

Review

Recent Advances in Ammonia Synthesis Modeling and Experiments on Metal Nitrides and Other Catalytic Surfaces

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Abstract: In this review, we explore the recent progress in catalytic materials for the ammonia syntheses that are based on metal nitrides and other catalytic surfaces. It comprises a detailed overlook of the various techniques used in ammonia synthesis research and the state-of-the-art modeling techniques employed to investigate new reaction mechanisms and more efficient processes for sustainable ammonia synthesis production. The review is discussed in the context of the reaction mechanisms developed and the recent progress that has been made with respect to thermal, electrochemical, and photocatalytic ammonia synthesis.

Keywords: ammonia synthesis; DFT; metal nitrides; photocatalytic; electrochemical

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1. Introduction

Industrial ammonia synthesis accounts for about 1.8% of our global energy requirement and, as a result, produces 500 million tons of carbon dioxide; therefore, any process that reduces the amount of energy required for this reaction will have a huge impact on the global sustainability of the process [1]. About 80% of Haber–Bosch-produced ammonia is used in fertilizers, which uses a potassium oxide-promoted iron catalyst, and this catalyst has been used for more than 100 years mainly for its low cost [2,3]. There are other catalysts that have been studied since then that are more active but perhaps do not have the long-term stability of the iron catalyst. For the iron catalyst, ammonia is produced by a Langmuir–Hinshelwood mechanism that was first described by Ertl and co-workers [4]. Some smaller industrial units currently use a promoted Ru catalyst, which is graphite-supported [5,6]. This catalyst is generally more active than the iron catalyst, but it is expensive due to the high cost of Ru. Nørskov and Hu, in two separate studies, have modeled the mechanism of ammonia synthesis on Ru surfaces [5,6]. This catalyst also undergoes the Langmuir–Hinshelwood mechanism for ammonia synthesis. Therefore, it would be interesting to see whether other catalysts that can undergo different mechanisms such as Eley–Rideal, Mars–van Krevelen, and combinations of them have higher activity. There are already a few reviews on ammonia synthesis but, with this review, we would like to give a comprehensive overview with respect to ammonia synthesis on metal nitrides and other catalytic surfaces in conjunction with the mechanism that occurs on these catalysts [7–14]. We placed special emphasis on reaction mechanisms in this review, which has been suggested as an approach to improve the efficiency of the ammonia synthesis catalyst [15].

In this review, we will present nitride catalysts and their associated mechanisms for ammonia synthesis. We will further explore new methods such as electrochemical and photochemical ammonia synthesis that have been suggested to reduce the cost of ammonia production. This will provide insight to fellow researchers throughout the world of what

catalyst formations are best and will suggest processes that they should be investigating in the near future.

1.1. Transition Metal Nitrides as Catalysts for Ammonia Synthesis

Transition metal nitrides have gained considerable attention in ammonia synthesis research due to their unique catalytic properties and the fact that they can utilize nitrogen vacancies on their surface as catalytic centers for activating dinitrogen [16]. These materials can facilitate nitrogen reduction, which is a crucial step in ammonia synthesis. The following sections provide an in-depth look at specific transition metal nitrides, their catalytic mechanisms, and their performance in ammonia synthesis.

Cobalt molybdenum nitride ($\text{Co}_3\text{Mo}_3\text{N}$), whose structure is shown in Figure 1, along with similar tertiary nitrides ($\text{M}_x\text{M}'_y\text{N}$, where M is a group VIB metal and M' is a group VIII metal) that were synthesized according to Topsøe's patented method, are known for their activity in ammonia synthesis at 400 °C and their high pressures when using a 3:1 hydrogen-to-nitrogen mixture [17]. The structure of cobalt molybdenum nitride is like a hexagonal array of Co_8 clusters embedded into a molybdenum nitride framework. This makes the catalyst bifunctional, where both metal and metal–support interactions are present. This type of catalyst is very versatile due to the unusual structure these metal nitrides have. $\text{Co}_3\text{Mo}_3\text{N}$ has been identified as a highly active catalyst for ammonia synthesis by various experimental studies [18,19].

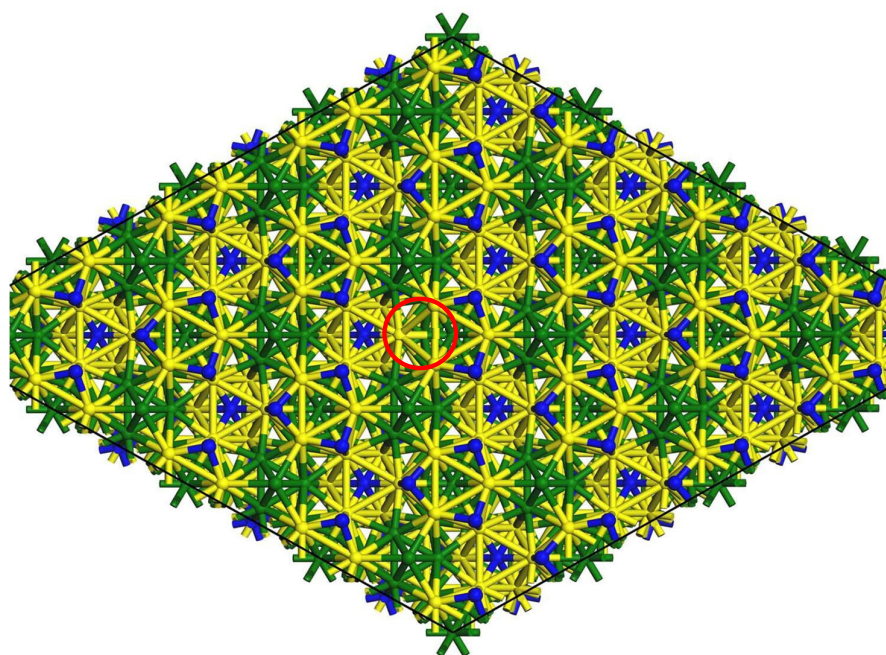


Figure 1. (1 1 1) Surface of cobalt molybdenum nitride ($\text{Co}_3\text{Mo}_3\text{N}$), where the nitrogen vacancy side is shown with a red circle. Nitrogen is represented in blue, molybdenum is represented in yellow, and cobalt is represented in green.

The study by Zeinalipour-Yazdi et al. explored the mechanisms of ammonia synthesis on $\text{Co}_3\text{Mo}_3\text{N}$ surfaces, emphasizing the role of surface defects such as nitrogen vacancies and intrinsic surface cavities. Using dispersion-corrected DFT calculations, their research compared the Langmuir–Hinshelwood (dissociative) and Eley–Rideal/Mars–van Krevelen (associative) mechanisms. The findings highlight that, apart from the conventional dissociative mechanism, an associative mechanism involving hydrazine and diazane intermediates also exists, where hydrogen reacts directly with surface-activated nitrogen to form ammonia under milder conditions. This associative mechanism exhibits lower activation barriers for the hydrogenation steps compared to the dissociative mechanism, making it kinetically

favorable. Their study underscored that, through surface defects, the ammonia synthesis activity on $\text{Co}_3\text{Mo}_3\text{N}$ can be significantly enhanced at lower temperatures, providing insights into optimizing this catalyst for more efficient ammonia production [20].

Further, the study by Zeinalipour-Yazdi and Catlow employed DFT to investigate the associative mechanisms for ammonia and hydrazine synthesis on $\text{Co}_3\text{Mo}_3\text{N}$ surfaces. Their research identified that the nitrogen intermediate, NNH_2 , can form readily on $\text{Co}_3\text{Mo}_3\text{N}$ surfaces through the Eley–Rideal chemisorption of H_2 on pre-adsorbed N_2 at nitrogen vacancies. This mechanism is energetically favorable, with the highest relative barrier being 213 kJ/mol, indicating a low-energy process for hydrazine synthesis via heterogeneous catalysis. Their study presented a potential energy diagram showing that the associative mechanism involves two high-barrier hydrogenation steps in the gas phase, contrasting with a significantly lower barrier for the formation of hydrazine on $\text{Co}_3\text{Mo}_3\text{N}$. Their research emphasized the efficient activation of N_2 at surface nitrogen vacancies, making $\text{Co}_3\text{Mo}_3\text{N}$ a promising catalyst for synthesizing hydrazine under mild conditions. The findings highlight that the Eley–Rideal mechanism could facilitate the production of hydrazine and ammonia, enhancing catalytic activity through surface defects [21].

This catalyst can operate via two primary mechanisms (which have been described by DFT in VASP): the Eley–Rideal/Mars–van Krevelen mechanism and the Langmuir–Hinshelwood mechanism. In this mechanism, which is shown in Figure 2, the active site is a nitrogen vacancy on the molybdenum nitride framework. Molecular nitrogen chemisorbs at the N-vacancies in an end-on configuration, followed by the dissociative chemisorption of molecular hydrogen. This leads to the formation of diazene and hydrazine intermediates, eventually producing ammonia. This hydrazine intermediate has a low barrier for decomposition into ammonia, which is the first stoichiometric ammonia molecule produced through this mechanism. The second stoichiometric ammonia molecule is produced in higher activated steps as it involves the hydrogenation of surface nitrogen that is then strongly absorbed to the surface of the metal nitride. Therefore, one disadvantage of this catalyst could be that the ammonia is produced on its surface by it being strongly bound to the surface. The energy profile for this mechanism indicates that the hydrogenation steps have lower barriers compared to the Langmuir–Hinshelwood mechanism, making it kinetically faster for ammonia synthesis on $\text{Co}_3\text{Mo}_3\text{N}$ [22].

In Figure 3, we illustrate a simplified schematic of the dissociative Langmuir–Hinshelwood mechanism of ammonia synthesis on a catalytic surface. The process begins with nitrogen molecules (N_2) adsorbing onto the catalyst surface.

Subsequently, hydrogen molecules (H_2) also adsorb onto the surface, dissociating into individual hydrogen atoms. The nitrogen atoms then react with the hydrogen atoms in a stepwise manner, forming intermediates such as NH , NH_2 , and, eventually, NH_3 (ammonia), which desorbs from the surface. The cycle repeats as new nitrogen and hydrogen molecules continue to adsorb and react on the catalyst surface. The nitrogen and hydrogen atoms are shown interacting through a series of intermediate steps leading to the formation of ammonia.

The Langmuir–Hinshelwood mechanism for ammonia synthesis involves a series of well-defined steps starting with the adsorption of molecular nitrogen (N_2) onto the surface of the catalyst. In this mechanism, nitrogen molecules are adsorbed in a side-on configuration at the active sites of the catalyst. This adsorption mode allows the nitrogen molecule to interact simultaneously with multiple active sites, leading to a significant activation of the $\text{N}\equiv\text{N}$ triple bond.

Once adsorbed, the nitrogen molecule undergoes dissociation into two nitrogen atoms, each of which are further adsorbed onto the catalyst surface in a bridged configuration. These bridged nitrogen species are highly reactive intermediates that play a crucial role in the subsequent steps of the reaction. The dissociation of the nitrogen molecule is facilitated by the strong interaction with the catalyst surface, which lowers the activation energy required to break the $\text{N}\equiv\text{N}$ bond.

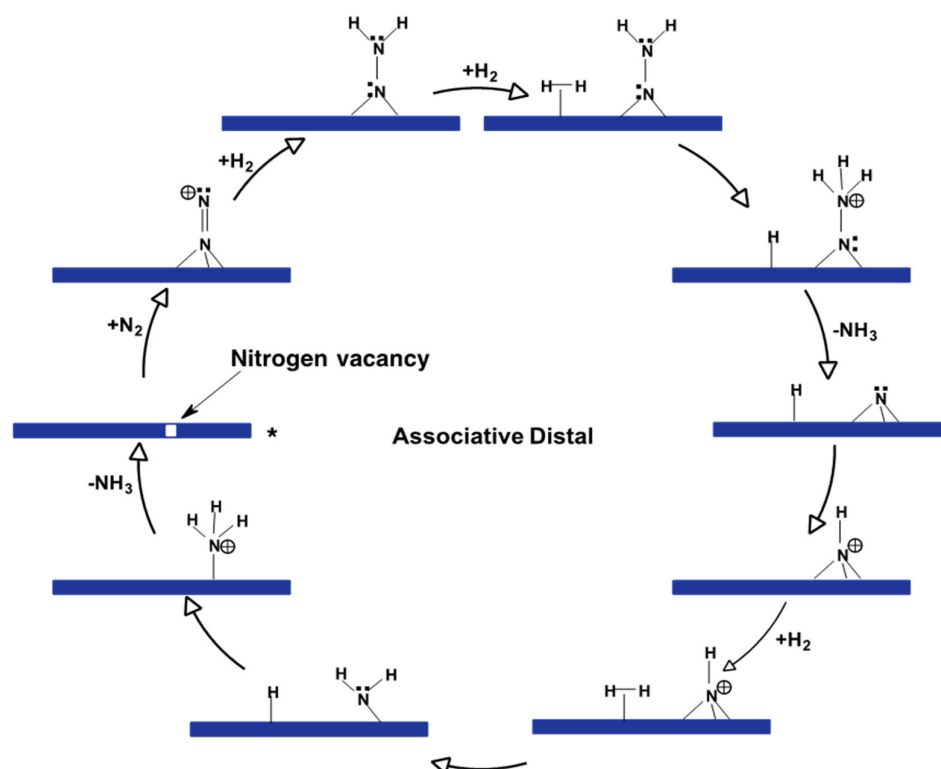


Figure 2. Simplified schematic showing the associative Eley–Rideal/Mars–van Krevelen mechanism of ammonia synthesis on cobalt molybdenum nitride. Asterisk indicates start of the process.

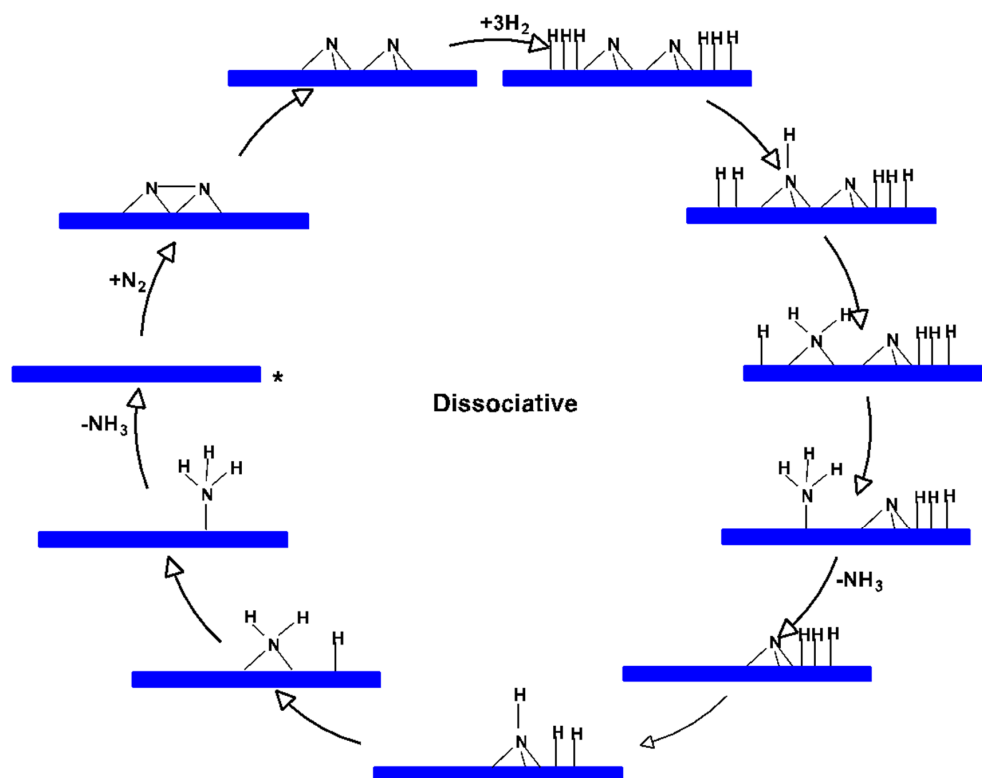


Figure 3. Illustration of the dissociative mechanism of ammonia synthesis on a catalytic surface. Asterisk indicates start of the process.

