Recent advances in thermocatalytic ammonia synthesis and decomposition

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Ammonia (NH$_3$) is widely used in the production of vital chemicals such as synthetic fertilizers and nitric acid. It has recently attracted great attention as an energy carrier due to its high hydrogen content (17 wt.% H), ease of transportation, and stability over time. However, for ammonia to fulfil this promise, a more efficient and sustainable method for its synthesis and decomposition must be developed. Significant scientific efforts have been devoted to achieving this via an in-depth understanding of the reaction mechanisms. This mini-review discusses the most relevant developments in heterogenous catalysts for ammonia synthesis and decomposition over the past two years, which has centered on structural and electronic modifications, single atom catalysis, and the use of dual/multiple catalytic sites for N$_2$ and H$_2$ activation to overcome the scaling relationship, and thereby achieve moderate reaction conditions.

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Ammonia synthesis

The vast majority of ammonia is produced via the Haber-Bosch (H−B) process, which involves a thermocatalytic reaction between nitrogen and hydrogen (N$_2$ +3H$_2$ ⇔ 2NH$_3$) [1−3]. Although the H−B process has been highly optimized over the last 100 years, it is energy- and cost-intensive. While ammonia synthesis from the elements is exothermic, hence should occur at ambient conditions, industrially, the reaction is performed at high temperature and pressure (>450 °C, 100 bar) over transition metal-based catalysts (typically Fe and Ru) [1,2]. The elevated temperature is needed to overcome the high dissociation energy (945 kJ mol^{-1}) of the stable triple bonds of N$_2$. The high temperature necessitates high pressure to shift the equilibrium

towards ammonia formation [3]. There is a great interest in developing alternative technologies that enable ammonia synthesis at moderate conditions. Electrochemical, plasma-based, and photochemical methods are being explored as a replacement for the H−B process [1,4]. However, these technologies are in their infancy and suffer from low yield, especially the electrochemical approach which requires high overpotentials. Given that the thermocatalytic approach can thermodynamically occur at ambient conditions, intense efforts have been devoted to developing new catalyst materials that can activate N$_2$ molecules under mild conditions (≤400 °C and ≤10 bar).

Ammonia synthesis on transition metal (TM) catalyst surfaces generally proceeds as follows: i. (dissociative) adsorption of N$_2$ and H$_2$, ii. reaction of adsorbed N* and H* species, and iii. the desorption of ammonia [5−9]. The dissociative chemisorption of N$_2$ has been identified as the rate-limiting step on TMs [2,10−12]. Following the Sabatier principle, the ideal catalyst should not only dissociate N$_2$ easily but also have a relatively weak to moderate binding strength for the intermediate NH$_x$ (x = 0, 1, and 2) species [6,13]. However due to the scaling relationship, the binding strength of N$_2$ on a metal surface scales with those of the intermediate NH$_x$ and NH$_3$. Hence, their interaction with TM surfaces cannot be independently tuned [6]. Consequently, despite the huge research effort over the last 100 years Ru and Fe remain the most active catalysts for this process. The most recent developments are geared towards the use of structural and electronic modifications, and dual/multiple catalytic sites for N$_2$ and H$_2$ activation to overcome the scaling relationship, thereby NH$_3$ synthesis under moderate conditions [14].

Structural modifications via size reduction

Ammonia synthesis catalysts often exhibit structure-dependent activity [15,16]. Hence their catalytic activity can be improved by changing their structure to increase the concentration of catalytically active facets or sites. For instance, the Fe C$_7$ sites (Fe surface atom with seven nearest neighbors) and the Ru B$_5$ sites (step sites on the Ru(001) surface) have been identified as the main sites for N$_2$ adsorption and dissociation, and thus exhibit higher activities [9,16,17]. Tuning the particle sizes has been the major approach to exploit such structure sensitivity because the concentration of Fe C$_7$ and Ru B$_5$ atoms depends on their particle sizes. This results in the adsorption, stabilization, and hydrogenation of molecular N$_2$ to NH$_3$ on the Ru clusters

[18]. Such improved catalytic activity has also been recently reported for Ru_3 clusters supported on g-C_3N_4 [19,20] and Sm_2O_3 [21], and in atomically dispersed Co-based catalysts where low coordinated Co atoms lead to catalytic active sites such as unoccupied Co 3d charges and tetrahedral cobalt(II) [22,23].

These examples and others, demonstrate the efficacy of structural modification via size reduction (sub-nanometric, atomic clusters, and single-atom), as a promising strategy to tune the catalytic activity of TMs in ammonia synthesis (Table 1). Particularly worth highlighting is single-atom catalysis which has been gaining increasing attention recently due to the profound changes that can occur in the electronic and structural properties, and hence the catalytic performance of catalysts, upon reduction of a TM catalysts to a single atom. For example, single-atom Ru catalysts were recently shown to exhibit associative, rather than the normal dissociative N_2 activation mechanism observed for Ru nanoparticles [18,24]. A similar observation has also been reported for Fe and Co. However, it is important to note that the exact impact of the catalyst structure and size can be obscured by the different catalyst supports and even additives used in the studies, which are also known to influence catalytic performance profoundly as will be explained in the next section.

