

Review

Advances in Gaseous Ammonia Decomposition for Hydrogen Production: Catalysts and Emerging Pathways

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Abstract

Ammonia (NH₃) is a compelling carbon-free hydrogen carrier. Its catalytic decomposition to produce a hydrogen/nitrogen (H₂/N₂) gas stream is central to the “NH₃-H₂” clean energy cycle, provided that residual NH₃ is removed to fuel-cell-grade purity downstream. This review integrates advances from the past five years across four major catalytic NH₃ decomposition pathways, encompassing conventional thermocatalysis, plasma-catalytic, photo(thermal), and electrically driven catalysis, within a unified mechanistic and practical framework, distinguishing it from existing single-pathway reviews. Noble metal catalysts, particularly Ru-based systems, achieve superior low-temperature activity through support engineering, promoter effects, and active-site construction. However, our analysis reveals that non-noble metal (Fe, Co, Ni) catalysts and their alloys, nitrides, and carbides have made substantial progress, with certain Co-based and bimetallic systems approaching Ru-level performance via interfacial oxygen vacancy engineering and electronic structure modulation. Emerging non-thermal routes effectively overcome thermodynamic barriers, enabling operation at temperatures 200–300 °C below conventional thermal requirements, though each faces distinct challenges in energy efficiency, stability, and scalability. Key challenges remaining across all pathways to practical implementation, including residual NH₃ removal and H₂ purification, catalyst deactivation and stability, heat management and energy efficiency, start-up/shut-down dynamics, as well as system integration and economics, are critically assessed. This review provides theoretical guidance and practical recommendations for developing scalable, low-temperature NH₃ decomposition technologies.

Keywords: ammonia decomposition; hydrogen production; ruthenium catalyst; non-noble metal; low-temperature catalysis; reaction mechanism

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1. Introduction

The global energy system is shifting away from fossil fuels towards a low-carbon, sustainable framework. In this transition, hydrogen (H₂) has solidified its reputation as a clean energy carrier. It boasts a high energy density (141.9 MJ·kg^{−1}, approximately three times that of gasoline) and emits no carbon at the point of use [1]. However, the widespread adoption of hydrogen as an energy carrier remains constrained by fundamental challenges in large-scale storage and distribution [2]. The two principal

storage options, high-pressure compression and cryogenic liquefaction, each present significant practical limitations. These methods involve safety risks, require substantial energy input for liquefaction and long-distance transport, and demand considerable capital investment in dedicated infrastructure [3]. These challenges have pushed

researchers to explore alternative storage media that are efficient, safe, and economically viable.

Ammonia (NH_3) has emerged as a competitive and industrially feasible hydrogen carrier, offering distinct merits that address the core limitations of traditional hydrogen storage systems. Notably, NH_3 possessed a high hydrogen content of 17.65%, which exceeds that of other carriers [4]. It can be readily liquefied under mild conditions (approximately 3 atm at 25 °C), facilitating low-cost storage and pipeline transport [5]. Most importantly, a mature, global-scale industrial infrastructure for NH_3 synthesis, storage, distribution, and transportation has been established over decades of large-scale agricultural and industrial application [6]. This established industrial ecosystem substantially lowers the infrastructure barriers to large-scale hydrogen energy deployment, positioning NH_3 as a key intermediate in the low-carbon hydrogen supply chain.

At the heart of a closed-loop “ NH_3 -to- H_2 ” energy cycle lies catalytic NH_3 decomposition. This process facilitates the direct conversion of NH_3 into a H_2/N_2 mixture (achieving fuel-cell-grade hydrogen purity requires downstream removal of residual NH_3 and, where needed, H_2/N_2 separation), thereby circumventing the generation of carbon-containing by-products, aligning perfectly with the requirements of green H_2 production and on-site H_2 supply [7,8]. This versatile technology boasts extensive application potential across a variety of sectors, including distributed on-site hydrogen refueling stations, proton exchange membrane fuel cell vehicles, offshore renewable energy-coupled H_2 production, and industrial high-purity H_2 supply [9].

Early studies on NH_3 decomposition primarily concentrated on high-temperature thermal catalysis, which necessitated reaction temperatures in excess of 600 °C to achieve satisfactory NH_3 efficiency [10]. Such harsh operating conditions not only resulted in excessive energy consumption, leading to a deterioration in the net energy benefit of H_2 production. Additionally, these conditions accelerated catalyst sintering, active site agglomeration, and irreversible deactivation, significantly restricting the long-term stability and economic viability of the technology. Over the past few decades, however, dramatic advances in catalytic material design, nanomaterial synthesis, and in situ/operando characterization techniques have driven considerable progress in NH_3 decomposition research, enabling breakthroughs in catalyst performance optimization, reaction mechanism elucidation, and low-temperature reaction kinetics regulation [11,12].

Ruthenium (Ru)-based catalysts exhibit exceptional capabilities for low-temperature N–H bond activation. This arises from their unique electronic structures and favorable d-band center positions, making them efficient catalysts for low-temperature NH_3 decomposition [13]. Conversely, non-noble metal-based catalysts (primarily Fe, Co, and Ni) have emerged as cost-effective alternatives owing to their earth-abundant reserves [14–16]. Their catalytic performance has been markedly boosted via rational structural engineering, support modification, heteroatom doping, and defect regulation. These strategies represent a core research direction for scalable, low-cost industrial applications [17,18]. Meanwhile, emerging catalytically intensified gaseous NH_3 decomposition pathways, encompassing plasma-assisted catalysis [19,20], photo(thermal) catalysis [21], and electrically driven catalysis [22], have been developed to overcome the inherent thermodynamic limitations and high energy demands of conventional thermal catalysis [23,24]. These strategies enable efficient NH_3 decomposition and enhanced H_2 yield under mild conditions.

Against the backdrop of recent advances, this review differentiates itself from the existing literature in several key aspects. While a number of recent reviews have focused on Ru-based thermal catalysis [12,13], non-noble metal systems [14,16], plasma catalysis [19,20] or photocatalysis [21], no comprehensive review integrates all four major gas-phase NH_3 decomposition pathways—thermocatalysis, plasma catalysis, photo(thermal)catalysis, and electrically driven catalysis—within a unified mechanistic and practical framework. Specifically, this review is designed to: (i) identify transferable catalyst design principles, including oxygen vacancy (O_v) engineering, d-band center modulation, surface protonics, promoter-induced electron donation, and lattice-N mediation (LNM), that underpin activity enhancements across all four routes; (ii) provide a critical cross-pathway comparison of operating temperature windows, energy inputs, catalyst stability, reactor complexity, and technology readiness levels (TRLs), summarized in a dedicated comparative table; and (iii) directly address the practical implementation gap, encompassing residual NH_3 purification, catalyst deactivation mechanisms, heat management, and fuel-cell-grade H_2 compatibility, that are frequently underemphasized in catalyst-centric reviews. By covering advances over the past five years and spanning both noble and non-noble catalytic systems from single atoms to high-entropy alloys, this review aims to offer mechanistic guidance for catalyst design and a strategic roadmap for the practical deployment of NH_3 -based H_2 production technology. The manuscript is organized as illustrated in Figure 1: thermocatalytic systems, plasma-catalytic systems, photo(thermal)catalytic systems, and electrically driven systems, followed by challenges and perspectives.

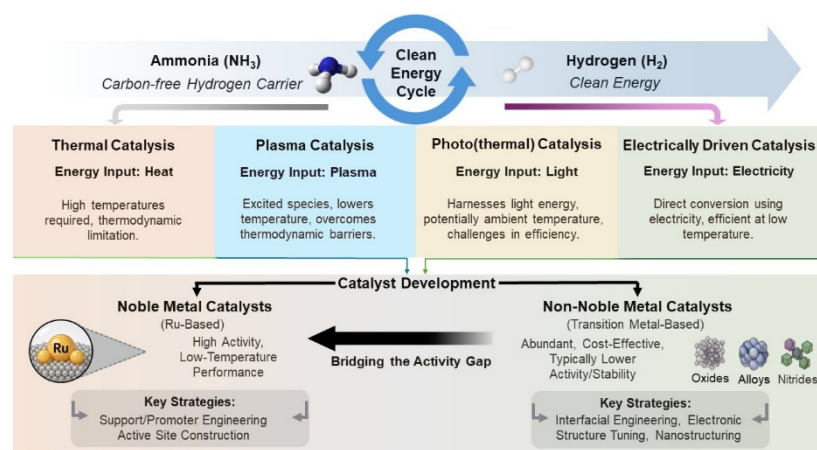


Figure 1. Schematic illustration for the technologies and catalysts in NH_3 decomposition.

2. Thermocatalytic NH_3 Decomposition

Thermocatalytic NH_3 decomposition is the classic model system for NH_3 decomposition, which plays a key role in elucidating N–H bond activation mechanisms and the operational principles of catalytic active sites. In this section, the structure-activity relationships in noble and non-noble metal-based catalytic systems were examined with a focus on how strategies such as support modification, additive doping, and structural regulation affect catalytic performance.

2.1. Ru-Based Catalysts

Under typical thermal conditions, the noble metals exhibit the following activity hierarchy for gas-phase NH_3 decomposition: $\text{Ru} > \text{Rh} > \text{Ir} > \text{Pt} > \text{Pd} > \text{Au}$ [25]. This trend can be rationalized by a volcano-plot analysis: the d-band center of metallic Ru is positioned closest to the Sabatier optimum, effectively balancing N–H bond activation

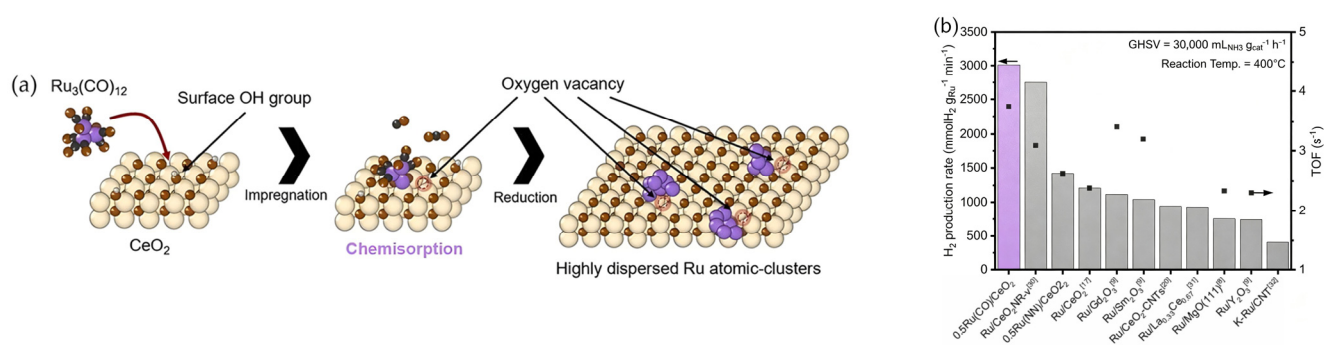
(favored by strong N binding) and recombinative N₂ desorption (facilitated by weak N binding) [26]. Pt and Pd bind surface N adatoms too weakly, which restricts the initial dehydrogenation kinetics despite their excellent performance in other hydrogenation/dehydrogenation reactions. At 400–450 °C, the turnover frequencies (TOFs) reported for optimized Ru catalysts typically exceed those of analogous Pt- or Pd-based systems by one to two orders of magnitude [27]. Au shows negligible activity for thermal NH₃ decomposition, yet it has demonstrated notable performance in plasmonic antenna-reactor configurations under light irradiation, where hot-carrier injection lowers the N–N coupling barrier via an associative hydrazine-mediated pathway [28]. Consequently, contemporary research on noble metal catalysts for thermal NH₃ decomposition has concentrated overwhelmingly on Ru, and this review reflects that emphasis.

In view of the scarcity and high cost of Ru, contemporary research efforts are largely directed towards maximizing atomic efficiency by reducing Ru loading while simultaneously enhancing intrinsic activity and thermal stability [29]. The field has moved from empirical optimization toward rational design grounded in metal-support interaction (MSI) tuning, defect engineering, and precise control over active site architecture [12]. This section provides a concise overview of recent advances in support engineering, promoter effects, and mechanistic understanding that collectively define the current state-of-the-art in Ru-based NH₃ decomposition.

2.1.1. Support Engineering

The support material plays a pivotal role in dictating the dispersion, electronic state, and sintering resistance of Ru nanoparticles (NPs), thereby profoundly influencing catalytic performance [30]. Rational design of the support entails the systematic tuning of surface chemistry and defect structure to optimize MSI [31–33].

Reducible oxides are extensively employed as supports due to their capacity to create O_v, which serve as anchoring sites for strong metal-support bonding and facilitate interfacial electron transfer. Ceria (CeO₂) received the most attention in this context. Shao et al. achieved near-complete NH₃ conversion at 500 °C with only 1.4 wt% Ru on CeO₂, an enhancement attributed to Ru–O–Ce interfacial bonding and Ce³⁺-mediated electron transfer [34]. Son et al. demonstrated the profound impact of precursor chemistry on Ru/CeO₂ catalyst. By employing Ru₃(CO)₁₂ as a precursor, chemisorption of the carbonyl precursor onto surface hydroxyls yielded robust Ru–O–Ce bonds and generated O_v, effectively suppressing Ru sintering and delivering a remarkable H₂ production rate of 180.84 mol H₂·g_{Ru}^{−1}·h^{−1} at 400 °C (Figure 2a,b) [35]. Composite CeO₂–γ-Al₂O₃ supports further enhanced performance: Patel et al. reported 87% conversion at 400 °C over Ru(1)Ce(10)/γ-Al₂O₃ with a TOF of 54.98 s^{−1}, leveraging the complementary roles of Ru (N–H cleavage), CeO₂ (redox cycling and hydrogen spillover), and γ-Al₂O₃ (high surface area and acidity) [36].



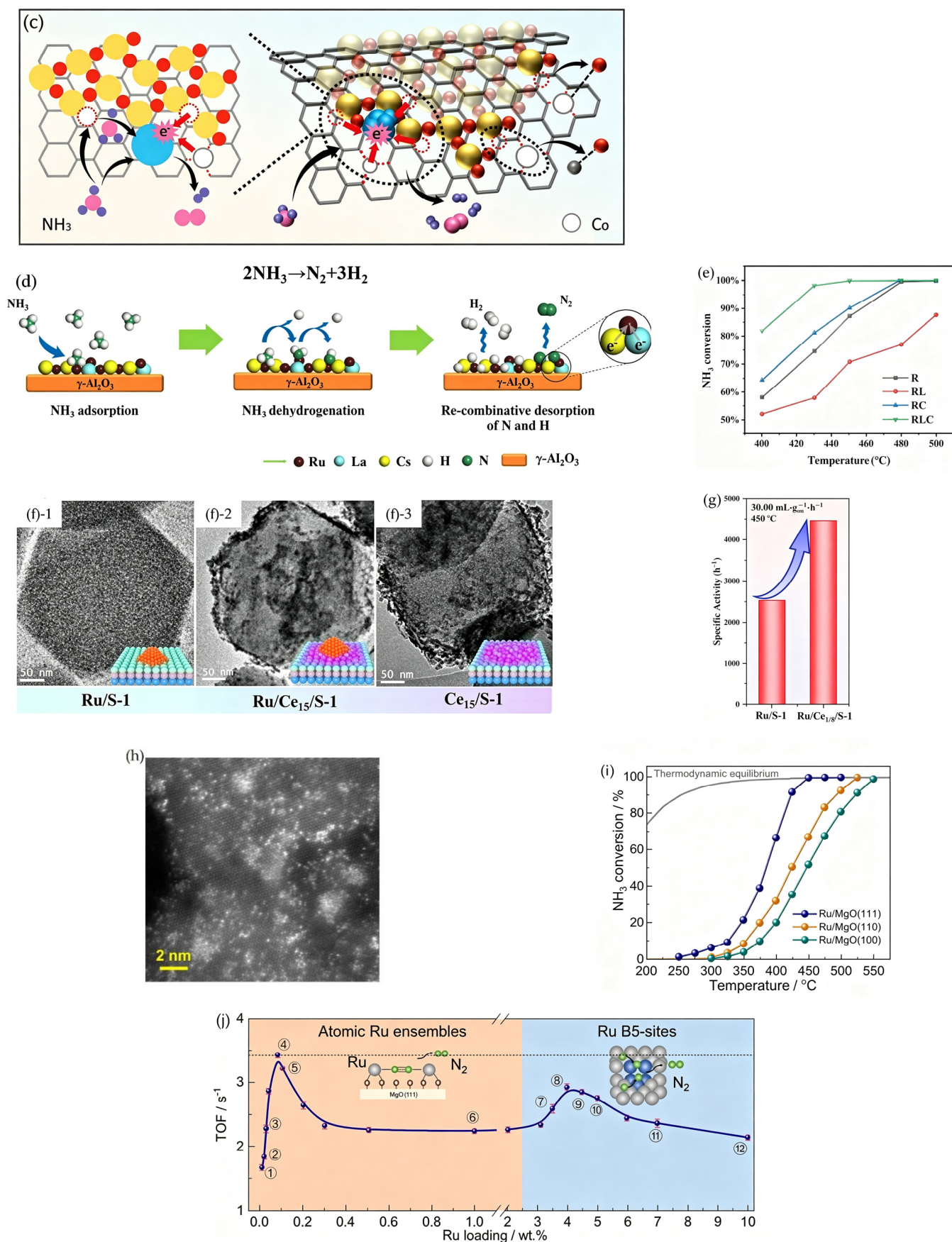


Figure 2. (a) Schematic illustration of the proposed Ru species morphology and interaction with CeO₂ during catalyst preparation using Ru₃(CO)₁₂ as a precursor. (b) Comparison of H₂ production rate and TOF with the reference at identical condition (GHSV = 30,000 g_{cat}⁻¹ h⁻¹, reaction temperature

= 400 °C) [35]. (c) Reaction pathway over the Ru/CeO₂-CNTs catalyst and the schematic diagram of electron transfer between defect sites and Ru NPs [37]. (d) Illustration of the speculative mechanism for the catalyst in promoting ammonia decomposition. (e) Catalytic activity of the Ru-based catalysts for NH₃ decomposition in the temperature range of 400–500 °C with GHSV = 5000 mL·g_{cat}^{−1}·h^{−1} [38,39]. (f) TEM images of Ru/S-1, Ru/Ce₁₅/S-1, and Ce₁₅/S-1 catalyst. (g) The specific activity at 450 °C with WHSV of 30,000 mL·g_{cat}^{−1}·h^{−1} of the Ru/S-1 and Ru/Ce₁₅/S-1 catalyst [40]. (h) HAADF-STEM images of 3.1 wt.% Ru/MgO(111). (i) NH₃ conversion as a function of reaction temperature over different supported Ru samples, reaction conditions: weight hour space velocity (WHSV) = 30,000 mL·g_{cat}^{−1}·h^{−1}. (j) The TOF values with error bars for ammonia decomposition as a function of Ru loading at 400 °C; the error bars in the figure represents standard deviation through three repeated measurements [41].

Aliovalent doping of CeO₂ offers an especially effective way to control defect concentration. Kim et al. systematically investigated yttrium (Y) doping in CeO₂ supports and established a comprehensive structure-defect-interaction-performance relationship [42]. The optimal Y incorporation (Ru/50Y-CeO_x) maximized the density of O_v, strengthened Ru–O–Ce interfacial bonding, and enhanced electron transfer, yielding 80% NH₃ conversion at 450 °C along with long-term stability over 168 h. Similarly, strontium (Sr) doping of CeO₂ has been shown to lower the O_v formation barrier and facilitate hydrogen spillover, thereby mitigating the H-poisoning of the active surface [43]. The introduction of zirconium (Zr⁴⁺) and rare-earth ions (Y³⁺, La³⁺) into the CeO₂ lattice to form CeZrO_x solid solutions further improves redox properties, oxygen storage capacity, and MSI [44]. Kim et al. extended the defect-engineering by incorporating silicon (Si) into CeO₂, in which Si-induced microstrain correlated with higher O_v content, facilitating N₂ recombinative desorption and achieving nearly 100% conversion [45]. Ce–Al composite supports also exhibit synergistic effects in boosting surface area, MSI, and electron transfer, enabling high NH₃ conversion at low Ru loading (0.8 wt%) [46].

Beyond CeO₂-based materials, other reducible and basic oxides offer complementary advantages. Wu et al. employed La₂Zr₂O₇, a pyrochlore-type oxide with intrinsic O_v, to induce strong electronic MSI (EMSI) that accelerated the rate-limiting N₂ recombination step [47]. Perovskite-type oxides constitute another versatile platform: Ru/BaTiO₃ catalysts demonstrated high conversion due to abundant basic sites, O_v, and strong MSI through Ru–O–Ti bond formation [48]. B-site doping with Al³⁺ in BaCeO₃ perovskites introduces additional O_v while optimizing NH₃ adsorption–desorption kinetics and lowering the activation energy (*E*_a) for N–H bond scission [49]. Jeon et al. demonstrated that Y³⁺ doping of BaCeO₃ facilitates lattice oxygen removal, promoting the encapsulation of Ru NPs by an oxygen-deficient suboxide overlayer [50]. The optimized Ru/BCY-10 catalyst (10 mol% Y) reached a H₂ formation rate of 768 mmol·g_{cat}^{−1}·h^{−1} at 450 °C, with the N₂ desorption energy reduced from 147 to 81 kJ·mol^{−1} and the apparent *E*_a fell from 91 to 62 kJ·mol^{−1}. Cation substitution in La_{1−x}Sr_xAlO₃ has also been shown to modulate the electronic state of Ru, thereby promoting N₂ binding and desorption [51]. Among rare-earth oxides, Sm₂O₃ and Y₂O₃ have demonstrated considerable promise [52]. Particularly, the choice of support precursor is itself a critical variable. Feng et al. showed that Ru/Y₂O₃ derived from Y₂(CO₃)₃ exhibited 2.37 times higher Ru dispersion and 1.84 times higher O_v concentration than that derived from Y(NO₃)₃·6H₂O [53]. Guan et al. demonstrated that Ru/MgO, despite possessing a lower surface area, displayed an abundance of strong basic sites and enhanced MSI; especially, the deposition-precipitation synthesis method afforded more uniform Ru dispersion and a 40 °C reduction in *T*₈₀ compared to conventional impregnation [54,55].