Following the dissociation, hydrogen molecules (H_2) adsorb onto the catalyst surface and dissociate into individual hydrogen atoms. These hydrogen atoms then migrate across the surface and react with the bridged nitrogen species in a stepwise manner. This stepwise hydrogenation leads to the formation of various nitrogen–hydrogen intermediates such as NH , NH_2 , and, ultimately, NH_3 (ammonia).

The final product, ammonia, desorbs from the catalyst surface, freeing up active sites for new nitrogen and hydrogen molecules to be adsorbed, thereby continuing the catalytic cycle. The efficiency of this mechanism depends on the ability of the catalyst to facilitate the adsorption, activation, and dissociation of nitrogen and hydrogen molecules, as well as the subsequent hydrogenation steps.

These species then undergo hydrogenation steps to form ammonia. The relative energy diagram shows that the hydrogenation steps in this mechanism have higher barriers compared to the associative distal Eley–Rideal/Mars–van Krevelen mechanism, making it less favorable kinetically [22].

Building on the understanding of nitrogen activation mechanisms, the study by Zeinalipour-Yazdi et al. presented a dispersion-corrected density functional theory (DFT-D3) investigation into the adsorption and activation of molecular nitrogen (N_2) and hydrogen (H_2) on Co_3Mo_3N surfaces. Their research identified two primary activation sites for N_2 , a Mo_3 triangular cluster at 3f nitrogen vacancies, and a surface cavity where N_2 is activated by Co_8 clusters. Their study revealed that H_2 can adsorb both molecularly on the Mo_3N framework and dissociatively on Co_8 or Mo_3 clusters exposed due to N-vacancies. N_2 adsorption occurs in three configurations (with the latter being particularly efficient for activation): side-on, end-on, and an unusual tilt end-on (155°). The findings suggest that the Co_3Mo_3N surface with high-nitrogen-vacancy density ($\sim 10^{13} \text{ cm}^{-2}$) is highly effective in activating N_2 by weakening the triple bond, facilitating the Mars–van Krevelen mechanism for ammonia synthesis. This study highlighted the potential of Co_3Mo_3N as a highly active catalyst for ammonia synthesis, with the unique tilt end-on configuration playing a crucial role in the activation process [23].

Following previous findings regarding the role of crystallographic orientation in catalytic activity, the study by Gudmundsson et al. investigated the nitrogen reduction reaction (NRR) on the (110) facets of transition metal nitrides (TMNs) using DFT. Their study compared the (110) facets with the previously examined (100) facets and found that the (110) facets generally exhibited higher overpotentials (OPs) and lower catalytic activity. Specifically, vanadium nitride (VN) showed the most promise among the tested TMNs, with a relatively low OP of -0.67 V and a favorable single-vacancy mechanism for ammonia formation. Their research highlighted that while the (110) facets of VN demonstrate some catalytic efficiency, they are still less active and selective compared to the (100) facets. Additionally, their study emphasized the importance of careful surface engineering to ensure the presence of optimal surface orientations as polycrystalline samples with mixed facets could negatively impact overall catalytic performance. This investigation underscores the critical need for precise control over the crystallographic orientation in developing effective TMN catalysts for ammonia synthesis [24].

A study by Al Sobhi et al. investigated the impact of substituting molybdenum (Mo) with tungsten (W) in Co_3Mo_3N and Ni_2Mo_3N on ammonia synthesis activity and lattice nitrogen reactivity. Their research found that tungsten substitution decreases the catalytic performance of both Co_3Mo_3N and Ni_2Mo_3N , with Co_3Mo_3N exhibiting a transformation to Co_6Mo_6N , indicating significant lattice nitrogen loss, while Ni_2Mo_3N retained its lattice nitrogen, showing limited reactivity. Computational calculations revealed that tungsten has minimal impact on the formation energy of surface nitrogen vacancies and the adsorption and activation of nitrogen molecules. Despite lower ammonia synthesis activity in tungsten-doped variants, both materials maintained stable performance over extended periods. The findings suggest that, while Co_3Mo_3N is a more promising candidate due to its higher lattice nitrogen reactivity, further modifications are needed to enhance its catalytic efficiency for industrial applications [25].

Expanding on the examination of lattice nitrogen reactivity in transition metal nitrides, the study by Daisley et al. focused on the ternary molybdenum nitrides $\text{Co}_2\text{Mo}_3\text{N}$ and $\text{Fe}_3\text{Mo}_3\text{N}$ and compared them with $\text{Co}_3\text{Mo}_3\text{N}$. The research investigated these materials under a 3:1 H_2/Ar mixture at temperatures up to 900 °C. The η -carbide-structured $\text{Co}_3\text{Mo}_3\text{N}$ demonstrated high reactivity, with significant nitrogen loss and transformation into $\text{Co}_6\text{Mo}_6\text{N}$, which is consistent with the Mars–van Krevelen mechanism. In contrast, the filled β -Mn-structured $\text{Co}_2\text{Mo}_3\text{N}$ showed stability up to 800 °C, decomposing only at 900 °C, suggesting a lower reactivity of its lattice nitrogen. $\text{Fe}_3\text{Mo}_3\text{N}$ exhibited minimal nitrogen loss up to 800 °C but decomposed at 900 °C, forming iron nitride and molybdenum metal. Their study highlighted that both the metal composition and phase significantly influence the bulk lattice nitrogen reactivity in these ternary nitrides, with $\text{Co}_3\text{Mo}_3\text{N}$ showing the highest reactivity due to its optimal nitrogen binding energy and favorable structural properties for nitrogen activation [26].

The study by Higham et al. investigated the catalytic ammonia synthesis mechanisms in $\text{Fe}_3\text{Mo}_3\text{N}$ and compared it with the previously studied $\text{Co}_3\text{Mo}_3\text{N}$. Using plane-wave DFT, their research examined surface nitrogen vacancy formation and two distinct ammonia synthesis mechanisms: the associative Mars–van Krevelen (ER–MvK) and the dissociative Langmuir–Hinshelwood (LH) mechanisms. The findings revealed that nitrogen vacancy formation on $\text{Fe}_3\text{Mo}_3\text{N}$ is thermodynamically more demanding than on $\text{Co}_3\text{Mo}_3\text{N}$, yet still feasible, suggesting that the surface lattice nitrogen vacancies in $\text{Fe}_3\text{Mo}_3\text{N}$ can facilitate ammonia synthesis. The calculations show that nitrogen activation is enhanced on $\text{Fe}_3\text{Mo}_3\text{N}$ compared to $\text{Co}_3\text{Mo}_3\text{N}$, with adsorption at and adjacent to the vacancy being more favorable. The associative ER–MvK mechanism provides a less energy-demanding pathway for ammonia synthesis, particularly for the initial hydrogenation processes. However, the LH mechanism shows high activation barriers for subsequent hydrogenation steps, indicating that, while both mechanisms are viable, the ER–MvK pathway is more kinetically accessible. Additionally, $\text{Fe}_3\text{Mo}_3\text{N}$ shares the same associative distal mechanism for ammonia synthesis as the $\text{Co}_3\text{Mo}_3\text{N}$ catalyst but is somewhat less active overall. These insights highlight the potential of $\text{Fe}_3\text{Mo}_3\text{N}$ as a catalyst for ammonia synthesis, particularly in the context of optimizing the $\text{Co}_{3-x}\text{Fe}_x\text{Mo}_3\text{N}$ system to enhance catalytic activity under milder conditions [27].

In extending the exploration of anti-perovskite nitrides for ammonia synthesis, a study by Daisley et al. investigated the catalytic activities of Co_3CuN , Ni_3CuN , and Co_3MoN . Experimental and theoretical analyses reveal that Co_3CuN demonstrates a higher conversion of lattice nitrogen to ammonia compared to Ni_3CuN , exhibiting activity at lower temperatures. The loss of lattice nitrogen in Co_3CuN was topotactic, resulting in the formation of Co_3Cu , whereas Ni_3CuN showed minimal activity at lower temperatures and required higher temperatures for significant nitrogen loss. Their study suggested that the metal composition influences the stability and activity of these nitrides, with computational modeling showing differences in nitrogen vacancy formation energies and the density of states at the Fermi level. Co_3MoN , unlike Co_3CuN and Ni_3CuN , maintains steady-state catalytic activity at 400 °C with a rate of $92 \pm 15 \text{ mmol h}^{-1} \text{ g}^{-1}$, highlighting the impact of metal composition on catalytic performance. These findings underscore the potential of anti-perovskite nitrides in ammonia synthesis through chemical looping; though regeneration using N_2 remains challenging, indicating a need for further optimization [28].

Ammonia synthesis on manganese nitride (Mn_6N_5) begins with nitrogen vacancies on the catalyst's surface, serving as active sites for the reaction. Molecular nitrogen (N_2) adsorbs at these vacancies in an end-on configuration, allowing one nitrogen atom to interact directly with the nitrogen vacancies [29]. This interaction significantly weakens the $\text{N}\equiv\text{N}$ triple bond. Concurrently, molecular hydrogen (H_2) adsorbs directly from the gas phase onto the end-on adsorbed nitrogen forming $>\text{NNH}_2$ species. Two such $>\text{NNH}_2$ species react with a hydrogen coming from the gas phase forming two $>\text{NNH}_3$ species. These $>\text{NNH}_3$ species dissociate forming ammonia and leaving behind surface nitrogen, which is adsorbed at the nitrogen vacancy. These nitrogen species become hydrogenated

forming NH_2 and then NH_3 , which desorbs from the surface. The NH_3 desorbs from the surface, freeing up active sites for new nitrogen molecules and perpetuating the catalytic cycle. This mechanism underscores the essential role of nitrogen vacancies and the stepwise hydrogenation process on Mn_6N_5 , highlighting the importance of tailoring the surface properties and active sites in order to achieve efficient ammonia synthesis [30].

Building on previous research, the study by Zeinalipour-Yazdi et al. employed dispersion-corrected density functional theory (DFT-D3) to investigate the chemisorption of H_2 and N_2 on cobalt-promoted Ta_3N_5 surfaces, focusing on the (100), (010), and (001) facets. Their study revealed that nitrogen adsorbs mostly molecularly in side-on, end-on, and tilt configurations, with the formation of azide functional groups at bridging nitrogen sites, exhibiting a formation energy of 205 kJ/mol. Hydrogen was found to chemisorb molecularly with adsorption energies ranging from -81 to -91 kJ/mol, but, at bridging nitrogen sites, it dissociates to form 4NH groups with an exothermic formation energy of -175 kJ/mol per H_2 molecule. The presence of cobalt promoters significantly enhances the dissociation of molecular hydrogen on the Ta_3N_5 surface primarily at nitrogen-rich sites, with adsorption energies between -200 and -400 kJ/mol. This enhancement in dissociation suggests that cobalt promoters play a critical role in facilitating the hydrogenation steps of ammonia synthesis on Ta_3N_5 by lowering the formation energy of nitrogen vacancies, thus increasing the catalyst's overall reactivity and efficiency [31].

Iron molybdenum nitride ($\text{Fe}_3\text{Mo}_3\text{N}$) follows a similar mechanism to $\text{Co}_3\text{Mo}_3\text{N}$ for ammonia synthesis but exhibits lower reactivity. The Eley–Rideal/Mars–van Krevelen mechanism on $\text{Fe}_3\text{Mo}_3\text{N}$ involves nitrogen vacancies and the subsequent hydrogenation of nitrogen species. Despite following a similar pathway as $\text{Co}_3\text{Mo}_3\text{N}$, $\text{Fe}_3\text{Mo}_3\text{N}$ has higher activation barriers for the hydrogenation steps. The desorption of ammonia from the catalyst surface requires less energy compared to the hydrogenation steps but, overall, $\text{Fe}_3\text{Mo}_3\text{N}$ is less reactive than $\text{Co}_3\text{Mo}_3\text{N}$ and Mn_6N_5 [22].

Recent studies have emphasized the significance of nitrogen vacancies in the catalytic activity of metal nitrides. Nitrogen vacancies act as active sites for the adsorption and activation of N_2 molecules. For example, in $\text{Co}_3\text{Mo}_3\text{N}$, the presence of nitrogen vacancies facilitates the associative Eley–Rideal mechanism, which has been shown to have lower activation barriers compared to the Langmuir–Hinshelwood mechanism [32]. This suggests that designing catalysts with a high concentration of nitrogen vacancies could enhance ammonia synthesis rates. In the Eley–Rideal/Mars–van Krevelen Mechanism nitrogen vacancies on the $\text{Co}_3\text{Mo}_3\text{N}$ surface, N_2 molecules are end-on adsorbed, which then react with the dissociated hydrogen to form ammonia. This mechanism is favored due to its lower activation barriers.

We observed that the best mechanism that has been suggested for the iron and ruthenium catalyst is the Langmuir–Hinshelwood mechanism. This involves the side-on adsorption of N_2 and its subsequent dissociation and hydrogenation on the catalyst surface. This mechanism has barriers that are higher for the hydrogenation steps than the associative distal Eley–Rideal/Mars–van Krevelen mechanism, thus clearly suggesting that the kinetically faster mechanism on $\text{Co}_3\text{Mo}_3\text{N}$ and $\text{Fe}_3\text{Mo}_3\text{N}$ is a different mechanism than what has been suggested for iron and ruthenium.

The manuscript by Hargreaves and Daisley provides an insightful overview of recent advancements in the development of nitrides, hydrides, and carbides as alternative heterogeneous catalysts for ammonia synthesis [33]. The paper emphasized the potential of these materials to facilitate sustainable ammonia production through mechanisms that are more akin to enzymatic nitrogen activation, thus potentially allowing for milder reaction conditions compared to the traditional Haber–Bosch process. The authors highlight that metal nitrides, such as $\text{Co}_3\text{Mo}_3\text{N}$, can operate via a Mars–van Krevelen mechanism, involving the direct hydrogenation of lattice nitrogen, which then leads to nitrogen vacancies that can be replenished during the reaction cycle. This process can be enhanced by incorporating elements like cobalt, which helps balance nitrogen adsorption strengths, thereby improving catalytic efficiency. Their study also explored the synergistic effects of combining nitrides

with other materials, such as hydrides, to overcome scaling limitations through dual-site mechanisms. For instance, nickel/lanthanum nitride catalysts exhibit high activity and stability by leveraging nitrogen vacancies for nitrogen activation and using nickel for hydrogen dissociation. The authors noted that the integration of alkali metal doping and hydrogen activation remains a relatively underexplored yet promising area for catalyst development. Overall, this work underscores the exciting potential and ongoing challenges in designing novel catalysts for localized, sustainable ammonia synthesis that is capable of operating under lower temperatures and pressures while maintaining high efficiency and durability [33].