Electronic and structural effects via promotors and supports

Promotors and dopants are often used to improve the catalytic performance of transition metals in ammonia synthesis [25,26]. The use of basic compounds such as alkali and alkaline earth metal oxides (e.g. K_2O and Cs_2O) [9,27–29] as promotors are well-established due to their ability to donate electrons easily to TMs. These basic promotors are still the most widely used, although other classes of dopants such as metal hydrides and nitrides are being explored. Dopants are added in minute quantities, and they are usually a metal (also metal halide or oxide) which can form an alloy with the TM catalysts or form a dual catalytic site. It is often not trivial to disentangle the role of promotors/dopants and supports because they both can influence the structure and electronic properties of a catalyst.

The chemical nature of catalyst supports, especially the acidity, determines the type of interaction with catalyst particles and the reactants/products, thus influencing the performance of catalysts via electronic and structural promotion, and stability (sintering and agglomeration). Electronic interaction with the catalyst can modify the adsorption strength of N_2 and the NH_x on the catalyst, thereby influencing the catalytic activity. Metal oxides (typically MgO, CeO_2) have been the main class of catalyst support but other materials such as lanthanides, various carbon materials [30,31], perovskites [32–34], graphene-carbon nitrides [20], oxyhydrides [35,36] and electrides [35,37–39] have recently attracted interest.
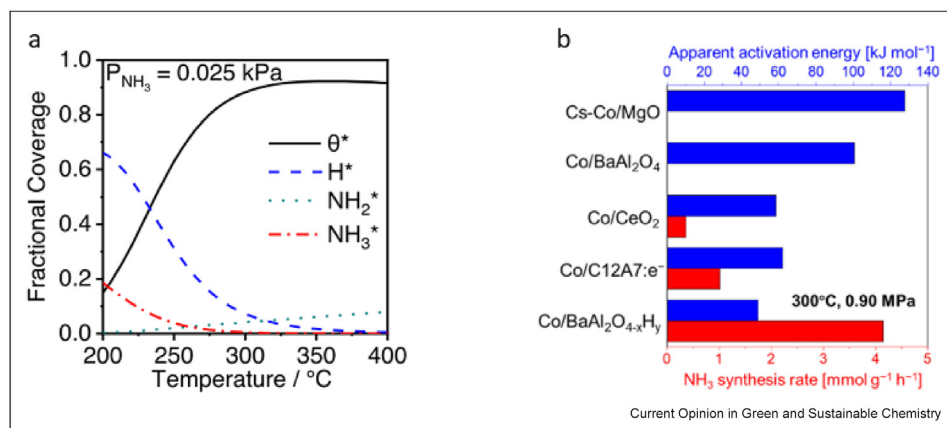
Feng, J. et al. recently reported that supporting sub-nanometer Ru clusters on ceria nanorods leads to higher catalytic activity toward ammonia at moderate temperatures than other metal oxide supports [40]. This was attributed to electron donation from ceria to Ru clusters which facilitates N_2 activation as well as limits hydrogen poisoning of Ru, which is known to deactivate Ru via the competitive adsorption with N_2 (Figure 1a) [35]. Li et al. further demonstrated that the synthesis method of the ceria influences the reaction rates [41] which was later linked to the strength of the basic sites on the ceria support [42]. Strong basicity leads to strong electron donation to the TM, as was recently shown for Co-based catalysts supported on

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Table 1

Overview of the catalytic activities of recently published TM-based NH_3 synthesis catalysts (E_a = activation energy).

Catalyst	(E_a) (kJ mol^{-1})	Temperature (°C)	Pressure (bar)	Activity (mmol NH_3 g^{-1} h^{-1})	Ref.
Ru SAC	64	400	10	4.69	[18]
Ru ACCs	59	400	10	7.42	[18]
Ru-2.8 nm	98	400	10	2.87	[18]
Ru-7.5 nm	98	400	10	2.50	[18]
Ru cluster/CeO_2	81	400	10	28.00	[40]
Ru NPs/CeO_2	54	400	10	15.90	[40]
Ru/CeO_2-w	52	400	10	22.62	[41]
Ru/LaCoSi	50	400	1	3.4	[39]
Ru/$BaAl_2O_{4-x}Hy$	66	340	9	13.30	[35]
Co/$BaAl_2O_{4-x}H_y$	49	340	9	8.3	[35]
Co/C12A7:e−	62	340	9	2.5	[35]
Co−N CNs	–	300	10	85.3	[22]
Co2-ACCs	49	400	10	8.5	[23]
Co SAC		400	10	4.6	[23]
Co NPs	75	400	10	2.6	[23]

Figure 1

a) Calculated fractional coverage of a Ru/CeO$_2$ of major adsorbed reaction species as a function of temperature [48] and **b**) the apparent activation energies and NH$_3$ synthesis rates of various Co-based catalysts [35]. Reproduced with permission from Jiang et al., Movick et al. [35,48].

several mixed oxides with different basic sites [43]. Likewise, the presence of anionic (oxygen) vacancies in partially reduced transition metal perovskites (barium niobate) [32] was recently shown to improve the catalytic properties of Ru via electron donation and mitigation of the detrimental effects of hydrogen poisoning of Ru [44].

