Noble-metal-free nanocatalysts for hydrogen generation from boron- and nitrogen-based hydrides

Qilu Yao, Yiyue Ding and Zhang-Hui Lu*

Hydrogen has attracted much attention as a globally accepted clean energy carrier. Currently, the search for safe and efficient hydrogen storage materials is one of the most difficult challenges for the upcoming hydrogen economy. Boron- and nitrogen-based hydrides, such as metal borohydrides (e.g. NaBH₄), ammonia borane (NH₃BH₃), ammonia (NH₃), hydrous hydrazine (N₂H₄·H₂O), and hydrazine borane (N₂H₄BH₃), have received much attention as potential chemical hydrogen storage materials because of their high hydrogen contents and the advantage of CO-free H₂ produced. In recent years, substantial efforts have been devoted to research highly efficient catalysts to significantly improve the kinetic properties for hydrogen evolution from the hydrolysis of sodium borohydride and ammonia borane, and selective decomposition of ammonia, hydrous hydrazine and hydrazine borane. Among them, non-noble metal catalysts have been widely considered as potential candidates due to their low cost, abundant reserves, and relatively high catalytic activities. In this review, we focus on the recent advances in non-noble metal catalyst design, synthesis and applications in hydrogen generation from boron- and nitrogen-based hydrides.

1. Introduction

The advancement of industrialization and economic growth means that human society is more heavily dependent on energy than ever before. The currently used fossil fuels (coal, crude oil, natural gas, etc.) are considered to be non-renewable energy and have limited reserves. In addition, the extraction, transport, and consumption of fossil fuels can also cause environmental pollution problems. Thus, it is urgent to find a clean and renewable alternative to fossil fuels. Hydrogen has been identified as a potential alternative energy carrier for future energy supplies because it is clean, renewable, and environment friendly, and has high energy density.1^-4 The use of hydrogen fuel cells in portable electronic devices or vehicles requires lightweight hydrogen storage or on-board hydrogen evolution. In particular, for vehicular applications, the most important requirements are safety, ease of control and fast reaction kinetics as well as high hydrogen content. To this

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end, the search for secure and efficient hydrogen storage materials has become extremely important.

In the last decades, several materials for hydrogen storage such as metal hydrides,\(^5\) carbonaceous materials,\(^6\) zeolites,\(^7\) metal organic frameworks,\(^8\) and organic hydrides,\(^9,10\) have been extensively investigated, while big challenges still remain. Chemical hydrogen storage materials have high hydrogen contents and store hydrogen in the form of chemical bonds, and they are considered as highly promising hydrogen sources for fuel cells.\(^11–14\) Among them, boron- and nitrogen-based hydrides, such as metal borohydrides (e.g. NaBH\(_4\), 10.8 wt%), ammonia borane (NH\(_3\)BH\(_3\), 19.6 wt%), ammonia (NH\(_3\), 17.7 wt%), hydrazine hydrazine (N\(_2\)H\(_4\)·H\(_2\)O, 8.0 wt%), and hydrazine (N\(_2\)H\(_4\), 15.4 wt%), have received much attention in recent years.\(^15–21\) These materials are not only high in hydrogen content, but are also easy to store and transport under mild conditions, making them highly potential hydrogen storage materials.

In order to achieve effective hydrogen evolution from boron- and nitrogen-based hydrides under ambient conditions, it is highly desired to develop economical, highly efficient and stable catalysts. To date, a lot of noble/non-noble metals and their composites have been developed as catalysts for hydrogen evolution from boron- and nitrogen-based hydrides.\(^21–26\) Among them, noble metal-based catalysts exhibit excellent catalytic activity, but they are unsuitable for large scale practical applications due to their high cost and insufficient reserves in the Earth’s crust.\(^27–30\) Therefore, the development of cost-effective catalysts is of great importance for practical applications. Non-noble metal (e.g. Fe, Co, Ni, etc.) catalysts have been considered as potential candidates due to their low cost, abundant reserves, and relatively high catalytic performances.\(^24,31,32\) In this review, we summarize the recent developments in non-noble catalysts for hydrogen generation from these boron- and nitrogen-based chemical hydrogen storage materials.

