties, electronic energy state configurations, redox potential, including the catalyst morphology, and the number of active sites on it (as shown in **Figure 3**). In addition to being essential for breaking $NH_3$ into nitrogen and hydrogen, the transfer of charges between the adsorption sites on the catalyst surface and its support may also be important for stabilising 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 $NH_3$ decomposition process differ, making it difficult to characterise the reaction using just one parameter [47].
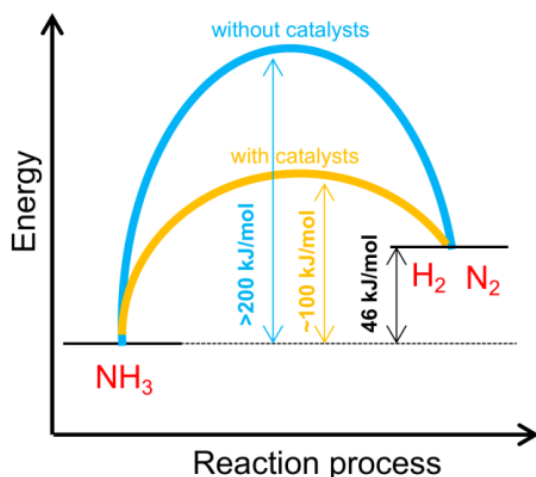
**Figure 3**. Energetic Overview of Ammonia Decomposition with and Without a Catalyst.

## 3.2. 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 $NH_3$. 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 $H_2$ via thermocatalytic $NH_3$ 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 $H_2$ manufacturing process. One such method is to subject a catalyst prepared for a combination of $NH_3$ and $O_2$ 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:

$$NH_3 + 1/4O_2 \rightarrow H_2 + 1/2N_2 + 1/2H_2O \ (\Delta H = -75 \text{ kJ/mol}) \quad (2)$$
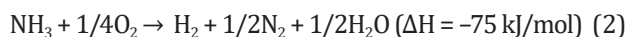
An acidic $RuO_2/\gamma\text{-}Al_2O_3$ catalyst was reported by Katsutoshi Nagaoka et al. to produce hydrogen utilizing ammonia and $O_2$ at room temperature, as shown in **Figure 4** [51]. They used an acidic $RuO_2/\gamma\text{-}Al_2O_3$ catalyst for the reaction of $O_2$ and ammonia at room temperature. 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 $RuO_2$ and acidic sites of $\gamma\text{-}Al_2O_3$. The findings demonstrated that both stages produced a considerable quantity of heat.

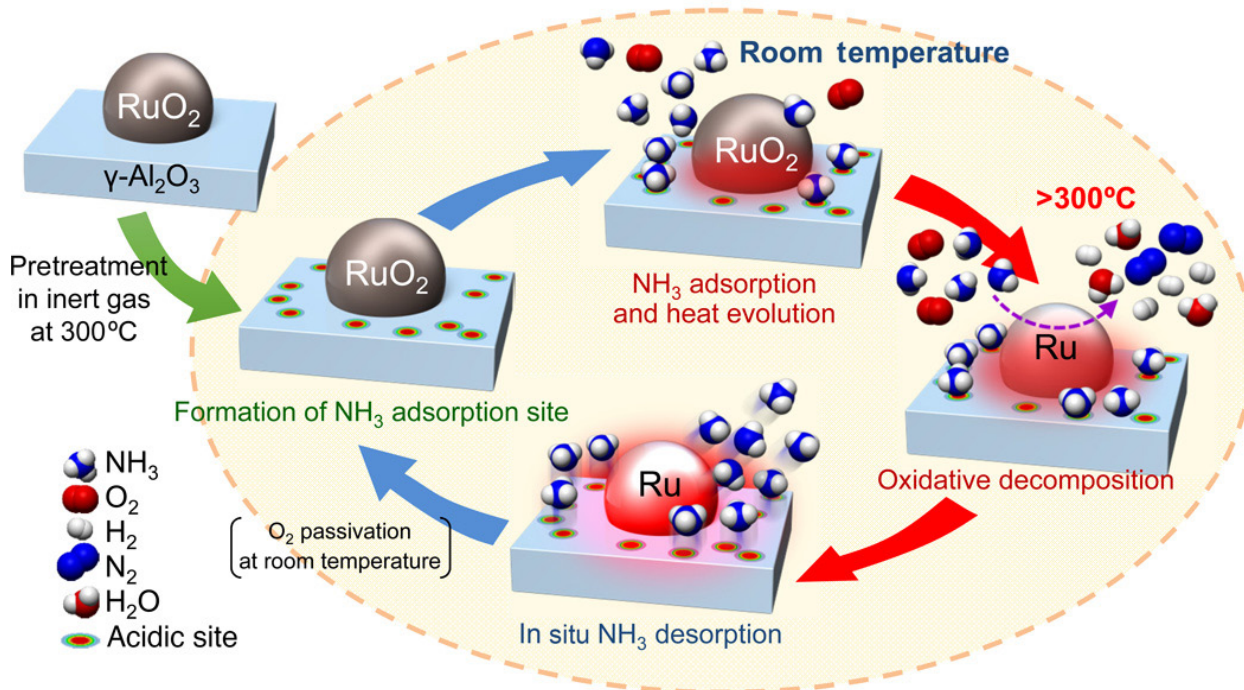# Catalytic cycle requiring no external energy



**Figure 4**. A cyclic Representation of Ru-Catalysed Oxidative Cleavage of Ammonia. Reproduced with Permission from Ref. [32]. Copyright © 2021, RSC.