Electrides are a relatively new class of catalyst supports for ammonia synthesis [35,38,45,46], with calcium aluminum-based oxide "C12A7:e$^-$" the most investigated so far [38,45]. Although the exact role is still under debate, most experimental and computational results suggest that the catalytic enhancement of electrides stems from their ability to readily donate the cage electrons to TMs, resulting in decreased activation energy and increased NH$_3$ synthesis rate (Figure 1b) [35,47,48]. It has also been hypothesized that the electrons aid the formation of hydride ions (H$^-$), which readily react with dissociated N atoms. This avoids high

hydrogen coverage on Ru and consequently suppresses its poisoning/deactivation [45,46,48−50].

On the other hand, a recent work by Gong et al. on a series of intermetallic electrides based on La-TM-Si [37,39] suggest a dual catalytic role (Figure 2a). Their results show that although electron donation from electrides generally promotes the rate-determining step (RDS), i.e., N$_2$ splitting, these ternary electrides also serve as the hydrogenation center for N atoms which becomes the new RDS because N$_2$ splitting is greatly enhanced. These results show that the role of electrides in ammonia synthesis is an important fundamental topic for further investigation.

The existence of the dual-site mechanism suggested for electrides has also been hypothesized for some TM-based catalysts when combined with lanthanum(La) or lanthanum nitride (LaN). Specifically, using experimental and DFT results Ye et al., recently credited the

Figure 2
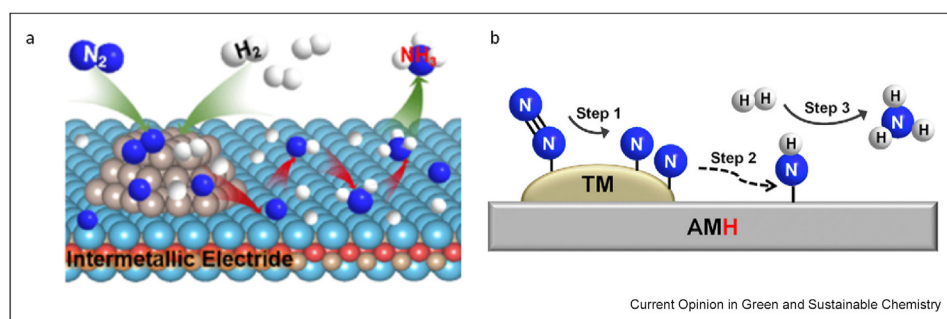
Model representation of **a**) ammonia synthesis reaction over Ru/La-TM-Si with N$_2$ bond weakening and hydrogen poisoning mitigation from the Ru metal center to the electride support [39]. and **b**) the activation of N$_2$ over the TM, followed by the N* transfer and hydrogenation on LiH to NH$_3$ [61,62]. Reproduced with permission from Gong et al., Wang et al. [39,62].

dual-site mechanism for the remarkable catalytic performance observed for LaN/Ni and LaN/Co in NH_3 synthesis, where H_2 is believed to be activated on the Ni or Co site, and nitrogen vacancies generated in the LaN are responsible for the activation of N_2 [51]. However, more recent works using model catalysts based on LaN and poor catalytic materials (Co and Ni) nanoparticles suggest that the profound increase in their catalytic activity stems from spin-promotion effect induced by the LaN on these ferromagnetic metals, rather than from dual-site mechanism [44,52]. Computational results show that LaN quenches/modifies the magnetic moment of the adjacent cobalt or Ni centres thereby enhancing their catalytic activity for nitrogen cleavage. This demonstrates that suppressing or altering the magnetic properties of magnetic-based catalysts is an attractive approach to tune their catalytic performance. A similar explanation goes for the improved performance when these TMs are combined with metal hydride promotors [44,52] These new findings highlight the fact that the exact roles of promotors are not yet well understood because their functionality seems to be highly dependent on the properties of the particular catalyst system.

Metal hydride-mediated ammonia synthesis

Metal hydrides are perhaps the most recent new catalytic materials for NH_3 synthesis. Alkali and alkaline earth metal oxides and hydroxides have been the typical promotors for ammonia synthesis [53–56]. Their hydride counterparts have lately garnered much attention as effective promotors for NH_3 synthesis due to their ability to improve catalytic activity at moderate conditions in both the chemical looping ammonia synthesis (CLAS) and normal catalytic routes. In the CLAS, the scaling relationship is overcome by decoupling the N_2 activation and hydrogenation steps via TM nitride formation (TM-N) followed by hydrogenation to NH_3 and the TM or TM hydride. The addition of LiH and BaH_2 to Ru was recently shown to improve the hydrogenation kinetics of transition metal nitrides (TM-N) to NH_3 in CLAS [57,58]. This was accredited to the formation of catalytic active complexes or intermediates such as Li_4RuH_6 and Ba_2RuH_6 [57,58]. While Li_4RuH_6 was found to assist the reaction by stabilizing the intermediate N_XH_Y species, Ba_2RuH_6 facilitates the dissociation of both N_2 and H_2. Extending the study to other alkali and alkaline earth metals (AMs) showed the following activity trend: Na < K < Ba < Li < C, suggesting that decreasing the AM-N_XH_Y bond strength increases the activity toward ammonia synthesis [59,60].

