Catalytic Decomposition of Ammonia for Hydrogen Production: Advances in Catalysts

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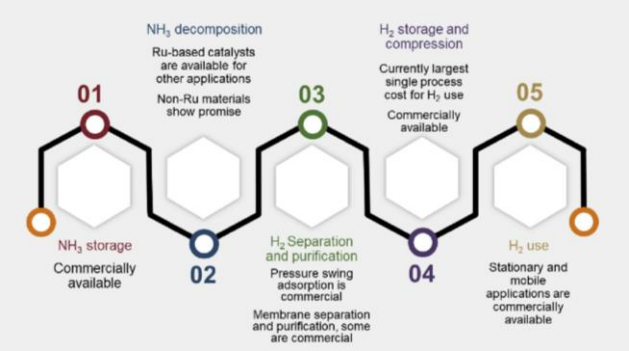
Abstract: Ammonia (NH_3) has emerged as a promising hydrogen carrier due to its high hydrogen content, ease of storage and transport, and well-established industrial infrastructure. This review focuses on recent advances in catalytic systems for ammonia decomposition aimed at hydrogen production. Special attention is given to the role of active phases, supports, and promoters in enhancing catalytic performance. Noble metals such as ruthenium (Ru) exhibit the highest activity but are limited by high cost and susceptibility to poisoning. As a result, alternative catalysts based on nickel (Ni), molybdenum (Mo), cobalt (Co), and their combinations have been extensively explored for their lower cost and favorable environmental profiles. The review compares catalysts in terms of turnover frequency (TOF), conversion efficiency, thermal stability, resistance to contaminants, and greenhouse gas emissions associated with their production. Overall, this review highlights the key technical challenges and opportunities in developing cost-effective and sustainable catalysts for ammonia cracking.
Keywords: Ammonia decomposition. Hydrogen production. Catalysis.
Abbreviations: NH_3, ammonia. H_2, hydrogen. N_2, nitrogen. TOF, turnover frequency. DFT, density functional theory. HTF, heat transfer fluid.

1. Introduction

The search for sustainable energy sources and alternatives to fossil fuels has driven global interest in the hydrogen economy. In this context, ammonia (NH_3) has emerged as a promising energy vector due to its high hydrogen content (17.8% by weight and a volumetric density of 121 kg H_2/m^3 at 10 bar), ease of storage and transport, and already well-established large-scale industrial infrastructure (SMITH et al., 2020) [10]. Moreover, ammonia does not emit carbon dioxide during its decomposition (KIM et al., 2018) [5], making it a relevant candidate to enable the energy transition.

Figure 1 illustrates the five main stages involved in energy production from H_2 stored in ammonia, highlighting the commercial availability of technologies at each stage.

Figure 1. The five stages of the energy production process from H_2 using ammonia as a carrier.



Source: [6] LAMB, et al., 2019.

Although hydrogen storage and utilization are already widely feasible, challenges remain in ammonia decomposition and hydrogen purification, requiring optimizations to reduce energy consumption and make the process more efficient. The thermocatalytic decomposition

reaction of NH_3 into hydrogen (H_2) and nitrogen (N_2), described by Equation 1, is thermodynamically favored above 400 °C but requires efficient catalysts to overcome high kinetic barriers (Ganley et al. 2004) [2].

$$2\,NH_3\,(g) \rightarrow N_2(g) + 3\,H_2(g) \qquad (1)$$
$$\Delta H^\circ{}_{400^\circ C} = +46{,}2\ kJ/mol$$

The reaction mechanism of catalytic ammonia cracking has been studied by several researchers through computational evaluations and is described by Equations 02 to 07 (Ganley et al. 2004) [2].

$$NH_3 \leftrightarrow NH_{3,ad} \qquad (2)$$

$$NH_{3,ad} \leftrightarrow NH_{2,ad} + H_{ad} \qquad (3)$$

$$NH_{2,ad} + H_{ad} \leftrightarrow NH_{ad} + 2H_{ad} \qquad (4)$$

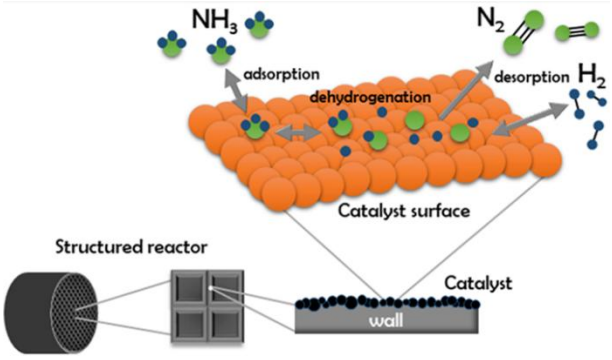
$$NH_{ad} + 2H_{ad} \leftrightarrow N_{ad} + 3H_{ad} \qquad (5)$$

$$2H_{ad} \leftrightarrow H_2 \qquad (6)$$

$$2N_{ad} \leftrightarrow N_2 \qquad (7)$$

The first reaction step is the adsorption of ammonia onto the active site, where successive N–H bond cleavages occur, leaving nitrogen and hydrogen atoms adsorbed on the catalyst surface. Following this step, the atoms recombine to form H–H and N≡N bonds, followed by the desorption of hydrogen and nitrogen gases and the release of the active sites (GANLEY et al., 2024) [2]. This process is illustrated in Figure 2, which depicts the stages of adsorption, recombination, and desorption of the products on the catalyst surface.