## 3.3. 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. However, Ru's high price and scarcity, which are 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.

Contrastingly, in noble metal catalysts, d-block metal catalysts exhibited reduced activity at low temperatures since their $NH_3$ 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].

As shown in **Figure 5a–e**, 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 [21,30]. Inokawa and colleagues studied Ni's catalytic activity by controlling its particle size. By adsorbing and breaking down $Ni(C_5H_5)_2$, on zeolite-Y, they created a CH zeolite catalyst. Following reduction at 400 °C in an $H_2$ environment, the TEM Fguire-5 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.

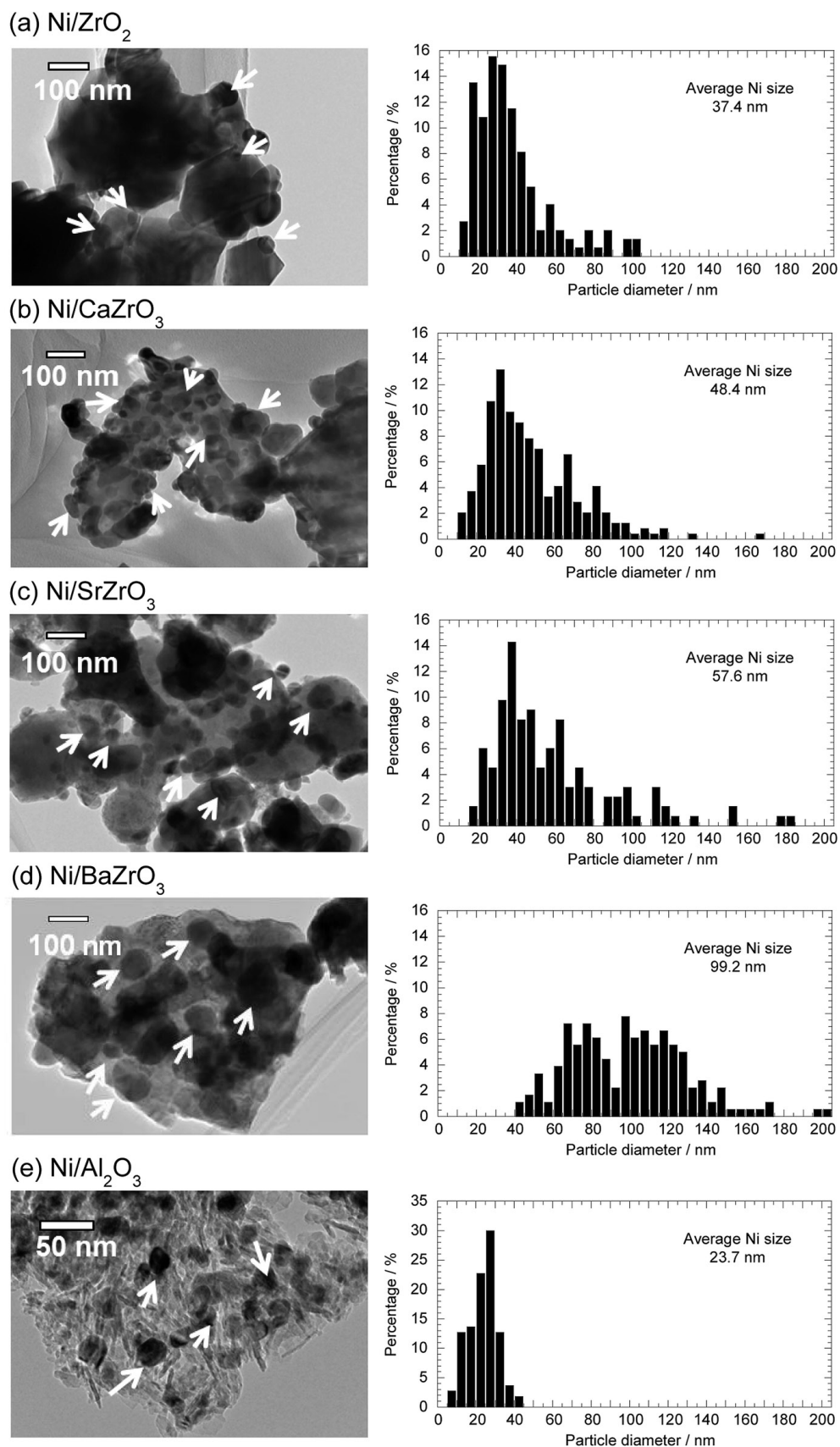**Figure 5**. TEM Images and Ni Particle Size Distribution Histograms of 40 wt% **(a)** Ni/ZrO$_2$, **(b)** Ni/CaZrO$_3$, **(c)** Ni/SrZrO$_3$, **(d)** Ni/BaZrO$_3$, and **(e)** Ni/Al$_2$O$_3$. Reproduced with Permission from Ref. [21]. Copyright © 2018, RSC.