The integration of experimental and computational approaches has been crucial in understanding the role of nitrogen vacancies and optimizing catalytic performance. Studies involving isotopic nitrogen exchange and computational modeling have shown that nitrogen vacancies are effective sites for N_2 activation and that the presence of surface defects can significantly influence catalytic activity [32]. Isotopic nitrogen exchange have been recently performed to better understand the role on nitrogen adsorbed to the surface of the catalyst on the kinetics of the reaction. Experiments have demonstrated the participation of lattice nitrogen in the ammonia synthesis reaction, indicating that nitrogen vacancies are replenished during the reaction cycle.

Computational modeling DFT calculations have supported experimental observations, showing that nitrogen vacancies have lower formation energies and are effective for N_2 activation at synthesis temperatures, but the exact role of the removal of lattice nitrogen is not yet clearly understood. Further computational studies are necessary that can identify the exact role of the surface versus lattice nitrogen removal and its participation in the mechanism of ammonia synthesis [32].

The addition of promoters to metal nitrides can further enhance their catalytic activity. For instance, doping Ta_3N_5 with cobalt has been shown to increase ammonia synthesis rates by facilitating hydrogen dissociation and nitrogen activation [31]. Similarly, lithium-doped Mn_6N_5 has exhibited improved activity and stability, highlighting the potential of dopants to modify surface chemistry and catalytic performance [34]. However, the role of dopants in the mechanism for ammonia synthesis on metal nitrides is currently not well understood on an atomistic basis, and further computational studies in this direction are necessary to find the exact formulation of metal nitride/promoter system that will have greater stability and activity for ammonia synthesis.

Chemical looping is an emerging approach in ammonia synthesis that leverages the Mars–van Krevelen mechanism. In this process, the lattice nitrogen in metal nitrides acts as an active species, which can be replenished in a separate regeneration step. Recent studies have explored various metal nitrides, such as manganese nitride and cerium nitride, for their potential in chemical looping systems [35].

Manganese nitride has been identified as a promising candidate for chemical looping due to its ability to form and utilize nitrogen vacancies. Doping with lithium has been shown to enhance the reactivity of lattice nitrogen, thereby improving ammonia formation rates [35].

Cerium nitride (CeN), especially when supported on nickel (Ni/CeN), exhibits a favorable formation of nitrogen vacancies, which play a crucial role in enhancing its catalytic activity for ammonia synthesis. The ammonia synthesis process on CeN involves both dissociative and associative pathways. In the dissociative pathway, nitrogen molecules adsorb at the nitrogen vacancies and dissociate into atomic nitrogen, which subsequently reacts with hydrogen to form ammonia. In the associative pathway, nitrogen molecules are hydrogenated stepwise without prior dissociation, forming intermediates such as NH and NH_2 before finally producing NH_3 [36]. This dual-pathway mechanism enhances the overall performance of the catalyst by allowing it to utilize multiple reaction routes.

The chemical looping process further contributes to the high activity of CeN in ammonia synthesis. This process involves the continuous cycling of nitrogen between the catalyst and the reaction environment, and it is facilitated by the Mars–van Krevelen mechanism.

In this mechanism, lattice nitrogen in CeN is involved in the reaction cycle, participating in the formation of ammonia and subsequently being replenished by nitrogen from the gas phase. This ensures a steady supply of active sites and maintains high catalytic efficiency over extended periods.

Chorkendorff and co-workers investigated the spin-mediated promotion of a cobalt catalyst for ammonia synthesis [37]. They found that suppressing the magnetism in the catalyst may be the key for lower temperature operations of the catalyst. They showed that one can use lanthanum to quench the magnetic moment of cobalt atoms on the surface of the catalyst. This results in a lower activation barrier for nitrogen cleavage compared to the barrier found on the iron catalyst.

Recent research has further expanded the understanding of molybdenum-based metal nitrides, specifically in focusing on lattice nitrogen-mediated ammonia production. This research employed a multistage design strategy to correlate the intrinsic activity of these catalysts with their electronic structures, utilizing DFT calculations as a critical tool. The study conducted by Qian et al. used DFT to investigate the electronic properties and catalytic behavior of molybdenum-based nitrides, such as Mo₂N and MoN. These nitrides were analyzed to understand their ability to activate nitrogen molecules and facilitate the ammonia synthesis process. The findings revealed that the lattice nitrogen in these materials played a crucial role in the reaction mechanism, participating directly in the formation of ammonia through both associative and dissociative pathways. The associative mechanism involved the stepwise hydrogenation of adsorbed nitrogen species, forming intermediates like NH and NH₂, while the dissociative mechanism involved the breaking of the N≡N bond to form atomic nitrogen, which then reacted with hydrogen to produce ammonia. Their study's computational approach provided detailed insights into the energy profiles and transition states of these reactions, highlighting the importance of electronic structure in determining the catalytic efficiency of molybdenum-based nitrides. Their research underscored the potential of these materials in sustainable ammonia production, offering a pathway to optimize catalysts for industrial applications [38].

Molybdenum-based nitrides, including Co₃Mo₃N, Fe₃Mo₃N, Ni₃Mo₃N, and Mo₂N, were employed as model catalysts. These materials were chosen to decouple the effects of electronic properties and geometrical features on catalytic activity.

It is obvious that there is still a great deal that can be discovered in thermal ammonia synthesis that utilizes nitrogen vacancies. In the following sections, we shall further explore the electrochemical synthesis of ammonia and photocatalytic synthesis.

The study by Hanifpour et al. investigated the electrochemical nitrogen reduction reaction (NRR) on transition metal nitride (TMN) thin films, specifically VN, CrN, NbN, and ZrN, using a micro-reactor flow-cell setup under ambient conditions. Employing chronoamperometry for ammonia production analysis, their research revealed that ZrN shows promising catalytic behavior, producing ammonia with higher reaction rates and current efficiencies in the presence of N₂ when compared to Ar. Conversely, VN and NbN initially produce ammonia through the reaction of surface nitrides but become inactive afterward, and CrN does not produce any detectable ammonia. Their study utilized electrochemical impedance spectroscopy (EIS), X-ray reflectivity (XRR), and X-ray photoelectron spectroscopy (XPS) to provide detailed insights into the stability and surface characteristics of the TMNs, emphasizing the critical role of nitrogen vacancies and surface dynamics in catalytic performance. These findings highlight the importance of the precise control and characterization in developing efficient electrochemical catalysts for ammonia synthesis [39].

The study by Abghoui et al. employed DFT to investigate the electrochemical reduction of nitrogen to ammonia at ambient conditions on transition metal nitride surfaces, specifically VN, ZrN, NbN, and CrN. Their study identified these nitrides as promising catalysts for ammonia synthesis due to their higher activity toward nitrogen reduction compared to the competing hydrogen evolution reaction (HER). Their research highlighted that VN, with its rocksalt (100) facet, can effectively reduce nitrogen to ammonia via a

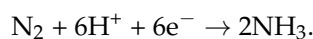
Mars–van Krevelen mechanism with only a -0.5 V overpotential, thus avoiding catalyst decomposition. Additionally, their study underscored the stability of these nitrides against poisoning and their potential to achieve sustainable and energy-efficient ammonia production at low temperatures and ambient pressures, offering a viable alternative to the traditional Haber–Bosch process. The comprehensive DFT analysis provided insights into the thermodynamics and kinetics of the nitrogen reduction reaction on these surfaces, guiding the development of efficient electrochemical ammonia synthesis catalysts [40].

The study by Lu et al. focused on the development of chemically durable nickel and cobalt lanthanum-nitride-based catalysts for ammonia synthesis. The authors addressed the challenge of high sensitivity to air and moisture in metal nitride complexes by introducing aluminum into the LaN lattice, forming La_3AlN . This modification creates La–Al metallic bonds that enhance chemical stability while retaining catalytic functionality. The resulting Ni/ La_3AlN and Co/ La_3AlN catalysts demonstrated significant catalytic activity without degradation after exposure to air and moisture, achieving reaction rates of $2410 \mu\text{mol g}^{-1} \text{h}^{-1}$ for Ni/ La_3AlN and $2735 \mu\text{mol g}^{-1} \text{h}^{-1}$ for Co/ La_3AlN at 400°C and 0.1 MPa. Their study highlighted the dual active-site mechanism, where La_3AlN facilitates N_2 absorption and activation, offering a promising approach for developing stable and efficient catalysts for ammonia synthesis [41].

The study by Bin Liu et al. investigated the manipulation of the geometric and electronic structures of manganese nitrides (Mn_4N and Mn_2N) for improved ammonia synthesis. This research highlighted that modifying Mn nitrides with transition metal heteroatoms (Cr, Fe, Co, Ni, and Mo) can significantly influence the binding energies of intermediate hydrogenation products and the overall ammonia formation process. DFT calculations reveal that, while the binding of NH on Mn nitride surfaces follows a linear relationship with lattice nitrogen, the binding of NH_2 and NH_3 is more sensitive to changes in the geometric and electronic structures. Their study also identified that the rate-determining step for ammonia synthesis involves the diffusion of lattice nitrogen, which can be facilitated by introducing single-atom dopants. This comprehensive approach provides insights into optimizing Mn nitrides as nitrogen carriers for efficient ammonia production, emphasizing the critical role of electronic structure modifications in enhancing catalytic performance [42].

1.2. Electrochemical Ammonia Synthesis

Electrochemical ammonia synthesis is a promising alternative to traditional thermal methods, offering the potential for ammonia production at ambient conditions using renewable energy sources. This approach not only reduces the energy requirements, but also provides a more sustainable pathway by potentially eliminating carbon emissions. The electrochemical nitrogen reduction reaction (NRR) involves the stepwise reduction of nitrogen (N_2) to ammonia (NH_3) at the cathode, with hydrogen (H^+) ions being supplied from the electrolyte. The basic reactions can be summarized as follows:



This process competes with the hydrogen evolution reaction (HER), which often occurs concurrently, thus affecting the selectivity and efficiency of ammonia production. Significant contributions have been made by various research groups, notably the group led by Skúlason and co-workers. They have developed detailed thermochemical data and computational models to identify potential catalysts for nitrogen reduction reactions. One notable study provided a comprehensive analysis of nitrogen-binding-energy descriptors, establishing new insights into the limiting potentials required for effective electrochemical ammonia synthesis [43]. Mo-based catalysts have shown promise due to their moderate nitrogen binding energy, which favors the NRR over HER. Studies indicate that molybdenum can serve as a robust catalyst under appropriate conditions [43]. Iron (Fe) is commonly investigated due to its abundance and catalytic properties. However, Fe also promotes HER, making it less selective for NRR in aqueous media [43]. Ruthenium (Ru) and rhodium

(Rh) have shown high activity for NRR but also suffer from significant HER competition, requiring further optimization for selectivity [43,44].

Recent studies have identified several overlooked catalysts that show potential for selective NRR. Manganese (Mn) has emerged as a highly reactive and selective catalyst for NRR, particularly at higher pH levels where HER is less favored [43]. Some post-transition metals such as gallium (Ga) and indium (In) have shown promise due to their poor HER promotion and strong nitrogen binding, making them suitable candidates for selective NRR in both aqueous and non-aqueous media [43]. Tantalum oxide (TaO_2), rhenium oxide (ReO_2), and osmium oxide (OsO_2) have been studied in recent computational studies, and it was found that these rutile oxides have a potential for electrochemical ammonia formation. These oxides were found to have significantly lower potential determining steps (PDSs) than previously reported, indicating their strong candidacy for NRR. TaO_2 , in particular, was identified as binding NNH stronger than H, making it a promising candidate for selective ammonia synthesis [45]. Recent DFT calculations on niobium carbonitride (NbCN) have identified NbCN as a highly effective catalyst for electrochemical NRR. It exhibits both activity and stability, and it is capable of self-regeneration and nitrogen-to-ammonia activation with a low potential-determining step energy of 0.58 eV. NbCN facilitates ammonia formation via a mixed associative Mars–van Krevelen (MvK) mechanism [46]. Tungsten carbonitride (WCN) has also shown promise for efficient ammonia synthesis, but it faces challenges related to higher activation energies and potential poisoning by other species in the electrolyte [46]. Recent research has shown that Fe_xO_y co-deposited on amorphous MoS_2 when supported on a gas diffusion layer electrode (GDL) significantly enhances NRR activity. The GDL/ MoS_2 -Fe-1 catalyst has exhibited an NH_3 yield of $7.38 \mu\text{mol h}^{-1} \text{cm}^{-2}$ and a Faradaic efficiency of 54.9% at -0.2 V vs. RHE at 25°C . This performance is attributed to the amorphous structure of MoS_2 providing abundant active sites and to Fe_xO_y enhancing electron transfer and nitrogen adsorption [47].

Recent DFT calculations have provided insights into the mechanistic pathways of NRR on the Ru(0001) surface. This study elucidated that the initial activation of N_2 to form NNH is the rate-limiting step, with an energy barrier of 0.8 eV at an applied potential of -0.6 V . The protonation steps involve low barriers of 0.0–0.25 eV, indicating efficient proton–electron transfer processes. The preferred pathway follows an associative distal mechanism, where the N–N bond is cleaved after the third proton–electron transfer, resulting in ammonia formation [44]. Homogeneous catalysts, typically molecular complexes with transition metals as their central atoms, are dissolved in the electrolyte. These catalysts operate through cyclic mechanisms where the metal centers coordinate with nitrogen, store charges, and facilitate the reduction process. However, the challenge lies in their separation and reuse post-reaction, which can hinder commercial applications [36]. The use of biological catalysts, inspired by the natural nitrogenase enzyme, is an emerging area in electrochemical NRR. These catalysts mimic the natural process of nitrogen fixation and offer a potentially sustainable approach to NH_3 synthesis. However, their practical application requires overcoming challenges related to stability and efficiency under electrochemical conditions [36].

A recent study demonstrated the effectiveness of nitrogen and phosphorus co-doped porous carbon (NPC) as an electrocatalyst for NRR. The NPC was prepared by pyrolyzing polyaniline aerogels in the presence of phytic acid. This co-doping introduced defects and heteroatoms that enhanced the catalyst's activity by providing more active sites and improving electron transfer [48]. The electrochemical performance of the N, P co-doped carbon mater (NPC) catalyst exhibited a high NH_3 yield of $7.38 \mu\text{mol h}^{-1} \text{cm}^{-2}$ and a Faradaic efficiency of 54.9% at -0.2 V vs. RHE in 0.1 M HCl electrolyte. The high surface area and porosity of NPC, combined with the synergistic effects of N and P co-doping, contributed to its superior performance [48]. Atomic structure modifications, such as defect engineering, surface orientation, and amorphization, have shown significant promise in improving the efficiency of electrochemical NRR. A recent review by Chen et al. summarized the progress in these areas, highlighting strategies like heteroatom doping and creating

atom vacancies to introduce extra active sites and enhance the intrinsic activity of catalysts. For example, heteroatom doping (e.g., metal atoms like Fe and non-metal atoms like B) can increase active sites and reduce the energy barrier for the rate-determining step of NRR by forming extraordinary coordination environments and electronic structures [49]. Additionally, surface orientation and the amorphization of catalysts can significantly influence their catalytic performance. Stepped facets and amorphous structures provide abundant active sites and unique electronic properties that enhance NRR efficiency [49]. Traditional metal electrodes like platinum and gold are often used, but their tendency to promote HER limits their effectiveness for NRR. Emerging materials such as metal nitrides and carbides are being explored for better selectivity and efficiency.