A conceptually different advance in Ru catalyst design involves nitrogen (N) incorporation into the support to create independent active sites that operate via an

associative pathway, thereby circumventing the Brønsted-Evans-Polanyi (BEP) scaling constraints inherent to conventional dissociative routes. Two recent systems showcase this LNM strategy. Ru/N-CeO₂ synthesized via a soft-urea-glass approach and then annealed in NH₃, contained only 1.6 wt% Ru but still reached 96% conversion at 450 °C with an apparent E_a of 65.2 kJ·mol⁻¹, much lower than that of undoped Ru/CeO₂ (90.5 kJ·mol⁻¹) [56]. Isotopic pulse Fourier transform infrared (FTIR) and ¹⁵NH₃/¹⁴NH₃ experiments confirmed a Mars-van Krevelen (MvK)-type associative mechanism at N-dopant sites, evidenced by the formation of ¹⁴N–¹⁵N (m/z = 29), with ~36.7% of N₂ produced via this pathway. In parallel, Ru/g-C₃N₄-AR catalysts exploit lattice N mediation to enhance NH₃ decomposition kinetics, achieving 99.01% conversion and a H₂ production rate of 5967 mmol·g_{cat}⁻¹·h⁻¹ at 500 °C and gas hourly space velocity (GHSV) = 18,000 mL·g_{cat}⁻¹·h⁻¹, a 72% efficiency improvement over N-free graphene sample (Ru/Gr-AR), with an apparent E_a of only 49.04 kJ·mol⁻¹ [57]. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and NH₃-temperature programmed surface reaction-mass spectrometry analyses showed that associative N₂ recombination preferentially occurs at lattice N sites on the g-C₃N₄ support, where electron transfer from Ru facilitates N–H activation while maintaining moderate product binding. In both systems, the spatial and electronic decoupling between Ru NPs and nearby N dopants allows efficient charge transfer for dehydrogenation without causing excessive N₂ adsorption. This breaks the traditional BEP scaling relations and opens up a versatile LNM strategy for low-temperature NH₃ decomposition.

In addition to chemical composition, the geometric architecture of the support is critical. Gong et al. tested commercial zeolites and found that 1Ru/Naβ exhibited superior performance due to its strong basicity, robust MSI, and favorable hierarchical pore structure [58]. Encapsulating ultrafine Ru NPs (1.5–3.5 nm) inside NaY zeolite micropores has been shown to increase the number of catalytically critical B-5 active sites and surface basicity, while providing exceptional anti-sintering durability [59]. El-Shafie et al. developed zeolite (SA-600A)-based catalysts co-promoted with Ru and Li [60]. The optimized formulation gave 99.87% NH₃ conversion at 490 °C under a GHSV of 3000 h⁻¹. The microporous framework confined the Ru NPs, and Li acted as an electronic promoter to enhance N₂ desorption. Spherical mesoporous silica with controlled pore sizes (~3 nm) allowed for an optimal Ru particle size (2.22 ± 0.29 nm) for B5 site formation, yielding an impressive H₂ generation rate [61]. Vertically aligned 2D porous frameworks have also been shown to prevent Ru aggregation and improve long-time durability [62].

Carbon-based composites offer additional degrees of freedom for MSI tuning. Ru/CeO₂-carbon nanotubes (CNTs) exploit a synergy between carbon defects and O_v to promote electron transfer and N adatoms (N*) desorption (Figure 2c) [37]. Carbon xerogels with N doping and sodium (Na) promotion have been reported to increase the decomposition rate considerably [63]. Carbonized Al₂O₃ nanofibers exhibited 2–3 fold higher activity than conventional supports, which can be traced to synergistic oxide-carbon properties [64]. Sustainable alternatives, such as hydrothermally derived carbon from chitosan, have also emerged as viable, low-cost supports [65]. Among inorganic alternatives, alkali metal silicates A₂SiO₃ (A = Li, Na, K) have revealed that strong EMSI forms between Ru and O_v within the silicate structure, leading to higher Ru dispersion and electron density [66]. Natural minerals like attapulgite (ATP) offer a cost-effective route, 1Ru/ATP achieving 100% conversion at 600 °C and excellent stability over 150 h [67].

2.1.2. Promoter Effects

The electronic density of Ru active sites is a key determinant of catalytic performance, especially in governing the energetics of the rate-determining N₂ desorption step [68,69].

Promoters, typically alkali, alkaline-earth, or rare-earth metals, tune this electronic environment mainly by donating electron density to Ru, thereby weakening the Ru–N bond and facilitating N₂ release [26].

Among single-element promoters, alkali metals (K, Na, Cs) have drawn the most attention because of their low ionization energies and strong electron-donating [29,69]. Su et al. found that K doping of Ru/MgO doubled the NH₃ decomposition efficiency at 350 °C [70,71]. The promotional effects were strong enough to shift the rate-determining step from N₂ desorption to the initial N–H bond cleavage. Ju et al. showed that adding K created super basic sites on γ -Al₂O₃, further boosting electron donation to Ru [72]. Similarly, Li et al. reported that Na-modified Ru/ γ -Al₂O₃ (Na:Ru = 2.0) achieved 82.3% conversion at 400 °C [73]. Their characterization indicated that Na⁺ preferentially occupies Lewis acid sites in the Al₂O₃ surface, raising the overall surface basicity, while in situ DRIFTS confirmed enhanced NH₃ coordination and dehydrogenation kinetics.

Cesium (Cs), which has the lowest ionization energy among stable alkali metals, has an especially strong effect. He et al. elucidated that Cs confined inside MCM-41 mesopores forms a Ru–O–Cs interfacial structure that increases the density of catalytically critical B5 site and generates electron-rich Ru species, which in turn lowers the temperature required for complete NH₃ decomposition by 70 °C [74]. In CeO₂-based systems, K promotes electron transfer to both the support and the Ru particles, simultaneously increasing the concentration of O_v and metallic Ru⁰ species and enabling complete NH₃ conversion at 525 °C [75]. Yang et al. used an in situ loading strategy to put K into Ru-MCM-41, which improved Ru dispersion and inhibited agglomeration, resulting in enhanced low-temperature activity [76]. Cs doping has also been shown to combat high-temperature deactivation of Ru/MgO catalysts by weakening the Ru–MgO interaction and stabilizing metallic Ru species, which helps the N₂ adsorption/desorption cycle [77].

While single-element promotion is effective, co-doping can produce synergistic benefits that exceed the additive contributions of individual promoters [78]. Shin et al. pioneered the co-doping of La and Cs into Ru/Al₂O₃: Cs improved Ru dispersion and strengthened MSI, while La served as an additional electron donor, and the combined effect afforded >99% conversion at 450 °C (Figure 2d,e) [38,39]. Le et al. demonstrated a conceptually similar synergy by pairing N-doped CeO₂ combined with Cs promotion [79]. N-doping increased the concentrations of O_v and Ce³⁺, tuning the support's electronic character, while Cs further enriched the electron density at Ru sites. The two effects together lower the energy barrier for recombinative N₂ desorption. Advanced interfacial engineering extends these ideas further. He et al. constructed Ru–O_v–Ce structures on Silicate-1, creating electron-rich Ru sites that optimize the recombination of surface N* and H* species, yielding specific activities as high as 4461 h^{−1} at 450 °C (Figure 2f,g) [40].

Underpinning all these promoter strategies is a single unifying principle: the basicity of the catalytic environment, whether it comes from the support, the promoter, or a mix of both, directly sets the electron density at Ru sites and thus governs N₂ desorption kinetics [80]. This correlation has been directly established across multiple support systems, where stronger basic character consistently accelerates N₂ release. CeO₂ supports are a perfect example. Interfacial electron back-donation from reduced Ce³⁺ to Ru raises the Ru electron density, which simultaneously lowers the NH₃ activation barrier and weakens N₂ binding at the surface [81]. The convergence of these findings underscores that rational promoter selection cannot be divorced from support design; rather, the two need to be co-optimized to create an electronic environment at the Ru active site that balances easy N–H activation with efficient N₂ desorption [12]. Striking that balance remains the central challenge in low-temperature NH₃ decomposition catalysis.

A critical evaluation of the promoter literature reveals several caveats that warrant careful consideration. First, the majority of promotional effects are reported under only a

single set of GHSV or weight hourly space velocity (WHSV) conditions, which severely hampers direct inter-study comparisons. For example, reported TOFs for K-promoted versus Cs-promoted Ru catalysts can differ by an order of magnitude across studies, largely owing to the wide range of space velocities employed (typically 3000–60,000 mL·g_{cat}^{−1}·h^{−1}). Second, the optimal promoter-to-Ru molar ratio depends strongly on the support material and therefore cannot be generalized across different catalyst systems. Third, although alkali metal promotion consistently lowers the apparent E_a for N₂ desorption, at higher promoter loadings the rate-determining step (RDS) often shifts to N–H bond cleavage. This shift can in fact impair catalytic performance at low temperatures, where the kinetics of N–H activation are inherently slow. To ensure reliable benchmarking, future studies should report the TOF at a well-defined temperature and WHSV, together with E_a , the Ru loading, and a minimum stability test duration.

2.1.3. Active Site Construction

The construction of optimal active sites on Ru-based catalysts is governed by a cascade of synthesis-level variables, including precursor identity, preparation route, atmosphere control, and post-treatment, that collectively determine particle size, metal-support interface quality, and residual impurity content [12].

The choice of Ru precursor has a first-order effect on both dispersion and site purity. Chloride-based precursors (RuCl₃), though widely available, leave behind residual Cl that poisons active sites by blocking N₂ adsorption and lowering surface basicity [68]. In contrast, Ru₃(CO)₁₂ can chemisorption strongly onto support hydroxyls and achieves high dispersion even at low loadings [35]. Recognizing this limitation, Yoo et al. developed a Cl-free synthesis route for Ru/Al₂O₃ catalysts, preserving active-site integrity and substantially improving long-term stability [82]. Koch et al. further demonstrated that the choice among multiple Ru precursors on γ -Al₂O₃ thoroughly changes surface speciation and low-temperature activity [83].

Beyond precursor chemistry, the preparation route itself dictates the strength of the MSI and the resulting electronic environment of the Ru NPs. Precipitation-derived Ru/Nd₂O₃ catalysts showed noticeably stronger MSI than their impregnated counterparts [84], a finding mirrored by Zhang et al. for Ru/ZrO₂. There, precipitation gave higher activity even though the Ru particle sizes were similar, highlighting that electronic modification, rather than geometric dispersion alone, controls performance [85]. The reduction atmosphere is another critical lever. Direct H₂ reduction prevents RuO₂ aggregation and yields highly dispersed sub-2 nm Ru NPs that are anchored by O_v [86,87]. Yan et al. showed that pretreatment under N₂ significantly increases O_v density in Ru-CeO₂ catalysts [88]. The treatment forms electron-rich interfacial Ru sites that optimize hydrogen transfer and counteract H-poisoning. These results collectively establish that the synthesis–atmosphere–MSI nexus must be co-optimized rather than treated as independent variables.

Spatial confinement strategies offer an effective means of simultaneously controlling particle size and enhancing sintering resistance. Encapsulation of Ru within metal–organic framework (MOF)-derived carbon matrices (Ru/CeO_x@NC) provides steric restriction that ensures high durability (<2% degradation over 6000 min) [89]. Polyol synthesis enables precise Ru particle-size tuning to generate B₅-site-rich Ru/MgAl₂O₄ nanocatalysts with reduced E_a [90]. A complementary approach was shown by depositing Ru quantum dots (QD < 2 nm) on a mesoporous MgO dendritic network (Ru QD/p-MgO) [91]. The hierarchical pore structure restricted QD growth while maintaining high accessibility. Tang et al. reported that amino-functionalized dendritic mesoporous silica microspheres permit ultrafine Ru NPs (2.22 ± 0.29 nm) optimized for B₅ site formation [92]. These confined architectures point to a general principle: geometric restriction

coupled with electronic tuning allows activity and stability to be simultaneously maximized. Synthesis strategies that combine confinement with interface engineering therefore represent the most robust route to high-performance, durable Ru catalysts.

Bimetallic catalyst design taps into electronic and geometric synergies that go beyond what single-metal systems can deliver. Ru/Co_xAlO catalysts derived from layered double hydroxides (LDHs) use Co doping to increase O_v concentration and enhance electron transfer to Ru [38]. A RuNi bimetallic catalyst derived from Ni phyllosilicate (Ru/SiO₂@NP) exhibited exceptional stability over 210 h at 600 °C, making it particularly promising for continuous-operation scenarios [93].

A conceptually distinct advance is the deliberate introduction of lattice strain to modulate the d-band electronic structure. A compressive-strained Ru/Y₂O₃-MgO catalyst was synthesized in which the compressive strain pushed the Ru d-band center downward [94]. This reduced the E_a for N–N bond formation and produced a record H₂ production rate of 148.794 mol·g_{Ru}^{−1}·h^{−1} at 450 °C with only 0.91 wt% Ru. Surface restructuring strategies offer yet another pathway. Creating a K–O–Ru interface in K–Ru/C catalysts through strong cation- π interaction suppresses Ru sintering and enhances surface basicity, promoting the rate-limiting N₂ recombination step [95]. These examples illustrate that engineering the mechanical and electronic environment around Ru, beyond conventional support or promoter effects adds new degrees of freedom for catalyst optimization.

At the same time, fundamental mechanistic insights are reshaping the long-held understanding of what constitutes the most active Ru site for NH₃ decomposition. The B5 step-edge ensemble has long been considered the dominant active site. However, a study on atomically dispersed Ru clusters on polar MgO(111) surfaces revealed that close-range Ru cluster ensembles are more active than either isolated single atoms or conventional B5 sites (Figure 2h–j) [41]. This finding challenges the long-held B5-site supremacy. Density functional theory (DFT) calculations coupled with microkinetic modeling have further refined the picture. Zou et al. found that a N₂H_y dehydrogenation mechanism can take over on defect sites under low-temperature or high-coverage conditions [96]. They also highlighted that Ru A4 and kink sites have superior intrinsic activity compared to B5 sites. Kulkarni et al. used ab initio-grounded microkinetic analysis to show that the identity of the rate-determining step itself shifts depending on alkali promotion and coverage regime [69]. This further emphasizes that no single site descriptor works universally.

The dynamic evolution of the active site under reaction conditions adds another layer of complexity. Study on Ru/TiO₂ catalysts showed that a Ru/TiO_xN_y interface forms during NH₃ exposure and leads to progressive deactivation by increasing the N–H bond cleavage barrier [97]. The key finding was that this deactivation is reversible through oxidation-reduction regeneration. In contrast, Yan et al. demonstrated that the electron-rich Ru/TiO_{2-x} interface, generated under controlled reduction, facilitates both NH₃ adsorption and N* desorption while mitigating H poisoning [98]. They observed a two-fold TOF enhancement over Ru/SiO₂. These studies collectively underscore that precise control over synthesis from precursor selection and atmosphere engineering to nanoscale confinement and strain must be guided by an evolving mechanistic understanding of the true active-site landscape, which extends well beyond the classical B5 paradigm.

This survey has identified several key trends and unresolved questions in the development of Ru-based catalysts. First, although support engineering (particularly the generation of O_v in CeO₂-based materials) consistently enhances activity, the degree of enhancement varies widely (2- to 10-fold) depending on the synthesis method, choice of precursor, and reduction conditions [35,42,43,45]. This variability highlights the need for standardized synthesis protocols and reporting practices. Second, alkali metal promoters (e.g., K, Cs, Na) universally facilitate N₂ desorption; however, the optimal promoter-to-

Ru ratio is highly support-dependent, ranging from 0.5:1 on MgO [70] to 2:1 on Al₂O₃ [73]. This indicates that promoter effects cannot be generalized without considering the electronic environment of the support. Third, the recent discovery that atomically dispersed Ru ensembles on MgO(111) outperform conventional B₅ sites challenges the long-standing paradigm of B₅-site supremacy and suggests that the structure-activity relationship for Ru catalysts is more complex than previously appreciated [41]. Fourth, the LNM strategy offers a conceptually new approach to circumvent BEP scaling relations [56,57]; however, the long-term stability of N-doped supports under reaction conditions and the scalability of their synthesis remain to be demonstrated. Collectively, these findings indicate that the most promising direction for advancing Ru catalysts lies in the integration of support defect engineering with precise control over the size and electronic state of Ru ensembles, guided by in situ characterization to track their dynamic structural evolution under operation conditions.

2.2. Non-Noble Metal Catalysts

The inherent scarcity and high cost of Ru impose fundamental limits on the scalability of noble-metal-based NH₃ decomposition systems [26]. Consequently, research has increasingly pivoted toward earth-abundant alternatives, primarily Fe, Co, and Ni, which offer distinct advantages in cost, availability, and industrial compatibility [16,99]. Despite differences in their electronic structures and N-binding characteristics, these three metal families share common kinetic challenges: the difficulty of balancing N–H bond activation against recombinative N₂ desorption, susceptibility to high-temperature sintering, and hydrogen or nitrogen poisoning of active surfaces [100].

2.2.1. Fe-Based Catalysts

Recent advances in Fe-based catalysts for NH₃ decomposition have centered on overcoming the intrinsic kinetic limitations imposed by strong Fe–N binding, which traditionally leads to surface nitride poisoning and sluggish recombinative N₂ desorption [101,102].

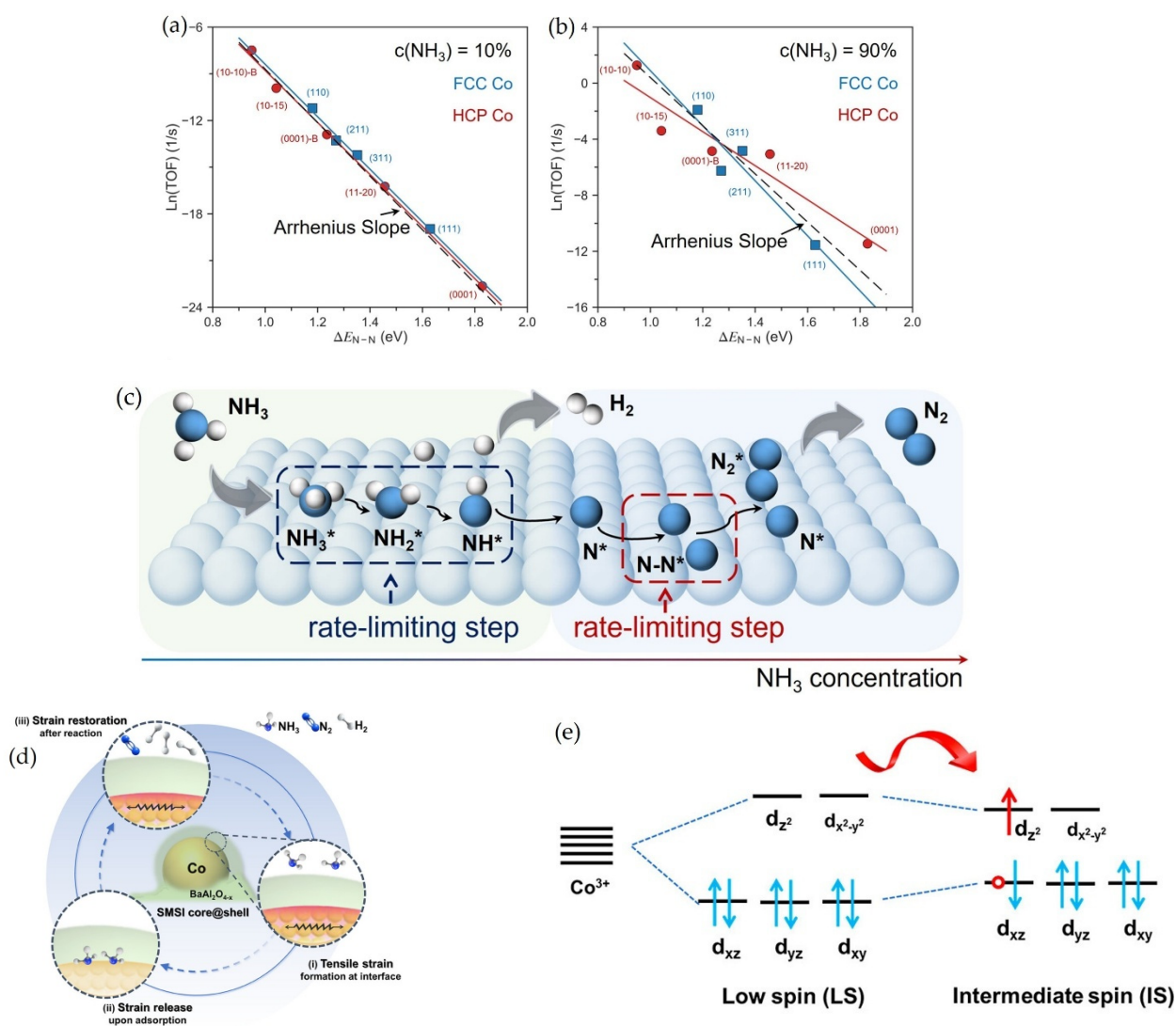
Metallic Fe has historically been considered as the active phase. However, detailed in situ and post-reaction characterizations have revealed a more nuanced “hidden active phase” phenomenon. A metastable Fe/Fe₄N mixing phase exhibits markedly higher dehydrogenation activity due to N-induced electronic modulation of adjacent Fe sites [103]. This insight has shifted the catalyst design philosophy. The goal is no longer to maintain a purely metallic surface but rather to stabilize an optimal Fe/Fe_xN equilibrium under reaction conditions. This mechanistic understanding has stimulated the development of fundamentally new catalyst architectures. One excellent example is embedding Fe in molten barium amide (Ba(NH₂)₂). A ternary Ba–NH₂–Fe species enables a bifunctional mechanism: Ba sites promote N–N coupling, while Fe sites handle hydrogen abstraction and desorption, yielding activity comparable to Ru catalysts at reduced temperatures [104]. Concurrently, the structural sensitivity of the reaction has been firmly established through studies on size-controlled Fe NPs, which demonstrate that TOF increases with particle size owing to a higher proportion of active step sites favorable for N recombination [105].

To address the practical challenges of high-temperature sintering and irreversible nitridation, several robust structural and compositional strategies have been validated. Structural promoters such as Cr in FeCrO_x bimetallic oxides [106] or the use of MgFe₂O₄ spinel precursors [107] can effectively inhibit Fe agglomeration while promoting the formation of stable, active Fe_xN species. The concept of utilizing industrial waste and byproducts has also proven viable. Modified fly ash [108] and direct reduced Fe from steelmaking [109] take advantage of their intrinsic Fe oxide and alkali promoter content

to create cost-effective, stable catalysts. Alkali metal doping (K, Na, Cs) of Fe-based catalysts has been shown to promote the formation of Fe_xN active phases and enhance N₂ desorption kinetics. At the frontier of Fe-based catalyst design, Fe-group single-atom catalysts (SACs) with discrete Fe–N–C or Fe–O coordination environments can alter the nature of the metal-adsorbate bond, weakening Fe–N interactions to facilitate dehydrogenation [110]. These multifaceted insights collectively pave the way for the rational design of next-generation Fe catalysts that can challenge noble-metal performance while keeping economic and sustainability advantages.