Metal hydrides have also been shown to increase the catalytic activity of TMs in direct ammonia synthesis via the dual-site mechanism (Figure 2b) [62]. The efficacy of hydrides is attributed to the reactive hydridic atoms from the metal hydrides which provide both the electrons and atomic hydrogen to break the dinitrogen bond and hydrogenate it to ammonia respectively [21,62–64]. Furthermore, in the presence of H_2 and N_2, alkali and alkaline earth metal hydrides can form a variety of amides and imides (A-M-H) which can further decompose into ammonia and the corresponding metal hydride [55]. Hence, the catalytic mechanism can go via TM-N or A-M-H depending on the stability of the intermediates.

The promotion effect of alkali and alkaline earth metal hydrides has been generally attributed to their role as a second active centre [53,55,61,65]. However, some metal hydrides have recently shown impressive catalytic activity at moderate conditions without transition metals, making them TM-free catalysts. The pioneering work of Chang et al. on potassium hydride-intercalated in graphite (potassium hydride carbide; KH_xC_y) showed that this TM-free catalyst is active for NH_3 synthesis at 300 °C and 10 bar (Figure 3a) [5]. A combination of experimental and DFT suggests that N_2 activation on the catalyst follows the associative mechanism, as reported for the Ru clusters and single-atom catalysts. The fact that the N_2 is not dissociatively adsorbed lowers the overall energy barrier for NH_3 synthesis. Following this report, a similar observation has been reported for 2D electride of Ba_2N with anionic electrons in the interlayer spacings (Figure 3c) [66]. Also, for CLAS, both LiH [67] and BaH_2 [68] have shown impressive catalytic activities without a TM (Figure 3b). These results demonstrate that metal hydrides are a fascinating new class of ammonia synthesis catalysts. However, characterization of hydride-containing materials is challenging due to their air sensitivity. This renders it difficult to unravel the exact catalytic mechanism(s), hence a major interesting scientific challenge.

Ammonia decomposition

Ammonia decomposition has also attracted attention due to the renewed interest in the compound as a carrier for green hydrogen fuel [69]. The decomposition reaction is endothermic, hence it occurs at higher temperatures (300–700 °C). The conversion rate is influenced by the catalyst and the reaction condition such as the feedstock concentration (dilution), the pressure, and the temperature. While at low temperatures (300–500 °C) and high NH_3 feed concentrations, the reaction is mainly limited by N–N bond formation, the N–H bond cleavage becomes rate limiting at higher temperatures and lower ammonia concentrations [9]. Ru on carbon nanotubes (Ru/CNT) has long been used as a model catalyst and promotors based on nitrates and other oxygen-containing salts of alkali and alkaline earth metals, promotors with lower electronegativity were found to be the best [30]. This promotional trend was observed for alkali oxide and hydroxide promotors but a different trend (Li > K > Na) was found for alkali metal

Figure 3
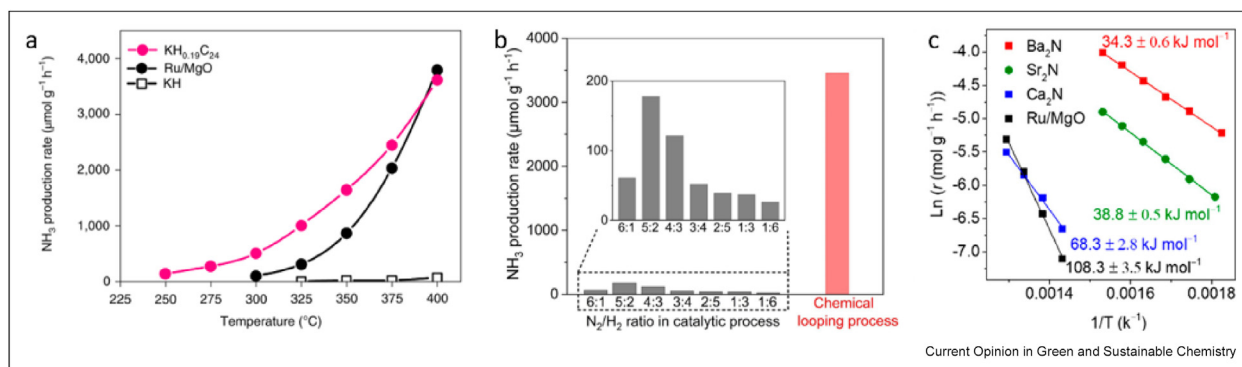
Ammonia synthesis activity of transition metal-free catalysts **a**) potassium hydride (carbide) and ruthenium-based catalysts as a function of temperature at 10 bar and $N_2:H_2$ 1:3 gas flow (thermocatalytic) [5], **b**) a comparison of NH_3 production rates of BaH_2 at 450 °C and 1 bar via thermo-catalysis and chemical looping processes, and **c**) the differences in activation energy for different metal-nitrides compared to a ruthenium-based catalysts [66]. Reproduced with permission from Chang et al., Zhang et al., Guan et al. [5,66,68].

amides, showing a clear dependence of the promotion mechanism on the chemical nature of the alkali metal, (e.g. hydride, hydroxide, or oxides) [70].