Aqueous electrolytes are commonly used due to their availability and ease of handling. However, the high proton concentration favors HER, necessitating the search for alternative electrolytes. Non-aqueous electrolytes such as ionic liquids offer a reduced proton environment, thus favoring NRR over HER. They are gaining attention for their ability to improve the selectivity of ammonia synthesis [43]. Optimal reaction conditions are crucial for maximizing the efficiency of electrochemical ammonia synthesis. Lower temperatures and ambient pressures are typically favorable, aligning with the principles of electrochemical processes. The applied potential must be carefully controlled to favor NRR while minimizing HER. Recent research has provided detailed guidelines on the appropriate potentials for various catalysts [43]. The mechanistic pathways for NRR on different catalysts can follow either an associative or dissociative mechanism. The associative mechanism involves the stepwise addition of protons and electrons to adsorbed N_2 , forming NH_3 via intermediates such as N_2H and NH . The dissociative mechanism involves the initial cleavage of the $N\equiv N$ bond, followed by the protonation of the resulting nitrogen atoms. This pathway is less favored at ambient conditions due to the high energy barrier for N_2 dissociation [43]. Despite this progress, several challenges remain: one is the Faradaic efficiency; and the other is the efficiency of converting electrical energy to chemical energy in the form of NH_3 , which remains low due to competing HER. The long-term stability of catalysts in the electrochemical environment is a critical issue, with many catalysts degrading over time. The cost of developing and scaling up new catalyst materials and processes needs to be addressed for commercial viability.

The study by Nørskov, Chorkendorff, and co-workers emphasized that special care needs to be taken in studies of electrochemical ammonia synthesis to avoid false positives [50]. In these experiments, the ammonia attributed to electrochemical nitrogen fixation was found to be due to the contamination from ammonia in the air; human breath or ion conducting membranes; or that generated from labile nitrogen-containing compounds (such as, for example, nitrates, amines, nitrites, and nitrogen oxides). They then continued to provide a protocol that should prevent false positives in experimental studies on the reduction of nitrogen to ammonia.

A study by Iqbal et al. explored the potential of transition metal carbonitrides (TMCNs) as electrocatalysts for nitrogen reduction reaction (NRR) under ambient conditions. Using DFT, their research examined the (111) facets of TMCNs, including VCN, NbCN, and WCN. Their findings revealed that VCN and NbCN are particularly promising for NRR via the Mars–van Krevelen mechanism, requiring low onset potentials of -0.52 V and -0.53 V vs. RHE, respectively. This low-energy requirement makes them efficient catalysts for ammonia synthesis at ambient conditions. Their study also highlighted that while WCN showed potential, it was more susceptible to poisoning in electrochemical environments. Their research underscored the importance of selecting materials with the right balance of activity and stability to enhance ammonia production efficiency. This comprehensive investigation into TMCNs provided valuable insights for developing sustainable and efficient electrocatalysts for ammonia synthesis [46].

A paper by Liu et al. reviewed the development of electrocatalysts for efficient nitrogen reduction reaction (e-NRR) under ambient conditions, emphasizing the need for novel catalysts to enhance practical applications. Their study highlighted the mechanisms

of NH_3 electrochemical synthesis and outlined strategies to improve catalytic performance by increasing exposed active sites or tuning electronic structures. Various novel electrocatalysts, including noble metal-based materials, single-metal-atom catalysts, non-noble metals, and metal-free materials, were systematically summarized. The review also discussed the role of surface control, defect engineering, and hybridization in improving catalytic efficiency. These insights provide valuable guidance for designing advanced catalytic systems for sustainable and efficient ammonia production through e-NRR, where the aim is to achieve higher energy efficiency and support decentralized ammonia production to reduce transportation costs and environmental impacts [51].

A study by Li et al. investigated the electrochemical promotion of ammonia formation on Fe-based electrode catalysts using proton-conducting-electrolyte-supported cells with $\text{H}_2\text{--Ar}$ and $\text{H}_2\text{--N}_2$ at temperatures between 550 °C and 600 °C under ambient pressure. Their research examined the ammonia formation rate using two types of cathodes: a porous pure Fe electrode with a shorter triple phase boundary (TPB) length; and a cermet electrode consisting of Fe-BCY (or W-Fe-BCY) with a longer TPB length. The results demonstrate that the porous pure Fe electrode outperformed the Fe-BCY cermet electrode, indicating that ammonia formation is primarily accelerated by the electrochemical promotion of catalysis (EPOC) effect on the Fe surface rather than the charge-transfer reaction at the TPB. The mechanism is dominated by a dissociative process, where the direct N_2 bond dissociation is accelerated with cathodic polarization on the Fe surface with a minor contribution from a proton-assisted associative mechanism at the TPB. Despite the relatively short TPB length, the porous pure Fe cathode achieves a high-ammonia formation rate of $1.4 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-1}$ ($450 \mu\text{g h}^{-1} \text{ mg}^{-1}$) under optimal conditions, suggesting that the effective double layer extends widely on the Fe electrode surface. This study highlights key processes for improving ammonia formation and underscores the effectiveness of the porous pure Fe electrode for electrochemical ammonia synthesis [52].

A study by Chen et al. presented a novel approach for enhancing electrochemical nitrogen reduction reaction (NRR) performance using non-noble metal sulfide catalysts integrated with a conductive matrix. Their research highlighted the self-organized growth of flower-like SnS_2 and forest-like ZnS nanoarrays on nickel foam through solvothermal conditions. These innovative structures exhibit strong-nitrogen-activation abilities that are further enhanced by their formation on 3D porous Ni foam, which provides a large surface area and facilitates easy electrolyte permeation. Nickel foam is chosen for its superior electrical conductivity and mechanical robustness, significantly outperforming carbon-based materials. The resulting $\text{SnS}_2\text{@Ni}$ and ZnS@Ni foams demonstrate high ammonia yields and faradaic efficiencies, rivaling or surpassing those of noble-metal-based catalysts. This work underscores the potential of integrating metal sulfides with conductive matrices to develop advanced hybrid catalysts for efficient and scalable ammonia synthesis [53].

A study by Cui et al. reviewed the progress and challenges in the electrocatalytic reduction of dinitrogen (N_2) to ammonia (NH_3) under ambient conditions. Their paper highlighted the urgent need for sustainable and eco-friendly energy pathways, given the increasing global population and depletion of fossil fuels. The authors focus on the development of heterogeneous electrocatalysts capable of facilitating the nitrogen reduction reaction (NRR) at room temperature and atmospheric pressure. They summarize the prevailing theories and mechanisms for NRR, the computational screening of promising materials, and the design of electrochemical systems to enhance activity, selectivity, efficiency, and stability. Their review emphasized the importance of overcoming challenges such as high energy consumption and negative environmental impacts associated with traditional ammonia synthesis methods like the Haber–Bosch process. Promising strategies to improve NRR electrocatalysts, such as cationic/anionic regulation, heteroatom doping, and defect/strain engineering, were proposed, along with a rational design of the catalyst/electrolyte and electrode/catalyst interfaces to suppress competing hydrogen evolution reactions. Their study provided a comprehensive overview of recent advancements and offered insights for future research directions in the field of electrocatalytic ammonia synthesis [54].

1.3. Additional Studies Performing Mechanistic Studies of Ammonia Synthesis

Recent research has further expanded the understanding of molybdenum-based metal nitrides, specifically focusing on lattice nitrogen-mediated ammonia production. This research employed a multistage design strategy to correlate the intrinsic activity of these catalysts with their electronic structures, utilizing DFT calculations as a critical tool. A study conducted by Qian et al. used DFT to investigate the electronic properties and catalytic behavior of molybdenum-based nitrides, such as Mo_2N and MoN . These nitrides were analyzed to understand their ability to activate nitrogen molecules and facilitate the ammonia synthesis process. The findings reveal that the lattice nitrogen in these materials plays a crucial role in the reaction mechanism, participating directly in the formation of ammonia through both associative and dissociative pathways. The associative mechanism involves the stepwise hydrogenation of adsorbed nitrogen species, forming intermediates like NH and NH_2 , while the dissociative mechanism involves the breaking of the $\text{N}\equiv\text{N}$ bond to form atomic nitrogen, which then reacts with hydrogen to produce ammonia. Their study's computational approach provided detailed insights into the energy profiles and transition states of these reactions, highlighting the importance of electronic structure in determining the catalytic efficiency of molybdenum-based nitrides. Their research underscores the potential of these materials in sustainable ammonia production, offering a pathway to optimize catalysts for industrial applications [38].

The Langmuir–Hinshelwood mechanism for ammonia synthesis involves a series of well-defined steps starting with the adsorption of molecular nitrogen (N_2) onto the surface of the catalyst. In this mechanism, nitrogen molecules are adsorbed in a side-on configuration at the active sites of the catalyst. This adsorption mode allows the nitrogen molecule to interact simultaneously with multiple active sites, leading to significant activation of the $\text{N}\equiv\text{N}$ triple bond. Once adsorbed, the nitrogen molecule undergoes dissociation into two nitrogen atoms, each of which is further adsorbed onto the catalyst surface in a bridged configuration. These bridged nitrogen species are highly reactive intermediates that play a crucial role in the subsequent steps of the reaction. The dissociation of the nitrogen molecule is facilitated by the strong interaction with the catalyst surface, which lowers the activation energy required to break the $\text{N}\equiv\text{N}$ bond. Following the dissociation, hydrogen molecules (H_2) adsorb onto the catalyst surface and dissociate into individual hydrogen atoms. These hydrogen atoms then migrate across the surface and react with the bridged nitrogen species in a stepwise manner. This stepwise hydrogenation leads to the formation of various nitrogen–hydrogen intermediates such as NH , NH_2 , and, ultimately, NH_3 (ammonia). The final product, ammonia, desorbs from the catalyst surface, freeing up active sites for new nitrogen and hydrogen molecules to be adsorbed, thereby continuing the catalytic cycle. The efficiency of this mechanism depends on the ability of the catalyst to facilitate the adsorption, activation, and dissociation of nitrogen and hydrogen molecules, as well as the subsequent hydrogenation steps.

In Figure 4, a free-energy diagram comparing the Langmuir–Hinshelwood (L-H) mechanism (in red) and the Eley–Rideal (E-R) mechanism (in black) for ammonia synthesis is shown. This figure highlights the stepwise reaction coordinates, showing the relative energy changes associated with each mechanism. The Langmuir–Hinshelwood mechanism involves nitrogen dissociation and hydrogenation on the catalytic surface, while the Eley–Rideal mechanism shows nitrogen directly reacting with hydrogen from the gas phase. The figure visually demonstrates the distinct energy barriers between the two mechanisms, emphasizing the catalytic efficiency of the process.

Continuing the investigation into transition metal catalysts for nitrogen reduction, the study by Ellingsson et al. focused on the activity of transition metal carbide (TMC) surfaces in the (100) facets of a rocksalt (RS) structure as potential catalysts for the nitrogen reduction reaction (NRR). Using DFT, their research modeled reaction pathways, estimated stability, assessed kinetic barriers, and compared adsorbate energies to determine the overall performance of various TMC surfaces. Their study found that pristine TMC surfaces without defects generally did not possess both exergonic nitrogen adsorption and the

capability to selectively protonate nitrogen to form ammonia in an aqueous solution. However, ZrC showed potential as a catalyst in non-aqueous electrolytes. Introducing carbon vacancies provided high coordination active sites on the surface, significantly improving nitrogen adsorption, selectivity toward ammonia, and lowering overpotential (OP) for NbC and WC. Despite this, NbC displayed an unfeasible kinetic barrier for nitrogen dissociation at ambient conditions, suggesting its suitability for high temperature/pressure ammonia synthesis. WC and VC emerged as promising materials for further experimental investigation in aqueous electrolytes due to their efficient nitrogen adsorption and favorable reaction pathways [55].

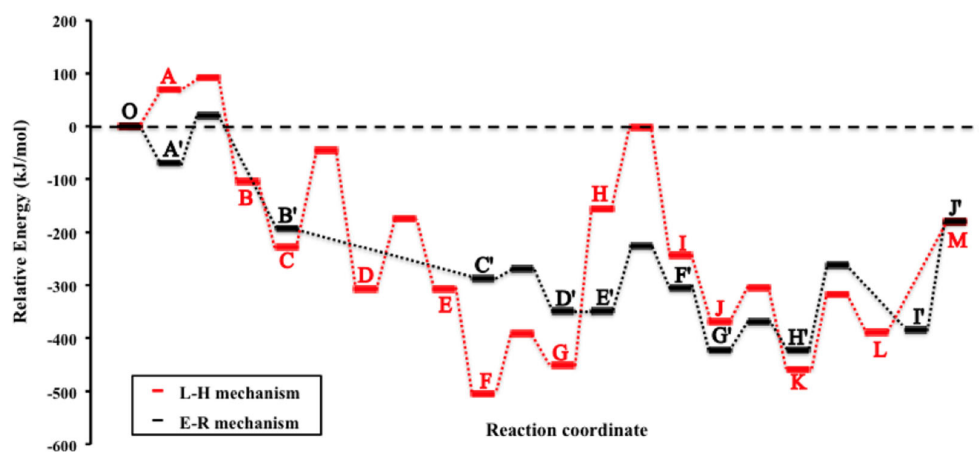


Figure 4. Relative energy diagram comparing the reaction profile of the Langmuir–Hinshelwood and the Eley–Rideal/Mars–van Krevelen mechanism on $\text{Co}_3\text{Mo}_3\text{N}$. Reproduced with permission from Ref. [20].

The use of electronic structure analysis in a study by Qian et al. revealed that the electron transfer between molybdenum and magnetic metals, along with the spin polarization characteristics of magnetic metals, are key descriptors of intrinsic catalytic activity. The modulation of these electronic properties through incorporating magnetic metals significantly enhances lattice nitrogen activity. This enhancement occurs because electron transfer increases the density of states at the Fermi level, facilitating nitrogen molecule activation by weakening the $\text{N}\equiv\text{N}$ bond. Additionally, spin polarization stabilizes reaction intermediates, lowering the activation energy for nitrogen dissociation and subsequent hydrogenation steps. These factors collectively improve the catalyst's ability to convert nitrogen to ammonia efficiently [38].

Expanding on the role of nitrogen vacancies in catalytic activity, the study by Abghoui et al. investigated the influence of incorporating titanium nitride (TiN) into the structure of chromium, vanadium, niobium, and zirconium nitrides. Using DFT analyses, their study found that combining TiN with vanadium nitride enhances the potential-determining step of the nitrogen reduction reaction (NRR) by up to 20% compared to pure vanadium nitride while maintaining a similar number of proton–electron transfer steps for forming ammonia. For chromium nitride, TiN incorporation improves the rate-determining step related to nitrogen adsorption and catalyst regeneration by around 90%. However, the integration negatively impacts niobium and zirconium nitrides, increasing the potential-determining step for niobium nitride and shifting the reaction pathway of zirconium nitride toward hydrogen evolution rather than nitrogen reduction. These results suggest that, while TiN can enhance stability and reactivity for certain nitrides, it can detrimentally affect others, highlighting the need for tailored approaches in catalyst design [56].

A recent mini-review by Gao et al. revisits the potential of Group 4–7 transition metals for heterogeneous catalytic ammonia synthesis, highlighting their ability to activate nitrogen under milder conditions than the traditional Haber–Bosch process. This review

emphasizes that, despite the tendency of these metals to form nitrides that are difficult to hydrogenate, their high affinity for N_2 makes them promising candidates for sustainable ammonia production. Their review covers recent advances in activating these metals through various strategies, including alloying, incorporating non-transition metal elements, and employing external fields like electricity and light. These approaches aim to enhance the catalytic activity by weakening strong metal–nitrogen bonds and facilitating nitrogen hydrogenation. This renewed focus on Group 4–7 transition metals could lead to the development of more efficient materials for ammonia synthesis, aligning with the goals of decentralized and flexible production systems [57].