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 showed that adding lanthanum to alumina enhanced catalytic efficiency and that the ideal ton of frequency utilizing $Ni/Al_2O_3$ catalyst was reached with Ni particle sizes ranging from 1.8 to 2.9 nm [53].

The catalytic performance of nickel is thought to be enhanced by adding rare earth metal promoters. In $Ni/Al_2O_3$ 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 ($ABO_3$). 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, $Ni/BaZrO_3$ proved the most efficient for $NH_3$ breakdown. Using catalysts based on $CeO_2$ and $Al_2O_3$, 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 $CeO_2$ was a better support material in terms of activity than $Al_2O_3$. However, Ru surface area loss from metal sintering with $Ru/Al_2O_3$ and Ru volatilization with $Ru/CeO_2$ 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, $Ru/CeO_2$ exhibits better performance in ammonia decomposition, but $Ni/CeO_2$ provides more benefits regarding catalyst lifespan and economic feasibility.
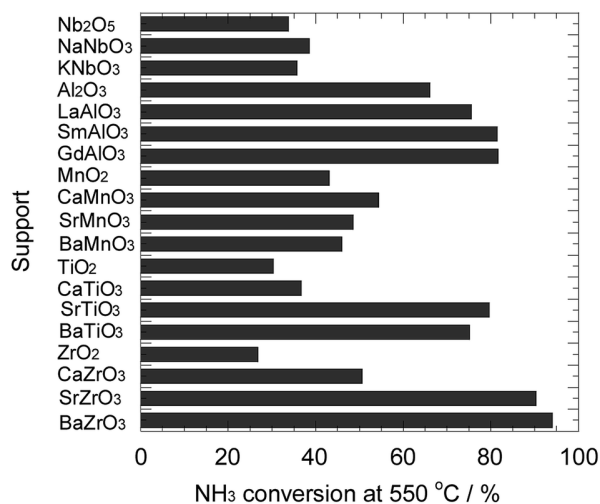


**Figure 6**. Catalytic $NH_3$ Decomposition Using Ni-Based Catalysts Supported on Different Oxides. Reproduced with Permission from Ref. [21]. Copyright © 2018, RSC.

## 3.4. Photocatalytic Decomposition of $NH_3$

The photocatalytic method of disintegrating ammonia into nitrogen and hydrogen is a potential technique that uses room-temperature, 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.
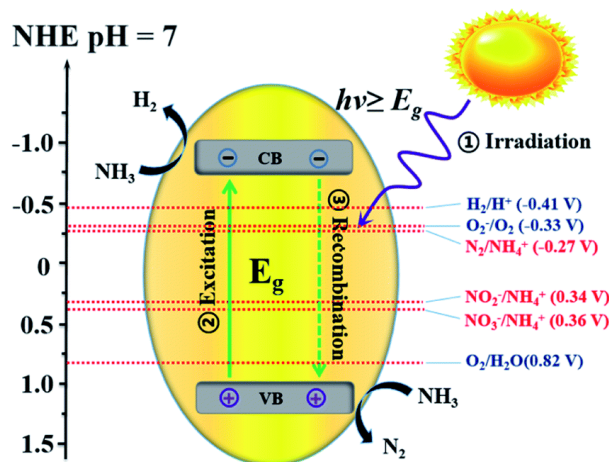


**Figure 7**. Photocatalytic Decomposition of Ammonia. Reproduced with Permission from Ref. [21]. Copyright © 2020, RSC.

In the photocatalytic process, these holes function as solid oxidisers, and the electrons which move to the conduction band act as reducing agents. These electrons can effectively reduce $O_2$ 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.

$$Photocatalyst + hv \rightarrow e^- + H^+ \qquad (3)$$

$$2NH_3 + 6h^+ \rightarrow N_2 + 6H^+ \qquad (4)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (5)$$
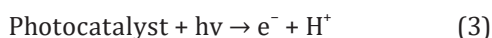
Thus far, a small number of photocatalysts have demonstrated efficacy in decomposing aqueous ammonia solutions. These include commonly used photocatalysts like graphene, ZnO, ZnS, $Mo_2N$, and $TiO_2$, as well as hybrid forms with metal loadings [56,57]. Utsunomiya et al. concentrated on the breakdown of ammonia in their investigation of the photocatalytic characteristics of $TiO_2$ impregnated with different metals. They investigated the mechanism of $NH_3$ breakdown and proposed three other lines of inquiry to clarify the procedure [58]. **Figure 8** describes the several pathways that lead to the degradation of $NH_3$. In route 2, neighbouring $NH_2$ radicals are coupled to generate $NH_2$-$NH_2$, whereas, in route 1, NH radicals are created by eliminating one atom of hydrogen from each of the two $NH_2$ 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 $N_2$ and $H_2$ synthesis through $NH_2$-$NH_2$ coupling route 2, which involves combining $NH_2$ radicals to generate $H_2N$-$NH_2$ and route 20 which involves $NH_2$ interacting with a single $NH_3$ 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 $NH_3$ breakdown most likely occurs via pathways 2 and 20, where $NH_2$-$NH_2$ formation occurs.