Recent focus has shifted away from Ru towards the use of other TM as well as TM-free catalysts. Alkali amides/imides, especially Li-based ($LiNH_2$ and Li_2NH), have been shown to lower the activation barrier significantly by stabilizing the intermediates M−N bonds [71,72]. Recent theoretical works have further confirmed the relevance of the surface disorder dynamics of these (non-stochiometric) lithium amide compounds ($Li_{2-x}(NH_2)_x(NH)_{1-x}$) for TM-free catalysts, indicating possible differences compared to the mechanism of TM-based catalysts [73,74]. Similar to the TM-free NH_3 synthesis catalysts [5], lithium amide/imide are also active for ammonia decomposition with and without transition metals [75,76], increasing the conversion at 440 °C from 54% up to 86% by adding TM to $LiNH_2$, and their performance also depends on the ammonia flow [5,78,79]. Similar to the multi-component catalysts for ammonia synthesis, the synergy between TM particles and imide compounds allows the separation of different mechanistic steps, i.e. a dual-site mechanism, combined with a promotional effect [77]. Synonymous with ammonia synthesis, electron donation from the basic sites of supports and promotors increases the catalytic performance of Ru in ammonia decomposition [78,79]. This was recently demonstrated using $XCeO_3$ (X: Mg, Ca, Sr, Ba) perovskite oxides as supports for Co, but was here limited to conversions up to 29% at 450 °C [34]. In summary, although not studied extensively as ammonia synthesis, recent progress on ammonia decomposition research is also centered on structural and electronic modifications of TMs, especially Ru, through alkali and alkaline earth-based promotors and basic supports.

Conclusion and outlook

This mini-review shows that the most recent developments in thermocatalytic ammonia synthesis and decomposition are centered on strategies that can modify the interaction strengths of N_2 and NH_x on TMs (especially Ru) and thereby improve the catalytic activity at moderate temperatures and pressure. The most promising approaches are structural and electronic promotion via size effects (nanoclusters/single atoms), support effects, promotors, and doping/alloying with other metals. Electrides, metal hydrides, and oxide perovskites have emerged as efficient promotors and/or supports. Other interesting new developments are chemical looping which can overcome the scaling relationship, and non-TM-based catalysts such as KH_xC_y which can activate N_2 at moderate temperatures via associative mechanism. The impressive and often intriguing results, especially from electrides and metal hydride-based catalysts, show that there is still much to understand in catalytic NH_3 synthesis and decomposition. The increasing use of computational approaches such as DFT and machine learning, will be crucial for achieving a more in-depth understanding of the catalytic mechanism and the discovery of new catalysts with improved performance.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Peter Ngene and Petra de Jongh report that financial support was provided by the European Commission. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

References

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest

1. Wang Q, Guo J, Chen P: **Recent progress towards mild-condition ammonia synthesis**. *J Energy Chem* 2019, **36**: 25−36.

2. Ravi M, Makepeace JW: **Facilitating green ammonia manufacture under milder conditions: what do heterogeneous catalyst formulations have to offer?** *Chem Sci* 2022, **13**: 890−908.

3. Aziz M, TriWijayanta A, Nandiyanto ABD: **Ammonia as effective hydrogen storage: a review on production, storage and utilization**. *Energies* 2020, **13**:3062.

4. El-Shafie M, Kambara S: **Recent advances in ammonia synthesis technologies: toward future zero carbon emissions**. *Int J Hydrogen Energy* 2023, **48**:11237−11273.

5.
* Chang F, *et al.*: **Potassium hydride-intercalated graphite as an efficient heterogeneous catalyst for ammonia synthesis**. *Nat Catal* 2022, **5**:222−230.
The authors demonstrate the conversion of dinitrogen and hydrogen to ammonia on transition-metal-free catalysts based on potassium hydride/graphite nanocomposites, the first non-TM-based heterogeneous catalysts for ammonia synthesis

6. Medford AJ, *et al.*: **From the Sabatier principle to a predictive theory of transition-metal heterogeneous catalysis**. *J Catal* 2015, **328**:36−42.

7. Ertl G: **Surface science and catalysis—studies on the mechanism of ammonia synthesis: the P. H. Emmett award address**. *Catal Rev* 1980, **21**:201−223.

8. Van Der Ham CJM, Koper MTM, Hetterscheid DGH: **Challenges in reduction of dinitrogen by proton and electron transfer**. *Chem Soc Rev* 2014, **43**:5183−5191.

9. Fang H, *et al.*: **Challenges and opportunities of Ru-based catalysts toward the synthesis and utilization of ammonia**. *ACS Catal* 2022, **12**:3938−3954.

10. Tabassum H, *et al.*: **Hydrogen generation via ammonia decomposition on highly efficient and stable Ru-free catalysts: approaching complete conversion at 450 °C**. *Energy Environ Sci* 2022, **15**:4190−4200.

11. Vojvodic A, *et al.*: **Exploring the limits: a low-pressure, low-temperature Haber-Bosch process**. *Chem Phys Lett* 2014, **598**: 108−112.

12. McEnaney JM, *et al.*: **Ammonia synthesis from N_2 and H_2O using a lithium cycling electrification strategy at atmospheric pressure**. *Energy Environ Sci* 2017, **10**:1621−1630.