Their study conducted by Iqbal et al. explored the potential of transition metal carbonitrides (TMCNs) as electrocatalysts for the nitrogen reduction reaction (NRR) to produce ammonia under ambient conditions. Using DFT calculations, the researchers examined the thermodynamic feasibility and activity of various TMCNs with rocksalt (RS) structures, focusing on their (100) facets. That study identified VCN and NbCN as the most promising candidates for ammonia production via the Mars–van Krevelen (MvK) mechanism, with low onset potentials of -0.52 V and -0.53 V versus the reversible hydrogen electrode (RHE). These carbonitrides demonstrated a preference for NRR over the hydrogen evolution reaction (HER), making them suitable for efficient ammonia synthesis. The comprehensive analysis included free-energy diagrams, adsorption energies, and kinetic barriers, providing valuable insights into the electrocatalytic behavior and stability of TMCNs. The results highlight the potential of VCN and NbCN as effective catalysts for sustainable ammonia production at ambient conditions, paving the way for further experimental validation and development [58].

The study by Abghoui et al. investigated the catalytic potential of transition metal sulfides (TMSs) for electrochemical nitrogen reduction reaction (NRR) to ammonia under ambient conditions. Using DFT calculations, the authors evaluated the performance of 18 different TMSs, including YS, ScS, ZrS, TiS, VS, CrS, NbS, NiS, FeS, MnS_2 , CoS_2 , IrS_2 , CuS_2 , OsS_2 , FeS_2 , RuS_2 , RhS_2 , and NiS_2 , in various crystal structures and facets. Their study focused on both associative and dissociative mechanisms, analyzing the adsorption free energies of key intermediates like NNH and H to determine their selectivity for NRR over hydrogen evolution reaction (HER). RuS_2 was identified as the most active sulfide for the associative mechanism with an overpotential of around 0.3 V, while TiS, VS, NbS, and CrS showed promise for both mechanisms, with overpotentials ranging from 0.7 to 1.1 V. The results highlight the importance of material selection and the potential of TMSs in providing efficient and sustainable pathways for ammonia synthesis, potentially mimicking the natural enzymatic process. Their study underscores the need for further experimental validation and optimization of these materials to enhance their catalytic performance for industrial applications [59].

In a study by Kitano et al., the electrochemical reduction of nitrogen to ammonia at ambient conditions on mononitrides of Zr, Nb, Cr, and V was investigated using DFT. Their study revealed that ZrN, NbN, CrN, and VN possess significant potential for catalyzing the nitrogen reduction reaction (NRR) due to their ability to stabilize intermediate species and facilitate the dissociation of nitrogen. The catalytic activities of these nitrides were evaluated based on their electronic properties, surface adsorption energies, and reaction pathways. The findings suggested that these materials could lower the energy barriers for nitrogen activation and the subsequent hydrogenation steps, making them promising candidates for ammonia synthesis under mild conditions. The theoretical insights provided by their study highlight the potential of transition metal nitrides as efficient and robust catalysts for electrochemical ammonia production at ambient conditions [60].

A study by Roy et al. demonstrated the efficacy of using dual active sites in bimetallic catalysts for ammonia synthesis under ambient pressure. Their research focused on Fe-based catalysts mixed with Ru, Co, and Ni, and these were synthesized using a mechanical milling method. The experimental results showed that Ru/Fe and Co/Fe catalysts significantly enhance ammonia synthesis at temperatures ranging from 400 °C to 550 °C,

with activation energies of $45.73 \text{ kJ mol}^{-1}$ and $46.38 \text{ kJ mol}^{-1}$, respectively. The kinetic studies revealed that the inclusion of Ru or Co to Fe shifts the rate-determining step to NH_x formation, which is facilitated by the electron donation from Fe to the co-catalysts. Their study highlighted the potential of bimetallic catalysts to operate efficiently under mild conditions, providing a promising approach for energy-efficient ammonia production [61].

The study by Araia et al. investigated the effects of metal loading and support particle size on the performance of Cs-promoted Ru catalysts supported on cerium oxide (CeO_2) for microwave-assisted ammonia synthesis at ambient pressure. Their research demonstrates that smaller CeO_2 support sizes (25 nm) result in higher ammonia production rates due to better dispersion and smaller Ru particle sizes, leading to more active sites. In contrast, larger support sizes (5 μm) exhibit lower activity. Their study also shows that increasing Ru loading enhances ammonia synthesis up to a point, after which the activity plateaus due to particle agglomeration. The findings highlight the potential of microwave-assisted synthesis to lower reaction temperatures and pressures, providing a more energy-efficient alternative to traditional methods [62].

The study by Goto et al. investigates the potential of anti-perovskite nitrides (Co_3ZnN , Ni_3ZnN , Co_3InN , and Ni_3InN) as nitrogen storage materials for chemical looping ammonia production. These nitrides were synthesized via ammonolysis of their respective precursor oxides and subsequently evaluated for their ammonia production capabilities under hydrogen. The findings revealed that all the nitrides produced significant amounts of ammonia, with Ni_3ZnN demonstrating the highest production rate. Their study highlighted that Ni-containing nitrides exhibited higher ammonia production rates compared to Co-containing nitrides, and this was likely due to the formation of intermediate phases (Ni_3ZnN_x and Ni_3InN_y) during the reaction, which facilitated the release of lattice nitrogen. This work emphasizes the potential of anti-perovskite nitrides in developing sustainable and efficient ammonia synthesis processes through chemical looping [63].

1.4. Photocatalytic and Plasma-Assisted Methods for Ammonia Synthesis

Photocatalytic and plasma-assisted methods for ammonia synthesis have garnered significant interest due to their potential to offer more sustainable and efficient alternatives to traditional thermal processes. These methods leverage unique mechanisms and advanced materials to enhance the ammonia production process. Photocatalytic ammonia synthesis utilizes light energy to drive the reduction of nitrogen to ammonia. This method often employs semiconducting materials that can absorb photons and generate electron–hole pairs, which then participate in the reduction and oxidation reactions necessary for ammonia formation. In this mechanism, nitrogen molecules adsorb onto the photocatalyst surface and the generated electron–hole pairs facilitate the breaking of the strong $\text{N}\equiv\text{N}$ bond, allowing for subsequent hydrogenation steps that lead to ammonia production. Various photocatalytic materials, such as titanium dioxide (TiO_2) and modified forms like doped TiO_2 , have been studied for their effectiveness in harnessing solar energy to drive these reactions. Recent research has focused on enhancing the performance of these materials by extending their absorption range into the visible light spectrum and improving charge separation efficiency [49].

On the other hand, plasma-assisted methods use non-thermal plasma to activate nitrogen and hydrogen molecules, facilitating their reaction to form ammonia at lower temperatures and pressures compared to the Haber–Bosch process. Non-thermal plasma provides a high-energy environment where electrons are energized to much higher temperatures than gas molecules, allowing the activation of nitrogen and hydrogen through collisions with energetic electrons. In these methods, nitrogen and hydrogen gases are introduced into a plasma reactor where they are exposed to an electric field, creating a highly reactive environment. The high-energy electrons in the plasma dissociate nitrogen molecules into reactive nitrogen atoms, which then react with hydrogen atoms to form ammonia. Studies have demonstrated that the synergy between plasma and catalysts can significantly improve reaction rates and reduce energy consumption. For instance,

microwave-assisted ammonia synthesis using a Cs-Ru/CeO₂ catalyst at ambient pressure has shown enhanced activity due to the improved dispersion of Ru particles and increased oxygen vacancies on the cerium oxide support [60,64].

The performance of Cs-Ru/CeO₂ catalysts under various temperatures and conditions for ammonia production is shown in Figure 5. Panel (a) shows the ammonia production rate at lower temperatures (260 °C to 360 °C), illustrating the efficiency of the catalyst at moderate conditions. Panel (b) extends this temperature range up to 500 °C, highlighting how the catalyst performs under higher temperatures. Panel (c) depicts the ammonia production rate over time at specific temperatures, demonstrating the catalyst's stability and activity over prolonged operation.

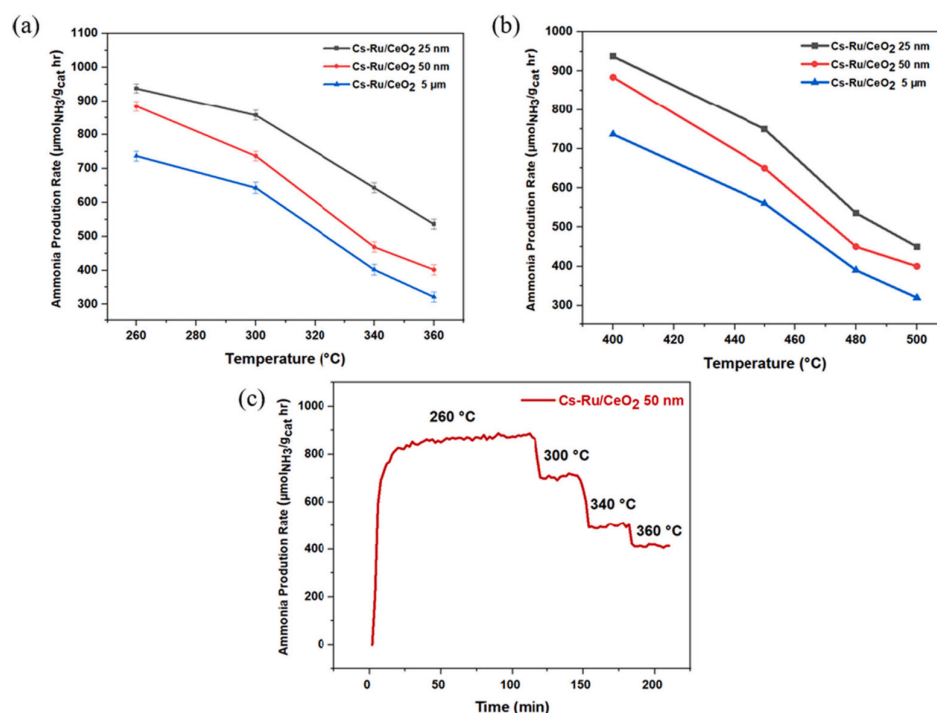


Figure 5. Performance of the Cs-Ru/CeO₂ catalysts under various temperatures and conditions for ammonia production. Reproduced with permission from Ref. [62].

Case studies and real-world applications of these methods have demonstrated their feasibility and potential benefits. Perovskite oxynitride-hydrides like BaCeO_{3-x}N_yH_z have been shown to be efficient catalysts for ammonia synthesis, operating through unique lattice N³⁻ and H⁻ ion-mediated mechanisms [60]. Additionally, microwave-assisted ammonia synthesis over Cs-Ru/CeO₂ catalysts has demonstrated significant ammonia production rates, highlighting the potential of these methods in replacing traditional ammonia synthesis processes [64]. Recent studies have also provided insights into the mechanisms and optimization strategies for these advanced catalytic systems, further underscoring their promise in achieving sustainable and efficient ammonia synthesis.

Recently there has been interest in making ammonia synthesis more sustainable with the use of solar energy as the driving force for the synthesis of ammonia [65].

Photocatalytic and plasma-assisted methods for ammonia synthesis have garnered significant interest due to their potential to offer more sustainable and efficient alternatives to traditional thermal processes. These methods leverage unique mechanisms and advanced materials to enhance the ammonia production process.

Photocatalytic ammonia synthesis utilizes light energy to drive the reduction of nitrogen to ammonia. This method employs semiconducting materials that can absorb photons and generate electron-hole pairs, which then participate in the reduction and oxidation reactions necessary for ammonia formation. The general mechanism involves the absorption

of light by the photocatalyst, leading to the excitation of electrons from the valence band to the conduction band, thus leaving behind holes in the valence band. The excited electrons can reduce nitrogen (N_2) to ammonia (NH_3), while the holes can oxidize water or other sacrificial agents [49].

Key advancements in photocatalytic ammonia synthesis have focused on developing efficient photocatalysts that can effectively absorb light and generate reactive species. Titanium dioxide (TiO_2) has been extensively studied due to its strong oxidizing power, chemical stability, and low cost. However, TiO_2 requires UV light for activation, which limits its practical application under sunlight. Modifications, such as doping with other elements or coupling with other semiconductors, have been employed to enhance its activity under visible light. For instance, modifications to traditional photocatalysts like TiO_2 and $g-C_3N_4$ have shown improved performance by extending their absorption range and enhancing charge separation efficiency [36,49].

Other semiconductor materials such as metal oxynitrides and nitrides have also been explored for their potential in photocatalytic ammonia synthesis. Perovskite oxynitride-hydrides like $BaCeO_{3-x}N_yH_z$ have shown promise as efficient catalysts. Kitano et al. reported that these materials could effectively utilize light to activate nitrogen molecules, leading to efficient ammonia synthesis under mild conditions. This process involves a Mars–van Krevelen mechanism where lattice N^{3-} and H^- ions are activated [60].

Photocatalytic processes involve three main steps: light absorption, charge separation, and surface reactions. The photocatalyst absorbs light, generating excited electrons and holes. The efficient separation of these charges is essential to prevent recombination. The separated charges then participate in redox reactions on the catalyst surface, leading to nitrogen reduction and ammonia formation. Photocatalytic ammonia synthesis generally follows associative or dissociative pathways. The associative pathway involves the stepwise hydrogenation of nitrogen molecules to form intermediates like hydrazine, which further reduce to ammonia. The dissociative pathway involves the initial dissociation of nitrogen molecules into nitrogen atoms, which are then hydrogenated to form ammonia.

Despite the potential, the efficiencies of these photocatalysts are still low due to their low photon utilization rate and the easy combination of excited electron–hole pairs. Further advancements in material design and synthesis are essential to improve the photocatalytic efficiency for large-scale applications [36,40].

Plasma-assisted methods use non-thermal plasma to activate nitrogen and hydrogen molecules, facilitating their reaction to form ammonia at lower temperatures and pressures compared to the Haber–Bosch process. Non-thermal plasma provides a high-energy environment where electrons are energized to much higher temperatures than the gas molecules, allowing the activation of nitrogen and hydrogen through collisions with energetic electrons [60].

In these methods, nitrogen and hydrogen gases are introduced into a plasma reactor where they are exposed to an electric field, creating a highly reactive environment. The high-energy electrons in the plasma dissociate nitrogen molecules into reactive nitrogen atoms, which then react with hydrogen atoms to form ammonia. Studies have demonstrated that the synergy between plasma and catalysts can significantly improve reaction rates and reduce energy consumption. For instance, microwave-assisted ammonia synthesis using a Cs-Ru/ CeO_2 catalyst at ambient pressure has shown enhanced activity due to the improved dispersion of Ru particles and increased oxygen vacancies on the cerium oxide support [40].

Microwave-assisted ammonia synthesis over Cs-Ru/ CeO_2 catalysts has demonstrated significant ammonia production rates, highlighting the potential for these methods to replace traditional ammonia synthesis processes [64]. Recent studies have also provided insights into the mechanisms and optimization strategies for these advanced catalytic systems, further underscoring their promise in achieving sustainable and efficient ammonia synthesis.