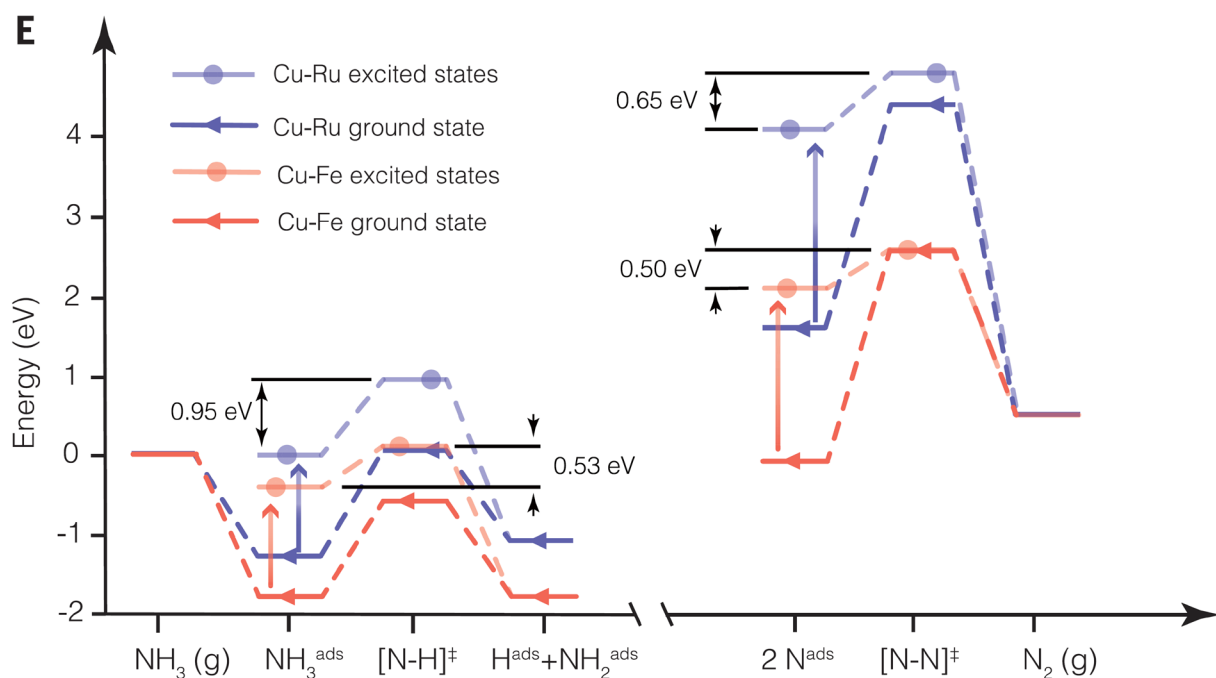**Figure 8**. The Energy Diagrams for Thermocatalysis (Ground State) and Photocatalysis (Excited States) on Cu-Fe- and Cu-Ru-ARs are Schematically Compared. Blue Arrows Point to Ru-N, While Red Arrows Point to Electrical Excitation on Fe-N. For Simplicity, Just the Two Feasible RDSs are Provided; Relocations of Nitrogen atoms are not Considered for This Reason. Reproduced with Permission from Ref. [58]. Copyright © 2022, Science.

Razak et al. suggested that the interaction of nitrogen atoms on the palladium surface was the cause of the linear $H_2$ synthesis from $NH_3$ over a Pd/TiO$_2$ 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 $NH_3$ when subjected to short-pulse laser light [58]. 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 9** illustrates. The results show that easily obtained metals may be used as affordable and efficient substrates for photocatalysis using plasmonic antenna-reactor technology.