2.2.2. Co-Based Catalysts

Co-based catalysts have emerged as leading non-noble metal alternatives to Ru. Compared to Fe, they offer a more favorable balance between N-binding strength and cost [16,100]. The fundamental challenge is the delicate balance required between N–H bond activation and associative N₂ desorption, a process that is highly sensitive to surface structure. DFT studies reveal strong structure-dependent. Stepped surfaces such as hexagonal close-packed (HCP) Co(10–10) and face centered-cubic (FCC) Co(110) are more active because of their favorable d-band centers [111]. Interestingly, the rate-limiting step shifts dynamically from N–N coupling to NH_x dehydrogenation depending on the NH₃ concentration (Figure 3a–c).



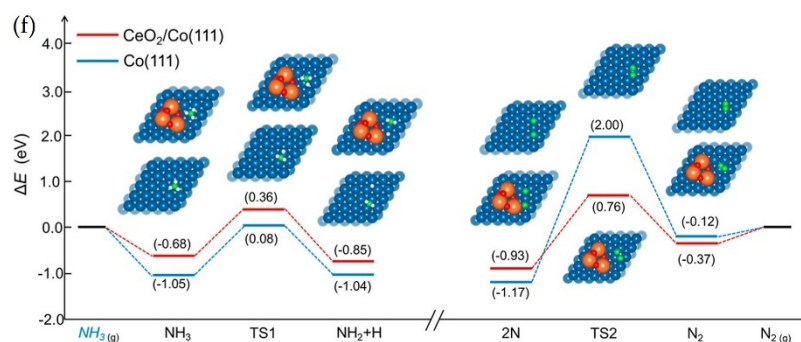


Figure 3. (a,b) Relations between the transition state energy of N–N coupling and the activity over various surfaces at the ammonia concentrations of 10% and 90% for HCP Co and FCC Co. (c) Schematic diagram of the shift in rate-limiting steps during the reaction proceeds. Light blue, blue, and gray spheres represent Co, N, and H atoms, respectively [111]. (d) Schematic of the dynamic lattice strain evolution mechanism for NH₃ decomposition over core@shell heterostructured Co@BaAl₂O_{4-x} catalyst. (e) Spin state regulation of Co³⁺ (from low spin to intermediate spin). (f) Energy diagrams of NH₃ dehydrogenation and N–N recombination on Co(111) and CeO_{2-x}/Co(111). The Co, Ce, N, O, and H atoms are marked in blue, orange, green, red, and white, respectively [112].

A primary strategy to improve the intrinsic activity and stability of Co catalysts involves tuning the MSI and engineering interfacial Ov. Supporting Co on Y₂O₃ [113,114] or Sm₂O₃ [115] not only stabilizes small NPs against sintering but also introduces abundant basic sites and Ov that facilitate N–H bond cleavage and accelerate N recombination. This concept is further advanced by the construction of inverse catalysts, such as CeAlO_x/Co [116] and MgO/Co [117], wherein oxide promoters anchored on Co surfaces generate robust interfacial Co–O–M linkages that suppress sintering, modulate electronic structure to mitigate hydrogen poisoning, and enhance NH₃ adsorption.

Rational design of precursor architectures has proven equally transformative. The exsolution of Co NPs from perovskite precursors (e.g., LaCoO₃ or SrCoO_{2.5}) under reducing NH₃ atmospheres produces finely dispersed, thermally stable metal particles that are strongly anchored to a La₂O₃ or Sr₅Co₄O₁₂ support matrix, a process that can be monitored via in situ techniques to optimize phase evolution [118–120]. Jeong et al. investigated the exsolution of single (Ni, Co, Fe) and alloy (NiCo, NiFe, CoFe) NPs from an La_{0.43}Ca_{0.37}M_xN_yTi_{1-(x+y)}O_{3-δ} perovskite [121]. They found that Co exsolution catalysts gave the highest NH₃ conversion (63.9% at 700 °C), while alloying with Fe (NiFe) improved performance compared to single-metal systems.

Pyrolysis of Co-based MOFs, particularly ZIF-67, enables the formation of Co NPs uniformly encapsulated within N-doped porous carbon (Co@NC) [114,122]. The morphology dictated by the ZIF-67 precursor impacts performance. Catalysts derived from the rhombic dodecahedron shape achieve superior activity and durability due to their optimal pore structure, high Co–N_x coordination density, and efficient mass transfer [123,124]. This MOF-derived strategy has been expanded to include promoters, such as La, forming amorphous LaCoO_x interfaces that synergistically boost activity through electron transfer and dual spatial confinement [123].

Adding promoters remains a cornerstone of catalyst optimization. Doping Co₃O₄ with alkali metals (Na, K) makes the oxide easier to reduce and generates electron-rich Co⁰ surfaces that markedly promote H₂ desorption; however, careful control of dopant basicity is required to avoid inhibiting NH₃ adsorption and N–N recombination [125,126]. Alkaline-earth and rare-earth dopants (Sr, Ba, Ce) introduced into CeO₂, LaAlO₃, or perovskite supports also increase surface basicity and Ov concentrations, thereby optimizing NH₃ adsorption strength and weakening the Co–N bond to facilitate N₂ release

[127–131]. The promotional effect of Mg in Co/CeO₂ catalysts is particularly loading-dependent. Mg can actually decrease activity at low Co loadings, yet at higher loadings (e.g., 20 wt%), it remarkably improves dispersion and reducibility, generating more O_v and strengthening the MSI [132]. The combination of CeO₂–Al₂O₃ bi-promoters in mesoporous CoCeAlO_x catalysts demonstrate a synergistic effect, wherein CeO₂ boosts activity, while Al₂O₃ provides structural stability [131,133]. Systematic optimization of Co loading on γ -Al₂O₃ has also revealed that higher Co loadings (e.g., 26 wt%) lead to weaker MSI and lower desorption energies, which enables higher NH₃ conversion at lower temperature [134].

Recent breakthroughs have demonstrated that the electronic structure of Co can be exquisitely tuned to overcome the scaling relations that normally restrict catalytic performance. The construction of a Co@BaAl₂O_{4-x} core@shell heterostructure, where tensile lattice strain at the interface elevates the Co d-band center, enhances NH₃ adsorption and N–H dissociation; the dynamic release and restoration of strain during the reaction cycle facilitates efficient N₂ desorption and prevents active-site poisoning (Figure 3d–f) [112]. In a parallel approach, nonoxidative Li species (e.g., LiNH₂) were used as promoters for Co/MgO catalysts. This leads to the formation of an amorphous LiN_xH_y overlayer, where interfacial N vacancies serve as the true active sites [135]. The flexible Li sites at these vacancies considerably lower the energy barrier for the initial N–H bond scission, producing Ru-free catalysts with near-optimal low-temperature activity [136]. Engineering CeO₂/Co/C catalysts with Ce–O–Co interfacial orbital coupling drives an electron spillover effect that shifts the Co spin state, enabling dynamic Co–N bonding that concurrently lowers the barriers for both NH₃ activation and N₂ recombination [136]. Even the spin state of Co has become a tunable parameter. Engineering a medium-spin state in Co/Li₂O–La₂O₃ catalysts achieves an optimal balance between NH₃ adsorption strength and N₂ desorption kinetics [137].

Advanced nanostructuring and innovative synthesis methods continue to push the boundaries of catalyst performance. Spray-flame synthesis can prepare metastable Mg_{1-x}Co_xO solid solutions, which upon controlled exsolution yield ultra-small Co clusters and single sites with remarkably high TOFs [138]. High-surface-area supports, such as SiC, TiC–SiC, or barium hexaaluminate effectively disperse Co NPs, enhance thermal conductivity, and provide resistance to methanation and sintering [139–141]. Deploying structured reactors, for instance, Co₃O₄ nanoarrays grown on Ni foam, represents a critical step toward practical, scalable on-board H₂ production [142].

In summary, the trajectory of Co-based catalyst development is defined by the rational integration of interfacial engineering, defect chemistry, electronic-structure tuning, and hierarchical nanostructuring. These multifaceted strategies collectively address the intrinsic kinetic and stability barriers of Co and position it as a cornerstone for sustainable H₂ production technologies.

2.2.3. Ni-Based Catalysts

Ni-based catalysts are the most extensively examined non-noble metal platform for catalytic NH₃ decomposition. This distinction comes from the favorable compromise Ni offers among crustal abundance, cost, and intrinsic activity for N–H bond activation [143]. However, their widespread application is often hindered by sintering of Ni NPs at the high temperatures, hydrogen poisoning of active sites, and sluggish kinetics of the rate-limiting recombinative N₂ desorption step [16,144]. Contemporary research has focused on sophisticated strategies to overcome these limitations. The main approaches involve rational design of catalyst supports, engineering interfacial electronic structures, and introducing promoters to modulate adsorption energetics.

(1) Support engineering

The catalyst support in Ni-based NH_3 decomposition systems functions not as an inert platform but an active modulator of Ni dispersion, electronic state, and interfacial reaction pathway [145].

A basic requirement for high catalytic efficiency is the generation and preservation of small, well-dispersed Ni NPs. Mesoporous silica architectures exemplify the confinement strategy. Zhou et al. demonstrated that small CeO_2 NPs stabilized on a high-surface-area $\gamma\text{-Al}_2\text{O}_3$ matrix simultaneously optimized Ni dispersion, modulated the reducibility of interfacial Ni atoms, and generated abundant surface O_v at the Ni– CeO_x interface, directly correlating with enhanced catalytic reactivity and stability [146]. Extending this principle, Xu et al. employed a solvent-free grinding method to confine high-loading NiO NPs (3–5 nm) entirely within the mesopores of SBA-15 silica, achieving 93.7% NH_3 conversion at 650 °C with sustained performance over 60 h [147]. Wu et al. explored high-loading (~40 wt%) Ni on SBA-15 with tunable textural properties [148]. They found that the variant with the largest specific surface area yielded superior performance because the mesopore could accommodate high metal loadings without particle agglomeration.

Carbon-based materials, such as carbon nanofibers (CNFs), offer high surface areas and unique structural properties. Di Stasi et al. explored CNFs doped with CeO_2 as a support, revealing a synergistic effect between the CNF structure and highly dispersed Ni/ CeO_2 nano-“catalytic islands” [149]. The CNFs provided a high surface area while CeO_2 created medium-strength basic sites that were crucial for promoting N_2 desorption. The resulting Ni-Ce40/CNFs catalyst achieved 90% NH_3 conversion at 600 °C across the carbon matrix.

LDHs are versatile precursors for synthesizing mixed oxide supports with tunable acid-base properties and intimate metal–oxide contact. Qiu et al. reported that a MgAl_2O_4 support derived from an LDH precursor (Ni/ MgAl_2O_4 -LDH) provided high surface area and highly dispersed Ni, leading to an NH_3 conversion of 88.7% at 600 °C, which was 1.68 times higher than a catalyst prepared by mechanical mixing [150]. Yan et al. tuned the Mg/Al ratio in LDH-derived $\text{Ni/Mg}_1\text{Al}_m\text{O}_x$ catalysts, revealing that an optimal acidity-basicity balance promotes both NH_3 adsorption (on acid sites) and N_2 desorption (facilitated by basic sites) [151]. The $\text{Ni/Mg}_1\text{Al}_{16}\text{O}_x$ catalyst, possessing the smallest Ni particles (3.4 nm) and optimal basicity, achieved 90% conversion at 574 °C. Further development of a Ni/ Al_2O_3 - La_2O_3 composite support from LDH precursors highlights the distinct roles of each component: Al_2O_3 provided a high specific surface area and ordered mesoporous structure that suppressed Ni particle growth, while La_2O_3 enhances the O_v concentration and support basicity, effectively alleviating H_2 poisoning and boosting the TOF [152]. The optimized catalyst exhibited a robust H_2 yield rate of $1828.2 \text{ mmol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ at 600 °C. Additional studies on Ni catalysts derived from Ni-Mg-Al and Ni-Ca-Al LDH precursors confirm that this synthetic approach consistently yields high dispersion and strong MSI, contributing to both excellent stability and activity [153,154].

Rare earth oxides offer a mechanistically different support paradigm based on their intrinsic basicity, redox flexibility, and ability to generate O_v . CeO_2 , with its reversible $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple, is a particularly effective support. Chen et al. compared Ni on CeO_2 nanorods (R), spheres (Sph), and spindles (Spi) [155]. The nanorod shape gave the highest activity due to its larger specific surface area and smaller Ni crystallites (3.3 nm), while the spindle morphology, with predominant exposed (110) facets, possessed the strongest basic sites capable of donating electrons to Ni and promoting associative N_2 desorption. Li et al. extended this morphological study by synthesizing $\text{Ni/Al}_{0.1}\text{CeO}_{0.9}\text{O}_x$ catalysts with spherical, flaky, and thready morphologies, confirming that the spherical catalyst with abundant $\text{CeO}_2(111)$ facets exhibited the strongest EMSI and highest activity

due to a greater number of Ni-O-Ce interface sites [156]. The synergistic combination of Al_2O_3 and CeO_2 into Al-Ce-O solid solutions further amplifies performance by generating abundant O_v that promote NH_3 activation and strengthen MSI [157].

Beyond CeO_2 , other rare-earth metal oxide supports represent a parallel development trajectory. Zhang et al. engineered Y_2O_3 supports with different morphologies and found that a needle-like Ni/Y11 catalyst achieved 100% conversion at 650 °C due to its large surface area, small Ni particle size, and suitable basicity [158]. A Ni/ Y_2O_3 catalyst synthesized via a sol-gel self-combustion method achieves a homogeneous dispersion of Ni and strong electron transfer from Y to Ni through a Y-O-Ni structure [159]. Bao et al. introduced Y as a dopant into Ni/ CeO_2 via a citrate sol-gel auto-combustion method [160]. They engineered a $\text{Ni}_{1-x}\text{Ce}_{0.5}\text{Y}_{0.5}\text{O}_x$ structure in which Y^{3+} incorporates homogeneously into the CeO_2 lattice, generating abundant and stable surface O_v while simultaneously reconstructing the local electronic environment of Ni active sites. The solid solution strategy extends to Ce-Zr systems. Zhu et al. demonstrated that Ni/ $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ catalysts, which benefit from the enhanced oxygen mobility and structural stabilization of the fluorite-structured Ce-Zr solid solution, could achieve near-complete NH_3 conversion at 550 °C with less than 5% activity loss over 60 h [161]. Musso et al. investigated Ni on yttrium zirconate ($\text{Y}_2\text{Zr}_2\text{O}_7$), demonstrating that the Y:Zr ratio can be adjusted to enhance O_v concentration and mitigate H_2 poisoning [162]. A Ni/ $\text{LaAl}_{12}\text{O}_{19}$ (lanthanum hexaaluminate, LHA) catalyst has shown high activity and impressive 260 h stability due to its strong basicity and the strong interaction between Ni and the LHA support [163]. Choi et al. explored a Yb_2O_3 - Co_3O_4 solid solution as a support, demonstrating that its intrinsic O_v could act as electron acceptors to promote associative N desorption [164].

Zeolitic supports introduce a qualitatively different design dimension through their crystallographically defined pore architectures, exchangeable cation sites, and tunable acid-base properties. Kim et al. examined zeolite 13X-supported Ni catalysts prepared by different methods [165]. The catalyst made by deposition-precipitation (Ni/13X-DP) exhibited the best performance due to strong MSI from Ni phyllosilicates and a uniform distribution of Ni within the zeolite pores. Gong et al. demonstrated that the activity of Ni supported on zeolite Y was influenced by the exchanged cation (Na, Mg, Ca, Sr, Ba, Ce, La), with the Ni/SrY catalyst achieving 98% conversion at 600 °C [166]. Cho et al. employed a surfactant-assisted melt infiltration (SAMI) method to prepare Mg-promoted Ni/USY catalysts [167]. This approach resulted in high dispersion and enhanced acid-base properties for improved activity and long-term stability.

The highly endothermic nature of NH_3 decomposition motivates exploration of thermally conductive support materials. Li et al. synthesized high-surface-area SiC-supported Ni catalysts and achieved 79.6% conversion at 550 °C [168]. Tuning the calcination temperature for a 30Ni/SiC-700 catalyst yielded 93.4% conversion at 600 °C and excellent stability over 450 h [169]. Martin et al. explored a TiC-SiC composite support, achieving a remarkable 91.5% conversion at 500 °C, with a H_2 production rate of $3678 \text{ mmol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ [170]. Beyond traditional packed-bed configurations, Degirmenci et al. developed Ni@ SiO_2 microspheres combined with activated carbon for microwave-assisted heating, achieving 98% NH_3 conversion at 500 °C with substantially reduced energy consumption [171]. Sui et al. modeled a Joule-heated catalytic reactor using a conductive washcoated honeycomb monolith (SiSiC), demonstrating superior heat transfer and catalyst utilization compared to conventional wall-heated reactors [172].

(2) Interface engineering

The atomic-scale architecture of the Ni-oxide interface has turned out to be a decisive factor in catalytic performance. It controls electron transfer, vacancy generation, and the coordination environment of active sites.

Liu et al. developed a CeO_2/Ni inverse catalyst via co-precipitation. Small CeO_2 islands (4.9 nm) decorated the Ni NPs (13 nm), creating a high density of Ni-CeO₂ interface sites with concentrated O_v and electron-enriched Ni atoms (Figure 4a,b) [173]. The same group also reported a mesoporous Ni-CeO₂ nanocomposite prepared by colloidal solution combustion synthesis, which achieved an intimately mixed architecture with strong MSI [174].

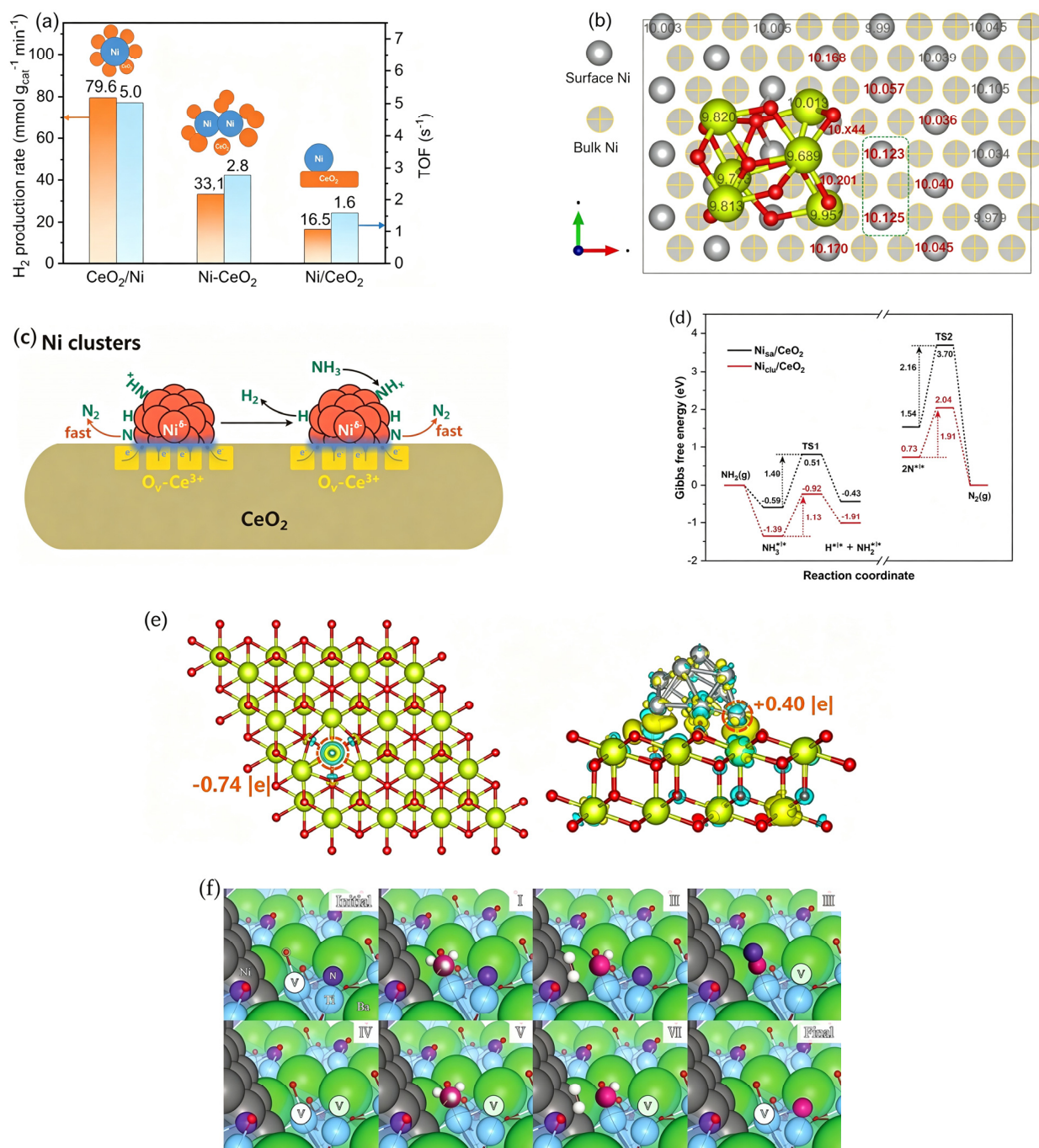


Figure 4. (a) H₂ production rate and TOF over CeO₂/Ni, Ni-CeO₂, and Ni/CeO₂ catalysts at 500 °C. (b) Top view of the optimized inverse CeO₂/Ni structure. The Bader charge of some atoms is marked [173]. (c) Schematic diagram of Ni clusters on CeO₂ nanorods. (d) Potential energy diagrams for NH₃ dissociative adsorption and associative desorption of N₂ on Ni_{SA}/CeO₂ and Ni_{Clu}/CeO₂. (e) The charge density difference analysis of Ni_{SA}/CeO₂ and Ni_{Clu}/CeO₂. The Ni, Ce, and O atoms are shown as gray, chartreuse, and red spheres, respectively. The yellow and blue areas represent charge

accumulation and depletion, respectively [175]. (f) Schematic illustration for ammonia decomposition over Ni/h-BaTiO_{3-x}N_y catalyst through N³⁻ vacancy mediated MvK mechanism. The NH₃ molecules adsorb onto the N³⁻ vacancy sites on the h-BaTiO_{3-x}N_y surface, and the N–H bond is cleaved at the Ni support interface with the aid of Ni NPs (steps I–II). Lattice N³⁻ reacts with adsorbed N adatoms to form surface dinitrogen molecules (step III). Lattice nitrogen is recovered by the decomposition of additional ammonia molecules at the Ni-support interface (steps IV–VI). Black, green, light-blue, blue purple, and red purple atoms in the atomistic models correspond to Ni, Ba, Ti, lattice N, and gas phase N, respectively. These atomistic models were visualized using the VESTA program [176].