Figure 2. Catalytic decomposition process of ammonia.



Source: [7] LUCENTINI, et al., 2021

Although the reaction is stoichiometrically simple, challenges related to kinetics, catalyst stability, and process integration with sustainable energy systems still impose barriers to its commercial implementation (Ganley et al., 2004) [2]. According to Makhloufi and Kezibri (2021) [8], no publicly disclosed large-scale processes or units for ammonia decomposition are currently known. This technological limitation underscores the importance of research focused on more efficient and economically viable catalysts.

Ruthenium (Ru)-based catalysts are highly active, but their high environmental impact, scarcity, and elevated costs make their use less feasible (PINZÓN et al., 2024) [9]. In this context, efforts have been directed toward developing catalysts as alternatives to noble metals and evaluating new supports and promoters. The objective of this article is to review the main advances in catalysts for ammonia decomposition.

2. Methodology

Based on the article's theme, a literature search was conducted to contextualize the text within the scope of scientific publications related to the proposed topic. The article search was carried out in two stages using the Derwent Innovation, Scopus, and Google Scholar platforms, covering the period of the last 10 years (2015–2025), with a few exceptions due to their relevance. The keywords used were: "ammonia decomposition," "NH_3 cracking," and "hydrogen production." In addition to the mentioned platforms, books, dissertations, theses, and other scientific literature documents aligned with the foundation of this study were also mapped.

3. Results and Discussion

Recent studies on ammonia decomposition have revealed significant advances both in the fundamental understanding of the process and in the development of more efficient catalytic and technological systems. Investigations based on density functional theory (DFT) indicate that the rate-limiting step of the process is the cleavage of the first N–H bond of the NH_3 molecule adsorbed on the metal surface. This step has activation barriers ranging from 120 to 140 kJ/mol for ruthenium (Ru)-based catalysts and from 160 to 180 kJ/mol for nickel (Ni), which helps explain the observed differences in catalytic activity between these metals (Di Carlo et al. 2013; Guo et al. 2024) [1;4].

Operating conditions play a fundamental role in system performance. For example, increasing the reaction temperature from 400 °C to 600 °C doubles the turnover frequency (TOF) for Ni/Al_2O_3 catalysts. However, further temperature increases beyond 600 °C result in higher energy consumption without significant improvements in conversion, becoming a practical limitation factor (Yuan et al., 2023) [11]. Regarding pressure, it has been observed that pressures above 5 bar inhibit H_2 desorption, causing a 7–10% decrease in NH_3 conversion for both Ru and Ni catalysts (Guo et al. 2024) [4].

Catalyst stability is another critical aspect for scale-up applications. Ru/Al_2O_3 exhibits significant degradation above 700 °C due to sintering, with a 30% reduction in TOF after 100 hours of continuous operation (Di Carlo et al., 2013) [1]. Meanwhile, Ni/Al_2O_3 shows greater thermal resistance but is highly susceptible to poisoning by impurities such as H_2S, experiencing a 50% drop in activity after only 20 hours of exposure to 5 ppm of the contaminant (Yuan et al. 2023) [11].

Other metallic catalysts have also been investigated, such as iridium, molybdenum, cobalt, and platinum in their active phases, as well as combinations with other metals like Co-Mo, Ni-Mo, Ni-Fe, and Cu-Zn. Among the catalysts studied, ruthenium supported on oxides or structured carbon exhibited the highest catalytic activity.

Table 1 presents the experimental turnover frequency (TOF) data obtained by Ganley et al.

(2004) [2], comparing 13 metals supported on alumina for ammonia decomposition. The suggested order of activity based on the data is: Ru > Ni > Rh > Co > Ir > Fe >> Pt > Cr > Pd > Cu >> Te, Se, Pb.