## 3.5. 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 $NH_3$ is adsorbed onto an electrode, OH$^-$ ions can cause $NH_3$ oxidation in an alkaline environment, or a low pH environment, oxidants like hypochlorous acid can cause $NH_4^+$ oxidation. These two processes can lead to electrocatalytic $NH_3$ decomposition in an aqueous electrolyte [63,64]. 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 $NH_3$. These materials have thoroughly been studied and are likely to mitigate the disadvantages concerned to acidic environments and electrode compositions.
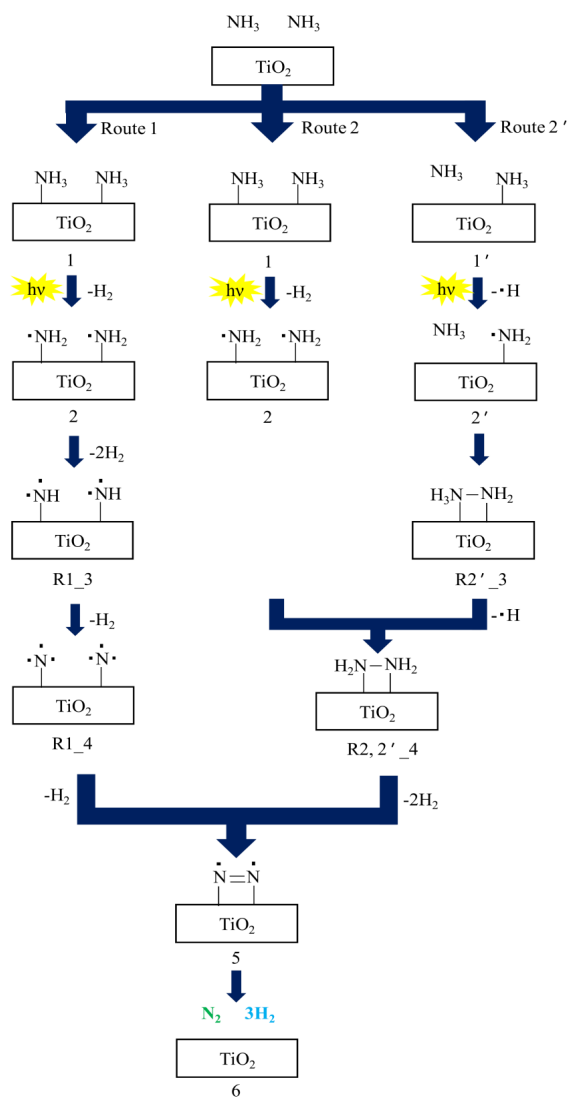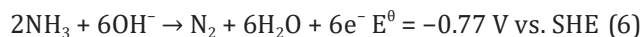


**Figure 9**. Mechanism of Ammonia Decomposition over TiO$_2$ Photocatalyst. Reproduced with Permission from Ref. [59]. Copyright © 2017, Elsevier.
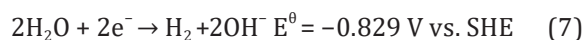
Ammonia solution is transformed into hydrogen and nitrogen gases in an ideal ammonia decomposition system, where ammonia is oxidized to nitrogen gas

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 $NH_3$ at the anode as a side process.
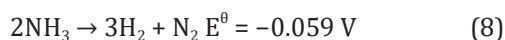
Reaction at anode:

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

Reaction at cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad E^\theta = -0.829 \text{ V vs. SHE} \quad (7)$$

Overall reaction:

$$2NH_3 \rightarrow 3H_2 + N_2 \quad E^\theta = -0.059 \text{ V} \quad (8)$$

Its simplicity and affordability are among the numerous advantages of electrocatalytic $NH_3$ breakdown for $H_2$ production. Still, issues like poor selectivity and delayed kinetics exist. Electrocatalysts of many kinds have been explored to improve the efficiency of electro-catalytic $NH_3$ 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 $NH_3$ 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 [65–68]. Recently, transition metal-based catalysts have shown potential for electrocatalytic $NH_3$ degradation using a range of structural and morphological engineering methods, including shape control, heteroatom doping, alloyed/core-shell creation, and self-supporting materials [64,69–72]. 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.
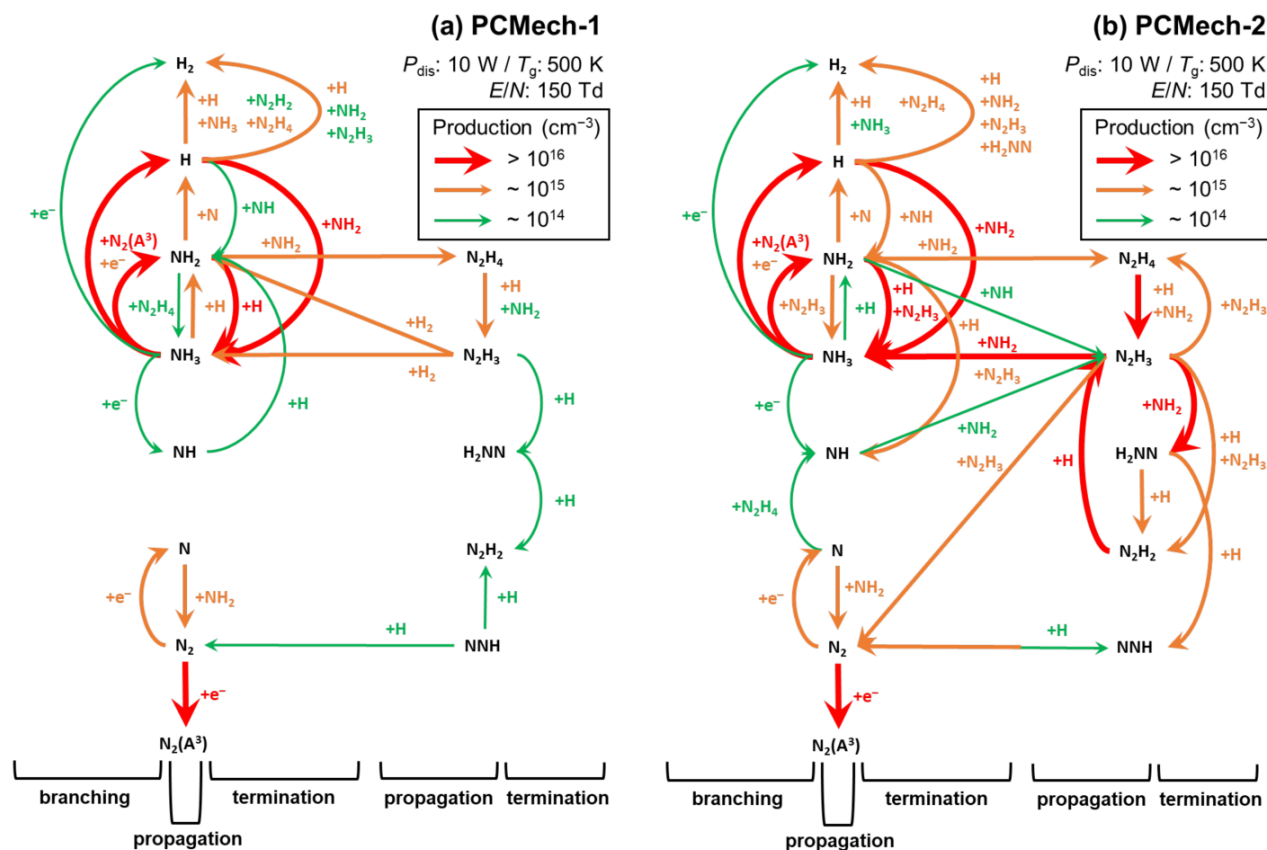


**Figure 10**. Schematic Representation of the Primary Chain Reactions for (**a**) PCMech-1 and (**b**) PCMech-2 for the $NH_3$/$N_2$ Combination (1/99 mol%) with Tg = 500 K, E/N = 150 Td, and Pdis = 10 W. Reproduced with Permission from Ref. [63]. Copyright © 2023, ACS.
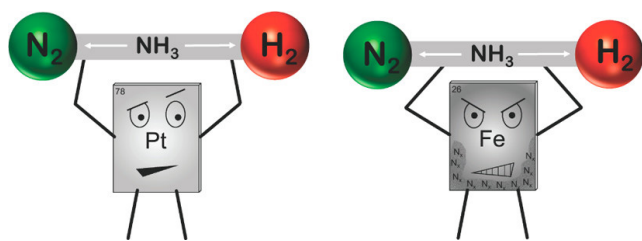
**Figure 11**. Ammonia Decomposition by Pt and Fe Catalysts. Reproduced with Permission from Ref. [32]. Copyright © 2023, ACS.

## 3.6. 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 [73].

Commonly used bimetallic catalysts are Ru-Ni, Ni-Co, Ni-Fe, etc [2,26,28,73–77]. 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 $NH_3$ breakdown than Ru. Tabassum and co-workers created a "K-CoNi alloy-MgO-CeO$_2$-SrO" catalyst, as shown in **Figure 12**. They synthesized this catalyst by spreading CoNi alloy nanoparticles evenly over a mixed oxide support comprising MgO–CeO$_2$-SrO boosted with potassium [2]. With a remarkable 97.7% conversion rate for $NH_3$, this catalyst performed exceptionally well at 450 °C and 6000 mL per hour per gram 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 $N_2$ and a significant decrease in the activation energy barriers.

$Pt_{0.9}Au_{0.1}/TiO_2$, a bimetallic alloy nanoparticle-supported $TiO_2$ photocatalyst with 90% Pt and 10% Au, was created by Shiraishi and associates [78]. Compared to $Pt/TiO_2$, this photocatalyst presented better catalytic activity, for converting ammonia into $H_2$ and $N_2$. The alloy's improved performance is partly due to the reduction of the Schottky barrier height at the metal/$TiO_2$ interface caused by the presence of Au. This enhances the transport of electrons from the $TiO_2$ conduction band to the metal particles.
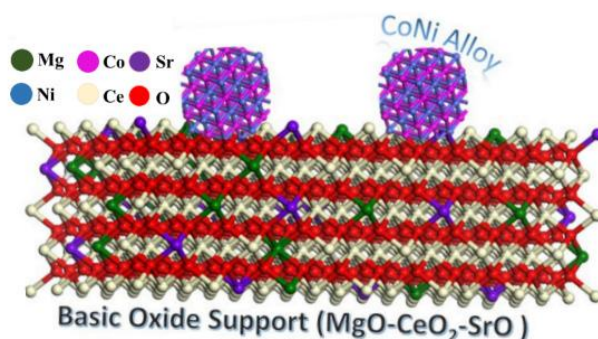