A mechanistically important advance is the recognition that catalytic interfaces undergo dynamic reconstruction under reaction conditions. Jin et al. revealed that an optimized NH₃ pretreatment dynamically assembled contiguous Ce³⁺–O_v–Ni⁰ triads at the Ni/CeO₂ interface, facilitating localized electron donation and lowering the activation barrier for N₂ desorption [177]. Yang et al. employed atomic layer deposition (ALD) to grow Ni clusters on CeO₂ nanorods, constructing an interfacial Ni^{δ-}–O_v–Ce³⁺ structure that substantially reduced the energy barrier for N–N coupling and N₂ desorption, achieving a H₂ production rate of 57.252 mol·g_{Ni}⁻¹·h⁻¹ (Figure 4c–e) [175]. Bao et al. doped Y into Ni/CeO₂ to form a Ni₁/Ce_{0.5}Y_{0.5}O_α catalyst, where Y-induced lattice distortion and charge imbalance generated abundant, stable surface O_v and simultaneously reconstructed the local electronic environment, reducing the energy barrier for N associative desorption by 0.21 eV and yielding 84% conversion at 550 °C [160].

Surface functionalization is a powerful tool for anchoring and stabilizing Ni species. Amino-functionalization of SiO₂ strengthens the interaction with Ni precursors, leading to well-dispersed Ni and accelerated desorption of N₂ and H₂ [178]. Similarly, La-induced surface reconstruction of BN generates LaBO₃ nano-islands that capture and confine Ni species, producing a high population of well-dispersed Ni clusters with enhanced catalytic performance [179].

(3) Promoter effects

The addition of a second metal as a promoter provides an effective lever for tuning Ni⁰ adsorption energetics and electronic structure. Alkaline earth metals are strong basic promoters that donate electrons to Ni. Zhang et al. evaluated Mg, Ca, Sr, and Ba as promoters for Ni/CeO₂, identifying Ba as the most effective due to its maximal enhancement of surface basicity and electron density on Ni, thereby facilitating N₂ desorption [180]. A synergistic effect between a Mg promoter and Span60 surfactant has also been reported in Ni/USY catalyst prepared by melt infiltration [167].

Rare earth elements exert multifaceted promotional effects that are not interchangeable. Usman et al. compared La, Ce, Nd, and Sm on Ni/Al₂O₃ and found that 5%La achieved the highest performance (90% conversion at 500 °C) by considerably lowering the *E_a* for NH₃ dissociation [181]. Bao et al. elucidated the distinct mechanistic roles of La, Ce, and Y in modifying Ni/MgO [182]. La most strongly mitigated H₂ inhibition, Ce delivered the highest TOF via enhanced O_v generation, and Y promoted N₂ desorption through electronic modulation. Wang et al. demonstrated that the La/Ce ratio in Ni/Ce_{1-y}La_yO_x maximizes O_v concentration and electron transfer to Ni, with the Ni/Ce_{0.5}La_{0.5}O_x achieving near-complete conversion at 540 °C [183]. Podila et al. observed that substituting 50% of La with Ce in LaNiO₃ perovskite yield 99% conversion at 550 °C, further underscoring that promoter effectiveness about matching the electronic perturbation to the specific kinetic bottleneck operative under given reaction conditions [184].

(4) Perovskite-derived catalysts

Perovskite oxides (ABO_3) represent a distinctive design paradigm, in which the active metal is not deposited externally but exsolved from the host lattice under reductive conditions, yielding metallic NPs crystallographically “socketed” into the resulting oxide matrix, a geometry that confers exceptional resistance to sintering and detachment. Alamoudi and Podila synthesized a series of Ce-based perovskites (CeXO_3 , $\text{X} = \text{Ni, Co, Fe}$) and observed substantial enhancement over impregnated counterparts, particularly for CeNiO_3 , attributed to O_v and enhanced metal reducibility [185]. Gamez et al. used a hard templating approach to create mesoporous LaNiO_3 with a high specific surface area, producing highly dispersed Ni NPs (7.0 nm) upon reduction [186]. High-pressure hydrogenation pretreatment of LaNiO_3 generated exceptionally small, stable Ni particles (~8 nm) with strong MSI, effectively suppressing agglomeration [187].

A-site substitution strategies further illustrate the compositional tunability of the perovskite platform. Duan et al. used a microwave-assisted deep eutectic solvent method to synthesize Sr-doped $\text{La}_{0.7}\text{Sr}_{0.3}\text{NiO}_3$, producing exsolved, socketed Ni NPs stabilized by strong MSI [188]. Sr-doping in $\text{La}_{1-x}\text{Sr}_x\text{NiO}_{3-\delta}$ creates an electron-rich environment around Ni that accelerates N_2 desorption, leading to a marked improvement in low-temperature activity [189]. Park et al. designed a dual-site substituted LaNiO_3 perovskite: Ba at the A-site to enhance electron density on Ni, and Co at the B-site to promote Ni exsolution and dispersion [190]. The result was 85.9% NH_3 conversion at 550 °C with 100 h of outstanding stability.

A mechanistically noteworthy extension is the use of hexagonal barium titanium oxynitride ($h\text{-BaTiO}_{3-x}\text{N}_y$) as a Ni support [176]. In this system, lattice N vacancies participate directly in the catalytic cycle through a Mars–van Krevelen mechanism. NH_3 fills a surface N vacancy, undergoes sequential dehydrogenation, and the resulting lattice N atom recombines with a neighbor to desorb as N_2 , regenerating the vacancy (Figure 4f) [176]. This lattice-mediated pathway substantially lowers the operating temperature while conferring remarkable water durability, a critically important practical consideration.

(5) Synthesis methods for precise control

The catalyst preparation method exerts a deterministic influence on the microstructural and electronic characteristics that govern catalytic behavior. Do et al. demonstrated that the coprecipitation–ammonia-driven homogeneous deposition (CADH) method is a powerful, scalable way to synthesize porous $\text{Ni/Al}_2\text{O}_3$ -based catalysts, achieving 99.9% NH_3 conversion at 600 °C with 200 h of stable operation [191,192]. The sol–gel self-combustion approach allows precise stoichiometric control and the formation of homogeneous solid solutions [161]. This route has been applied to synthesize Ce–Zr solid solution-supported Ni catalysts with high surface area and abundant O_v .

The NH_3 evaporation-hydrothermal (AEH) method generates Ni phyllosilicate precursors that produce very small, stable Ni NPs upon reduction. Ren et al. compared Ni/SiO_2 catalysts prepared by AEH, impregnation, and evaporation-induced self-assembly [193]. The AEH-derived catalyst possessed the smallest Ni NPs (~3.0 nm) and the strongest Ni– SiO_2 interaction, resulting in the highest catalytic activity and stability. Yang et al. used a similar approach to synthesize an Si_3N_4 -derived Ni phyllosilicate, producing small (4.2 nm), highly dispersed Ni NPs inlaid in an unreduced phyllosilicate matrix that achieved 100% conversion at 700 °C and maintained 90% of its initial activity over 100 h [194].

The role of organic modifiers during impregnation has been addressed in detail. Hu et al. identified citric acid as the most effective additive (compared with β -cyclodextrin

and PVP) because it reduces Ni particle size and increases the population of strong basic sites and O_v [195]. Ulucan et al. conducted a comprehensive in situ/operando study that compared coprecipitation and wet impregnation methods for Ni/MgO catalysts [196]. They found that coprecipitation method leads to a more homogeneous distribution of Ni^{2+} in the $Mg_{1-x}Ni_xO$ solid solution precursor and smaller, more uniformly dispersed Ni NPs upon activation.

(6) Kinetic studies and mechanistic insights

A rigorous kinetic framework is essential for rationalizing the design strategies listed above. On metallic Ni surfaces, NH_3 decomposition proceeds through sequential dehydrogenation ($NH_3^* \rightarrow NH_2^* \rightarrow NH^* \rightarrow N^*$). The recombinative desorption of N adatoms ($N^* + N^* \rightarrow N_2$) is generally identified as the RDS at moderate to high temperatures. However, studies on modified Ni catalysts reveal important mechanistic divergences. Qin et al. used DFT to study NH_3 decomposition on Ni-doped $BaZrO_3$ perovskite surfaces, identifying the second dehydrogenation step ($NH_2^* \rightarrow NH^* + H^*$) as the RDS, with surface O_v facilitating the overall reaction [197]. Cheng et al. studied a high-entropy oxide (HEO) perovskite $La_{1.0}(Ni_{0.2}Fe_{0.2}Co_{0.2}Mn_{0.2}Cr_{0.2})O_3$ and employed d-band center theory to show that the HEO-Ni site exhibited an optimal NH_3 adsorption energy, balancing reactant activation and product desorption [198].

This RDS plasticity shifting between N_2 desorption and NH_3 dehydrogenation depending on the electronic and structural environment carries profound design implications. Yadav et al. developed a microkinetic model for NH_3 decomposition over Ni/Al_2O_3 , confirming that both N_2 desorption and NH_2^* dehydrogenation function as the RDS depending on the temperature, and derived a comprehensive rate equation that accurately captured the inhibitory effects of H_2 and NH_3 [199]. This implies that optimal catalyst architecture is not universal but contingent upon which elementary step is rate-limiting under specific operating conditions.

(7) Stability and durability

The predominant deactivation mechanism for Ni catalysts under NH_3 decomposition conditions is thermally driven sintering, which reduces the population of active surface sites. Purcel et al. conducted an 800 h stability test on a co-precipitated Ni/Al_2O_3 catalyst, documenting continuous sintering and a 13.5% activity loss, while an industrial reference catalyst stayed stable under identical conditions [200]. Kim et al. demonstrated that exsolution-derived Ni NPs from a 2D MWW-type zeolitic Ni silicate maintained 90% of their initial conversion for 100 h at 550 °C, with a very low deactivation rate of 0.7% [201].

The most compelling stability demonstrations arise from systems that address sintering and hydrogen poisoning simultaneously. The CADH-derived catalysts of Do et al. showed no obvious decrease during 100 h of continuous operation [192]. The $Ni/LaAl_{12}O_{19}$ catalyst exhibited 260 h stability due to strong MSI [163]. At the extreme limit, Ni SAs embedded in a $Ni_xMg_{1-x}O$ solid solution interfaced with CeO_2 ($Ni_xMg_{1-x}O/CeO_2$) create $Ni^{\delta+}-O-Ce$ sites [144]. These sites make N-H bond cleavage efficient while promoting hydrogen spillover to the CeO_2 surface, mitigating hydrogen poisoning and accelerating N-N bond formation. The result is near-equilibrium NH_3 conversion at 525 °C and outstanding stability for over 5000 h, a landmark result that redefines durability expectations for non-noble metal catalysts [144]. Li et al. reported a pyramidal Ni NP catalyst ($Ni/Al_{1.8}Ce_{0.2}O_x$ -etched) that maintained performance for over 1000 h [202], and Yu et al. demonstrated 30Ni/SiC-700 with 450 h of stable operation [169].

A comparative assessment of Fe, Co, and Ni catalysts reveals distinct performance profiles. Co-based systems exhibit the highest intrinsic activity, approaching Ru-level performance in optimized formulations (e.g., K-CoNi-MgO- CeO_2 -SrO [203]), yet they suffer from a higher cost than Ni and a lower crustal abundance compared to Fe. Ni-based

catalysts offer the most favorable balance of cost, availability, and stability. The $\text{Ni}_x\text{Mg}_{1-x}\text{O}/\text{CeO}_2$ system, for example, has demonstrated exceptional durability over 5000 h [144], but it typically requires elevated operating temperatures ($>550^\circ\text{C}$) to achieve $>90\%$ conversion. Fe-based catalysts are the most economical and have been advanced by waste-to-catalyst strategies such as the use of red mud [204,205]; however, they are prone to deactivation caused by strong N binding and bulk nitridation. It is increasingly recognized that dynamic phase transformations ($\text{Fe} \rightarrow \text{Fe}_x\text{N}$, $\text{Co} \rightarrow \text{CoN}$) generate the true active species under reaction conditions [103,206,207], suggesting that catalyst design should aim to stabilize optimal metal-nitride equilibria rather than preserve purely metallic surfaces. Interface engineering—particularly the construction of inverse catalyst structures (e.g., CeO_2/Ni [173], MgO/Co [117]) and core@shell heterostructures (e.g., $\text{Co@BaAl}_2\text{O}_{4-x}$ [112])—has emerged as a powerful strategy to overcome the activity-stability trade-off, with the metal-oxide interface enabling both electronic modulation and structural stabilization. Nonetheless, the scalability of these sophisticated nanostructures and their performance under industrially relevant conditions (e.g., elevated pressure, feed impurities, and thermal cycling) remain largely unexplored.

2.3. Alloy Catalysts

Non-noble metal catalysts offer clear cost advantages for NH_3 decomposition. However, a persistent activity gap relative to Ru reflects a fundamental electronic-structure mismatch with the Sabatier optimum [208]. Monometallic Fe binds N too strongly, which pushes the system toward surface nitridation and deactivation. Co and Ni exhibit, on the other hand, bind N comparatively weak, which limits initial NH_3 activation [209]. The resulting dilemma, optimizing one elementary step at the expense of another, is a direct manifestation of the BEP scaling relation, wherein activation barriers for NH_3 dissociation and N_2 desorption are anti-correlated along a single binding-energy coordinate [7,17].

Alloying provides a systematic way to escape this scaling constraint by combining metals with complementary electronic characteristics into multicomponent phases whose collective d-band structure deviates from the linear interpolation of the parent metals [210]. Through judicious selection of alloy composition, one can engineer intermediate N binding energies that approach the top of the activity volcano, simultaneously enhancing NH_3 activation kinetics and N_2 desorption thermodynamics [211,212]. This section surveys recent progress in alloy catalysts for NH_3 decomposition, encompassing Fe-based, Ni-based, Ru-based bimetallic systems, and emerging high-entropy alloys (HEAs), with an emphasis on the mechanistic principles linking alloy composition, electronic structure modulation, and catalytic performance as elucidated by DFT calculations and advanced characterization techniques.

2.3.1. Fe-Based Alloy Catalysts

The central challenge for Fe-based catalysts is the excessively strong Fe–N interaction, which traps atomic nitrogen on the surface and promotes bulk nitride formation, ultimately leading to deactivation [68]. Alloying Fe with a second metal that has a weaker N affinity offers a direct electronic way to moderate this binding strength while preserving Fe's capacity for N–H bond activation. Qi et al. developed FeCu alloy catalysts on MgO and showed that Cu incorporation tunes the Fe–N binding energy through a fundamentally electronic mechanism [213]. The $\text{Fe}_{1-x}\text{Cu}_x/\text{MgO}$ catalyst increased NH_3 conversion from 29.7% to 73.8% at 500°C relative to monometallic Fe/MgO (Figure 5a). DFT calculations and in situ X-ray absorption spectroscopy (XAS) together revealed that FeCu alloying reduces the N–N recombination energy barrier from 2.265 eV on a pure Fe cluster to 1.77 eV on a FeCu cluster, a reduction attributed to a Cu-induced

3d-3d orbital coupling that reshapes the d-p hybridization between Fe active sites and N intermediates (Figure 5b). The electronic perturbation simultaneously moderates NH_3 adsorption-dehydrogenation energetics and facilitates N_2 desorption, precisely the dual optimization demanded by the Sabatier principle.

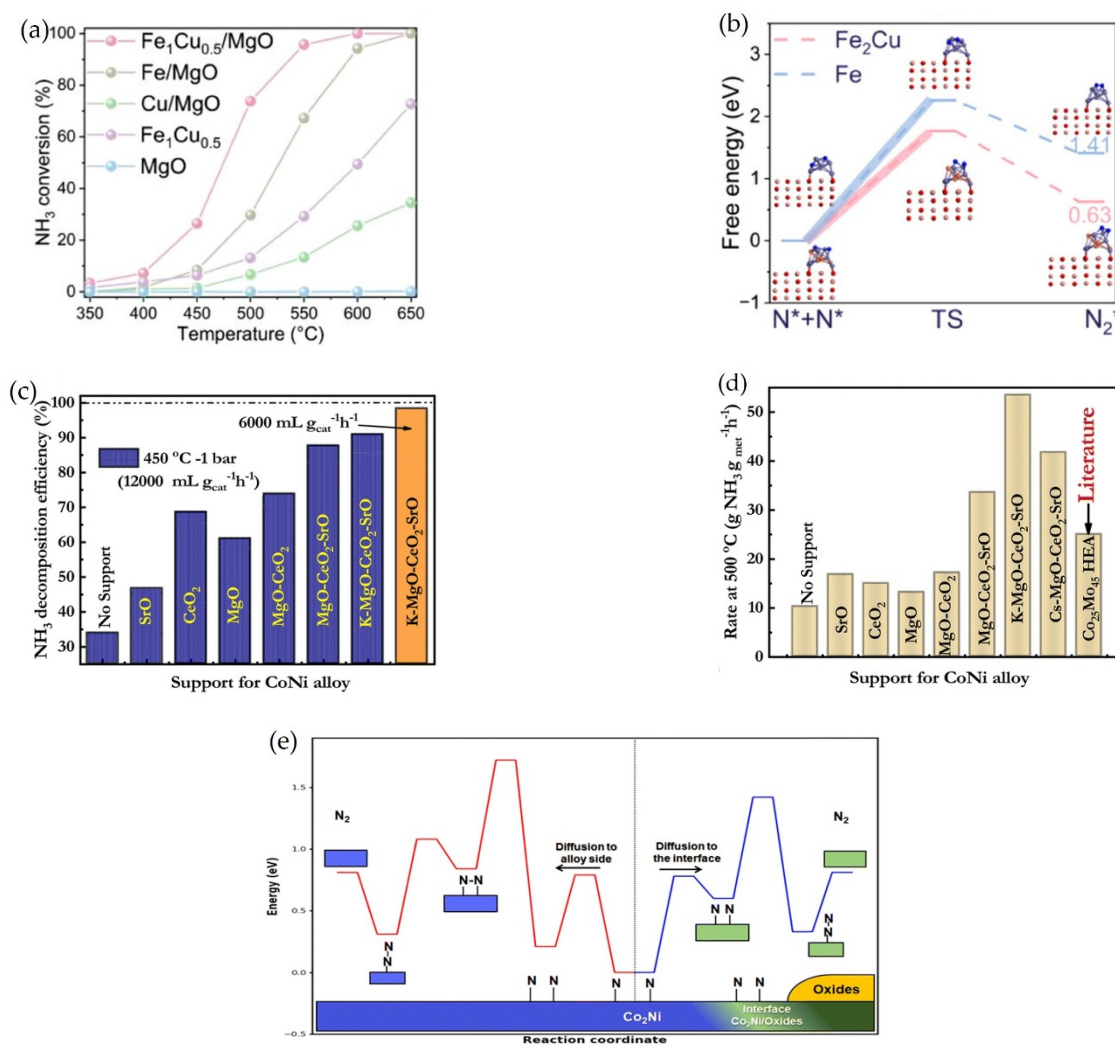


Figure 5. (a) Comparison of ADR performance of $\text{Fe}_1\text{Cu}_x/\text{MgO}$ catalysts at different temperatures (GHSV = 12,000 h^{-1}). (b) Comparison of reaction energy changes during detailed N-N recombination desorption of ADR on Fe_2Cu clusters and Fe clusters [213]. (c) Comparison of NH_3 decomposition efficiency (with >99.99% NH_3) of K-CoNi_{alloy}-MgO-CeO₂-SrO with different mixed oxide support. (d) NH_3 reaction rate for different ADR catalysts developed and those reported in the literature. (e) The energy profiles of NH_3 dissociation and N_2 formation on the alloy (left side) and alloy-oxide interfaces (right side). The studied oxides include CeO₂ and MgO, showing the same trends [203].

Meng et al. investigated unsupported FeCo, FeNi, and FeCu bimetallic catalysts to isolate intrinsic bimetallic synergy from support effects [210]. FeCo exhibited the highest performance, achieving nearly 100% NH_3 conversion at 600 $^{\circ}\text{C}$ with robust thermal stability exceeding 200 h. Structural characterization revealed that Fe and Co form a single-phase alloy with optimal lattice compatibility, while DFT calculations indicated that FeCo alloying enhances NH_3 adsorption and activation while simultaneously lowering the N recombination barrier. The origin of this dual enhancement lies in the formation of strong covalent Fe-Co metallic bonds that generate elevated electron density at the active surface, facilitating both NH_3 activation and intermediate transformation.

2.3.2. Ni-Based Alloy Catalysts

Section 2.2 addressed Ni catalysts modified by support engineering, interface design, and promoters, the present section focuses specifically on Ni-based bimetallic and multimetallic alloy phases in which a secondary metal is incorporated directly into the Ni lattice, producing a fundamentally different electronic and geometric environment at the active surface.

Zhao et al. conducted a systematic DFT investigation of 29 Ni-based binary alloys, establishing quantitative composition–binding energy relationships [214]. Early transition metal dopants strengthen N binding (shifting the system toward the strong-binding side of the volcano), whereas post-transition and main-group dopants (Cu, Zn, Ga, In, Sn) weaken N adsorption, thereby promoting the N recombination step. An optimal N adsorption energy range of -5.0 to -4.3 eV was identified to be the range that balances dehydrogenation and N recombination kinetics. NiZn and NiCu₃ emerged as the most promising candidates, exhibiting the lowest energy barriers for NH₃ dehydrogenation (1.58 eV for NiZn) and N recombination (1.57 eV for NiCu₃), respectively. A complementary machine learning analysis underscored the importance of dopant electronic characteristics (d-orbital radius, atomic radius, polarizability) in tuning N adsorption strength, providing transferable descriptors for alloy screening.

Yoon et al. investigated NH₃ decomposition over Ni-based alloys using DFT calculations and microkinetic simulations, revealing a volcano-shaped dependence of catalytic activity on nitrogen adsorption energy [215]. Their analysis predicted Ni_{10.64}Fe_{0.36} as an optimal composition, a prediction subsequently validated by experiment, demonstrating the predictive power of binding-energy descriptors for rational alloy design.

Beyond conventional alloy synthesis, the thermal decomposition of ordered intermetallic precursors offers a route to nanostructured composites with inherent confinement. The thermal decomposition of CeNi₅ intermetallics produces a Ni/CeO₂ nanocomposite whose interconnected microstructure physically confines the Ni NPs, preventing thermally induced growth and sustaining high activity under demanding reaction conditions [216].