1.5. Single-Atom and Cluster Catalysts for Ammonia Synthesis

Single-atom and cluster catalysts have emerged as promising candidates for ammonia synthesis due to their unique electronic structures and high surface-to-volume ratios. These catalysts offer distinct advantages, including maximized atom efficiency and tunable electronic properties, which are crucial for the activation of nitrogen molecules and the subsequent synthesis of ammonia.

Single-atom catalysts (SACs) consist of isolated metal atoms dispersed on a support material. These catalysts exhibit unique properties that are different from their bulk counterparts. The isolated metal atoms in SACs provide uniform active sites, which can enhance the selectivity and efficiency of the catalytic process. Additionally, the strong metal–support interactions in SACs can significantly modify the electronic properties of the metal atoms, thereby influencing their catalytic activity.

Recent studies have demonstrated the potential of SACs in ammonia synthesis. For example, single-atom ruthenium (Ru) catalysts supported on carbon or metal oxides have shown remarkable activity for ammonia synthesis at relatively low temperatures and pressures. The isolated Ru atoms provide highly active sites for nitrogen activation, while the support material helps in stabilizing the active sites and facilitating electron transfer processes. This combination of factors results in improved catalytic performance compared to conventional catalysts [49,60].

In Figure 6, we show the comparative analysis of the ammonia synthesis rates and turnover frequencies (TOF) for different catalysts, including Ru single-atom catalysts (SNCs) and Ru nanoparticles (NPs). Panel (a) shows the NH_3 synthesis rate for different catalyst systems, indicating that 0.5Ru-SNCs outperform the others. Panel (b) highlights the turnover frequency (TOFRu), demonstrating that the single-atom catalysts (SNCs) have a higher TOF than nanoparticles. Panel (c) examines the NH_3 synthesis rate at different pressures, with higher pressures leading to better performance. Panel (d) shows the stability of 0.5Ru-SNCs over time, emphasizing its durability during long-term reactions.

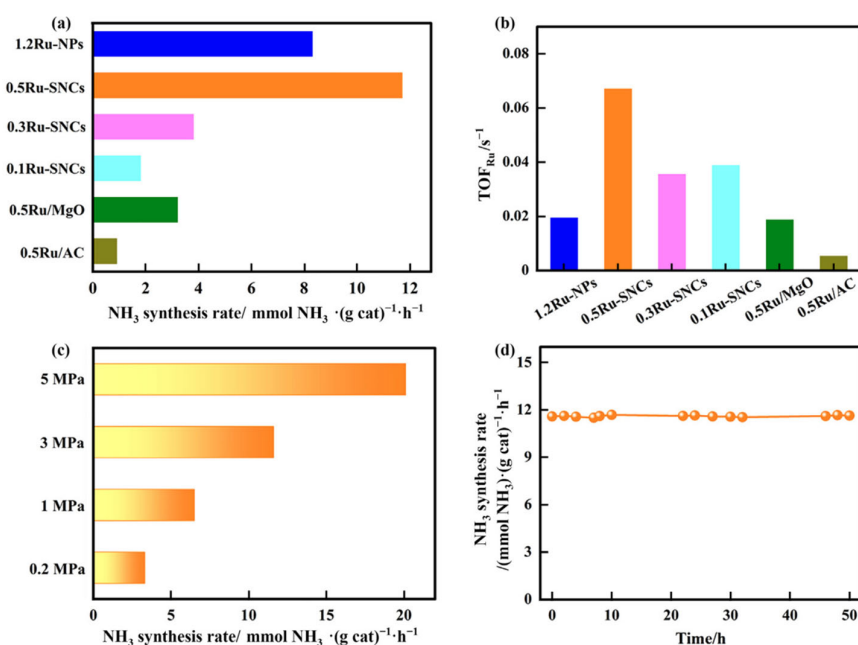


Figure 6. Graph showing the ammonia synthesis rates and turnover frequencies (TOF) over different catalysts reproduced with permission from Ref. [66].

Cluster catalysts, which consist of small aggregates of metal atoms, also show significant promise for ammonia synthesis. These clusters possess unique geometric and electronic structures that can enhance their catalytic activity. The small size of the clusters

provides a high density of active sites, while the electronic interactions between the metal atoms in the cluster can facilitate the activation of nitrogen molecules.

One notable example is the use of iron (Fe) and cobalt (Co) clusters for ammonia synthesis. These metal clusters have been shown to effectively activate nitrogen and hydrogen molecules, leading to the formation of ammonia. The catalytic activity of these clusters is influenced by their size, composition, and support material. Studies have shown that optimizing these parameters can lead to significant improvements in catalytic performance [36,40].

The mechanisms underlying the catalytic activity of single-atom and cluster catalysts for ammonia synthesis involve several key steps. The first step is the adsorption of nitrogen molecules onto the active sites of the catalyst. This is followed by the activation and dissociation of the nitrogen molecules into reactive nitrogen atoms. The dissociated nitrogen atoms then react with hydrogen atoms to form ammonia. The efficiency of these steps is highly dependent on the electronic structure of the catalyst, which can be tuned by adjusting the size, composition, and support material of the catalyst [67].

For single-atom catalysts, the strong metal–support interactions play a crucial role in modulating the electronic properties of the isolated metal atoms. These interactions can facilitate the transfer of electrons to the nitrogen molecules, thereby enhancing their activation. For cluster catalysts, the electronic interactions between the metal atoms in the cluster can create a highly reactive environment that promotes the dissociation of nitrogen molecules and the subsequent formation of ammonia [36,60].

Despite the promising results, several challenges need to be addressed to fully realize the potential of single-atom and cluster catalysts for ammonia synthesis. One major challenge is the stability of these catalysts under reaction conditions. The isolated metal atoms in SACs and small metal clusters can be prone to agglomeration, which can lead to a loss of catalytic activity. Developing strategies to stabilize these catalysts, such as using strong metal–support interactions or encapsulating the metal atoms or clusters in a protective matrix, is crucial for enhancing their stability.

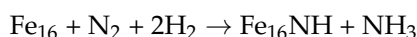
Another challenge is the scalability of these catalysts for industrial applications. While single-atom and cluster catalysts have shown excellent performance in laboratory-scale studies, scaling up these catalysts for large-scale ammonia production requires a careful consideration of factors such as catalyst synthesis, reactor design, and process optimization. Future research should focus on developing new materials and strategies to address these challenges. This includes designing support materials that can provide strong stabilization for the isolated metal atoms or clusters, optimizing the size and composition of the clusters to maximize their catalytic activity, and exploring new synthesis methods to produce these catalysts on a large scale. Additionally, gaining a deeper understanding of the mechanisms underlying the catalytic activity of these catalysts through advanced characterization techniques and theoretical studies will be crucial for guiding the design of more efficient catalysts.

Single-atom and cluster catalysts offer a promising approach for ammonia synthesis, with the potential to achieve high catalytic efficiency and selectivity. By addressing the challenges associated with stability and scalability, and by continuing to advance our understanding of their catalytic mechanisms, these catalysts could play a significant role in the development of sustainable and efficient ammonia synthesis technologies [64].

A study by Liu et al. explored a novel Fe₃ single-cluster catalyst anchored on the θ -Al₂O₃(010) surface for ammonia synthesis. Unlike the traditional Haber–Bosch process that relies on the dissociative mechanism, this catalyst employs an associative mechanism where adsorbed N₂ is first hydrogenated to form NNH before dissociating. This process significantly reduces the N–N bond dissociation barrier, enhancing the turnover frequency (TOF) for ammonia production. The large-spin polarization and low-oxidation state of the iron cluster play crucial roles in N₂ activation. Microkinetic simulations indicate that the calculated TOF for the Fe₃/ θ -Al₂O₃(010) catalyst is comparable to that of the Ru B5 site, which is known for its high catalytic activity. This innovative approach demonstrates the

potential for ammonia synthesis under milder conditions, bypassing the limitations of the Brønsted–Evans–Polanyi (BEP) relation and bridging the gap between heterogeneous and homogeneous catalysis [68].

The work by Gutsev et al. explored the catalytic formation of ammonia on a 16-atom iron nanocluster (Fe_{16}) using DFT with a generalized gradient approximation and an all-electron basis set. Their research delved into both the associative and dissociative pathways for N_2 attachment to the Fe_{16} cluster and examined the subsequent steps leading to ammonia formation. The findings indicate that the reaction



is exothermic by 1.02 eV. Their study also identified two mechanisms for NH_3 detachment, noting that spin fluctuations play a significant role in the bond formation and rupture processes on the catalyst surface. The detailed computational analysis provided valuable insights into the fundamental processes of nitrogen reduction on iron nanoclusters, which could contribute to the development of more efficient catalysts for ammonia synthesis [69].

In their study, Fuller et al. explored the potential of discovering significantly improved ammonia synthesis catalysts through a hierarchical high-throughput approach. This method involves a combination of machine learning, high-throughput experimentation, and catalyst optimization techniques. By systematically screening a vast array of catalyst compositions and process conditions, the researchers aim to identify promising candidates that outperform conventional catalysts. Their approach led to the discovery of catalysts that exhibited higher activity and stability under milder conditions, highlighting the importance of integrating advanced computational and experimental methods in catalyst development [70].

The study conducted by Kamiguchi et al. presented a novel approach for efficient ammonia synthesis using Angstrom-sized molybdenum (Mo) clusters supported on HY-zeolite. These clusters, prepared by the impregnation of a molybdenum halide cluster complex with an octahedral Mo_6 metal core, retain their small size (approximately 7 Å) after the removal of halide ligands through hydrogen activation. This innovative method allows for effective N_2 activation and continuous ammonia synthesis at relatively mild conditions of 200 °C and 5.0 MPa. The catalytic activity of these clusters is attributed to the cooperation of multiple Mo sites, which promotes $\text{N}\equiv\text{N}$ bond cleavage and efficient ammonia synthesis. Their study highlighted the stability of these clusters during the synthesis process and the significant reduction in energy barriers for N-H bond formation when compared to conventional catalysts. Their research demonstrated the potential of ultra-small Mo clusters in achieving efficient and sustainable ammonia production [71].

The study by Cao et al. explored ammonia synthesis via an associative mechanism on the alkaline earth metal sites of $\text{Ca}_3\text{CrN}_3\text{H}$. The authors demonstrated that the nitride hydride compound $\text{Ca}_3\text{CrN}_3\text{H}$ exhibited robust ammonia synthesis activity. This compound activates dinitrogen through active sites where calcium provides the primary coordination environment. DFT calculations revealed that an associative mechanism is favorable for this catalyst, and it is distinct from the dissociative mechanism typically found in traditional Ru or Fe catalysts. Their study highlighted the potential of alkaline earth metal hydride catalysts and related 1D hydride/electrides for ammonia synthesis, emphasizing the significant role of calcium in the catalytic process. Their research emphasized the importance of considering alternative active sites, such as alkaline earth metals, for developing efficient catalysts for ammonia synthesis, potentially paving the way for more sustainable and effective catalytic processes [72].

The study by Zhou et al. reported the development of subnanometer Ru clusters (0.8 nm) anchored on hollow N-doped carbon spheres (Ru-SNCs) as a highly efficient catalyst for ammonia synthesis under mild conditions via an associative route. The Ru-SNCs catalyst exhibited a superior ammonia synthesis rate of $11.7 \text{ mmol of NH}_3 \cdot \text{g cat}^{-1} \cdot \text{h}^{-1}$ at 400 °C and 3 MPa, outperforming traditional Ru nanoparticle catalysts. Characterization techniques, including UV-vis absorption spectroscopy and in situ DRIFTS, identified

N_2H_4 species as the main intermediates, confirming the associative mechanism, which bypasses the direct dissociation of N_2 . Their work demonstrates the potential of Ru-SNCs catalysts in achieving efficient ammonia synthesis at reduced energy consumption and lower CO_2 emissions, aligning with the goals of sustainable and carbon-neutral chemical processes [66].

In their study, Lu et al. presented a significant advancement in the development of lanthanum-nitride-based catalysts for ammonia synthesis. Their research emphasized the creation of chemically durable catalysts using nickel and cobalt that were incorporated into a lanthanum nitride (LaN) matrix. These catalysts demonstrated remarkable activity and stability under harsh reaction conditions, which are essential for efficient ammonia production. Their study showed that the LaN-supported nickel and cobalt catalysts exhibit enhanced catalytic performance due to the strong interaction between the metal atoms and the lanthanum nitride support. This interaction facilitates the activation and cleavage of nitrogen molecules, which is a critical step in the ammonia synthesis process. The durability of these catalysts under reaction conditions suggests their potential for long-term industrial applications, reducing the frequency of catalyst replacement and thereby improving the overall efficiency and cost-effectiveness of the ammonia synthesis process [73].

The study by Fang et al. presented theoretical insights into the thermal reduction of N_2 to NH_3 over single metal atoms incorporated into nitrogen-doped graphene. Using DFT calculations, their study investigated the reaction mechanisms and catalytic activities of different metal atoms in N-doped graphene. Their findings reveal that the catalytic activity is significantly influenced by the type of metal atom and its coordination environment. Specifically, CoN_4^- and FeN_4^- -embedded graphene sheets, where the metal atom is fourfold-coordinated, are inactive for N_2TR due to the poor stability of adsorbed H_2 and N_2 molecules. In contrast, CoN_3/G and FeN_3/G , where the metal atom is threefold coordinated, show catalytic activity for N_2TR , facilitating ammonia synthesis through an associative mechanism. Their study identified the formation of an NHNH^* intermediate as a crucial step in the reaction pathway. Further analysis showed that FeN_3/G exhibits superior catalytic activity compared to CoN_3/G , and this was attributed to its preference for a high spin-polarized state during the N_2TR process. Their research provided valuable theoretical insights into the design and development of graphene-based single-atom catalysts with high activity for ammonia synthesis through N_2 thermal reduction [74].

1.6. In Situ and Operando Methods for Ammonia Synthesis

The use of in situ and operando methods is vital for understanding the dynamic processes and mechanisms occurring on the surface of catalysts during ammonia synthesis. These advanced techniques enable the real-time monitoring of structural, electronic, and chemical changes, providing insights that are critical for the development of more efficient and robust catalysts, i.e., insights that are not accessible through ex situ techniques.

In their study, Laassiri et al. employed a combination of in situ neutron diffraction, isotopic exchange reactions, and DFT calculations to investigate the role of lithium dopant in enhancing the reactivity of manganese nitride ($\text{Mn}_6\text{N}_{5+x}$) for ammonia synthesis. The in situ neutron diffraction studies revealed that lithium doping significantly reduces the nitrogen vacancy formation energy (NVFE), which enhances nitrogen mobility and reactivity. The structural modifications facilitated by lithium doping allowed for the formation of ammonia at lower temperatures (300 °C) compared to undoped manganese nitride, which remained stable and inactive under similar conditions. Isotopic exchange experiments demonstrated that lithium enhances both nitrogen and hydrogen activation, resulting in higher reactivity for ammonia synthesis. DFT calculations supported these findings, indicating that lithium doping increases the number of active sites for nitrogen adsorption and activation. This comprehensive approach underscores the importance of dopant incorporation in optimizing the performance of nitride materials for ammonia synthesis, providing valuable insights for developing more efficient catalysts [75].