**Figure 12**. CoNi Alloy Supported on MgO–CeO$_2$–SrO. Reproduced with Permission from Ref. [2]. Copyright © 2022, RSC.

In their investigation into the plasma-catalyzed breakdown of $NH_3$, Yi et al. created and evaluated a variety of bimetallic catalysts, such as Fe-Co, Mo-Co, Fe-Ni, and Mo-Ni [79]. 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 $NiCO_2N$ 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 $NiCO_2N$ composite provided the best catalytic performance in the hydrogen evolution (HER) and ammonia electrolysis [80].

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 $NH_3$ breakdown. The miscibility limit of bime-

tallic 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 $NH_3$ conversion efficiency may approach 100% when reaction was carried out at 500 $^0$C. Moreover, the HEA catalyst's alloy composition and surface adsorption characteristics can be precisely adjusted, showcasing its enormous potential for real-world uses [81].
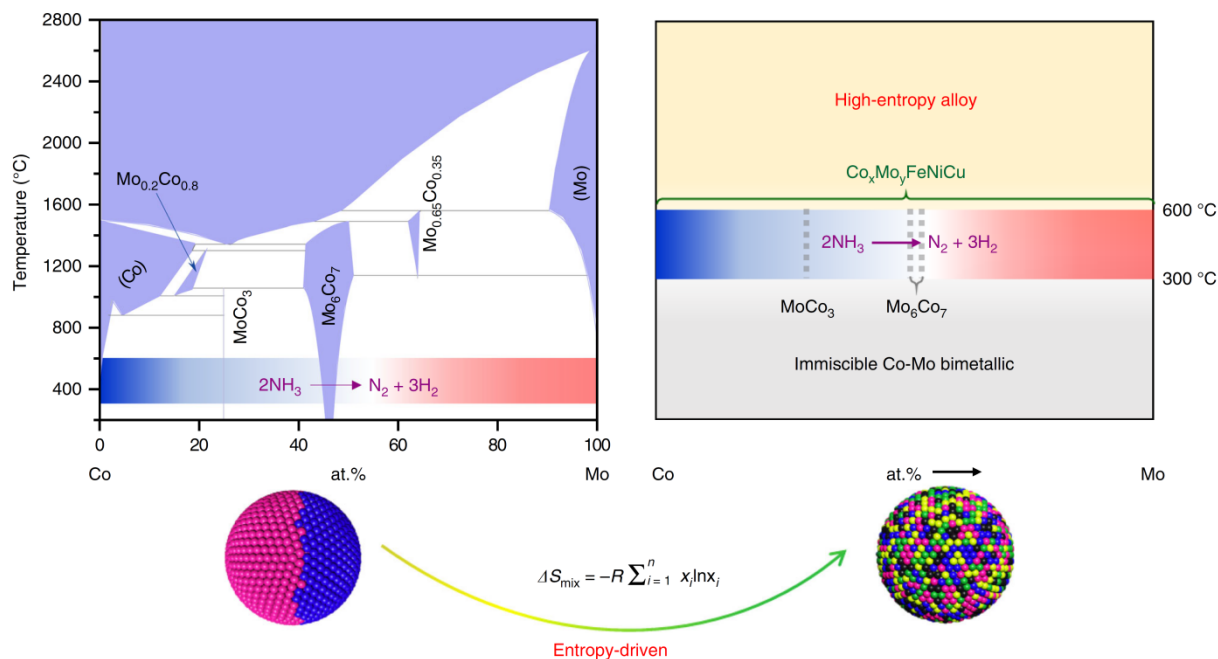


**Figure 13**. HEA Catalysts Breaking the Miscibility Limitation of Conventional Binary Alloys. Reproduced with Permission from Ref. [2]. Copyright © 2019, Nature.

## 3.7. 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 $NH_3$ to produce a range of nitrides and amides [82]. Bergstrom and Fernelius in 1933 comprehensively analyzed the interaction between alkali metals and ammonia to synthesise extended amides [83]. These alkali amides have further been utilised in different industries to synthesise different organic chemicals. Sodium and potassium amides were first synthesised by Gay-Lussac and Thenard in 1807. Subsequently, lithium, rubidium, and caesium amides have been synthesized from the molten alkali metals and gaseous ammonia. $LiNH_2$ was synthesised by Titherley in 1894 and has since been often used as a reagent in chemical synthesis [84].