Li et al. developed CoNi alloy catalysts on Zr-modified Y₂O₃, with the CoNi(1:2)/5%Zr-Y₂O₃ formulation achieving 90.9% NH₃ conversion at 550 °C [217]. The synergistic interaction between Co and Ni generates an intermediate M–N bond strength. H₂ temperature-programmed reduction (H₂-TPR) confirmed a strong interaction between the CoNi particles and the mesoporous support that prevents sintering at high temperatures. Yadav et al. found a similar synergy for Al-supported systems: a bimetallic 12Ni₃Co/Al catalyst exhibited the highest activity and lowest E_a (42.8 kJ·mol⁻¹) among a series of Ni/Al₂O₃ and Ni-Co/Al₂O₃ catalysts, attributable to alloy formation with reduced particle size and enlarged effective surface area that mitigated H₂ poisoning [218].

A landmark study by Tabassum et al. showed that CoNi alloy performance can be elevated to near-Ru levels through deliberate engineering of the metal-oxide interface [203]. A K-promoted CoNi alloy (Co:Ni = 2:1) dispersed on a ternary MgO–CeO₂–SrO mixed oxide support achieved 97.7% NH₃ conversion at 450 °C (GHSV = 6000 mL·h⁻¹·g⁻¹) and a H₂ production rate of 3465 mmol·g_{cat}⁻¹·h⁻¹ at 500 °C (Figure 5c,d). DFT calculations revealed the mechanistic origin of this performance. While the CoNi alloy surface has localized charge polarization favorable for NH₃ activation, the rate-determining N–N recombinative desorption barrier is substantially reduced at the metal-oxide interface (0.82 eV on CeO₂/Co₂Ni) relative to the bare alloy surface (1.52 eV) (Figure 5e). The Ce⁴⁺/Ce³⁺ redox couple generates O_v that enhance MSI, while SrO incorporation and K promotion increase surface basicity, facilitating electron donation and N₂ desorption. In a membrane reactor at 500 °C, the catalyst maintained complete conversion for over 600 h,

establishing that rational interface engineering enables non-precious metal systems to approach noble metal performance levels.

2.3.3. Ru-Based Alloy Catalysts

Alloying Ru with less expensive metals addresses the dual objectives of reducing precious metal loading and fine-tuning the electronic environment of Ru active sites. The key mechanistic question is how neighboring heteroatoms change the d-band character of surface Ru—and therefore its N binding energy—without disrupting the favorable position of Ru near the volcano apex. Wei et al. introduced a quantitative descriptor called “coordination impact” to capture how nearest-neighbor heteroatoms affect the electronic structure of Ru sites in RuM alloys [219]. A systematic survey across multiple alloy compositions revealed a volcano-shaped relationship between this descriptor and catalytic reaction rates, consistent with the Sabatier principle. RuMn and RuMo intermetallic alloys occupy the top of the volcano with optimal activity attributable to a moderate electronic perturbation of the Ru d-band (Figure 6a). Experimental tests confirmed that RuMn comfortably outperforms pure Ru, demonstrating the coordination environment, not merely elemental identity.

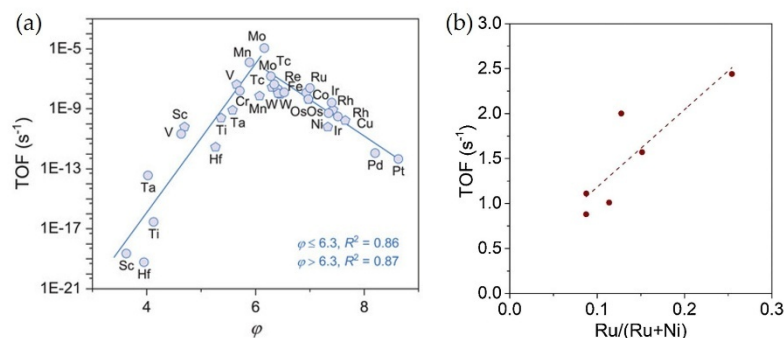


Figure 6. (a) The relation between the coordination impact descriptor and TOF for different alloy catalysts [219]. (b) Correlation between TOF_{H2} values and the Ru/(Ru + Ni) (wt. %) [220].

Lucentini et al. conducted a comparative evaluation of bimetallic Ni-Ru/CeO₂ against its monometallic counterparts, demonstrating that the intimate electronic interaction between Ni and Ru generates a catalyst with exceptional activity and stability [220]. The bimetallic system delivered a TOF for H₂ production exceeding 2 s⁻¹ at 400 °C, surpassing the majority of reported Ni-based and unmodified Ru-based catalysts. The boost comes from the synergistic modulation of N binding energy at Ni–Ru interfacial sites (Figure 6b).

2.3.4. Trimetallic and High-Entropy Alloy Catalysts

The extension from binary to multicomponent alloys introduces combinatorial complexity, but it also opens up qualitatively new dimensions: multiple distinct active-site motifs, composition-dependent local chemical ordering, and emergent properties absent in the constituent binaries [211,221].

Yuan et al. synthesized CoMo@NC catalysts using N-doped carbon (NC) derived from a ZIF-67 template [222]. The rhombic dodecahedral structure facilitates electron transfer, while the synergistic interaction between Co and Mo promotes the in situ formation of Co₃Mo₃N, a bimetallic nitride phase that provides additional active sites for NH₃ decomposition via a distinct reaction pathway involving nitrogen vacancy cycling. Sun et al. extended the bimetallic paradigm to a trimetallic NiFeCo alloy catalyst, which achieved ~80% NH₃ conversion at 550 °C with sustained stability [223]. A distinctive mechanistic feature of this system is the formation of the interstitial compound Fe₂Ni₂N

during nitridation, which markedly promotes NH_3 dehydrogenation by providing additional coordinatively unsaturated sites. Adding Co enhances the interplay among Fe, Co, and Ni, lowering the energy barrier for the RDS. DFT calculations revealed that the 3d orbital manifold of the NiFeCo phase is expanded and shifted to higher energy compared to the bimetallic counterparts, facilitating electron transfer adsorbed intermediates and thereby accelerating NH_2^* dehydrogenation.

High-entropy alloys (HEAs), solid solutions with five or more elements in near-equimolar proportions, represent a fundamentally different way to design catalysts. Their huge compositional space and inherent chemical disorder produce a statistical distribution of active-site geometries with continuously tunable binding energies, offering the possibility of approaching the Sabatier optimum across an ensemble of sites rather than at a single, uniform site [224,225]. Kobayashi et al. synthesized a quinary IrRhRuCoNi HEA powder and showed it outperformed a single Ru catalyst for liquid NH_3 electrolysis, attributing the enhancement to multielemental synergistic effects [226]. Although that study focused on electrolysis, the underlying principle that HEA compositions can access electronic states that binary alloys is directly transferable to thermal NH_3 decomposition.

Identifying active-site motifs within the disordered HEA structure is a major mechanistic challenge. Wang et al. addressed this by building an integrated computational framework combining cluster expansion–Metropolis Monte Carlo simulations with microkinetic analysis to investigate NH_3 decomposition on a Co–Cu–Fe–Mo–Ni HEA [227]. Their analysis identified highly active B5-step sites as Cu-deficient multi-metal configurations. Temperature-induced Cu surface segregation was found to suppress catalytic activity by disrupting these motifs. From this, they drew actionable design principles: keep Cu away from B5 sites, but preserve the conformational disorder that generates the ensemble of near-optimal binding energies.

A further mechanistic subtlety is revealed by Morris et al., who demonstrated that even though macroscopically homogeneous mixing characteristic of HEAs, pronounced local chemical ordering, specifically preferential Ru–Ir bonding pairs, exists at the atomic scale and substantially influences catalytic behavior [228]. In their quinary HEA-5 system, the higher coordination number of Ir atoms around surface Ru active sites weakens Ru–N interactions, thereby promoting the kinetically limiting nitrogen recombination and desorption step. This finding underscores that the relevant descriptor for HEA catalyst design is not bulk composition alone but rather the local coordination environment of the active site—a principle that connects directly to the coordination impact descriptor introduced by Wei et al. for binary Ru alloys [219].

Alloying has been demonstrated as an effective strategy to overcome the constraints imposed by BEP scaling relations, yet several challenges remain. First, the optimal alloy composition exhibits pronounced system dependence: FeCu delivers the best performance for Fe-based systems [213], CoNi for Ni-based systems [203,217], and RuMn/RuMo for Ru-based systems [219]. This strong compositional specificity suggests that alloy design should be guided by computational screening approaches, such as DFT and machine learning, rather than by relying on empirical trial-and-error. Second, whether the alloy forms a single-phase solid solution or a phase-separated structure significantly impacts the catalytic performance [210]; achieving the targeted phase demands precise control over synthesis parameters, including temperature, atmosphere, and precursor chemistry. Third, high-entropy alloys (HEAs) provide access to an unprecedented compositional space but introduce new complexities: the statistical distribution of active sites obscures mechanistic understanding [227], and local chemical ordering (e.g., preferential Ru–Ir bonding [228]) can profoundly influence catalytic behavior in ways that are not captured by the bulk composition alone. The most

promising direction appears to be interface-engineered alloy catalysts, in which the alloy component optimizes binding energetics while the oxide interface facilitates N_2 desorption [203], thereby enabling earth-abundant elements to deliver catalytic performance approaching that of Ru.

2.4. Transition Metal Nitride/Carbide Catalysts

Beyond conventional supported metals, transition metal nitrides (TMNs) and carbides (TMCs) have emerged as a distinct and promising class of catalysts for NH_3 decomposition [229]. These interstitial compounds, formed by incorporating N or C atoms into the lattice of a parent transition metal, exhibit a unique combination of properties: high electrical conductivity, thermal stability exceeding that of the parent metal, and, most consequentially, electronic structures that approximate those of Group VIII noble metals. The physical origin of this “noble-metal-like” character lies in the contraction of the metal d-band upon interstitial atom insertion: the hybridization between metal d-states and nonmetal p-state broadens and shifts the d-band, modifying the density of states near the Fermi level in a manner that enables fine-tuning of the metal–N bond strengths that govern NH_3 decomposition kinetics [5,230]. This electronic-structure rationale has motivated extensive investigation of TMNs and TMCs, particularly Mo-based systems, as cost-effective alternatives to Ru. The following subsections are organized along a progression from phase-structure and surface chemistry (the intrinsic determinants of activity) through dispersion and interfacial strategies (engineering levers for performance optimization) to multicomponent and activation approaches (frontier directions), with the unifying thread being the interplay between interstitial-atom-induced d-band modification and the resultant modulation of elementary step energetics.

2.4.1. Mo-Based Nitrides

Molybdenum nitrides (MoN_x) have attracted the most sustained attention among TMN catalysts, owing to the favorable position of Mo in the periodic table, its d-band width and filling, when modified by interstitial nitrogen, produce M–N binding energies that are intrinsically closer to the Sabatier optimum than those of many other first-row TMNs [231].

MoN_x exists in multiple crystallographic phases with very different catalytic behaviors, the most important being cubic $\gamma\text{-Mo}_2\text{N}$ and hexagonal $\delta\text{-MoN}$. Huo et al. conducted a systematic comparison of $\gamma\text{-Mo}_2\text{N}$ and $\delta\text{-MoN}$ nanocrystals confined within two-dimensional mesoporous SBA-15/reduced graphene oxide (rGO) hybrid nanosheets [230]. DFT calculations provided a direct electronic-structure explanation for the observed activity difference: the associative desorption of N atoms—the RDS—proceeds a much lower barrier on $\text{Mo}_2\text{N}(100)$ (2.56 eV) than on $\text{MoN}(100)$ (3.22 eV), reflecting the weaker Mo–N binding in the N-deficient γ phase (Figure 7a) [231]. The $\text{Mo}_2\text{N}/\text{SBA-15}/\text{rGO}$ catalyst delivered an NH_3 decomposition rate of $1834.8 \text{ mmol}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$ at 600°C , one of the highest reported for Mo-based systems, with the rGO component further weakening Mo–N bonds via electron donation, facilitating N_2 desorption.

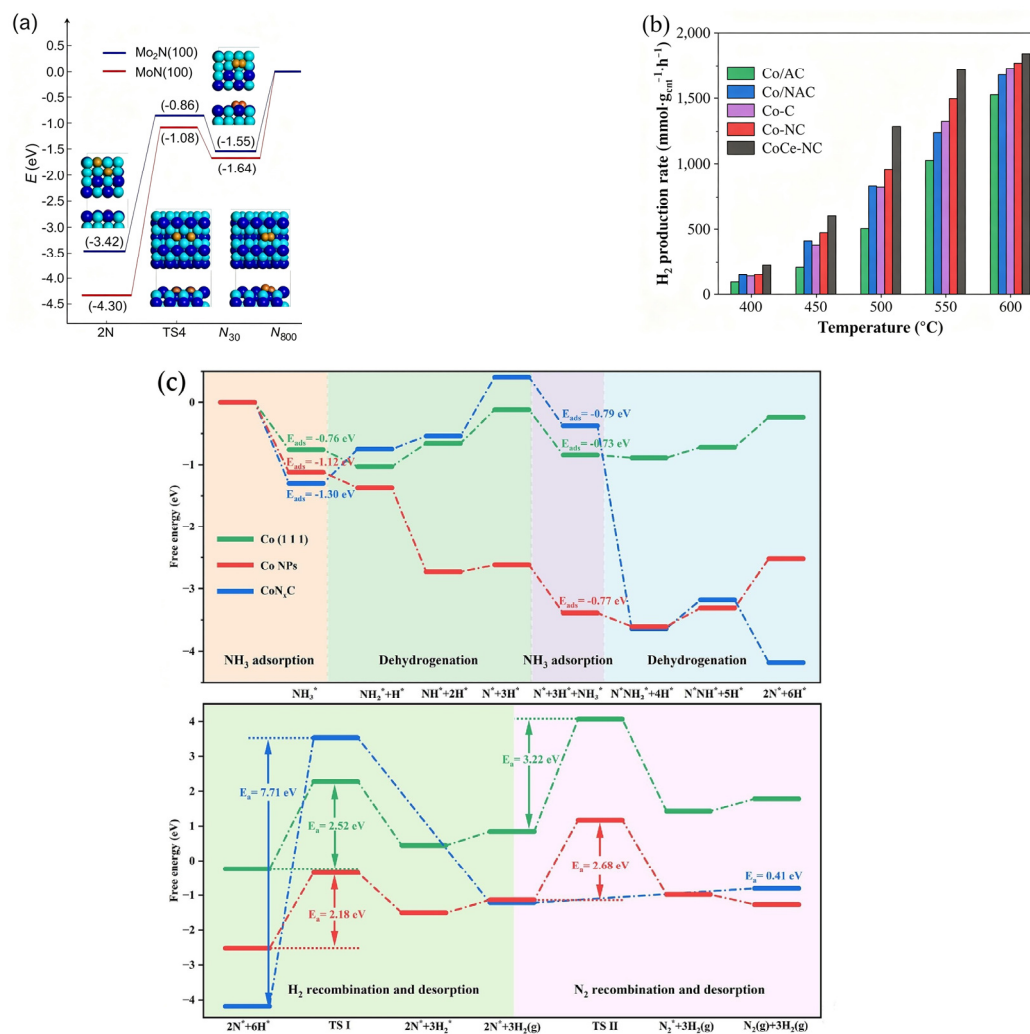


Figure 7. (a) The associative desorption of nitrogen atoms on Mo₂N (100) and MoN (100) [231]. (b) The H₂ production rate at different temperatures. (c) Free energy changes throughout the NH₃ decomposition reaction on different Co active sites [207].

A more subtle part of MoN_x surface chemistry is the role of residual oxygen. Shi et al. synthesized γ -Mo₂N catalysts with systematically varied the oxygen content and demonstrated that higher oxygen levels (HO- γ -Mo₂N) increases the average oxidation state of surface Mo, thereby strengthening Mo–NH₃ interactions and promoting NH₃ activation [232]. At 550 °C, the HO- γ -Mo₂N catalyst achieved a H₂ formation rate 3.3 times higher than its low-oxygen counterpart. The mechanistic insight is that surface oxygen species serve a dual kinetic function: they enhance NH₃ activation by increasing Lewis acidity, while simultaneously facilitating hydrogen spillover—migrating H adatoms away from active Mo–N sites and mitigating hydrogen poisoning. This dual role of surface oxygen, simultaneously promoting the first and alleviating inhibition of the last elementary steps, constitutes a valuable and transferable design principle for nitride catalysts.

Maximizing the density of accessible active sites requires strategies to disperse the nitride phase while maintaining structural integrity. Wei et al. employed a molybdate-intercalated Mg–Al hydrotalcite-like precursor to prepare Mg(Al)O-supported Mo_{2+x}N species [233]. The layered precursor structure provided spatial confinement during nitridation, yielding compositionally uniform, highly dispersed nitride NPs. The optimized Mo_{0.5}Mg₃Al nitride catalyst achieved nearly complete NH₃ conversion at 625

°C and exhibited remarkable stability over 100 h with no significant aggregation, attributable to the strong MSI and the mixed oxide matrix. This result demonstrates that the principles of MSI engineering, well established for conventional supported metal catalysts, are directly transferable to nitride systems.

Introducing a second transition metal into the nitride framework offers additional electronic tunability beyond that accessible through phase selection or surface modification alone. Ternary nitrides, particularly $\text{Co}_3\text{Mo}_3\text{N}$, have consistently demonstrated superior performance compared to binary counterparts. Lee et al. reported that $\text{Co}_3\text{Mo}_3\text{N}$ exhibited higher intrinsic activity than $\text{Ni}_3\text{Mo}_3\text{N}$, achieving ~100% NH_3 conversion at 550 °C [234]. X-ray photoelectron spectroscopy (XPS) attributed this to a higher average Mo valence state and stronger Lewis acidity in $\text{Co}_3\text{Mo}_3\text{N}$, which facilitates N–H bond cleavage at the rate-limiting dehydrogenation step. Decorating with Ni NPs further enhanced low-temperature activity, with the $\text{Ni}/\text{Co}_3\text{Mo}_3\text{N}$ catalyst achieving 71% conversion at 500 °C and maintaining stable performance for 30 h.

The $\text{Fe}_3\text{Mo}_3\text{N}$ ternary nitride represents a parallel development. Hund et al. confirmed its η -6 crystal structure and evaluated its catalytic performance for NH_3 decomposition, demonstrating that the Fe–Mo–N ternary system provides yet another compositional variable for tuning M–N binding energetics [235]. Bimetallic CoMo nitride systems [236] and Co-doped graphdiyne-derived catalysts [237] further illustrate that engineering the coordination environment at multi-metal interfaces, whether through $\text{Co}_3\text{Mo}_3\text{N}$ active phases or Co–C interfacial sites, yields enhanced low-temperature activity and stability beyond that achievable with binary nitrides.

Two other strategies address the kinetic limitations of Mo-based nitrides from complementary directions. First, alkali metal promotion tunes the electronic environment of the nitride surface. Bamufleh and Zaman studied Li, K, and Cs promotion of bulk Mo_2N and found K to be the most effective promoter [238]. K- Mo_2N achieved 100% NH_3 conversion at 600 °C and 80% at 550 °C under a GHSV of 6000 h^{-1} . XPS analysis revealed that K acts as an electron donor to the Mo–N phase, enhancing surface basicity and promoting kinetically limiting N–N recombinative desorption step, with no appreciable deactivation over 20 h. Second, non-conventional energy input can dramatically improve energy efficiency. Dutta et al. demonstrated that microwave-driven NH_3 decomposition over $\text{Co}_2\text{Mo}_3\text{N}$ achieved >90% conversion at 400 °C with an E_a of 31 $\text{kJ}\cdot\text{mol}^{-1}$, much lower than the 37 $\text{kJ}\cdot\text{mol}^{-1}$ observed under conventional thermal conditions [239]. The energy efficiency of microwave-assisted process was approximately 90 times higher than that of the conventional thermal process at 400 °C. The reason is selective volumetric heating of the electrically conductive nitride phase. This result highlights the potential synergy between the intrinsic electrical properties of TMNs (high conductivity) and advanced reactor concepts (microwave, Joule heating) as an emerging design frontier.

2.4.2. Fe-Based Nitrides

For Fe-based catalysts, a distinctive mechanistic feature distinguishes them from Mo-based nitrides. Under NH_3 decomposition conditions, metallic Fe undergoes progressive nitridation, and the resulting Fe_xN phases, rather than the initial metallic state, constitute the true catalytically active species [240]. Understanding and controlling this in situ phase transformation is therefore central to Fe-nitride catalyst design.

Purcel et al. conducted a comprehensive transient kinetic and in situ X-ray diffraction investigation of a promoted wüstite-based bulk Fe catalyst, establishing that nitride formation follows a sequential two-step pathway: $\text{Fe} \rightarrow \text{Fe}_4\text{N} \rightarrow \text{Fe}_2\text{N}$ [206]. The decomposition of Fe_4N to α -Fe and N_2 was identified as the RDS, with an E_a of 172 $\text{kJ}\cdot\text{mol}^{-1}$, a value closely matching the apparent E_a for NH_3 decomposition (173 $\text{kJ}\cdot\text{mol}^{-1}$), confirming the intimate coupling between bulk nitride phase dynamics and surface catalytic kinetics.

Molecular dynamics simulations further demonstrated that N migration into the Fe bulk is kinetically favored over surface recombinative desorption, providing an atomistic rationale for the propensity toward bulk nitridation.

The kinetics of active Fe_xN formation can be substantially accelerated by adding promoters. Indriadi et al. showed that putting as little as 0.1 wt% highly dispersed Pt on Fe/SiO_2 accelerated the Fe_2N formation rate by more than threefold [241]. The mechanism involves a reverse hydrogen spillover process: dissociated H atoms migrate from Fe to Pt for recombination and desorption, thereby exposing additional Fe surface sites for NH_3 adsorption and promoting N diffusion into the Fe lattice. Alkali metal doping provides an alternative electronic promotion route. Yan et al. demonstrated that Rb-doped Fe_2O_3 catalysts, pretreated under NH_3 , achieved 95.5% NH_3 conversion at 550 °C, with enhancement attributed to increased electron density in the Fe_3N active phase and improved NH_3 adsorption capacity [242].