Table 1. Turnover Frequency (TOF) of catalysts tested at 580 °C and 1 atm

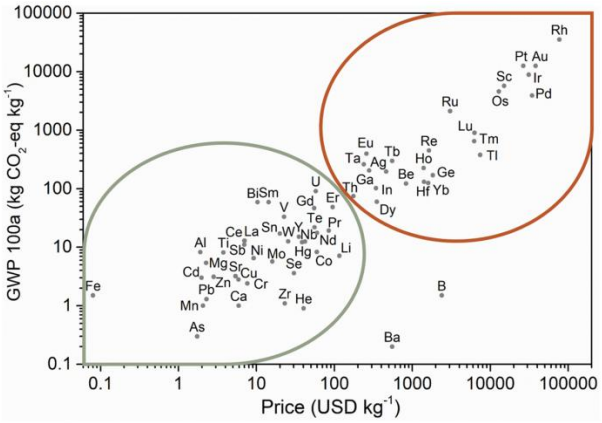
Catalyst	Dispersion (%)	TOF (s^{-1})	TOF/Ru TOF
0,5 wt% Ru/Al_2O_3	48	6,85	1
1,0 wt% Ni/Al_2O_3	0,9	4,21	0,61
0,5 wt% Rh/Al_2O_3	65	2,26	0,33
1,0 wt% Co/Al_2O_3	2,3	1,33	0,19
1,0 wt% Ir/Al_2O_3	47	0,786	0,11
1,0 wt% Fe/Al_2O_3	0,7	0,327	0,048
1,0 wt% Pt/Al_2O_3	31	0,0226	0,0033
1,0 wt% Cr/Al_2O_3	1,9	0,022	0,0032
0,5 wt% Pd/Al_2O_3	39	0,0194	0,0028
1,0 wt% Cu/Al_2O_3	5,1	0,013	0,0019
1,0 wt% Te/Al_2O_3	4,2	<0,0056	<0,00082
1,0 wt% Se/Al_2O_3	2,9	<0,0044	<0,00065
1,0 wt% Pb/Al_2O_3	16	<0,0024	<0,00035

Source: Adapted from Ganley et al. (2004) [2]

Despite ruthenium's excellent performance, its high cost and significant greenhouse gas (GHG) emissions during industrial processing limit its application. Alternative metals such as nickel, molybdenum, copper, and cobalt have lower average costs and reduced CO_2 equivalent emissions.

Figure 3 below presents a graph comparing the greenhouse gas emissions impacting global warming during the processing and production of various metals over a 100-year period, alongside their market prices (LUCENTINI et al., 2021) [7].

Figure 3: Association between price and GHG emissions in metal production, based on a 100-year timeframe



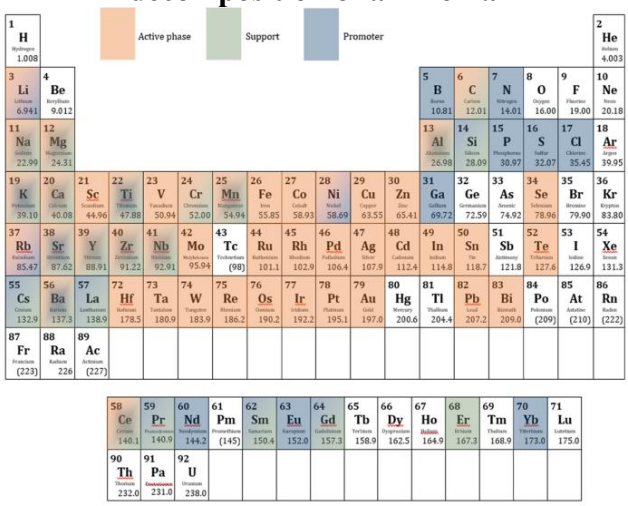
Source: LUCENTINI et al (2021) [7]

It is observed that ruthenium belongs to the group of metals with high market prices and considerable CO_2 equivalent emissions. However, alternative metals such as nickel, molybdenum, copper, and cobalt fall into the group with lower average costs, as well as lower GHG emissions during their processing.

Besides the catalyst's active phase, it is crucial to address the supports and promoters that work together with the active phase. Figure 4 shows a simplified periodic table composed of chemical elements that contribute to the catalytic

decomposition of ammonia, as well as their possible functions (active phase, support, or promoter). A comparative summary of the main catalysts explored in the literature is presented in Table 2.

Figure 4: Simplified periodic table of elements that may play a role in the catalytic decomposition of ammonia



Source: LUCENTINI et al (2021) [7]

4. Conclusion

Catalytic ammonia decomposition is established as a technologically viable and strategically relevant route for clean hydrogen production, especially within the context of the global energy transition. The analysis presented in this article highlights that Ru-based catalysts remain the most effective in terms of activity and conversion, despite cost limitations.

Ni/Al_2O_3 stands out as an economically attractive alternative, offering competitive performance at a lower cost and greater availability, despite its vulnerability to poisoning by impurities.

Table 2. Quantitative Comparison of Catalysts

Catalyst	TOF (s^{-1})	Conversion (%)	Temperature (°C)	Cost (US$/kg)	Notes	Reference
Ru/Al_2O_3	6,85	>99,8	580	~3.200	High activity; consistent performance under varying pressures; Sintering above 700 °C	Ganley et al. 2004 [2]
Ni/Al_2O_3	4,21	95	600	~18	Good cost-activity balance; moderate resistance to sintering; sensitive to H_2S	Yuan et al. 2023 [11]
Mo/C	-	100	400	-	25% lower energy consumption; lifespan of approximately 200 hours before metallic Mo agglomeration.	Güler et al. 2017 [3]
$La_{0,9}Sr_{0,1}NiO_3$	-	90	600	-	Stability of approximately 500 hours (less than 10% decline); support-free; based on rare earth elements.	Guo et al. 2024 [4]

Source: Authors, 2025

Therefore, it is recommended to deepen studies focused on developing catalysts that are more stable and less costly. Catalytic innovation will be fundamental to establishing ammonia decomposition as a key step in the hydrogen value chain.

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