Similarly, the study by Hanifpour et al. employed a comprehensive set of in situ and operando techniques to investigate the electrochemical nitrogen reduction reaction (NRR) on transition metal nitride (TMN) thin films, specifically VN, CrN, NbN, and ZrN, under ambient conditions. Using a micro-reactor flow-cell setup, they combined chronoamperometry with flow-injection analysis for ammonia detection, achieving a detection limit as low as 1 ppb. Their study demonstrated that ZrN showed promising catalytic behavior, with higher reaction rates and current efficiencies in the presence of N_2 compared to Ar, indicating its potential for NRR. In contrast, VN and NbN produced ammonia initially by reacting to the nitrides of their surface layers but became inactive thereafter. CrN did not produce any detectable ammonia under the experimental conditions. The integration of electrochemical impedance spectroscopy (EIS), X-ray reflectivity (XRR), and X-ray photoelectron spectroscopy (XPS) provided detailed insights into the stability and surface characteristics of the TMNs, highlighting the critical role of nitrogen vacancies and surface dynamics in catalytic performance [39].

In Figure 7, we show a comparison of the ammonia synthesis rates for various catalysts, including 5% Ni_2Mo_3N/SiO_2 , 5% $Os_3(CO)_{12}/SiO_2$ hydroxylated, 5% Ru/Al_2O_3 , 10% $CoRe/MgO$, and 5% $Ru/Al_2O_3 + 1\% KOH$. The figure highlights the substantial performance boost achieved with KOH promotion, demonstrating how catalyst enhancement can significantly improve synthesis rates, thus leading to more energy-efficient and economically viable ammonia production.

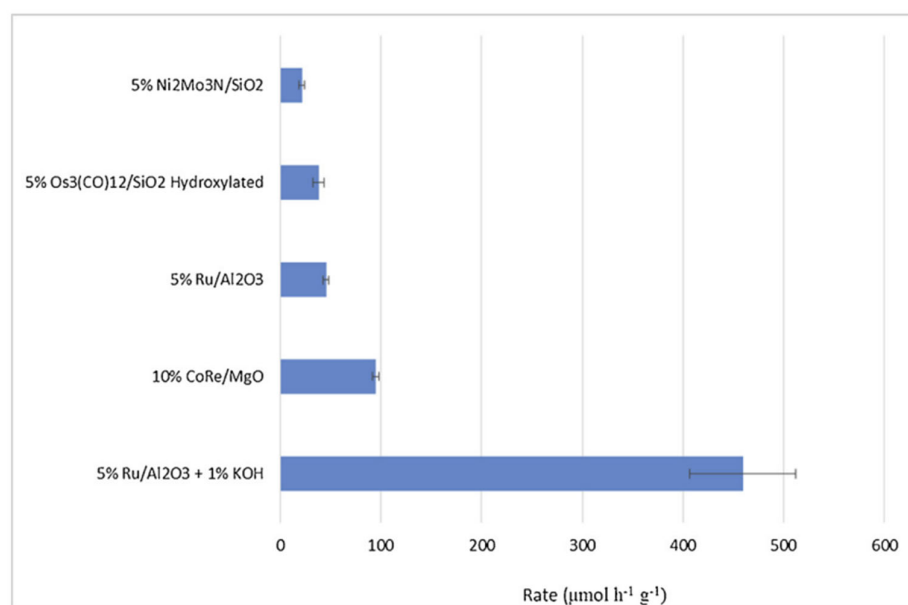


Figure 7. Comparison of the ammonia synthesis rate over various catalysts. Reproduced with permission from Ref. [76].

These studies exemplify how in situ and operando techniques provide a detailed characterization of catalytic processes and enable the identification of active sites and intermediates. This approach is essential for developing highly efficient and robust catalysts capable of operating under mild conditions, advancing the field of ammonia synthesis. By integrating experimental observations with computational predictions, researchers can gain a comprehensive understanding of the catalytic processes, thereby paving the way for the design of more effective and durable catalysts.

1.7. Improving the Process Conditions of Ammonia Synthesis

Ammonia production is one of the most energy-intensive chemical processes, consuming approximately 1–2% of the world's energy production. The main operating cost influencing the price of ammonia is the cost of hydrogen, which constitutes about 70%

of the total cost according to the U.S. Department of Energy. Moreover, 3% of global anthropogenic CO₂ emissions are attributed to steam methane reforming: a major route for hydrogen production in ammonia synthesis [77].

Several strategies have been proposed to improve ammonia synthesis rates, including operating reactors under unsteady-state conditions and the decrease in the hydrogen partial pressure in the feed. Studies have shown that higher ammonia synthesis rates can be achieved with lower H₂:N₂ ratios than the stoichiometric 3:1 ratio. For instance, unsteady-state reactor operation has been suggested for various types of ammonia synthesis catalysts, with rate improvements observed under cyclic operation conditions depending on the catalyst type. Additionally, the absorption of synthesized ammonia on supported absorbents, such as MgCl₂ on zeolite-Y, has been studied to enhance ammonia separation, reducing the need for high-pressure condensers [77].

Co₃Mo₃N catalysts have shown potential as nitrogen-transfer reagents, with significant ammonia synthesis rates observed at 300–400 °C and at atmospheric pressure. Kojima and Aika reported an ammonia synthesis rate expression for Co₃Mo₃N at 400 °C and 31 bar pressure based on power law kinetics. This expression reflects the positive dependency of the reaction rate on the reactants and the poisoning effect of the product [77].

Simulations have been performed to evaluate the effect of lower H₂:N₂ ratios on both the investment and operating costs of the ammonia synthesis process. An ammonia synthesis loop consisting of a packed-bed reactor, a flash column, a compressor, and auxiliary units was devised and operated isothermally at 673 K and 100 bar pressure with different H₂:N₂ ratios (3:1 and 1:1). The simulations indicated that operating with a lower H₂ ratio could reduce the reactor volume, compressor duties, and capacities while maintaining constant ammonia production [77].

Improving the process conditions for ammonia synthesis is critical for enhancing the efficiency and sustainability of this essential industrial process. The study by Daisley et al. presented an empirical screening of various supported catalysts for ammonia synthesis, highlighting the impact of different process conditions on catalytic performance. Their research explored the performance of catalysts such as Ru/Al₂O₃, Os₃(CO)₁₂/SiO₂, CoRe/MgO, and Ni₂Mo₃N/SiO₂ under varying temperatures and pressures. Among these, Ru/Al₂O₃ exhibited the highest activity, particularly when promoted with potassium (K⁺), which enhances electron density on the Ru surface, thereby improving catalytic activity. Their study emphasizes the role of alkali metal promoters in enhancing the performance of Ru-based catalysts.

Operating conditions such as temperature and pressure significantly influence the activity of ammonia synthesis catalysts. Their study found that increasing the reaction temperature from 400 °C to 500 °C generally increased the activity of most catalysts, although the thermodynamic favorability of ammonia synthesis decreases with rising temperature. For example, the ammonia synthesis activity of supported Os-based materials was prominent at 500 °C, with the supported Os₃(CO)₁₂ catalysts demonstrating significant activity that was comparable to Ru-based systems.

In Figure 8, the ammonia synthesis rates of various supported catalysts, including 10% CoRe/MgO, 5% Ru/Al₂O₃, 5% Os₃(CO)₁₂/SiO₂, and other modified versions with KOH and hydroxylation, are shown. The data highlight how catalyst modifications, such as the addition of KOH to Ru/Al₂O₃ and CoRe/MgO, lead to significant improvements in ammonia synthesis rates. This figure emphasizes the importance of optimizing catalyst compositions and reaction conditions to achieve higher synthesis efficiency.

The use of different supports also plays a crucial role in catalyst performance. For instance, CoRe supported on MgO showed enhanced activity due to the basic nature of the support, which helps mitigate hydrogen inhibition and stabilize active phases. This highlights the importance of support selection in optimizing catalyst performance for ammonia synthesis.

Additionally, this study discussed the potential of ternary nitrides such as Ni₂Mo₃N/SiO₂. These materials offer high catalytic activity due to their unique structural properties and the

presence of multiple active sites, which facilitate nitrogen adsorption and activation. The empirical screening conducted by Daisley et al. provided valuable insights into the structure–activity relationships of various catalysts, guiding further development and optimization of ammonia synthesis processes.

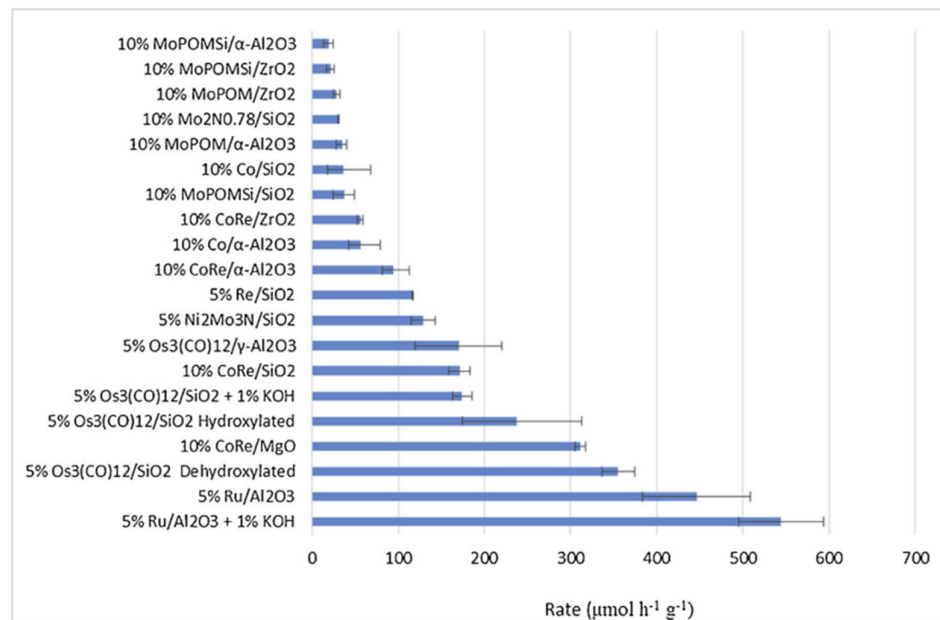


Figure 8. Ammonia synthesis rates of the various supported catalysts. Reproduced with permission from Ref. [76].

In conclusion, the improvement of process conditions for ammonia synthesis involves optimizing catalyst composition, operating the temperature, pressure, and use of promoters and supports. These strategies collectively enhance the efficiency and sustainability of ammonia production, making it more viable for industrial applications [76,77].

Recent research has highlighted the potential of manganese nitride-based materials as nitrogen-transfer reagents for nitrogen chemical looping in ammonia production. The study by Laassiri et al. systematically investigated the reactivity of lattice nitrogen in various manganese nitride systems, such as Fe-Mn-N, Co-Mn-N, K-Mn-N, and Li-Mn-N, for ammonia synthesis. Among these, Li-Mn-N exhibited the highest reactivity, converting up to 15.8% of the total available lattice nitrogen into ammonia at 400 °C. The enhanced reactivity was attributed to the role of lithium in facilitating nitrogen mobility and reactivity at lower temperatures. Their research also indicated that, while Fe, Co, and K dopants did not significantly improve nitrogen reactivity, the incorporation of lithium drastically improved performance, making Li-Mn-N a promising candidate for ammonia synthesis under mild conditions. Additionally, their study underscored the importance of lattice nitrogen mobility and the potential benefits of using manganese nitride materials in developing more efficient and sustainable ammonia synthesis processes [34].

In their study, Laassiri et al. investigated the nitrogen-transfer properties of tantalum nitride-based materials, specifically focusing on the role of doping with transition metals such as Re, Fe, and Co. The researchers prepared various Ta_{3-x}M_xN_y (M = Re, Fe, and Co; x = 0, 0.25, 0.5, and 1) materials with different microstructural features through high-temperature ammonolysis and soft chemistry-synthesis techniques. They found that the nitrogen reactivity of tantalum nitride is predominantly influenced by the chemical composition and the nature of the transition metal dopant rather than the microstructural properties. Doping with low levels of Co significantly enhanced the reactivity at lower temperatures, making it the most effective dopant among those tested. The improved reactivity was attributed to the increased nitrogen mobility within the tantalum nitride lattice, which operates through a Mars–van Krevelen mechanism. That study highlighted

the potential of doping tantalum nitride with transition metals to develop highly active nitrogen-transfer materials for ammonia synthesis under milder conditions [78].

The work by Qian et al. investigated the dynamic evolution of the $\text{Co}_3\text{Mo}_3\text{N}$ bimetallic nitride surface during ammonia synthesis. Using a combination of ab initio thermodynamics and temperature-programmed experiments, the authors demonstrated that the $\text{Co}_3\text{Mo}_3\text{N}$ catalyst adjusts its surface states in response to various reaction conditions. Their study revealed that hydrogenated surfaces and subsurface defects are more thermodynamically stable than clean surfaces under typical ammonia synthesis conditions. This surface evolution significantly impacts the electronic structure and reaction performance of the catalyst. The presence of surface hydrogen inhibits nitrogen dissociation but does not affect lattice nitrogen hydrogenation, while subsurface nitrogen defects modulate the charge of molybdenum species, influencing the dissociation process. These insights into the realistic surface states are crucial for understanding reaction mechanisms and designing high-performance nitride catalysts [79].

The study by Brown et al. presented the first evidence of ammonia synthesis via the bulk diffusion in cobalt molybdenum (CoMo) particles during a chemical looping ammonia synthesis (CLAS) process. Their research demonstrated that CoMo bimetallics, when subjected to nitridation under pure N_2 gas, could produce ammonia without the presence of gaseous H_2 . This unexpected phenomenon suggests a dynamic surface interaction involving a shrinking core and counter-diffusion mechanism, where nitrogen diffuses inward and oxygen diffuses outward, stabilizing the core and forming HxMoO_3 . Their study utilized various characterization techniques, including X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and time on stream (TOS) experiments, to investigate the surface and bulk chemistry of CoMoO_4 particles. Their findings indicate that the ammonia synthesis in this system follows the Mars–van Krevelen mechanism, involving both surface and bulk nitrogen interactions and potentially providing new insights into ammonia synthesis and catalyst design [80].

In the study by Wang et al., the effects of the support and promoter on ruthenium (Ru) catalyst activity for microwave-assisted ammonia synthesis were investigated. Their research highlighted that cesium (Cs)-promoted Ru/CeO_2 catalysts exhibit considerable activity at 533 K and ambient pressure. The combined theoretical and experimental approaches demonstrated that the strong interaction between Ru and CeO_2 leads to the formation of highly dispersed Ru particles, which favor ammonia synthesis. The higher electron-donating ability of CeO_2 and the lower electronegativity of the Cs promoter result in a higher electron density on Ru, reducing the $\text{N}\equiv\text{N}$ dissociation barrier. That study underscored the potential of microwave-assisted catalytic processes in activating stable molecules for ammonia synthesis under mild conditions, providing a promising alternative to the energy-intensive Haber–Bosch process [81].

In the study by Wang et al., the ternary ruthenium complex hydrides Li_4RuH_6 and Ba_2RuH_6 were presented as efficient catalysts for the mild-condition ammonia synthesis from N_2 and H_2 . These catalysts differed significantly from traditional iron or ruthenium-based catalysts in terms of electronic, compositional, and structural properties, exhibiting remarkable catalytic performance under mild conditions. Their study demonstrated that the dynamic and synergistic involvement of the electron-rich $[\text{RuH}_6]^{4-}$ anionic centers, along with Li/Ba cations and hydridic hydrogen, facilitates an associative reaction mechanism with a narrow energy span. This results in superior ammonia production rates at temperatures below 373 K, outperforming existing conventional heterogeneous catalysts. Their findings provide valuable insights into catalyst designs for mild-condition ammonia synthesis, bridging the gap between heterogeneous and homogeneous nitrogen fixation at the molecular level [82].