One noteworthy translational development is turning red mud (RM)—the hazardous alkaline byproduct of aluminum production, generated at ~120 million tons per year and containing 35–40 wt% Fe_2O_3 into a feedstock for Fe_xN catalyst synthesis [204,205]. Kurtoğlu and Uzun showed that acid digestion of RM in 6 M HCl, followed by controlled calcination, reduction, and NH_3 activation, enables systematic tuning of Fe_xN NP size and degree of nitridation [205]. An inverse correlation between Fe_xN crystallite size and H_2 production rate was established: smaller NPs (e.g., 23 nm) substantially outperformed larger ones (>30 nm) under differential conversion conditions. The optimized catalyst (MRM-2-C900@700) achieved stable NH_3 conversion of $98.8 \pm 0.5\%$ at $120,000 \text{ cm}^3\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ ($7290 \text{ mmol H}_2\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$) and $87.1 \pm 0.5\%$ at $240,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ for >70 h without deactivation at 700 °C, performance surpassing most Fe-based and many non-noble metal catalysts. Characterization confirmed surface-accessible $\epsilon\text{-Fe}_2\text{N}$ NPs as the active phase, with performance enhancement attributed to the removal of Cl/S impurities and retention of trace alkali promoters (K, Na) from the RM precursor [204,205]. This waste-to-catalyst strategy shows how fundamental Fe_xN structure-activity relationships can be translated into a cost-effective and sustainable technology.

2.4.3. Co-Based Nitrides

In the Fe system, the nitride phase itself is the main active species. Co-based exhibit a qualitatively different mechanism in which synergistic cooperation between metallic Co NPs and CoN species determines overall catalytic performance. Kang et al. designed a series of C-supported Co catalysts and, using extended X-ray absorption fine structure, carbon monoxide temperature-programmed desorption, and DFT calculations, elucidated the distinct mechanistic roles of different Co species [207]. Metallic Co NPs were the optimal active sites for NH_3 decomposition (RDS barrier of 2.68 eV). CoN alone exhibited poor catalytic performance (barrier of 7.71 eV) (Figure 7b). However, a pronounced synergy was observed that the Co–CoN interface: CoN sites facilitate the initial adsorption and activation of NH_3 , while adjacent metallic Co NPs provide energetically favorable pathways for the recombinative desorption of H_2 and N_2 , collectively lowering the overall energy barriers below those of either phase in isolation. The optimized CoCe–NC catalyst, derived from a Ce-doped ZIF-67 precursor, achieved complete NH_3 conversion at 600 °C with a H_2 production rate of $1840 \text{ mmol}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$ (Figure 7c).

This metal-nitride bifunctional mechanism represents a conceptual bridge between the conventional supported-metal paradigm and the bulk nitride paradigm: rather than viewing metallic and nitride phases as competing (or sequential) states of the same catalyst, the Co system reveals that deliberately engineering their co-existence at the nanoscale can unlock cooperative catalytic pathways inaccessible to either phase alone.

2.4.4. Emerging Nitrides and N-Vacancy-Mediated Mechanisms

The preceding sections have established that phase structure, surface chemistry, multicomponent composition, and promoter addition collectively govern the catalytic performance of Mo-, Fe-, and Co-based nitrides. A mechanistically significant recent development stretches beyond these established systems: the recognition that N vacancies (N_v) in binary metal nitrides can serve as catalytically active sites that mediate NH_3 decomposition via a MvK-type mechanism, similar to the role of O_v in reducible oxide supports. Miyazaki et al. examined NaCl-type binary transition metal nitrides containing La, Ce, Y, Zr, or Hf as catalytic supports for transition metal NPs. They found a clear correlation between N_2 desorption temperature and catalytic activity, which they rationalized in terms of the ionic radii of the metal cations [243]. In this N_v -mediated pathway, NH_3 fills a lattice nitrogen vacancy, undergoes stepwise dehydrogenation, and the resulting lattice N recombines with a neighbor to regenerate the vacancy upon N_2 desorption, a fundamentally different catalytic cycle from conventional surface-mediated mechanisms, one that may circumvent the BEP scaling constraints limiting metallic surfaces. The exploration of unconventional nitride compositions continues to expand the catalyst design space. Hojamberdiev et al. recently reported on Li_2ZrN_2 , characterizing its crystal structure, electronic properties, and catalytic activity for NH_3 decomposition and demonstrating its viability as a non-transition-metal nitride platform [244]. These emerging platforms suggest that the design principles established for Mo- and Fe-based nitrides, d-band modulation via interstitial atoms, surface vacancy engineering, and promoter-mediated electronic tuning, are widely transferable across the transition metal nitride family, while each system introduces unique mechanistic features that merit further investigation.

2.4.5. Carbides

Molybdenum carbides (MoC_x) share the same electronic-structure logic as their nitride counterparts. Interstitial C atoms contract the Mo d-band, but differ in the quantitative details of M–N binding and surface chemistry. The performance of MoC_x is tightly linked to surface stoichiometry and phase identity.

Sun et al. conducted a detailed comparison of α - MoC (cubic) and β - Mo_2C (hexagonal) [245]. The β - Mo_2C catalyst, characterized by a higher surface Mo/C atomic ratio (1.48 versus 0.73 for α - MoC), exhibited a TOF of 1.3 s^{-1} at $450\text{ }^\circ\text{C}$, more than ten times higher than that of α - MoC . A linear correlation between the surface Mo/C ratio and the H_2 yield was established, confirming that Mo-rich surfaces are intrinsically more active for NH_3 decomposition. This finding parallels the phase-dependent behavior of Mo nitrides (γ - $Mo_2N > \delta$ - MoN). In both cases, the metal-rich, N/C-deficient phase provides weaker M–N binding and thus faster N_2 desorption, consistent with the Sabatier principal prediction for systems positioned on the strong-binding side of the activity volcano.

MoC_x also serves as an effective support for transition metal NPs. A 5Co/ Mo_2C catalyst activated in H_2 /Ar or NH_3 /Ar at $400\text{ }^\circ\text{C}$ achieved $\sim 90\%$ NH_3 conversion at $500\text{ }^\circ\text{C}$; H_2 pre-activation enhanced the surface Co/Mo ratio and charge transfer, increasing the number of active Co sites [246]. Optimizing Co loading to 7.5 wt% gave 93.7% conversion at $450\text{ }^\circ\text{C}$, which was attributed to optimal dispersion and crystallite size ($\sim 16.8\text{ nm}$). Among promoters, La improved activity by increasing basicity and Co dispersion, whereas K and Cs caused agglomeration and site blocking. This is a cautionary counterpoint to the uniformly beneficial effect of K on Mo nitrides, highlighting that promoter effectiveness is support-specific and cannot be assumed transferable across TMN and TMC platforms.

Emerging computational work on two-dimensional MXene carbides (V_2C , Ti_2C , Mo_2C) has extended the design space beyond bulk phases: DFT calculations predict that

V₂C surfaces offer the most favorable balance between NH₃ adsorption and N-atom desorption energetics among the three MXenes examined, with the desorption of nitrogen atoms confirmed as the RDS [247]. These predictions still need experimental validation, but suggest that two-dimensional carbide architectures may offer fundamentally different active-site geometries and electronic environments compared to their bulk counterparts.

3. Plasma-Catalytic NH₃ Decomposition

Plasma-catalytic ammonia decomposition has arrived as an attractive electrified route to carbon-free hydrogen, capable of circumventing the thermodynamic and kinetic constraints that govern conventional thermal catalysis [20,248]. In non-thermal plasma (NTP) environments, dielectric barrier discharge (DBD), gliding arc, and microwave plasmas, energetic electrons generate a rich mixture of vibrationally excited NH₃, reactive radicals ($\cdot\text{NH}_2$, $\cdot\text{NH}$, $\cdot\text{H}$), and ions, enabling appreciable conversion at temperatures far below those required for thermal processes alone [19]. The resulting non-equilibrium chemistry opens up a distinct catalytic design space in which plasma activation and heterogeneous surface reactions can be strategically coupled through catalyst formulation and process intensification.

3.1. Noble-Metal Catalysts

Among noble metals, Ru-based catalysts are still the performance benchmark for plasma-catalytic NH₃ decomposition. Shawon et al. demonstrated that operating a DBD reactor under adiabatic (thermally insulated) conditions amplifies the synergy between plasma-generated species and low-loading Ru/Al₂O₃ catalysts, achieving 73% conversion at 19 W over a 0.05 wt% Ru catalyst that was entirely inactive thermally [249]. Similarly, Gao et al. achieved near-complete NH₃ conversion at 400 °C using highly monodisperse Ru NPs on a perovskite MgTiO₃ support [250]. Their work highlighted the role of strong MSI and favorable dielectric properties in modulating discharge characteristics and catalytic performance. Wang et al. constructed a Ru/La₂O₃ plasma catalytic system where DBD coupling markedly enhanced N–H bond dissociation, delivering an energy efficiency of about 20.7 mol·g_{cat}^{−1}·kWh^{−1} at 99% NH₃ conversion with exceptional long-term stability [251]. This result illustrates that the support in plasma-catalytic ammonia decomposition systems functions not merely as a dispersion medium but as an electronic regulator that modulates surface bond strengths and N/H desorption energetics. Comparative studies by Wang et al. further showed that Ru/La₂O₃ outperformed CeO₂- and SiO₂-supported analogs under DBD plasma, an effect attributed to the high surface basicity of La₂O₃ that facilitates reactant capture and to favorable plasma discharge behavior [252].

3.2. Earth-Abundant Transition Metal Catalysts

To mitigate the cost and scarcity limitations of Ru, extensive effort has been directed toward earth-abundant metals (Ni, Co, Fe) and their compounds. Zhou et al. investigated M/Al₂O₃ (M = Ni, Co, Fe, Cu, Mo) catalysts in a DBD reactor, employing in situ DRIFTS and synchrotron vacuum ultraviolet-photoionization mass spectrometry to reveal that Ni/Al₂O₃ achieved the highest activity due to enhanced NH₃ adsorption on Lewis acid sites and accelerated N₂ desorption [253]. In the context of gliding arc discharges, Ronduda et al. compared supported (Ba-Co/CeO₂) and bulk (Co/Ce/Ba) cobalt catalysts [254]. The supported version was more active and thermally stable owing to a higher population of weak hydrogen adsorption sites and strong surface basicity that promotes recombinative desorption. Perron et al. similarly found that Co/ α -Al₂O₃ and Ni/ α -Al₂O₃ catalysts improved NH₃ conversion and reduced energy consumption compared to a homogeneous gliding discharge system when processing highly concentrated NH₃ feeds

[255]. Furthermore, Zhou et al. showed that a plasma-assisted preparation strategy for Ni/Al catalysts enhanced Ni dispersion and reducibility, amplifying the synergy with DBD plasma to achieve 85% conversion at 330 °C [256].

3.3. Carbides, Nitrides, and Non-Metallic Catalysts

Beyond conventional oxide-supported metals, TMCs and TMNs have come forward as materials that are intrinsically plasma-active. Yu et al. reported over 95% NH_3 conversion using a low-pressure-synthesized Mo_2N catalyst in a DBD reactor without any external heating, attributing the high activity to a surface Mo/ Mo_2N composite structure [257]. Wang et al. further elucidated that smaller Mo_2N powder particles promote a more favorable surface discharge mode, thereby enhancing reactive species transport to the catalyst surface [258]. Multi-scale modeling by Ibrahim et al. delivered fundamental insights into the plasma-surface interplay, demonstrating that plasma-induced vibrational excitation of NH_3 on $\text{Co}_3\text{C}(001)$ and $\text{Co}_3\text{N}(001)$ surfaces shifts the RDS from $\text{N}\equiv\text{N}$ bond formation (thermal regime) to $\text{NH}_3(v)$ dissociation (plasma regime), leading to a dramatic increase in TOFs of up to 6 orders of magnitude and enabling operating-temperature reductions in several hundred degrees (Figure 8a) [259]. Even metal-free carbon film platforms have shown promise: Moszczyńska et al. demonstrated effective NH_3 splitting over N-doped carbon films under low-temperature plasma with near-100% H_2 selectivity, illustrating that surface functionality alone can be tuned for plasma-driven catalysis [260].

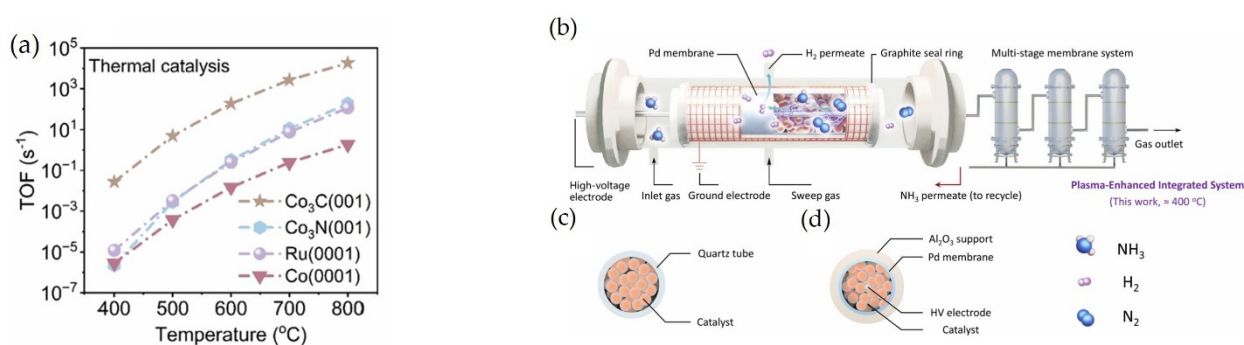


Figure 8. (a) Temperature-dependent TOFs showing that $\text{Co}_3\text{C}(001)$ exhibits substantially higher activity than $\text{Co}_3\text{N}(001)$, $\text{Ru}(0001)$, and $\text{Co}(0001)$ [259]. (b) The novel integrated Plasma-Enhanced Dual-Membrane Ammonia Decomposition System (PEDMADS), which couples plasma-catalysis with in situ H_2 separation and downstream NH_3 recovery. (c,d) Corresponding cross-sectional views of the packed catalyst bed in the conventional reactor and PEDMADS reactor, respectively [261].

3.4. Role of Support Dielectric Properties

The dielectric constant of the support exerts a decisive influence on microdischarge behavior in packed-bed DBD reactors. Andersen et al. observed a linear correlation between microdischarge frequency and NH_3 conversion [262]. MgAl_2O_4 ($\epsilon \sim 8.3$) gave the highest conversion among the tested materials, whereas high- ϵ materials such as BaTiO_3 were actually detrimental because they quenched the discharge. Ruiz-Martín et al. corroborated this finding in a BaTiO_3 -moderated ferroelectric packed-bed reactor, where the back-reaction of N_2 and H_2 to re-form NH_3 became significant at elevated power and flow rates, limiting net decomposition yield and reinforcing the importance of in situ H_2 removal [263].

3.5. Mechanistic Insights

Mechanistic understanding of plasma-catalytic NH_3 decomposition has advanced through the combined application of in situ spectroscopy and kinetic modeling. In a catalyst-free DBD system, Gao et al. used voltage-current waveform analysis and optical emission spectroscopy to show that under optimized electric field strength and pulsing conditions, the generation rates of radical and vibrational species can match the NH_3 supply rate, enabling substantial decomposition activity at near-ambient bulk temperatures [264]. The introduction of a highly active catalysts further amplifies conversion by providing selective surface pathways for these gas-phase excited species, establishing a synergistic paradigm of gas-phase excitation coupled with surface-selective conversion.

At the level of elementary processes, Zheng et al. developed a comprehensive kinetic model for non-equilibrium plasma-enhanced ammonia decomposition over Fe-based catalysts that simultaneously accounts for the evolution of electron and vibrational species populations alongside the stepwise dehydrogenation mechanism on the catalyst surface [265]. This model reveals that plasma conditions substantially enhance the chemisorption capacity of NH_3 through charge transfer that comes from EMSI. Nevertheless, the RDS under plasma conditions is still associative nitrogen desorption rather than initial NH_3 adsorption or N–H bond scission. Notably, the model indicates that N_2 formation proceeds predominantly via a Langmuir–Hinshelwood pathway, even in the presence of abundant gas-phase radicals, rather than an Eley–Rideal mechanism. Taken together, these findings suggest that the primary role of plasma is to accelerate atomic N generation and facilitate its desorption by modifying the surface electronic structure, without fundamentally overriding the intrinsic surface reaction pathway.

Bang et al. complemented these efforts by matching temperature-controlled DBD experiments with plasma-chemical kinetic modeling, identifying significant deficiencies in available thermal NH_3 pyrolysis mechanisms and electron-impact cross-section data for N_xH_y species [266]. In situ XPS and FTIR studies by Xia et al. gave a direct view of plasma-induced surface transformations [267]. They demonstrated that high-energy plasma-generated species suppress Ru NP sintering while also inducing O_v on CeO_2 supports that act as anchoring sites for N-containing intermediates. Wang et al. further quantified the kinetic benefit of plasma assistance, showing that the apparent E_a for NH_3 decomposition over Ru-promoted Ni, Co, and Fe bimetallic catalysts decreases from $89 \text{ kJ}\cdot\text{mol}^{-1}$ (thermal) to $43.6 \text{ kJ}\cdot\text{mol}^{-1}$ (plasma-assisted) for Ru-Ni-Ce/ Al_2O_3 [268].

3.6. Reactor Engineering and Process Intensification

To overcome thermodynamic equilibrium constraints and improve overall process efficiency, several reactor and process intensification strategies have been developed. Meng et al. designed a plasma-enhanced dual-membrane system that combines a DBD reactor with an ultrathin Pd membrane for in situ H_2 removal, along with a downstream cascade of Silicalite-1 membranes for NH_3 recovery (Figure 8b–d) [261]. The system reached a high H_2 space-time yield of $1567 \text{ mmol}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$ at 400°C with a much smaller carbon footprint. Van Steenwegen et al. proposed a reversed plasma-catalysis configuration in which a thermocatalytic reactor is positioned upstream of a warm gliding arc plasmatron [269]. The extra heat from the plasma drives the endothermic cracking in the catalyst bed, attaining 98.2% overall conversion while reducing catalyst loading by up to 60%. High-throughput plasma sources are also getting active attention. Antunes et al. achieved >99% conversion with a hydrogen energy yield of $447 \text{ L}\cdot\text{kWh}^{-1}$ using an electrodeless microwave plasma torch at atmospheric pressure [270]. Niu et al. reported 100% NH_3 conversion and a H_2 production rate of $40.61 \text{ mol}\cdot\text{h}^{-1}$ in an atmospheric-pressure nitrogen microwave plasma torch [271]. A comprehensive benchmarking study

by Peng et al. put plasma technology in perspective within the broader NH_3 -to- H_2 landscape, noting that while plasma decomposition offers rapid dynamic response and inherent modularity, achieving cost parity with thermal cracking requires further improvements in energy efficiency, targets that are being progressively addressed by the catalyst and process innovations reviewed above [272].

Collectively, these studies establish plasma-catalytic NH_3 decomposition as a versatile, electrified route for sustainable H_2 release. The field has moved from simple proof-of-concept to a mechanistically informed design framework. In this framework, catalyst formulation (active metal, support chemistry, dielectric properties), plasma source selection, and reactor architecture are co-optimized. Continuing advances in real-time diagnostics, multi-scale modeling, and process integration, especially in situ product removal and waste-heat recovery, are poised to deliver the energy efficiency and scalability required for integration into a decarbonized energy infrastructure.

4. Photo(thermal)catalytic NH_3 Decomposition

Photocatalytic and photothermal catalytic NH_3 decomposition has emerged as a sustainable strategy for carbon-free H_2 production, leveraging solar energy to overcome the kinetic and thermodynamic barriers inherent in the conventional thermocatalytic process. It is critical to clarify the temperature regimes for these systems. In pure photocatalytic processes, the reaction is driven by photogenerated charge carriers and proceeds at near-ambient temperatures (typically $<200\text{ }^\circ\text{C}$). In photothermal catalysis, by contrast, light-to-heat conversion raises the temperature to an intermediate range (typically $300\text{--}500\text{ }^\circ\text{C}$); these temperatures are substantially lower than those required for conventional thermocatalytic operation, yet they are sufficient to drive the endothermic reaction. The approach integrates the unique benefits of photoexcitation where energetic charge carriers activate strong N–H bonds and key intermediates with the local heating effects derived from the excellent light-to-heat conversion of advanced catalyst materials. Depending on the main energy-transfer pathway, the field can be broadly partitioned into three regimes: (i) pure photocatalysis, in which hot carriers or photogenerated electron–hole pairs drive bond activation at near-ambient temperatures; (ii) photothermal catalysis, in which solar-to-heat conversion supplements or replaces external heating to reach the temperatures required for associative N_2 desorption; and (iii) plasmonic antenna-reactor systems, which exploit localized surface plasmon resonance (LSPR) to inject hot electrons into catalytically active sites, thereby modifying both activation barriers and surface coverages. Recent progress across all three regimes—plasmonic nanostructures, SACs, MOF-derived nanocomposites, oxide- and carbon-supported transition metals, and modified nitrides—has deepened the mechanistic understanding and expanded the catalyst design space for solar-driven NH_3 -to- H_2 conversion.

4.1. Pure Photocatalysis

Plasmonic nanostructures have shown impressive low-temperature activity by funneling hot carriers into bond-breaking events. Bui et al. developed a Cu-decorated Au plasmonic nanocone array that achieved a high H_2 evolution rate at near-room temperature under visible light [28]. DFT calculations showed that the N–N coupling barrier is lowered through a hydrazine-mediated associative pathway at the Cu–Au interface (Figure 9a,b). This concept has been broadened through the antenna-reactor (AR) paradigm, in which a plasmonic Cu antenna generates hot electrons that transiently occupy the antibonding orbitals of M–N bonds on an adjacent reactor metal. In Cu–Fe and Cu–Ru AR systems, this mechanism enables earth-abundant Fe to approach the photocatalytic efficiency of Ru under ultrafast pulsed or light emitting diode (LED) illumination by dramatically lowering the activation barrier for associative N_2 desorption

[273]. The practical scalability of this approach has been demonstrated in gram-scale photoreactors driven by inexpensive LEDs, suggesting a viable pathway toward decentralized H₂ production.