2. Metal borohydrides

Metal borohydrides, such as LiBH\(_4\), NaBH\(_4\), KBH\(_4\) and Mg (BH\(_4\))\(_2\), have received considerable interest as promising hydrogen storage materials due to their high gravimetric hydrogen capacities.\(^33–43\) Compared to LiBH\(_4\), KBH\(_4\) and Mg(BH\(_4\))\(_2\), NaBH\(_4\) is more widely studied because it provides a safe and low-cost route to produce hydrogen.\(^16,21,13\) Thus, NaBH\(_4\) is taken as a representative for discussion.

Hydrogen stored in NaBH\(_4\) can be released by either thermolysis or hydrolysis.\(^33,44–48\) However, the thermolysis of NaBH\(_4\) is not conceivable because it requires high temperature (>500 °C), and it inevitably produces toxic species. Alternatively, hydrolysis can be used to release H\(_2\) from NaBH\(_4\) easily and in a controllable way under friendly conditions.\(^33,47,48\) As shown in eqn (1), half of the hydrogen produced originates from water, which is also an advantage of this reaction. In addition, the byproduct of this hydrolysis reaction (NaBO\(_2\)) is nontoxic and can be recycled for regeneration, which facilitates its use in fuel cells. In general, NaBH\(_4\) is not stable in aqueous solution and can spontaneously release H\(_2\) without catalysts. However, the self-hydrolysis is too slow and uncontrollable, and only 7–8% of NaBH\(_4\) can be converted. In order to suppress the self-hydrolysis, NaOH is often added into the NaBH\(_4\) solution as a stabilizer. The alkaline NaBH\(_4\) solution can only be hydrolyzed by using suitable catalysts.

\[
\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2 \quad (1)
\]

Unlike the simple hydrolysis reaction formula shown in eqn (1), the detailed mechanism of the hydrolysis of NaBH\(_4\) over transition metal catalysts is complicated and not fully understood.\(^49–53\) As early as in 1971, Holbrook and Twist proposed a plausible mechanism for metal (M) catalyzed hydrolysis of NaBH\(_4\).\(^49\) Firstly, BH\(_4^-\) ions are chemisorbed on a metal active site surface, forming M–BH\(_4^-\) and M–H intermediate species. Subsequently, M–BH\(_4^-\) reacts with OH\(^-\) and H\(_2\)O, possibly \(\text{via} \) a BH\(_3\) intermediate, to form BH\(_3\)(OH\(^-\))\(^+\) and M–H intermediate species. Then, the intermediate BH\(_3\)(OH\(^-\))\(^+\) finally converts into B(OH\(^-\))\(^2-\) by the replacement of B–H bonds with B–OH\(^-\) bonds. Meanwhile, the intermediate M–H reacts with another M–H to generate H\(_2\) and to regenerate the metal active sites. Peña-Alonso et al. suggested that the intermediate M–H directly reacts with H\(_2\)O to generate H\(_2\).\(^50\) Guella et al. proposed a mechanism based on \(^{11}\)B NMR measurements, and suggested that the rate-controlling step of the metal catalyzed hydrolysis of NaBH\(_4\) is the cleavage of the O–H bond in water.\(^51,52\) It is worth noting that the catalytic hydrolysis of NaBH\(_4\) is closely related to the metal active sites, as there is a charge transfer between the metal active sites and NaBH\(_4\) or intermediates. Therefore, the development of efficient metal catalysts is very important.