Investigations by Fuller et al. explored the impact of alkali promoters on the activity and stability of ammonia synthesis catalysts. Alkali metals, such as potassium, cesium, and rubidium, were found to significantly enhance the catalytic performance by increasing the electron density on the active sites, thereby facilitating the nitrogen activation process. The

presence of these promoters alters the electronic environment of the catalysts, reducing the energy barriers for nitrogen dissociation and subsequent hydrogenation steps. This modification leads to higher turnover frequencies (TOF) and improved overall catalytic efficiency. Their research highlighted that the optimal choice and concentration of alkali promoters are crucial for maximizing the performance of ammonia synthesis catalysts, providing valuable insights into the design of more effective catalytic systems for industrial applications [83].

The study by Wang et al. investigated the use of a cobalt-based catalyst for ammonia synthesis under mild conditions. Their research focused on a nitrogen-anchored cobalt single-atom catalyst (Co-N-C) that demonstrates both dynamic and steady-state active sites. The Co-N-C catalyst exhibits a high ammonia synthesis rate of $116.35 \text{ mmol NH}_3 \text{ gCo}^{-1} \text{ h}^{-1}$, and this is facilitated by atomically dispersed cobalt coordinated with pyridine nitrogen, which reacts with surface hydrogen to produce ammonia via a chemical looping pathway. Pyrrolic nitrogen anchors the single cobalt atoms, forming $\text{Co}_1\text{-N}_{3.5}$, which aids in nitrogen adsorption and the step-by-step hydrogenation of nitrogen to ammonia. Their study emphasized that the dual active sites in Co-N-C allow for efficient NH_3 production by bypassing the N_2 dissociation bottleneck, making it feasible under milder conditions compared to traditional catalysts [84].

The work by Uner and co-workers examined the process economics of ammonia synthesis over $\text{Co}_3\text{Mo}_3\text{N}$ by optimizing the hydrogen-to-nitrogen (H_2) feed stoichiometry. Through the ammonia synthesis rate measurements at atmospheric pressure and 400°C , it was determined that the synthesis rate remains independent of the H_2 ratio for stoichiometries above 0.5:1. However, for ratios below 0.5:1, there is a linear dependency of the synthesis rate on the H_2 stoichiometry. Static measurements of hydrogen adsorption isotherms at various temperatures indicated that the $\text{Co}_3\text{Mo}_3\text{N}$ surface becomes saturated with strongly bound hydrogen at around 100 Torr, corresponding to an H_2 ratio of approximately 0.5:1. These findings confirm the significant role of strongly bound hydrogen in the ammonia synthesis process. Using these data, the researchers modified an existing kinetic expression to develop a conceptual design that incorporates a late mixing strategy for the hydrogen stream. The economic analysis of this design demonstrated that employing low hydrogen stoichiometries could reduce both investment and operating costs by a factor of two, highlighting the potential for more cost-effective ammonia production [77].

1.8. Enhancing Ammonia Synthesis Catalyst Activity

Recent advancements in the field of ammonia synthesis have focused on the catalytic potential of confined cobalt molybdenum nitride (CoMo-N) nanoparticles. A notable study by Sfeir et al. reported on the development of highly active CoMo-N catalysts that were supported on SBA-15, a mesoporous silica material known for its high surface area and thermal stability. This innovative approach leverages the dispersion of CoMo-N nanoparticles within SBA-15 to enhance their structural and textural properties, which are crucial for catalytic performance. Their research demonstrated that SBA-15-supported CoMo-N catalysts exhibited significantly higher catalytic activity compared to unsupported $\text{Co}_3\text{Mo}_3\text{N}$. Specifically, the CoMo-N/SBA-15 catalysts with 10, 20, and 30 wt% metal loadings achieved ammonia synthesis rates of 1714, 1429, and $810 \text{ } \mu\text{mol gactive phase}^{-1} \text{ h}^{-1}$, respectively, thus far surpassing the rate of $259 \text{ } \mu\text{mol g}_{\text{catalyst}}^{-1} \text{ h}^{-1}$ for the bulk $\text{Co}_3\text{Mo}_3\text{N}$ catalyst. This improvement was attributed to the increased surface area and enhanced dispersion of the active phase, which promoted better nitrogen activation and hydrogenation. Their study underscored the importance of nanoconfinement and structural optimization in designing efficient catalysts for sustainable ammonia production [85]. Recent studies have also demonstrated that the catalytic activity of molybdenum nitride (Mo-N) catalysts can be significantly influenced by the interaction between the molybdenum nanoparticles and their support material. The work by Sfeir et al. explored the catalytic performance of Mo-N catalysts supported on mesoporous silica (SBA-15) and titanium dioxide (TiO_2). Their research highlighted that SBA-15-supported Mo-N catalysts exhibit higher catalytic activity

for ammonia synthesis compared to those supported on TiO_2 . The superior performance of SBA-15-supported catalysts was attributed to the high dispersion of Mo nanoparticles within the SBA-15 matrix, which provides a high surface area and thermal stability. Conversely, Mo-N catalysts supported on TiO_2 showed poor catalytic activity and were prone to rapid deactivation due to strong metal–support interactions (SMSIs) that led to a charge transfer from the reducible support to the active phase. This charge transfer was confirmed by X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) analyses, which revealed changes in the oxidation states and electronic properties of the Mo species. Their study concluded that the nature of the support material played a crucial role in modulating the catalytic efficiency of Mo-N catalysts, with non-reducible supports like SBA-15 being more favorable for maintaining high activity and stability in ammonia synthesis. Switching the on/off molybdenum nitride catalytic activity in the ammonia synthesis through modulating metal–support interaction seems to be an efficient method for enhancing ammonia synthesis activity [86].

In the studies of Hosono and co-workers on the Co-Mo bimetallic nanoparticles prepared via sodium naphthalenide reduction, it was found that Co-Mo bimetallic nanoparticles (NPs) exhibit activity levels similar to Ru NPs [87]. These Co-Mo bimetallic NPs with various compositions were prepared on CeO_2 by sodium naphthalenide-driven reduction, which had a much higher activity than the monometallic Co/ CeO_2 and Mo/ CeO_2 catalysts. This suggests that the synthesis method of the catalyst can significantly affect the resulting activity for ammonia synthesis in the Co-Mo systems.

In another study by Abghoui et al., the potential of mononitrides as catalysts for nitrogen reduction to ammonia under ambient conditions was explored using DFT. Their research highlighted that transition metal nitrides (TMNs) such as ZrN, NbN, CrN, and VN show promise due to their ability to adsorb and activate N_2 molecules on their surfaces. Among these, ZrN exhibited the most favorable properties for N_2 adsorption and activation, with a lower energy barrier for nitrogen reduction, suggesting a higher catalytic activity for ammonia synthesis. Their study provided critical insights into the electronic and structural properties of these mononitrides, contributing to the understanding of how these materials can be optimized for efficient ammonia production under mild conditions [25].

In Figure 9, free-energy diagrams for the nitrogen reduction reaction (NRR) on transition metal nitride surfaces, including VN, ZrN, CrN, and NbN, are shown. The plots display the reaction pathways on different crystal facets (RS(100), RS(111), ZB(100), and ZB(110)), illustrating the energy barriers and reaction intermediates as nitrogen is reduced to ammonia. The figure highlights the rate-determining step (PDS) for each catalyst, demonstrating how various nitride surfaces influence the efficiency of the NRR process. These energy profiles emphasize the advantages of certain nitride catalysts in reducing energy barriers, contributing to more efficient ammonia synthesis under milder conditions.

The study conducted by Araia and co-workers explored the effects of carbon nanotubes (CNT) on a Cs–Ru/ CeO_2 catalyst for microwave-assisted ammonia synthesis. Their research demonstrated that a mechanical mixing of Cs–Ru/ CeO_2 with CNT significantly enhances catalytic activity when compared to chemically synthesized catalysts. Their study highlighted that the mechanically mixed catalyst achieved an ammonia production rate of $1822 \mu\text{mol NH}_3/\text{g}_{\text{cat}} \text{ h}$ at 260°C , outperforming the individual components and chemically synthesized mixtures. This improvement was attributed to the increased dielectric properties and electrical conductivity provided by the CNT, which enhance microwave heating and facilitate electron transfer. The synergistic effect between the CNT and Cs–Ru/ CeO_2 was also noted to improve interfacial polarization, further boosting catalytic performance. Their research suggests that the combination of Ru-based catalysts and the use of CNT as microwave susceptors can significantly optimize ammonia synthesis under milder conditions [88].

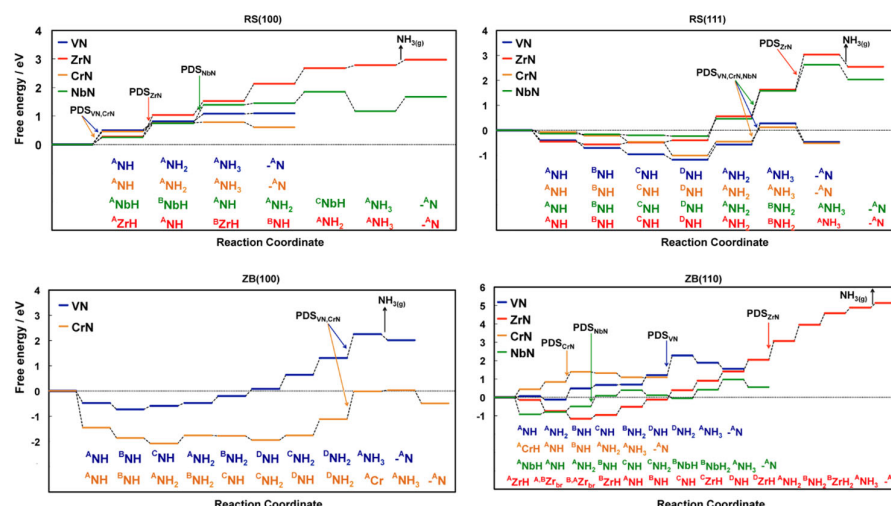


Figure 9. Free-energy diagrams of the nitrogen reduction reaction (NRR) on transition metal nitride surfaces, including VN, ZrN, CrN, and NbN. Reproduced from Ref. [40].

The study by Zhou et al. focused on integrating dissociative and associative mechanisms for efficient ammonia synthesis using a TiCN-promoted Ru-based catalyst. The developed Ru/3TiCN/ZrH₂ catalyst demonstrated a superior ammonia synthesis rate of 25.6 mmol g_{cat}^{−1} h^{−1} at 400 °C and 1 MPa. The researchers found that TiCN transfers electrons to the Ru centers and reduces Ru metal particle aggregation, generating more B5 sites that facilitate N₂ dissociation. Additionally, the formation of nitrogen vacancies on TiCN, assisted by Ru, promotes the associative mechanism for N₂ hydrogenation. This dual mechanism enhances the overall catalytic performance under mild conditions. Their study's findings highlighted the synergistic effects of Ru and TiCN in improving N₂ activation, providing valuable insights for developing advanced catalysts for ammonia synthesis [89].

In a work by Fuller et al., a hierarchical high-throughput catalyst screening (HHTCS) was employed to enhance the efficiency of ammonia synthesis via the Haber–Bosch process using Fe-based catalysts. Their study specifically focused on the Fe(211) surface, one of the most active iron catalyst facets, and they investigated 49 potential metal dopants to identify those that could significantly increase the turnover frequency (TOF) for ammonia synthesis. The screening identified cobalt (Co) as the most promising dopant, leading to a decrease in the overall reaction free-energy barrier by 0.19 eV. Kinetic Monte Carlo simulations predicted that the TOF for the Co-doped surface would increase by a factor of 2.8 compared to the undoped Fe(211) surface. This enhancement could potentially lower the operating pressure of the Haber–Bosch process from 200 atm to around 40 atm at 773 K while maintaining the same TOF, thus improving the catalytic efficiency of ammonia synthesis under industrial conditions. That study underscored the potential of Co-doped Fe catalysts in achieving more sustainable and cost-effective ammonia production processes [90].

The paper by Inoue et al. investigated the direct activation of cobalt catalysts by the electride 12CaO·7Al₂O₃ (C12A7[−]) for ammonia synthesis. Their research highlighted that while cobalt is known for its catalytic potential in ammonia synthesis, its activity is typically low due to insufficient nitrogen adsorption energy. However, this issue is effectively addressed by utilizing C12A7[−], which has a low work function of 2.4 eV, significantly enhancing the ammonia synthesis activity of cobalt. That study demonstrated that Co/C12A7[−] can initiate ammonia synthesis at a remarkably low temperature of 200 °C; this is in contrast to Co/C12A7₂[−], which requires 400 °C. The activation energy of Co/C12A7[−] is approximately 50 kJ/mol, which is comparable to advanced cobalt-based catalysts like Co₃Mo₃N and LiH-Co. This significant reduction in activation energy is attributed to the effective electron donation from C12A7[−] to the cobalt nanoparticles, facilitating N₂ dissociation. That study provided valuable insights into improving the

efficiency of cobalt catalysts for ammonia synthesis by leveraging the electronic properties of electride supports [91].

The study by Singh et al. explored the significant potential of innovative materials development strategies for improving ammonia synthesis under mild conditions, moving away from the traditional high-energy Haber–Bosch process. The authors highlighted various approaches, including defect engineering, structure manipulation, and the design of single-atom catalysts (SACs), which have shown promise in enhancing catalytic performance. Their review emphasized the need for catalysts that can efficiently perform at lower pressures and temperatures, aligning with the goals of sustainable and eco-friendly ammonia production. Defects and structural manipulation in catalysts, such as introducing vacancies or doping, can significantly alter electronic structures and enhance activity. Additionally, their paper outlines some strategies to produce ammonia under mild conditions, underscoring the role of computational tools like DFT in guiding the design of both electrochemical and thermochemical catalysts. This comprehensive approach aims to reduce the energy consumption and environmental impact of ammonia synthesis, making the process more economically viable and environmentally friendly [92].

A paper by Hosono addressed the significant challenge of synthesizing ammonia efficiently using carbon-footprint-free hydrogen under mild conditions. Their review outlined various methods of N₂ activation for ammonia synthesis, highlighting the chronological progress in heterogeneous catalysts from the traditional use of iron oxide in the Haber–Bosch process to modern advancements. Their article emphasizes the importance of developing support materials with low work functions to reduce the activation barrier for N₂ dissociation. Electride materials, which maintain bulk-like properties on their surfaces, are identified as promising candidates for this purpose. The key requirements for effective catalysts include high efficiency at low temperatures, compositions free of ruthenium, and chemical robustness in ambient conditions. That paper provided a comprehensive overview of the current state of catalytic N₂ activation and the technical challenges that need to be addressed to achieve green ammonia synthesis [93].

2. Conclusions

Ammonia synthesis research has become a global task with many new results published every month. In this review article, we provided a comprehensive overview of the recent advances in ammonia synthesis research with respect to thermal, electrochemical, photocatalytic ammonia synthesis, and ammonia synthesis via electrolysis. We found that these processes require further optimization to result in a shift in the industry, which will use more sustainable and efficient methods. It remains critical to understand, via calculations, the mechanism happening in these new catalysts. This will stimulate more careful experiments under new conditions that will eventually lead to new catalytic systems that are superior to the existing ones. We anticipate that this review will trigger the interest of scientists globally in this topic and lead to new discoveries that will have an economic impact on societies.

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