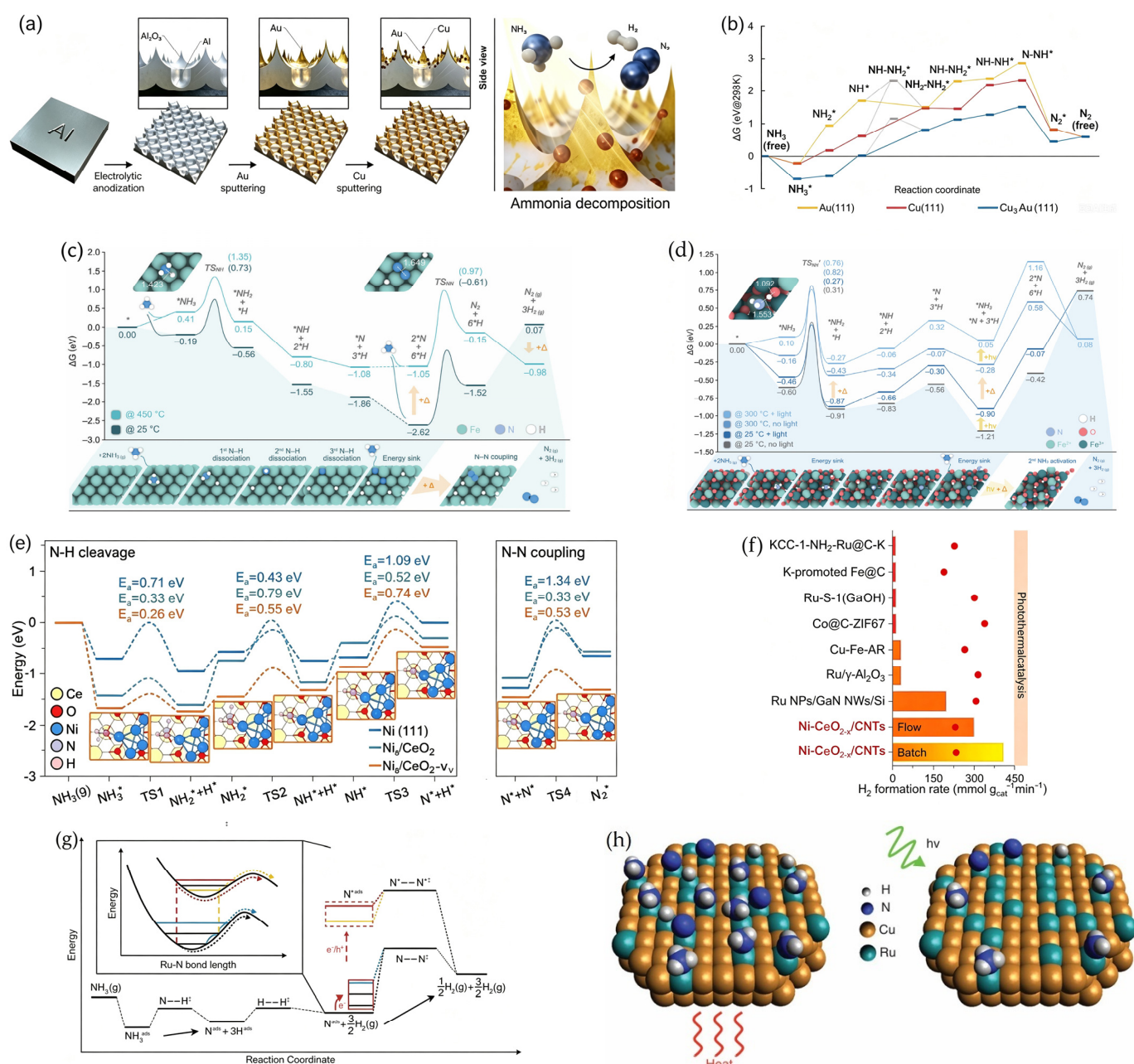


Figure 9. (a) Schematics of the sequential fabrication steps for the plasmonic NCs array used in ammonia decomposition. (b) Gibbs free energy changes (ΔG) during ammonia (NH₃) decomposition on pristine Au(111) and Cu(111) surfaces, as well as on Cu₆@Au(111) [28]. (c) Gibbs energy profile for NH₃ decomposition on the Fe(110) surface. (d) Gibbs energy profile for NH₃ decomposition on the Fe₃O₄(111) surface [274]. (e) Energy profiles for NH₃ decomposed on Ni(111), Ni₃/CeO₂ and Ni₃/CeO₂-O_v surfaces. The optimized structure of each intermediate is depicted. (f) Summary of H₂ formation rate achieved in this work and versus state-of-the-art systems [275]. (g) Schematic energetics of elementary reaction steps for NH₃ decomposition. (h) Schematics of surface coverage under heating versus light-illumination conditions. In contrast to thermocatalysis (left), photocatalysis and hot carrier generation (right) can promote desorption of “poisoning” adsorbed intermediates. hv, light [276].

Semiconductor photocatalysts, most prominently TiO_2 , have been extensively investigated for gas- and liquid-phase photocatalytic NH_3 decomposition. Yang et al. provided a comprehensive review of both highlighting strategies like bandgap tuning, heterojunction formation, and cocatalyst integration to improve charge separation and light utilization [21]. A particularly illustrative example is the dual-cocatalyst system of Ag and NiO on TiO_2 [277]. Work-function gradients establish an $\text{Ag} \rightarrow \text{TiO}_2 \rightarrow \text{NiO}$ directional electron cascade that improves charge separation while tuning the Ni d-band center for N–N coupling, yielding a H_2 production rate of $2366.9 \mu\text{mol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$. Beyond binary oxides, layered perovskites offer distinctive structural advantages. Protonated HPrNb_2O_7 , for instance, stabilizes hydrazine intermediates within its interlayer galleries through an associative dehydrogenation pathway facilitated by thermally generated O_v and hydrogen bonding, achieving an H_2 evolution rate of $1311.2 \mu\text{mol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ at a mild temperatures of 200°C [278].

4.2. Photothermal Catalysis

The photothermal regime combines photoexcitation with the heat from broadband light absorption. It turned out to be particularly effective for reducing the operating temperature of non-noble metal catalysts. Carbon-based supports, owing to their broad spectral absorption and high thermal conductivity, serve as ideal photothermal transducers. Sousa et al. synthesized an Fe-based catalyst derived from the pyrolysis of Fe-BTC MOF, where Fe NPs embedded in a graphitic carbon matrix achieved up to 55% NH_3 conversion under illumination without external heating [274]. Mechanistic studies and DFT calculations uncovered a temperature-dependent duality. At lower temperatures, photogenerated electrons in the Fe_3O_4 phase raise intermediate energies to prevent a thermodynamic sink, whereas metallic Fe dominates catalytic turnover at higher temperatures (Figure 9c,d). Yu et al. further demonstrated this principle with iron-incorporated ordered mesoporous carbon (Fe@OMC) catalysts that exhibited a dramatic reduction in apparent E_a under photothermal conditions ($23.2 \text{ kJ} \cdot \text{mol}^{-1}$) compared to thermal catalysis ($69.4 \text{ kJ} \cdot \text{mol}^{-1}$), achieving near-complete NH_3 conversion at 500°C with excellent long-term stability [279].

A landmark advance in N–N coupling barrier engineering was reported by Tan et al., who constructed a $\text{Ni-CeO}_{2-x}/\text{CNTs}$ photothermal catalyst featuring closely interfaced Ni NPs and defect-rich CeO_{2-x} nanodomains on CNTs [275]. The resulting Ce–O_v–Ni interface upshifted the Ni d-band center, reducing the N–N coupling barrier from 1.34 eV to 0.53 eV and achieving an exceptionally high H_2 production rate of $17.904 \text{ mol g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ under full-spectrum light, a performance surpassing even many Ru-based thermal catalysts (Figure 9e,f).

A critical challenge in both thermal and photothermal of photothermal NH_3 decomposition over Ru is surface poisoning by adsorbed hydrogen (H^*) [280]. Liu et al. showed that on a $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$ photothermal catalyst, hot carriers generated under illumination effectively cleave Ru– H^* bonds [281]. This relieves the hydrogen poisoning and allows robust NH_3 -to- H_2 conversion for over 1200 h, a stark contrast to the rapid deactivation observed under purely thermal conditions. In a complementary and methodologically rigorous study, Beck et al. examined $\text{Ru}/\text{Al}_2\text{O}_3$ under visible-photon illumination at low partial pressures and concluded that the only detectable effect was photon-induced heating of the catalyst bed, with no evidence of any non-thermal photochemical contribution under their specific conditions [280]. This work highlights the importance of precise temperature measurement and calorimetric controls in disentangling photothermal from photochemical contributions, and it serves as a benchmark method for evaluating claims of photocatalytic effects.

The atomic-level dispersion of active metals represents a frontier strategy for maximizing atom utilization efficiency under solar-driven conditions. Li et al. reported that Ni SAs supported on CeO₂ nanosheets (SA Ni/CeO₂) delivered a robust H₂ yield of 212.64 mmol·g_{cat}^{−1}·h^{−1} at 300 °C under thermal conditions, and when integrated into a solar heating device, the system achieved a stable 94.8 mmol·g_{cat}^{−1}·h^{−1} under one-sun irradiation, a performance two orders of magnitude greater than conventional weak solar-driven systems [282]. In a parallel atomic-dispersion strategy, Co SAs on CeO₂ (SA Co/CeO₂) achieved a 291-fold enhancement over Co NPs, with a H₂ production rate of 174.6 mmol·g_{cat}^{−1}·h^{−1} at 450 °C and a solar-driven rate of 162 mmol·g_{cat}^{−1}·h^{−1} under two-sun illumination, directly powering a H₂ fuel cell [283].

TMNs provide a complementary materials platform. Xia et al. showed that K-modified Co₃Mo₃N with an optimal K content (0.864%) promotes the recombinative desorption of N₂, achieving 86.5% NH₃ conversion at 500 °C and a remarkable solar-to-fuel efficiency of 14.4% when driven by a solar simulator [284]. The importance of tuning the local electronic environment modulation has been further shown by loading Ru on gallium-modified silicalite-1 (Ru-S-1(GaOH)), which creates an alkaline microenvironment that enhances the electron density at the Ru center, facilitating N–H bond cleavage and H atom recombination. Under photothermal conditions, this catalyst reduced the temperature required for a TOF exceeding unity from 430 °C to 375 °C [285].

4.3. Mechanistic Frameworks: Disentangling Photochemical and Photothermal Contributions

A central challenge pervading the field is the rigorous deconvolution of non-thermal (hot-carrier or photochemical) effects from photothermal heating. The Halas group has made seminal contributions through their Cu–Ru AR platform, demonstrating that under LSPR conditions illumination reduced the apparent E_a for NH₃ decomposition from 1.21 eV (dark) to approximately 0.35 eV, further decreasing to roughly 0.27 eV at optimized light intensities (Figure 9g,h) [276]. Concurrently, the reaction order shifted from near zero-order under thermal conditions to near first-order, indicating that photoexcitation not only lowers the N₂ recombination barrier but also reduces nitrogen surface coverage through hot-electron-mediated desorption, thereby liberating active sites and fundamentally altering the kinetic regime. The resulting “light-dependent E_a ” framework provides a unified kinetic description that quantitatively separates photogenerated carrier effects from photothermal contributions.

Complementary work on AR architectures has shown that hot carriers from photoexcitation can transiently activate both M–N and N–H bonds, influencing two classic bottleneck steps: initial NH₃ dehydrogenation and associative N₂ desorption [286]. The redistribution of surface coverage, particularly the lower occupancy of strongly adsorbed nitrogen species, further liberates active sites, enabling the reaction to proceed along a more thermodynamically favorable pathway.

From an energy-partitioning perspective, studies on Au–Pt model systems have demonstrated that absorbed photon energy is distributed between carrier-induced heating and carrier-mediated reduction in the activation barrier at reaction sites [287]. Critically, even a minor fraction of absorbed energy allocated to activation-energy reduction can produce rate-constant enhancements that would require substantially greater energy input if achieved through heating alone. This analysis supports a mechanistic framework in which local charge injection and transition-state stabilization by photoexcited carriers are the decisive kinetic factors. Photothermal heating plays a synergistic role primarily by modifying surface coverages and diffusion kinetics.

Turning catalytic progress into real-world H₂ production requires reactor-level optimization. Yu et al. developed a multi-channel membrane reactor for solar thermochemical NH₃ decomposition, using a fully coupled three-dimensional numerical

model to demonstrate that adding more membrane channels and applying vacuum pumping enhance both NH_3 conversion and H_2 recovery [288]. A four-channel design lifted H_2 recovery by 13.2% and NH_3 conversion by 5.9% compared to a single-channel setup. This kind of system-level integration combining efficient solar concentration, membrane separation, and catalytic conversion is vital to bridge the gap between laboratory-scale demonstrations and deployable solar H_2 production technologies.

To sum up, the field of light-driven NH_3 decomposition is advancing rapidly along multiple complementary fronts. Pure photocatalytic systems—particularly plasmonic AR architectures—offer the transformative possibility of activating earth-abundant metals under mild conditions. Semiconductor platforms provide tunable electronic structures for charge-directed catalysis. Photothermal catalysis effectively bridges the activity gap by harnessing the full solar spectrum to drive reactions at intermediate temperatures with unprecedented rates and stability, as the breakthrough d-band engineering at Ni-CeO_{2-x} interfaces shows. SACs and modified nitrides stretch the design space further by maximizing atom utilization and enabling direct solar-to-fuel conversion with efficiencies above 14%. The ongoing refinement of mechanistic frameworks for disentangling photochemical and photothermal contributions, anchored by quantitative kinetic models and rigorous calorimetric controls, supplies the intellectual foundation for rational catalyst optimization. Coupled with advances in membrane reactor design and solar concentration technologies, these catalytic innovations chart a credible pathway toward a sustainable, carbon-free hydrogen economy in which NH_3 serves as a versatile solar energy carrier.

5. Electrically Driven Catalytic NH_3 Decomposition

Electrified catalytic NH_3 decomposition under an applied direct current (DC) electric field has emerged as a compelling strategy for low-temperature, on-demand H_2 production. It is important to distinguish this approach from conventional electrochemical (electrolytic) NH_3 decomposition. In conventional electrocatalysis, NH_3 is decomposed in a liquid electrolyte at electrode surfaces under applied potential, typically at room temperature, but this route suffers from low conversion rates, issues with H_2 purity, and the complexities of electrolyte management. By contrast, the electrically driven thermal catalysis discussed in this section operates by applying a DC electric field across a conventional gas-phase, packed-bed heterogeneous catalytic reactor. In this configuration, the electric field functions as an electronic promoter: it drives surface proton hopping at metal-oxide interfaces (surface protonics), enhances metal-support electron transfer, and promotes the recombinative desorption of N_2 and H_2 , without any electrochemical oxidation of NH_3 . The reaction medium remains entirely gaseous, the catalyst structure is preserved, and no liquid electrolyte is involved. Moreover, the electrical energy supplied by the electric field is orders of magnitude smaller than the Faradaic energy input required in conventional electrolysis. This distinction is critical for properly interpreting the operating temperatures and energy efficiencies reported in this section. By exploiting unique interfacial phenomena—most notably surface protonics and electric-field-induced electron redistribution on semiconductor supports—this strategy circumvents the high thermal budgets of conventional thermocatalysis while accessing kinetic regimes that are thermodynamically favorable yet kinetically inaccessible under purely thermal conditions [289]. The significance of this approach is most pronounced below 300 °C, where thermal catalysis, although thermodynamically feasible, is severely limited by sluggish N–H bond scission kinetics and product-induced surface poisoning. In the presence of an electric field, carrier activation, interfacial charge migration, and proton hopping collectively modify surface coverages and lower the effective energy

barriers for RDSs, enabling selected catalyst systems to achieve near-equilibrium conversion performance at remarkably low temperatures.

Sekine and co-workers laid the mechanistic groundwork for this approach. They showed that applying a weak DC field across a Ru/CeO₂ catalyst bed dramatically enhances NH₃ conversion at temperatures as low as 398 K, achieving conversions that even surpass thermodynamic equilibrium limitations under equivalent thermal conditions [22]. Critically, this remarkable low-temperature activity proceeds via a mechanistically distinct associative pathway involving N₂H₂ intermediates, rather than the conventional dissociative route based on N-atom recombination. Triviño et al. further clarified how essential the metal-support interface is [290]. They showed that the TOF based on perimeter sites (TOF-p) remains constant under an electric field, which confirms that the reaction is governed by surface proton hopping at the Ru–CeO₂ boundary. This process effectively alleviates the rate-limiting N₂ desorption step. Ofuchi et al. provided additional mechanistic resolution by demonstrating that surface protonics at low temperatures is facilitated by the migration of protons through the oxide support lattice, enabling H⁺ species generated by N–H bond scission to be rapidly transported away from the active metal site, thereby preventing hydrogen poisoning and sustaining catalytic turnover [22].

5.1. Support Chemistry and Electronic Modulation

The choice of support is critical in electric-field-assisted catalysis, as it must exhibit appropriate semiconducting properties to sustain surface protonic conductivity without inducing dielectric breakdown. Ceria-based materials have emerged as the dominant support platform owing to their facile Ce⁴⁺/Ce³⁺ redox cycling and the associated generation of O_v. Wang et al. compared Ru/CeO₂ and Ni/CeO₂ catalysts under identical electric field conditions, revealing that the electric field promotes the formation of M–O–Ce bonds, enhances electron transfer from CeO₂ to the metal, and lowers the apparent *E*_a by nearly 80% [291]. This electronic activation enables Ni/CeO₂ to achieve 60% conversion at 400 °C, and remarkably maintaining 15% conversion even at 150 °C, with stable operation over 48 h, demonstrating that electric-field assistance can render non-noble metals viable for low-temperature NH₃ decomposition.

The promotional effect of Ce as an electronic modifier was investigated by Wang et al., who found that Ce doping of Co/SiC catalysts considerably outperforms K and Mg promotion [292]. The applied electric field drives a Ce⁴⁺ → Ce³⁺ redox cycle accompanied by substantial O_v generation. These vacancies act as electron traps that strengthen EMSI, enriching electron density on nearby Co sites and facilitating N₂ desorption at temperatures below 150 °C with a rapid H₂ production response time of approximately 10 s.

Maslova et al. conducted a comparative analysis across a structurally varied set of Ce-based materials, including CeO₂, metal-loaded CeO₂, CePO₄, Sr-doped CePO₄, and CeZrO₄, revealing that an optimal metal loading on ceria-based supports, beyond which metal clustering diminishes activity [293]. A particularly instructive finding is the divergent influence of support microstructure: in non-porous systems, the electrical properties (dielectric constant and charge transfer resistance) predominantly govern NH₃ conversion, whereas in porous systems, porosity and specific surface area exert a more significant influence than bulk electrical characteristics. Further investigations by Maslova et al. into La-based supports demonstrated that NiO/La₂O₃ catalysts achieve stable NH₃ decomposition at ambient temperature under a DC electric field, with catalytic activity correlating with the semiconducting properties of NiO and the progressive hydroxylation of La₂O₃ during reaction, which facilitates proton transfer from Ni to the support [294].

The role of support basicity and hydrogen spillover was further clarified by studies demonstrating that Al doping of CeO_2 improves surface hydrogen adsorption and spillover efficiency, thereby improving the performance of surface protonics and shifting the H_2 reaction order from negative to zero [295]. That transition effectively mitigates hydrogen poisoning, one of the principal deactivation mechanisms for Ru-based catalysts, by ensuring that dissociated hydrogen is rapidly transported away from the active site through the oxide lattice.

5.2. Catalyst Formulation

Ru- CeO_2 nanocluster catalysts are the performance benchmark for electric-field-assisted NH_3 decomposition. Triviño et al. showed that under optimized conditions, this system achieves 100% conversion at 450 °C and exceptional conversions of up to 34% at 200 °C at a GHSV of 30,000 $\text{mL}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$, with long-term stability and the ability to reach thermodynamic equilibrium conversions at temperatures about 100–200 °C lower than required without the field [290].

To mitigate the cost and scarcity of Ru, significant progress has been made with earth-abundant transition metals integrated into conductive or semiconductor matrices. Wang et al. demonstrated an electrically driven gaseous ammonia decomposition reactor using SiC-mediated Ru/ Al_2O_3 catalysts, achieving 85% NH_3 conversion at ca. 230 °C without external heating (Figure 10a) [296]. The outstanding performance was attributed to the effective current carrier activation effect, which promotes N–N recombination and hydrogen migration at low temperature (Figure 10b). In parallel, Co-based SiC composite catalysts were shown to have a strong synergistic effect with the electric field; Co directly loaded on highly conductive SiC facilitates proton (H^+) and electron transport, leading to a 73% NH_3 conversion at around 200 °C (Figure 10c) [297]. Wang et al. further demonstrated that coupling Ce-doped $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ supports with non-noble metals (Fe, Co, Ni) under an electric field delivers substantial low-temperature activity, with the electric field shifting the rate-determining step and promoting N_2 desorption through enhanced charge transfer at the metal-support interface [298].

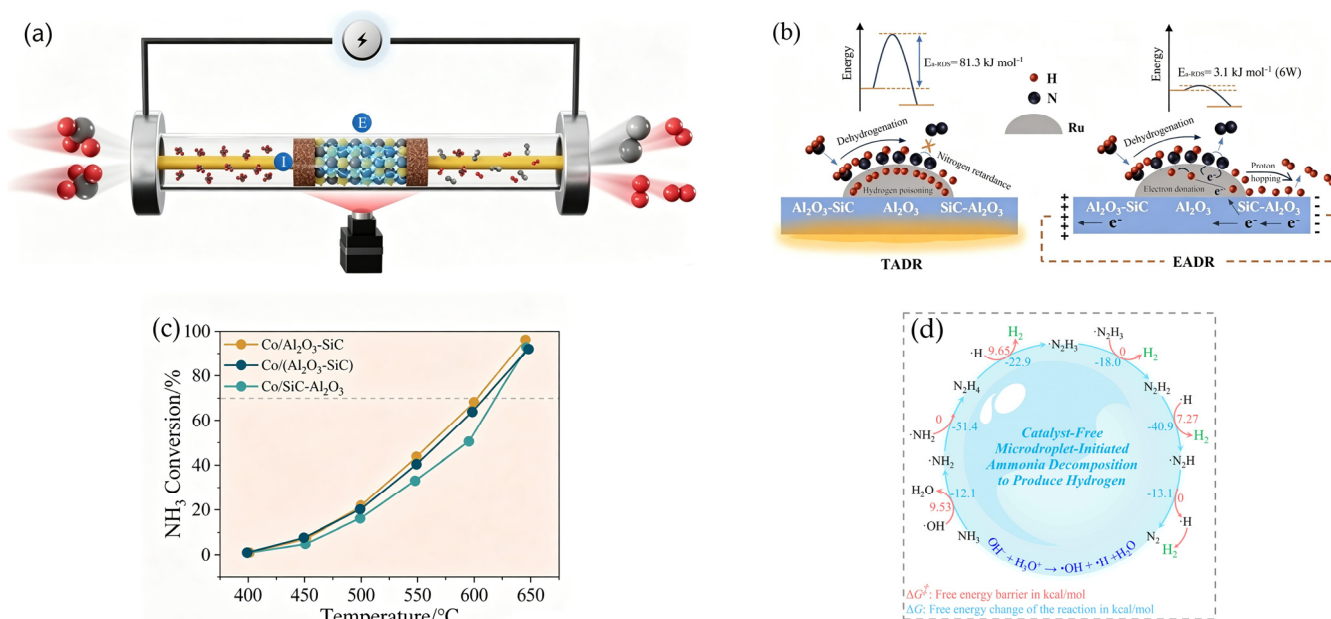


Figure 10. (a) Schematic of a self-designed EADR experimental system. (b) Schematic illustration of the mechanisms of TADR and EADR at low temperatures [296]. (c) Catalytic activity of conventional thermal NH_3 decomposition, WHSV: 12,000 $\text{mL}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$ [297]. (d) Proposed pathways and reaction energy barriers toward NH_3 decomposition at the gas-liquid interface of microdroplets [299].