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, $NH_3$ 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.

$$MH + NH_3 \rightarrow MNH_2 + H_2 \qquad (9)$$
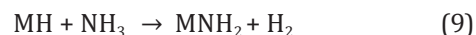
Leng et al. conducted the synthesis of $LiNH_2$, $NaNH_2$, $KNH_2$, $Mg(NH_2)_2$, and $Ca(NH_2)_2$ by reacting ammonia gas with respective metal hydrides (MH). This process was carried out at ambient temperature, with a pressure of 0.5 MPa [85]. Simultaneously, Kojima and coworkers examined the potential for recycling metallic amides. They introduced $LiNH_2$, $NaNH_2$, and $KNH_2$ 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 [86,87]. In LiNH$_2$, 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 LiNH$_2$ is relatively low compared to the hydrides (LiH) created by an ionic link. The LiNH$_2$ decomposes at a higher temperature, forming the end product Li$_3$N. Similarly, NaNH$_2$ and KNH$_2$ as exhibited the same behaviour. The breakdown tendencies of Mg(NH$_2$)$_2$ and Ca(NH$_2$)$_2$ are less than those of LiNH$_2$ 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 Mg$^{2+}$ and [NH$_2$] would be higher than that between Li$^+$ and [NH$_2$]. This study effectively elucidates the accelerated synthesis of LiNH$_2$ 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.

$$NaNH_2 \rightarrow 1/2Na + N_2 + H_2 \qquad (10)$$

$$Na + NH_3 \rightarrow 1/2\ H_2 + NaNH_2 \qquad (11)$$
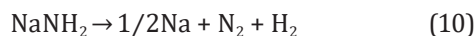
The researchers have successfully created NaNH$_2$ as a highly efficient catalyst for breaking down ammonia. This catalyst facilitates the use of ammonia by incorporating the balanced breakdown and creation of NaNH$_2$ from sodium metal [82]. The decomposition efficiency of 99.2% at a temperature of 530 °C, using 0.5 g of NaNH$_2$ and a flow rate of 60 cm$^3$(STP) min$^{-1}$ of NH$_3$, demonstrates that the as-received NaNH$_2$ performs just as well as a ruthenium catalyst in continuously decomposing NH$_3$ 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 [88]. A compound with imide-like characteristics might be produced during the break-down process. Recently, an article has been published by our research group that describes the breakdown route of sodium amide. This is the first time that mass spectroscopy and in situ transmission electron microscopy (TEM) have been used to study such a process [89]. NH$_3$ 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, Na−N−H, Li/Mg−N−H, and Ca−N−H, etc [89–92].

## 4. Conclusions

The catalytic decomposition of ammonia (NH$_3$) into hydrogen (H$_2$) and nitrogen (N$_2$) has emerged as a promising pathway for sustainable hydrogen production, addressing critical challenges in energy storage, transportation, and carbon-free fuel generation. This review systematically examined the advancements in thermocatalytic, photocatalytic, and electrocatalytic NH$_3$ decomposition, highlighting the pivotal role of catalyst design in enhancing efficiency, stability, and cost-effectiveness. Thermocatalysis remains the most mature technology, with Ru-based catalysts exhibiting superior activity but facing scalability issues due to cost, while Ni-based and bimetallic catalysts (e.g., Ni-Co, Ru-Ni) offer viable alternatives by leveraging synergistic effects to optimize nitrogen desorption and reduce energy barriers. Photocatalysis provides a low-energy route under ambient conditions, though limited by slow kinetics and catalyst stability, with innovations in plasmonic and earth-abundant materials (e.g., Cu-Fe alloys) showing potential for solar-driven NH$_3$ splitting. Electrocatalysis enables mild-condition H$_2$ production, yet struggles with selectivity and sluggish kinetics, though transition metal-based electrocatalysts (e.g., Ni-Co nitrides) and reactor designs are advancing toward practical applications. Multi-metallic and hydride systems (e.g., high-entropy alloys, alkali metal amides) demonstrate breakthroughs in activity and recyclability, though mechanistic understanding and scalability require further exploration. Future efforts must focus on optimizing non-precious metal catalysts, elucidating reaction mechanisms through advanced characteriza-

tion, integrating $NH_3$ decomposition with renewable energy sources, and addressing industrial scalability challenges in cost and durability. By overcoming these hurdles, $NH_3$ decomposition can accelerate the transition to a sustainable energy future, offering a pragmatic solution to global energy and environmental challenges. The review underscores the need for interdisciplinary collaboration—materials science, catalysis, and engineering—to unlock the full potential of $NH_3$-derived hydrogen as a cornerstone of decarbonized energy systems.

## Author Contributions

Conceptualization, M.A.A. and M.S.A.; methodology, M.M.; software, M.S.A.; validation, M.M.; formal analysis, R.A.; investigation, R.A.; resources, M.M.; data curation, M.M.; writing—original draft preparation, M.A.A.; writing—review and editing, M.A.A.; visualization, M.A.A.; supervision, M.S.A. project administration, R.A.; funding acquisition, R.A. All authors have read and agreed to the published version of the manuscript.

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It is a review article so all of data is available.

## Conflicts of Interest

The authors declare no conflict of interest.

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