Schlesinger and coworker first found that adding an acid into aqueous NaBH\(_4\) solution can significantly accelerate the hydrolysis reaction.\(^54\) Since then, a number of catalysts have been investigated to accelerate the NaBH\(_4\) hydrolysis. Noble-

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metal-based catalysts such as Ru, Rh, Pt, Pd and relevant alloys display excellent catalytic performances, but the high cost and scarcity of noble metals limit their industrial applications.31,35-36 Low-cost and Earth-abundant transition metal (Co, Ni, and Fe), metal boride and metal phosphide catalysts are viable alternatives.31,32 Among them, Co-based catalysts have been proven to be highly effective at catalyzing NaBH₄ hydrolysis (Table 1).31,59-61

2.1. Metal catalysts

Cobalt catalysts have been reported to be effective in catalytic hydrolysis of NaBH₄.31,59 These are usually deposited on a support material in the form of Co²⁺ ions and then reduced to metal Co. Microporous and mesoporous materials are considered as suitable support materials because it can effectively limit the growth or sintering of metal nanoparticles (NPs). Özkar and coworkers reported the synthesis of intrazeolite Co nanoclusters by using ion-exchange of Co²⁺ ions with the extra-framework Na⁺ ions in zeolite-Y followed by reduction with NaBH₄.62 The obtained intrazeolite Co nanoclusters provided 36,000 turnovers in the hydrolysis of NaBH₄ and retained 59% of their initial catalytic activity after the fifth run. Later on, Kwon and coworkers developed a hydroxyapatite-supported Co (Co/HAP) pre-catalyst, which showed long-term stability, retaining 75% of its initial catalytic activity over 20 days of use.63 Auroux and coworkers chose various materials with different acid/base surface properties as supports (hydroxalcates, KF/Al₂O₃, and heteropolyanions) to immobilize Co NPs.64 Among them, a heteropolyanion supported Co pre-catalyst showed the highest hydrogen generation rate in NaBH₄ hydrolysis.

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<td>6060</td>
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Table 1: Catalytic activities for hydrogen evolution from the hydrolysis of NaBH₄ by different catalysts.
Various carbon supported Co catalysts have been reported, which have the advantages of relatively low cost and excellent catalytic hydrogen production performance.\textsuperscript{55–69} Gou and co-worker found that Co supported on colloidal carbon spheres (Co/CSS) obtained from glucose exhibited a high HGR (10 400 mL min\(^{-1}\) g\(^{-1}\)) for NaBH\(_4\) hydrolysis at 293 K, whereas Co supported on carbon aerogels (Co/ACs) showed a higher HGR of 11 220 mL min\(^{-1}\) g\(^{-1}\).\textsuperscript{66,67} Zhang \textit{et al.} fabricated a Co@C pre-catalyst by using Co-MOF as the starting precursor.\textsuperscript{68} The Co@C-700 pre-catalyst exhibited higher catalytic activity than Co@C-600 and retained 93.1\% of its initial catalytic activity after five cycles in NaBH\(_4\) hydrolysis. Recently, Li \textit{et al.} synthesized nitrogen-doped mesoporous graphitic carbon encapsulated Co NPs (Co@NMGC) by a simple one-step pyrolysis of a complex of Co(NO\(_3\))\(_2\)-6H\(_2\)O and ethylenediaminetetraacetic acid (EDTA).\textsuperscript{69} Co@NMGC annealed at 773 K showed high catalytic activity and remarkable durability, retaining 82.5\% of its initial catalytic activity after 20 hydrolysis cycles.