Computational studies have provided fundamental mechanistic underpinning for the experimental observations. Zhang et al. investigated the adsorption and dehydrogenation mechanisms of NH_3 over Cu- and Mo-doped CNTs using first-principles methods, revealing that a positive electric field enhances both NH_3 adsorption strength and dehydrogenation kinetics, while a negative field inhibits them [300]. The RDS was found to be metal-dependent: third hydrogen dissociation for Cu–CNT and associative nitrogen desorption for Mo–CNT, providing design criteria for selecting active metals in electric-field-assisted systems.

5.3. Reactor Innovation

Beyond conventional packed-bed reactors, innovative designs are being integrated with electric-field concepts to improve process dynamics and scalability. Ponikvar et al. developed a dynamically responsive NH_3 decomposition system based on magnetic induction heating of a CoNi/Ru– Al_2O_3 nanocomposite, achieving rapid H_2 release with a minute-scale response time and a tunable H_2/NH_3 ratio [301]. This concept of electrified, rapid-response heating is particularly attractive for on-board or intermittent renewable energy applications, where system compactness and dynamic load-following capability are paramount.

In a fundamentally distinct yet conceptually illuminating approach, Li et al. demonstrated that catalyst-free NH_3 decomposition can occur spontaneously at the gas–liquid interface of water microdroplets under ambient conditions, driven by hydroxyl and hydrogen radicals generated by the strong interfacial electric field [299]. While not a catalytic process in the traditional sense, this work underscores the intrinsic chemical potential of high electric fields to trigger N–H bond activation and N–N coupling in the complete absence of catalytic materials or external heating, providing a conceptual lower bound for the energy input required to decompose NH_3 via electric-field activation (Figure 10d).

Collectively, these advances establish electrically driven catalysis as a transformative and energy-efficient paradigm for ammonia decomposition. The convergence of three mechanistic pillars, surface protonics at metal-oxide interfaces, electric-field-induced O_2 generation and EMSI enhancement, and electrothermal coupling via Joule heating, provides a rich design space for engineering catalysts that operate efficiently at temperatures 200–300 °C below conventional thermal requirements. The systematic progression from noble-metal benchmarks (Ru/ CeO_2) to earth-abundant alternatives (Ni/ CeO_2 , Co/SiC, NiO/ La_2O_3) demonstrates that electric-field assistance can compensate for the intrinsically weaker M–N binding of non-noble metals. Looking forward, the integration of electric-field catalysis with membrane-based H_2 separation, renewable electricity inputs, and compact reactor architectures holds significant promise for decentralized, on-demand H_2 production from NH_3 .

6. Challenges and Perspectives

6.1. Challenges in Practical Applications

Translating laboratory-scale NH_3 decomposition catalysts into industrial-scale H_2 production encounters several significant challenges that warrant detailed examination.

Residual NH_3 removal and H_2 purification. The claim that NH_3 decomposition yields “pure H_2 ” must be qualified, as the product stream is a H_2/N_2 mixture containing residual unconverted NH_3 (typically 0.1–5%, depending on conversion). For proton exchange membrane (PEM) fuel cell applications, even trace levels of NH_3 (<0.1 ppm) can severely degrade the membrane by reacting with sulfonic acid groups in Nafion membranes, thereby reducing proton conductivity and cell efficiency. Although N_2 is not

chemically deleterious, it dilutes the H₂ stream and lowers the hydrogen partial pressure, impairing fuel cell performance. Downstream purification is therefore essential. Available technologies include: (i) pressure swing adsorption, which achieves >99.99% H₂ purity but adds significant capital and operating costs; (ii) Pd-based membrane separation, which offers high H₂ selectivity and can be integrated with the decomposition reactor, but faces challenges with H₂ embrittlement and cost; (iii) NH₃ scrubbing using acid solutions (e.g., H₂SO₄) or water, which is effective but generates waste streams; and (iv) selective catalytic oxidation of residual NH₃, which requires an additional catalyst and an oxygen source. The choice of purification technology depends on the application scale and the target H₂ purity; membrane reactors currently represent the most promising integrated solution for distributed H₂ production.

Catalyst deactivation and stability. Sustaining long-term catalyst stability under industrially relevant operating conditions remains a critical challenge. The primary deactivation mechanisms include: (i) thermal sintering of metal NPs at elevated temperatures (>550 °C), leading to a loss of active surface area; (ii) poisoning by impurities in the NH₃ feed, particularly sulfur compounds (commonly present in NH₃ derived from fossil feedstocks) and oxygen-containing species; (iii) nitridation of non-noble metals (especially Fe), which can alter the active phase composition; and (iv) carbon deposition when carbon-containing supports or impurities are present. An examination of the literature (Table 1) reveals that, although many catalysts exhibit excellent initial activity, stability tests rarely exceed 100 h, and only a limited number of studies have demonstrated operation beyond 1000 h. Among non-noble systems, the Ni_xMg_{1-x}O/CeO₂ catalyst (5000 h stability [144]) and K-promoted CoNi/MgO–CeO₂–SrO (600 h in membrane reactor [203]) stand out as exceptional benchmarks. Achieving >5000 h of stable operation with less than 10% activity loss is a realistic target for industrial deployment, demanding careful optimization of catalyst composition, support selection, and operating conditions.

Table 1. Performance comparison of different NH₃ decomposition catalysts in various reaction systems.

Reaction System	Catalysts	Metal Loading (wt%)	Catalyst Mass (g)	NH ₃ Conversion (%)	Temperature (°C)	GHSV (mL·g _{cat} ⁻¹ ·h ⁻¹)	H ₂ Production Rate (mmol·g _{cat} ⁻¹ ·h ⁻¹)	Stability (h)	E _a (kJ·mol ⁻¹)	TOF (s ⁻¹)	Ref.
Thermal catalysis	Ru(CO)/CeO ₂	0.5	0.1	48	400	30,000	904.2	-	89	3.73	[35]
	Ru/Sr _{0.1} Ce _{0.9} O ₂	0.97	0.1	92	450	30,000	1578.966	100	48	-	[43]
	Ru/Ce–Al	0.8	0.2	95	500	15,000	850.2	48	51.48	-	[46]
	RuLaCs/Al ₂ O ₃	1.0	0.2	99	450	5000	3348	100	-	-	[39]
	Ru/CeO ₂ –N	0.4	0.05	43.8	450	30,000	880	100	114.5	-	[88]
	Co–N/TiC–SiC	2.5	0.1	81.8	450	60,000	168	24	-	-	[140]
	25Co/SiC	25	0.1	73.2	550	30,000	1476	200	-	-	[141]
	CeO ₂ /Ni	Ni: 59.4	0.1	72.4	500	30,000	2454	100	113.3	5.0	[173]
	LaNiO ₃	Ni: 7.8	0.1	90	550	18,000	2352	100	85.14	-	[187]
	NiPs–Red	Ni: 20.0	0.1	93.6	650	60,000	3762	100	78.7	-	[194]
	FeCu/MgO	Fe: 22.7 Cu: 10.71	0.1	98	550	12,000	139.1	150	93.38	-	[213]
	Ni/YO _{1.5}	Ni: 72	-	90	500	10,000	-	50	-	-	[216]
	CoNi/Zr–Y ₂ O ₃	Co: 7.1 Ni: 14.1	0.2	90.9	550	9000	550	30	35	-	[217]

	K-CoNi-MgO-CeO ₂ -SrO	Total metal: 60	0.1	97.7	450	6000	7	600	56.79	11.14	[203]
	NiFeCo	Ni:34.5 Fe: 59.1 Co: 6.54	0.2	80	550	60,000	-	40	69.4	-	[223]
	CoMo@NC	Co: 12.15 Mo: 10.48	0.1	97.57	550	30,000	1959.6	300	69.17	-	[222]
	Mo ₂ N/SBA-15/rGo	MoN/Mo ₂ N: 23.9	0.03	98	600	60,000	1834.8	50	96.8	-	[230]
	γ-Mo ₂ N	-	0.03	97	600	60,000	1113.9	155	102.3	-	[232]
	Co-doped graphdiyne	14	0.05	100	550	30,000	1000	18	47.5	-	[237]
	Co-La/Mo ₂ C	7.5	0.1	90	400	60,000	97.2	50	-	-	[246]
Plasma catalysis	Ru/MgTiO ₃	0.62	0.1	92	450	36,000	1445	48	43.2	4.9	[250]
	Ru/La ₂ O ₃	1.5	-	97	525	1600	11,700	45	41	1.96	[251]
	Ba-Co/CeO ₂	Co: 31.2	30	96	508	6000	-	-	-	-	[254]
	Ru-Ni-Ce/CeO ₂	2.5	0.5	98	400	3600	237.7	200	43.56	-	[268]
Photo(thermal) catalysis	HPNO	-	50	43.4	550	30,000	1.3112	6 cycles	11.7	-	[278]
	Fe@OMC	5	0.1	98	500	6000	372	80	23.2	1.691	[279]
	Ru/γ-Al ₂ O ₃	4.91	0.1	84.8	420	30,000	1700	1200	78.68	-	[281]
	SA Co-CeO ₂	-	0.02	-	450	-	1746	96	-	0.87	[283]
	K-Co ₃ Mo ₃ N	K: 0.864	0.3	86.5	500	6000	347.5	100	70.7	-	[284]
Electrically driven catalysis	Ru/CeO ₂	3	0.2	100	400	3000	200.9	48	9.75	-	[291]
	Ce-Co/SiC	Co: 18	0.1	32	150	12,000	257.1	80	21.9	-	[292]
	Ru/Al ₂ O ₃ -SiC	2	0.2	85	230	12,000	682.92	100	54.8	-	[296]
	Co/SiC-Al ₂ O ₃	15.13	0.1	73	200	12,000	586.6	100	5.86	-	[297]
	Ni/Ce _{0.25} Zr _{0.75} O ₂	9.247	0.3	60	300	4000	162	30	12.03	1.34	[298]

Notes: The temperatures for photo(thermal) systems indicate the catalyst bed temperature under illumination, which may include both photochemical and photothermal contributions. The temperatures for electrically driven systems indicate the catalyst bed temperature during electric field application; these are distinct from conventional electrocatalysis in liquid electrolyte at room temperature.

Heat management and energy efficiency. NH₃ decomposition is highly endothermic, with a reaction enthalpy of +46.2 kJ·mol⁻¹ of NH₃ decomposed, which corresponds to approximately +30.8 kJ·mol⁻¹ of H₂ produced. For a large-scale plant producing 1000 m³ H₂·h⁻¹, the theoretical minimum reaction heat requirement is approximately 0.38 MW. While actual industrial systems require higher energy input due to thermal losses and heating inefficiencies, this makes heat management a critical design consideration. In conventional packed-bed reactors, the endothermic reaction creates significant axial and radial temperature gradients, leading to non-uniform conversion and the formation of hot or cold spots that accelerate catalyst deactivation. Innovative reactor designs currently under development include: (i) heat-exchanger reactors that couple the endothermic decomposition with exothermic combustion of a portion of the H₂ or NH₃; (ii) fluidized-bed reactors that provide excellent heat transfer and temperature uniformity; and (iii) membrane reactors that shift the equilibrium by selectively removing H₂. For emerging

pathways, energy efficiency is even more critical: plasma-based systems typically achieve <20% electrical-to-chemical energy efficiency, while photo(thermal) systems are constrained by solar energy capture and conversion efficiencies. Electrically driven thermal catalysis (via Joule heating or electric field) enables the direct conversion of renewable electricity to heat, potentially achieving higher overall efficiency than plasma systems, but it still requires optimization to compete with conventional thermal cracking processes that can utilize waste heat.

Start-up/shut-down dynamics. Integrating NH_3 decomposition with intermittent renewable energy sources (wind, solar) necessitates rapid start-up and shut-down capabilities. Conventional thermal catalytic systems involve lengthy warm-up periods (hours) and are not well-suited for frequent cycling, which can accelerate deactivation through thermal stress. In contrast, plasma and electrically driven systems offer much faster response times (seconds to minutes), making them more compatible with dynamically varying renewable electricity input. However, rapid thermal cycling introduces mechanical stress in reactor components and catalysts, potentially compromising long-term durability. A hybrid approach that combines a thermal catalyst bed for base-load operation with a plasma or electric-field stage for dynamic load-following may provide an optimal solution.

System integration and economics. The economic viability of NH_3 decomposition for H_2 production depends not solely on catalyst performance but also on the overall system balance. Key factors include: (i) the cost and purity of the NH_3 feedstock; (ii) the capital cost of the decomposition reactor and associated auxiliary equipment (e.g., heat exchangers, compressors, and purification units); (iii) operating expenses (energy input, catalyst replacement, maintenance); and (iv) the market value of the produced H_2 , which is determined by its purity, delivery mode, and market conditions. The thermal catalytic pathway is currently more technologically mature; however, its carbon reduction potential is constrained by the carbon intensity of the ammonia synthesis process. Emerging electrified pathways, in contrast, currently face higher capital costs, but may achieve lower operating costs when powered by low-cost renewable electricity. System-level optimization encompassing heat integration, co-product utilization (e.g., recovery of N_2 as a valuable byproduct), and economics of scale is essential for achieving commercial viability.

6.2. Conclusions and Perspectives

The field of NH_3 decomposition for H_2 production is transitioning from fundamental catalyst studies toward integrated system engineering and multi-mechanism coupling. Over the past five years, significant advances have been achieved across all four major catalytic pathways, accompanied by clear trends in catalyst design, mechanistic understanding, and reactor engineering. To facilitate a systematic cross-pathway comparison, Table 2 summarizes the key characteristics, advantages, and limitations of thermal catalysis, plasma catalysis, photo(thermal) catalysis, and electrically driven catalysis. This comparison highlights that, while thermal catalysis remains the most mature and cost-effective option for large-scale applications, emerging electrified pathways offer distinct advantages for low-temperature operation, modular deployment, and compatibility with renewable energy sources.

Table 2. Comparative analysis of four catalytic ammonia decomposition pathways for H₂ production.

Feature	Thermal Catalysis	Plasma-Catalysis	Photo(thermal) Catalysis	Electrically Driven Catalysis
Operating temperature	400–650 °C	Near ambient–500 °C	Photocatalytic: RT–200 °C Photothermal: 150–500 °C	150–400 °C
Energy input	Thermal energy (external heating)	Electrical energy (plasma discharge)	Solar/light + thermal energy	Electrical energy (DC field/Joule heating)
Typical catalysts	Ru, Ni, Co, Fe, alloys, nitrides/carbides	Ru, Ni, Mo ₂ N, supported on dielectrics)	Plasmonic metals, Ru NPs, semiconductors	Ru, Ni, Co on conductive/semiconductive supports
Advantages	Mature technology, high TRL, well-understood mechanisms	Fast start-up, mild bulk temperature	Renewable energy coupling	Fast response, low-temperature operation, electrical integration
Disadvantages	High energy consumption, sintering, slow start-up	Low energy efficiency, reactor complexity, scale-up challenges	Low efficiency for photocatalysis	Complex field distribution, limited understanding of mechanism, stability issues
Energy efficiency	High (with heat recovery)	Moderate (Specific energy input-dependent)	Photocatalytic: very low Photothermal: moderate to high	Moderate (depends on electric field strength)
H ₂ purity	High (requires separation)	Moderate (potential NH ₃ slip)	High (requires separation)	High (requires separation)
Catalyst stability	Sintering at high temperatures	Plasma erosion, support degradation	Photocorrosion, carbon support oxidation	Electric-field-induced sintering, dielectric breakdown
Reactor complexity	Simple (packed bed)	Complex (DBD, gliding arc, microwave)	Moderate (photoreactor)	Moderate (reactor configuration)
Technology readiness level (TRL)	8–9 (commercial deployment)	4–6 (pilot-scale)	2–3 (laboratory research)	3–4 (laboratory to early pilot)
Main scale-up bottlenecks	Heat management, catalyst cost	Electrical efficiency, reactor scaling	Light penetration, quantum efficiency	Field uniformity, mechanism understanding
Optimal application scenarios	Centralized large-scale H ₂ production	Distributed, fast-response H ₂ production	Off-grid applications in solar-rich regions	On-demand, renewable-coupled H ₂ production

Notes: TRL: technology readiness level (1 = basic concept; 9 = full commercial deployment). Operating temperatures refer to the external reactor/furnace temperature.

Advances in catalyst design have resulted in a significant enhancement in decomposition efficiency (Table 1). Noble metal catalysts, primarily leveraging the superior low-temperature activity of Ru, benefit from support modification, alkali/rare-earth metal doping, and strong MSI. These strategies have been shown to facilitate high metal dispersion, low-temperature activation, and lower apparent activation energies. In non-noble metal systems, the energy barriers associated with N–N bond formation are effectively lowered, and hydrogen poisoning is mitigated through approaches such as the engineering of interfacial O_v, the construction of inverse catalyst structures, and the development of multimetallic alloys. Consequently, high catalytic activity is achieved at a reduced cost. Photocatalytic and photothermal catalytic systems leverage the synergy

between photogenerated charge carriers and thermal effects to facilitate NH_3 decomposition without the necessity for externally applied high temperatures, thereby substantially expanding the scope of applications in low-temperature contexts. Plasma catalysis has been demonstrated to generate highly reactive radicals and vibrationally excited species via non-equilibrium electron excitation, thereby enabling efficient decomposition at temperatures below thermal equilibrium. Electrically driven catalysis, through electric field-induced interfacial electron regulation and proton migration, has been shown to markedly enhance reaction kinetics in the low-temperature regime, offering viable pathways for distributed and onboard H_2 production. Despite the diversity of these technical approaches, current NH_3 decomposition H_2 production technologies still face several common challenges.

Building on the foundations established in this review, future research should be pursued along the following interconnected directions to overcome existing challenges and accelerate the practical deployment of NH_3 decomposition for H_2 production:

(1) Catalyst design targets for non-noble metal systems. To approach the practical deployment threshold for distributed H_2 generation, non-noble metal catalysts must achieve the following performance metrics: NH_3 conversion > 90% at $\leq 550^\circ\text{C}$ under a GHSV $\geq 30,000\text{ mL}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$, an apparent E_a below $80\text{ kJ}\cdot\text{mol}^{-1}$, and stable operation for $\geq 500\text{ h}$ with <10% activity loss. Based on the literature surveyed, the most promising pathways toward these targets include: (i) CoNi alloy catalysts featuring engineered metal-oxide interfaces (e.g., K-CoNi/MgO-CeO₂-SrO type systems, which have already demonstrated >600 h stability [203]); (ii) Ni catalysts stabilized in solid-solution or inverse-catalyst architectures (e.g., $\text{Ni}_x\text{Mg}_{1-x}\text{O}/\text{CeO}_2$ [144], with a demonstrated stability of 5000 h); and (iii) bimetallic nitride systems (Co₃Mo₃N and Fe₃Mo₃N), which offer noble-metal-like electronic structures without precious metal content. HEA catalysts represent a longer-term direction that requires more systematic experimental validation beyond the proof-of-concept demonstrations currently available.

(2) Low-temperature operation below 300°C : targets and preferred strategies. Achieving >50% NH_3 conversion below 300°C represents the most transformative near-term target for on-board and distributed applications. Among the strategies reviewed, electric-field-assisted catalysis (exploiting surface protonics on Ru/CeO₂ and Ni/CeO₂) currently constitutes the most extensively demonstrated non-thermal route below 300°C ; Triviño et al. reported 34% conversion at 200°C [290]. Plasma-catalytic systems offer the highest theoretical low-temperature activity because vibrational excitation can bypass thermal activation barriers, yet energy efficiency at sub-500 W power levels remains a critical unresolved challenge. For all low-temperature routes, the key mechanistic priorities are: quantification of the N–N recombination barrier under non-thermal conditions; characterization of hydrogen-poisoning dynamics at low temperatures (where H^* surface coverages are high); and identification of the RDS under electric-field and plasma conditions for different catalyst families.

(3) Reactor integration: specific priorities. The most actionable near-term priorities in reactor engineering are: (i) integration of Pd-based or Pd-alloy membrane reactors with optimized thermal catalysts to simultaneously achieve >95% NH_3 conversion and >90% H_2 recovery at $450\text{--}500^\circ\text{C}$, targeting a system-level H_2 purity compatible with PEM fuel cell use (<0.1 ppm NH_3); (ii) development of compact, modular electric-field-assisted reactors that can maintain a uniform field distribution at catalyst-bed scales exceeding 100 g, which is a current engineering gap; (iii) integration of waste heat recovery in plasma-catalytic systems to raise the net energy efficiency from the presently demonstrated ~30–50% to >70%; and (iv) dynamic load-following characterization—specifically, evaluating catalyst activity and selectivity during ramp-rate tests from cold start to full operation—for all non-thermal routes, for which essentially no data currently exist.

(4) Mechanistic and kinetic priorities. The most critical mechanistic uncertainties identified in this review are: (i) the precise nature of active sites under reaction conditions (e.g., whether metallic, nitride, or mixed-phase Co and Fe species serve as the true active species in Fe- and Co-based systems under flowing NH_3); (ii) the role of surface proton hopping in electrically driven systems at temperatures above 300 °C, where deconvoluting field-enhanced thermal contributions from purely non-thermal effects becomes challenging; (iii) the quantitative energy partitioning between photothermal heating and hot-carrier-mediated barrier reduction in photo(thermal) catalytic systems—the Beck et al. calorimetric standard should be adopted across the field as a benchmarking protocol [280]; and (iv) the coverage-dependent shift in the RDS (N_2 desorption versus NH_2^* dehydrogenation) under realistic high-conversion, high-GHSV conditions, a phenomenon that is well established for Ru by microkinetic models [41,69] but remains largely uncharacterized for non-noble metal systems.

In summary, the field of NH_3 decomposition for H_2 production technology is undergoing a transition from fundamental catalyst studies toward integrated system engineering, low-temperature operation, and multi-mechanism coupling. In the future, it is anticipated that the convergence of low-cost, high-efficiency catalysts with innovative reactor designs will play a pivotal role in hydrogen industrialization and renewable energy utilization, thereby providing robust support for the realization of a green and low-carbon energy system.

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