13. Sabatier P: **La catalyse en chimie organique**. 1920.

14. Barbieri M: **Industrial synthesis of ammonia: a patent landscape**. *SSRN Electron J* 2022. https://doi.org/10.2139/ssrn.4268048.

15. Peng X, *et al.*: **Size-dependent activity of supported Ru catalysts for ammonia synthesis at mild conditions**. *J Catal* 2022, **408**:98−108.

16. Spencer ND, Schoonmaker RC, Somorjai GA: **Iron single crystals as ammonia synthesis catalysts: effect of surface structure on catalyst activity**. *J Catal* 1982, **74**:129−135.

17. Honkala K, *et al.*: **Ammonia synthesis from first-principles calculations**. *Science* 2005, **307**:555−558.

18.
* Li L, *et al.*: **Size sensitivity of supported Ru catalysts for ammonia synthesis: from nanoparticles to subnanometric clusters and atomic clusters**. *Chem* 2022, **8**:749−768.
Authors demonstrate a difference in ammonia synthesis mechanism when ruthenium catalysts reach sub-nanometer scale, leading to an associative mechanism with an extremely low reaction barrier.

19. Lin J, *et al.*: **Macroporous carbon-nitride-supported transition-metal single-atom catalysts for photocatalytic hydrogen production from ammonia splitting**. *ACS Catal* 2023, **13**: 11711−11722.

20. Zhang Y, *et al.*: **Defective g-C3N4 supported Ru3 single-cluster catalyst for ammonia synthesis through parallel reaction pathways**. *Nano Res* 2023, **16**:3580−3587.

21.
* Zhang X, *et al.*: **Synergizing surface hydride species and Ru clusters on Sm2O3 for efficient ammonia synthesis**. *ACS Catal* 2022, **12**:2178−2190.
Authors demonstrate that the presence of surface hydride species on a metal-oxide support improves the ammonia synthesis activity of ruthenium cluster by donating electrons to ruthenium and actively participating in the reaction pathway.

22. Zhou Y, *et al.*: **Boosting efficient ammonia synthesis over atomically dispersed Co-based catalyst via the modulation of geometric and electronic structures**. *CCS Chem* 2022, **4**: 1758−1769.

23.
* Peng X, *et al.*: **Studies of a highly active cobalt atomic cluster catalyst for ammonia synthesis**. *ACS Sustainable Chem Eng* 2022, **10**:1951−1960.
Authors demonstrate based on in-situ spectroscopy that the Co_2 atomic clusters with strong inter-clustering interactions exhibit excellent catalytic performance under mild conditions for sustainable ammonia synthesis.

24. Sivan SE, *et al.*: **Facile MOF-derived one-pot synthetic approach toward Ru single atoms, nanoclusters, and nanoparticles dispersed on CeO2 supports for enhanced ammonia synthesis**. *J Catal* 2022, **408**:316−328.

25. Ertl G, Lee SB, Weiss M: **Adsorption of nitrogen on potassium promoted Fe(111) and (100) surfaces**. *Surf Sci* 1982, **114**: 527−545.

26. Urabe K, Aika KI, Ozaki A: **Activation of nitrogen by alkali metal-promoted transition metal. VI. Hydrogen effect on isotopic equilibration of nitrogen and rate-determining step of ammonia synthesis on potassium-promoted ruthenium catalysts**. *J Catal* 1976, **42**:197−204.

27. Ju X, Feng J, Wang J, Guo J, Liu L: **One-step synthesis of cesium decorated Ru nanoparticles on MgO as efficient catalyst for ammonia synthesis**. *Catal Lett* 2023, **153**: 1615−1624.

28. Faria JA: **Renaissance of ammonia synthesis for sustainable production of energy and fertilizers**. *Curr Opin Green Sustainable Chem* 2021, **29**, 100466.

29. Chen Z, *et al.*: **Iron-single sites confined by graphene lattice for ammonia synthesis under mild conditions**. *ACS Catal* 2023, **13**:14385−14394.

30. Wang SJ, *et al.*: **Investigation on modification of Ru/CNTs catalyst for the generation of COx-free hydrogen from ammonia**. *Appl Catal B Environ* 2004, **52**:287−299.

31. Chen C, *et al.*: **Ru-based catalysts for ammonia decomposition: a mini-review**. *Energy Fuel* 2021, **35**:11693−11706.

32. Zhao Y, *et al.*: **Anionic defects enhanced ammonia synthesis over Ru catalyst supported on barium niobate reduced with CaH2**. *Catal Lett* 2023, **1**:1−15.

33. Kitano M, *et al.*: **Low-temperature synthesis of perovskite oxynitride-hydrides as ammonia synthesis catalysts**. *J Am Chem Soc* 2019, **141**:20344−20353.

34. Al-attar OA, Podila S, Al-Zahrani AA: **Preparation and study of XCeO3 (X: Mg, Ca, Sr, Ba) perovskite-type oxide supported cobalt catalyst for hydrogen production by ammonia decomposition**. *Arabian J Sci Eng* 2023, **48**:8667−8677.