Magnetic catalysts can be easily recycled with a permanent magnet from a spent NaBH\(_4\) system after hydrogen production.\textsuperscript{70–72} Chen \textit{et al.} synthesized a magnetic Co/IR-120 pre-catalyst by a combination of ion-exchange and reduction methods.\textsuperscript{70} A stable generation rate of highly pure hydrogen near 200 mL min\(^{-1}\) g\(^{-1}\) was achieved over the Co/IR-120 pre-catalyst in 100 mL of 5 wt\% NaBH\(_4\) solution. Kim and co-workers reported novel Co NPs supported on magnetic carbon (Co/Fe\(_3\)O\(_4@C\)) via a modified wetness impregnation–chemical reduction method.\textsuperscript{71} The abundant oxygen-containing-groups on the surface of the carbon layer can effectively immobilize and stabilize the Co NPs, thereby enhancing their catalytic activity for the hydrolysis of NaBH\(_4\). Ferromagnetic metals Co, Ni, and Fe were supported on porous SiO\(_2\) via an incipient wetness impregnation method.\textsuperscript{32} The catalytic activities of ferromagnetic metal/SiO\(_2\) followed the order Co/SiO\(_2\) > Ni/SiO\(_2\) > Fe/SiO\(_2\). Furthermore, various other Ni-based catalysts have been reported, but Co-based catalysts have been found to be the most superior in terms of the maximum hydrogen generation rate.\textsuperscript{73–75}

2.3. Metal boride catalysts

Schlesinger and co-workers first found that Co\(_2\)B was active for hydrogen evolution from the hydrolysis of NaBH\(_4\).\textsuperscript{54} Afterwards, there have been many reports on the preparation and catalytic activity of Co–B catalysts.\textsuperscript{60,61,76–81} It has been reported that the structure and catalytic activity of Co–B catalysts were sensitive to their preparation conditions. Jeong and co-workers prepared a Co–B pre-catalyst by the chemical reduction method using NaBH\(_4\) as a reductant.\textsuperscript{76} The obtained Co–B catalyst was amorphous and showed excellent catalytic performance for hydrogen generation from an aqueous alkaline NaBH\(_4\) solution, which was comparable to that of a Ru catalyst. Wu and co-worker found that amorphous Co–B after heat treatment showed much higher catalytic activity than the untreated sample, which is attributed to the formation of the crystalline state of Co–B.\textsuperscript{77} In addition, the Co–B catalyst treated at 500 °C exhibited the best crystallization and showed the highest hydrogen generation performances. When the Co–B catalyst was heated at 700 °C, the catalytic activity of the catalyst drastically decreased due to the decomposition of Co–B to form metal Co.

To further obtain efficient Co–B catalysts, the synthesis parameters such as the cobalt salt, ratio of NaBH\(_4/\text{Co}^{2+}\), calcination temperature and solvent type are investigated. Kim and coworkers examined the catalytic activity of a Co–B catalyst prepared by using different Co precursors (CoCl\(_2\) and CoSO\(_4\)) and NaBH\(_4/\text{Co}^{2+}\) molar ratios (0.67, 1.5, and 3) at different calcination temperatures (130, 250 and 450 °C).\textsuperscript{82} With CoCl\(_2\) as the precursor, a NaBH\(_4/\text{Co}^{2+}\) molar ratio of 1.5, and a calcination temperature of 250 °C, the hydrogen evolution rate of the Co–B catalyst was the highest. Demirci and coworkers further confirmed that CoCl\(_2\) is the best precursor, which showed a four times higher hydrogen generation rate than those of other Co salts (Co(CH\(_3\)COO)\(_2\), CoSO\(_4\), Co\(_2\)F\(_2\) and Co(NO\(_3\))\(_2\)).\textsuperscript{83} The sizes, morphologies, and properties of the Co–B catalyst are also greatly influenced by the solvents used. Zhao and coworkers found that the Co–B catalyst was more likely to agglomerate as the viscosity of the solvent increased.\textsuperscript{84} The catalytic activities of Co–B catalysts prepared in different solvents are in the order of MeOH > H\(_2\)O > EtOH > PrOH.