35. Jiang Y, *et al.*: **Boosted activity of cobalt catalysts for ammonia synthesis with BaAl2O4-xHy electrides**. *J Am Chem Soc* 2023, **145**:10669−10680.
* Authors present a novel oxyhydride electride that can significantly promote ammonia synthesis over Co via increased electron donation.

36. Tang Y, *et al.*: **Metal-dependent support effects of oxyhydride-supported Ru, Fe, Co catalysts for ammonia synthesis**. *Adv Energy Mater* 2018, **8**, 1801772.

37. Gong Y, *et al.*: **LaRuSi electride disrupts the scaling relations for ammonia synthesis**. *Chem Mater* 2022, **34**:1677−1685.

38. Hosono H: **Electride catalysts for ammonia synthesis**. In *CO2 free ammonia as an energy carrier: Japan's insights*. Taylor & Francis; 2022:325−338. https://doi.org/10.1007/978-981-19-4767-4_21.

39. Gong Y, *et al.*: **Unique catalytic mechanism for Ru-loaded ternary intermetallic electrides for ammonia synthesis**. *J Am Chem Soc* 2022, **144**:14.
* The authors demonstrate that ternary intermetallic electrides with the same crystal structure can result in different promotional effects on Ru catalysts by lowering the nitrogen activation energy.

40. Feng J, *et al.*: **Sub-nanometer Ru clusters on ceria nanorods as efficient catalysts for ammonia synthesis under mild conditions**. *ACS Sustainable Chem Eng* 2022, **10**: 10181−10191.

41. Li C, *et al.*: **Revealing hydrogen migration effect on ammonia synthesis activity over ceria-supported Ru catalysts**. *Appl Catal B Environ* 2023, **320**, 121982.

42. Hirabayashi S, Ichihashi M, Takeda Y: **Optimization of ruthenium particle size and ceria support for enhanced activity of Ru/CeO2 cluster catalysts in ammonia synthesis under mild conditions**. *Catal Lett* 2023, **1**:1−7.

43. Ronduda H, *et al.*: **Development of cobalt catalyst supported on MgO−Ln2O3 (Ln = La, Nd, Eu) mixed oxide systems for ammonia synthesis**. *Int J Hydrogen Energy* 2022, **47**: 6666−6678.

44. Cao A, *et al.*: **A spin promotion effect in catalytic ammonia synthesis**. *Nat Commun* 2022, **13**:1−7.
* Authors provide an overview of recent experimental results and developed a model to explain the role of the promotors, which includes changes in the active site structure due to promoters as well electrostatic interactions.

45. Lin B, Nowrin FH, Rosenthal JJ, Bhown AS, Malmali M: **Perspective on intensification of Haber−Bosch to enable ammonia production under milder conditions**. *ACS Sustainable Chem Eng* 2023, **11**:9880−9899.

46. Kitano M, *et al.*: **Ammonia synthesis using a stable electride as an electron donor and reversible hydrogen store**. *Nat Chem* 2012, **4**:934−940.

47. Humphreys J, Lan R, Tao S: **Development and recent progress on ammonia synthesis catalysts for Haber−Bosch process**. *Adv. Energy Sustain. Res.* 2021, **2**, 2000043.

48. Movick WJ, Kishimoto F, Takanabe K: **Dynamic surface-coverage alteration based on microkinetic analysis for enhanced ammonia synthesis over ruthenium catalysts at low temperatures**. *Chem Eng J* 2023, **452**, 139525.

49. Kammert J, *et al.*: **Nature of reactive hydrogen for ammonia synthesis over a Ru/C12A7 electride catalyst**. *J Am Chem Soc* 2020, **142**:7655−7667.

50. Kitano M, *et al.*: **Electride support boosts nitrogen dissociation over ruthenium catalyst and shifts the bottleneck in ammonia synthesis**. *Nat Commun* 2015, **6**:1−9.

51. Ye TN, *et al.*: **Vacancy-enabled N2 activation for ammonia synthesis on an Ni-loaded catalyst**. *Nature* 2020, **583**: 391−395.

52. Zhang K, *et al.*: **Spin-mediated promotion of Co catalysts for ammonia synthesis**. *Science* 2024, **383**:1357−1363.
* Authors of [44 and 52] combined theoretical and experimental works to demonstrate for the first time that suppressing/altering the magnetic properties of magnetic-based catalysts (such as Ni and Co) by the addition of promotors or additives such as LaN and metal hydrides, is an attractive approach to tune the catalytic performance in ammonia synthesis.

53. Gao W, Guo J, Chen P Hydrides: **Amides and imides mediated ammonia synthesis and decomposition**. *Chin J Chem* 2019, **37**:442−451.

54. Feng S, *et al.*: **A multi-functional composite nitrogen carrier for ammonia production via a chemical looping route**. *J Mater Chem A* 2021, **9**:1039−1047.

55. Guo J, Chen P: **Interplay of alkali, transition metals, nitrogen, and hydrogen in ammonia synthesis and decomposition reactions**. *Acc Chem Res* 2021, **54**:2434−2444.

56. Al Maksoud W, *et al.*: **Active and stable Fe-based catalyst, mechanism, and key role of alkali promoters in ammonia synthesis**. *J Catal* 2021, **394**:353−365.

57. Wang Q, *et al.*: **Ternary ruthenium complex hydrides for ammonia synthesis via the associative mechanism**. *Nat Catal* 2021, **4**:959−967.

58. Liu C, *et al.*: **Formation of a complex active center by Ba2RuH6for nondissociative dinitrogen activation and ammonia Formation**. *ACS Catal* 2022, **12**:4194−4202.

59. Wang Q, *et al.*: **Ruthenium complex hydride catalyst as a platform for ammonia synthesis: the effect of alkali or alkaline earth elements**. *ACS Catal* 2023, **13**:9882−9890.
* Authors demonstrate the differences between ruthenium complex hydrides and conventional AM-promoted Ru metal catalysts, providing insight into the fundamentals of ammonia synthesis.

60. Wang Q, Guo J, Chen P: **Complex transition metal hydrides for heterogeneous catalysis**. *Chem Catal* 2023, **3**, 100524.

61. Wang P, *et al.*: **Breaking scaling relations to achieve low-temperature ammonia synthesis through LiH-mediated nitrogen transfer and hydrogenation**. *Nat Chem* 2017, **9**: 64−70.

62. Wang Q, Guan Y, Guo J, Chen P: **Hydrides mediate nitrogen fixation**. *Cell Reports Phys Sci* 2022, **3**, 100779.

63. Guan Y, *et al.*: **Barium chromium nitride-hydride for ammonia synthesis**. *Chem Catal* 2021, **1**:1042−1054.

64. Zhang X, *et al.*: **The role of lanthanum hydride species in La2O3 supported Ru cluster catalyst for ammonia synthesis**. *J Catal* 2023, **417**:382−395.

65. Chang F, *et al.*: **Alkali and alkaline earth hydrides-driven N2 activation and transformation over Mn nitride catalyst**. *J Am Chem Soc* 2018, **140**:14799−14806.

66. Zhang Z, *et al.*: **A 2D Ba2N electride for transition metal-free N2 dissociation under mild conditions**. *J Am Chem Soc* 2023, **145**:53.
* Authors demonstrate the use of transition metal free dinitrogen dissociation via the formation of the $(N_2)^{2-}$ anion in the interlayer spacing of Ba2N.

67. Tagawa K, Gi H, Shinzato K, Miyaoka H, Ichikawa T: **Improvement of kinetics of ammonia synthesis at ambient pressure by the chemical looping process of lithium hydride**. *J Phys Chem C* 2022, **126**:2403−2409.

68. Guan Y, *et al.*: **Transition-metal-free barium hydride mediates dinitrogen fixation and ammonia synthesis**. *Angew Chem Int Ed* 2022, **61**, e202205805.
* Authors demonstrate the use of transition metal-barium hydride as chemical looping synthesis ammonia catalysts, where both the hydrogen vacancies and adjacent lattice hydrogen participate in the conversion.

69. Ristig S, *et al.*: **Ammonia decomposition in the process chain for a renewable hydrogen supply**. *Chem-Ing-Tech* 2022, **94**: 1413−1425.

70. Chang F, *et al.*: **Influence of alkali metal amides on the catalytic activity of manganese nitride for ammonia decomposition**. *Catal Today* 2017, **286**:141−146.

71. Guo J, *et al.*: **Lithium imide synergy with 3d transition-metal nitrides leading to unprecedented catalytic activities for ammonia decomposition**. *Angew Chem Int Ed* 2015, **54**: 2950−2954.

72. Guo J, *et al.*: **Highly active MnN-Li2NH composite catalyst for producing COx-free hydrogen**. *ACS Catal* 2015, **5**:2708−2713.

73. Yang M, Raucci U, Parrinello M: **Reactant-induced dynamics of lithium imide surfaces during the ammonia decomposition process**. *Nat Catal* 2023, **6**:829−836.

74. Mambretti F, Raucci U, Yang M, Parrinello M: **How does structural disorder impact heterogeneous catalysts? The case of ammonia decomposition on non-stoichiometric lithium imide**. *ACS Catal* 2024, **14**:1252−1256.

75. Makepeace JW, Wood TJ, Hunter HMA, Jones MO, David WIF: **Ammonia decomposition catalysis using non-stoichiometric lithium imide**. *Chem Sci* 2015, **6**:3805−3815.

76. Brooker-Davis, Makepeace C, Wood J, Thomas: **Enhancement
* of the catalytic activity of lithium amide towards ammonia decomposition by addition of transition metals**. *J. Ammon. Energy* 2022, **1**:46.
Authors examined the catalytic mechanisms and formation of a ternary hydride phase for lithium amide ammonia decomposition catalysts in the presence of transition metals.

77. Ogasawara K, *et al.*: **Ammonia decomposition over CaNH-supported Ni catalysts via an NH2–vacancy-mediated mars-van Krevelen mechanism**. *ACS Catal* 2021, **11**:11005−11015.

78. Zhang X, *et al.*: **Ru nanoparticles on Pr2O3 as an efficient catalyst for hydrogen production from ammonia decomposition**. *Catal Lett* 2022, **152**:1170−1181.

79. Zhang T, *et al.*: **Steering ammonia decomposition over Ru nanoparticles on ZrO2 by enhancing metal-support interaction**. *Catal Sci Technol* 2023, **13**:5205−5213.