Although optimization of the synthesis parameters can improve the catalytic properties, the exothermic nature of the reduction reaction involves high surface energy and is easily prone to aggregation, leading to deteriorated activity. An efficient route to avoid agglomeration and increase the active surface area of Co–B particles is by doping with transition metals (Cr, Mo, W, etc.).\textsuperscript{85–91} These dopant metals, mainly in the form of oxides, act as atomic barriers that are able to significantly increase the surface area of the catalyst by avoiding agglomeration. Additionally, these dopant metals can also act as electron donors to increase the electron density on the active metal, which can further improve the catalytic activity of the Co–B catalyst. For instance, Patel \textit{et al.} conducted a systematic and comparative study on transition metal (Cr, Mo, W, Cu, Ni and Fe) doped Co–B catalysts for hydrogen generation by hydrolysis of NaBH\(_4\).\textsuperscript{86} They found that the hydrogen generation rate of Co–B catalysts doped with Cr, W, Mo, and Cu is about 3–4 times higher than that of the undoped catalysts. Ni and Fe are only able to slightly enhance the catalytic activity of the Co–B catalyst. In recent years, Co–B catalysts doped with Mn,\textsuperscript{92} Ti,\textsuperscript{93} Ce\textsuperscript{94} and Zn\textsuperscript{95} have been investigated and they also showed positive promotion effects on the hydrogen evolution of NaBH\(_4\) hydrolysis. Another efficient route to enhance the catalytic performance is by supporting Co–B NPs in a support material, such as carbon,\textsuperscript{96–98} Al\(_2\)O\(_3\),\textsuperscript{99} CeO\(_2\),\textsuperscript{99} TiO\(_2\),\textsuperscript{99,101} and Ni foam.\textsuperscript{102,103} The above supports can effectively inhibit the agglomeration of metal NPs and increase the active sites of the catalysts, and therefore can effectively improve the catalytic activity of the catalysts.

Other metal boride catalysts such as Ni–B, Cu–B, and Fe–B are also investigated for hydrogen evolution from the hydrolysis of NaBH\(_4\). Kim and co-workers reported a Ni–B–silica
nanocomposite pre-catalyst via an in situ reduction method.\textsuperscript{104} The obtained amorphous pre-catalyst was active, providing a hydrogen generation of 1916 mL min\textsuperscript{-1} g\textsuperscript{-1}. Later on, a stable and physically adhesive Ni-B on Ni foam was prepared by Lee and coworkers via a dipping-chemical reduction process and it exhibited high catalytic activity towards the hydrolysis of NaBH\textsubscript{4}.\textsuperscript{105} Zhang and coworkers prepared an amorphous Ni-B pre-catalyst via an ultrasonic complexing reduction route.\textsuperscript{116} They found that the chemical composition and phase state of the Ni-B pre-catalyst were greatly influenced by its complexing ability. The stronger the complexing ability of the complex, the smaller the size and the higher the dispersibility of the formed Ni-B, resulting in a higher catalytic activity of Ni-B. Recently, a Ni-B/NiFe\textsubscript{2}O\textsubscript{4} magnetic pre-catalyst with a metal loading of 10 wt% retained 85% of its initial activity after the fifth run, and the Ni-B/NiFe\textsubscript{2}O\textsubscript{4} can be easily separated from the reaction solution using an external magnet.\textsuperscript{107}

Lee reported a Fe-B/C cloth pre-catalyst by electrochemical adsorption techniques.\textsuperscript{108} The hydrogen generation rate using the Fe–B/C cloth pre-catalyst can achieve 813 mL min\textsuperscript{-1} g\textsuperscript{-1} at room temperature. The Fe–B/Ni foam catalyst was also prepared by the same group for hydrogen generation from NaBH\textsubscript{4} in a mixture solution of H\textsubscript{2}O and CH\textsubscript{3}OH.\textsuperscript{109} They found that using methanol as an additive to water can increase and stabilize the rate of hydrogen generation, but with lower gravimetric capacity. Bekirogullari compared the catalytic activities of Cu–B, Fe–B, and Ni–B pre-catalysts for hydrogen evolution from NaBH\textsubscript{4}.\textsuperscript{110} The results reveal that the catalytic activities of these metal borides followed an order of Cu–B > Ni–B > Fe–B.

### 2.3. Metal phosphide catalysts

Like Co–B, the other counterpart Co–P catalysts were also able to produce hydrogen from hydrolysis of NaBH\textsubscript{4}.\textsuperscript{111,112} Kwon and co-workers first reported a Co–P pre-catalyst electrodeposited on a Cu substrate in a sulfate based solution containing H\textsubscript{3}PO\textsubscript{2}– ions.\textsuperscript{111} They found that the amorphous Co–P pre-catalyst with 13 at% P showed the best hydrogen generation rate of 954 mL min\textsuperscript{-1} g\textsuperscript{-1} in a solution of 1 wt% NaOH and 10 wt% NaBH\textsubscript{4} at 303 K, which is 18 times higher than that of a pure Co pre-catalyst. To further obtain efficient Co–P catalysts, the synthesis parameters such as the pH value, reactant concentration and deposition time are investigated.\textsuperscript{113,114} Chen’s group found that the Co–P pre-catalyst formed at a pH value of 12.5, a NaH\textsubscript{2}PO\textsubscript{2} concentration of 0.8 M, and a deposition time no more than 6 min showed the highest catalytic activity for the hydrolysis of NaBH\textsubscript{4} solution.\textsuperscript{113} By tuning the deposition temperature, nanostructured Co–P/Cu sheets with different morphologies (nanoplatelets, nanospheres, pores and nanoclews) were selectively obtained.\textsuperscript{114} Notably, the nanostructured Co–P pre-catalyst deposited at 50 °C displayed novel hierarchical architectures and exhibited the highest catalytic properties with a high hydrogen release rate of 2275.1 mL min\textsuperscript{-1} g\textsuperscript{-1} and a low apparent activation energy of 27.9 kJ mol\textsuperscript{-1}.

The Co–P based catalysts prepared by chemical and electrodeposition methods are usually formed in powder form. Compared to nanoparticle catalysts, monolithic catalysts have obvious advantages such as no aggregation, easy separation and reuse, and they can be utilized as an on/off switch for on-demand hydrogen generation.\textsuperscript{115,116} Sun’s group designed 3D cobalt phosphide nanosheet arrays on Ti mesh (CoP/Ti mesh) via a topotactical conversion reaction.\textsuperscript{115} The obtained 3D monolithic pre-catalyst showed high catalytic activity, providing a maximum hydrogen generation rate of 6100 mL min\textsuperscript{-1} g\textsuperscript{-1} for NaBH\textsubscript{4} hydrolysis in alkaline media and an activation energy of 42.01 kJ mol\textsuperscript{-1}. Similarly, Liu and coworkers reported the synthesis of a CoP nanowire array integrated on a Ti mesh (CoP NA/Ti) for hydrolytic dehydrogenation of NaBH\textsubscript{4} in basic solutions.\textsuperscript{116}

Not only binary Co–P but also ternary Co–M–P (M = W, Ni, Cu, Fe, etc.) catalysts have been developed as robust catalysts for hydrogen generation from the hydrolysis of NaBH\textsubscript{4} alkaline solution.\textsuperscript{117–123} Ma and coworkers found that the catalytic activity of the amorphous Co–P pre-catalyst could be markedly improved by incorporating W.\textsuperscript{117} However, the hydrogen generation rate of the Co–W–P pre-catalyst lost 49% of its activity after 5 cycles. Furthermore, by depositing Co–W–P on γ-Al\textsubscript{2}O\textsubscript{3} and carbon cloth, the catalytic activity and stability of the pre-catalyst can be significantly improved.\textsuperscript{118,119} Kim et al. synthesized porous Co–Ni–P on Cu substrates by electrodeposition.\textsuperscript{120} The three-dimensional Co–Ni–P pre-catalyst formed at a high cathodic current density (>0.5 A cm\textsuperscript{-2}) had a larger surface area than the two-dimensional pre-catalyst formed at a low cathodic current density (0.01 A cm\textsuperscript{-2}), which significantly increased the rate of hydrogen generation in the alkaline NaBH\textsubscript{4} solution. Diverse nanostructures of Co–Ni–P pre-catalysts have been prepared on Cu sheets via the electroless plating method by tuning the depositional pH value.\textsuperscript{121} Compared with football-, granular-, and shuttle-like Co–Ni–P, mockstrawberry-like Co–Ni–P exhibited the highest catalytic properties. It has been reported that the alloying of Cu into Co–Cu–P was also able to improve their catalytic activity in hydrogen production via NaBH\textsubscript{4} hydrolysis.\textsuperscript{122} Lately, Fe-doped CoP nanoarrays on Ti foil (Fe-CoP/Ti) have been investigated by Sun’s group as a robust catalyst for NaBH\textsubscript{4} hydrolysis, resulting in a hydrogen generation rate of 6060 mL min\textsuperscript{-1} g\textsuperscript{-1} and an activation energy of about 39.6 kJ mol\textsuperscript{-1}.\textsuperscript{123}

Overall, Co-based catalysts are demonstrated to be cost-effective, active and stable catalysts for hydrogen generation from the hydrolysis of NaBH\textsubscript{4}. In addition, most of the reported metal borides/phosphides are in an amorphous state.\textsuperscript{61,124} The materials in the amorphous state have great structural distortion and high concentrations of unsaturated coordination sites, which make them show high catalytic activity. After heat treatment, the amorphous metal borides can be transformed into a crystalline state, because of which they usually exhibit higher catalytic performance. However, the material after heat treatment is often a mixture of the metal, borides and/or oxides. Thus, its composition and surface structures are complex, and it is difficult to identify the real active sites. Furthermore, the mechanism of their catalytic hydrogen production is not clear. Particularly, what is the exact active
composition of Co and B or P to achieve high catalytic activity? Therefore, future research can be focused on mechanistic studies of the hydrolysis reaction at the surface of the Co-based catalysts.

3. Ammonia borane

Ammonia borane (NH₃BH₃, AB) is a stable solid at room temperature with a density of 0.780 g cm⁻³ and a melting point of 112–114 °C.²¹⁵ Owing to its high hydrogen content (19.6 wt%), low molecular weight (30.9 g mol⁻¹), and nontoxic and environmentally friendly nature, NH₃BH₃ has been considered as a promising hydrogen storage material.¹²⁶–¹³³ Hydrogen stored in NH₃BH₃ can be released by either thermal decomposition in the solid phase or catalytic solvolysis (hydrolysis and methanolysis) under mild conditions.¹²⁶,¹³⁴–¹³⁸ There are considerable works involving hydrogen release from the thermal decomposition of NH₃BH₃.¹³⁴–¹³⁷ Although pure NH₃BH₃ possesses 3 equivalents of H₂, only 2 equivalents could be released at a temperature of 200 °C. In order to maximize the efficacy of NH₃BH₃, higher temperatures are needed, which also results in the release of the by-product borazine. To decrease the thermolysis temperature and suppress the volatile byproducts, various approaches have been achieved, including nano-confinement, catalysis, dispersion in ionic liquids and organic liquids, and the synthesis of derivatives (e.g., metal amidoboranes).¹³⁹–¹⁴² Generally speaking, thermal decomposition of NH₃BH₃ requires high temperature and the reaction is relatively difficult to control. In contrast, the hydrolytic (eqn (2)) or methanolytic (eqn (3)) dehydrogenation of NH₃BH₃ can be conducted at room temperature with a stoichiometric hydrogen release in the presence of suitable catalysts.²⁵,¹²⁶,¹³⁸ The effective gravimetric hydrogen storage capacity (GHSC) of an NH₃BH₃ hydrolysis system [NH₃BH₃·2H₂O] is about 8.9 wt%, which is higher than that from NH₃BH₃ methanolysis [NH₃BH₃·4MeOH, 3.9 wt%].

\[
\text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4\text{BO}_2 + 3\text{H}_2 \quad (2)
\]

\[
\text{NH}_3\text{BH}_3 + 4\text{MeOH} \rightarrow \text{NH}_4\text{B(OMe)}_4 + 3\text{H}_2 \quad (3)
\]

In 2006, Xu’s research group firstly found that a stoichiometric amount of hydrogen could be released from the hydrolysis of NH₃BH₃ by using noble metal-based (Pt, Ru, and Pd) catalysts.¹²⁶ Since then, numerous studies have been reported on hydrogen generation from the hydrolysis of NH₃BH₃.¹⁴³–¹⁴⁸ Also, several reviews have been reported on the research progress on the hydrolysis of NH₃BH₃.²¹,²⁵,¹²⁷,¹⁴⁹–¹⁵³ Here, we have mainly summarized the most active noble-metal-free nanocatalysts for the hydrolytic (Table 2) or methanolytic (Table 3) dehydrogenation of NH₃BH₃.

3.1. Monometallic catalysts

Xu’s research group reported that non-noble-metals Co, Ni and Cu supported on different supports [Al₂O₃, SiO₂ and C] were catalytically active, whereas supported Fe was inactive in hydrolytic dehydrogenation of NH₃BH₃ at room temperature.¹⁵⁴ Unexpectedly, amorphous Fe NPs synthesized by in situ reduction (Fe/NH₃BH₃ = 0.12) with NH₃BH₃ and NaBH₄ exhibited noble metal-like catalytic activity in the hydrolysis of AB (Fig. 1).¹⁵⁵ The high activity of the amorphous metal NPs could be attributed to their amorphous structure, which has a much greater structural distortion and therefore a much higher concentration of active sites for the reaction than its crystalline counterpart. Then, the amorphous Co and Ni NPs were also found to exhibit enhanced catalytic performance in comparison with their crystalline counterparts.¹⁵⁶,¹⁵⁷ In particular, the amorphous Co NPs showed the highest catalytic activity with a TOF of 44.1 min⁻¹ for hydrogen production from the hydrolysis of NH₃BH₃, which is the highest among the non-noble metal catalysts ever reported.¹⁵⁶

Co-Based catalysts have been widely studied in recent years due to their relatively higher catalytic activity and low cost.¹⁵⁸–¹⁶⁵ Xu’s research group synthesized dendrimer-encapsulated Co NPs ([G6-OH(Co₆₀)]) through the complexation of Co²⁺ cations with the internal tertiary amine of sixth-generation hydroxyl-terminated poly(amideamine) dendrimers followed by reduction with NH₃BH₃ and NaBH₄.¹⁵⁸ The synthesized [G6-OH(Co₆₀)] was highly dispersed (1.6 nm) and active for the hydrolysis of NH₃BH₃. Duan et al. constructed a Co@g-C₃N₄ core–shell nanostructure anchored onto the surface of rGO sheets [Co@g-C₃N₄ rGO], where g-C₃N₄ shells could protect Co cores from aggregating or leaching and rGO sheets could strengthen the magnetic momentum transfer of Co NPs from the external magnetic field.¹⁵⁹ The self-stirring mode in the batch reactor and the magnetic fixing, stirring, and separating mode in the continuous-flow slurry-bed reactor provided an excellent catalytic process with Co@g-C₃N₄ rGO as the pre-catalyst. To further improve the activity of Co-based catalysts for NH₃BH₃ hydrolysis, post-modified supports have been used. Lu and coworkers reported well-dispersed Co NPs with an average size of 2.6 nm on PEI-decorated GO, and the resultant Co@PEI-GO nanocomposites showed excellent activity (39.9 min⁻¹) due to the chelation effect of PEI with precursor metal ions.¹⁶⁰

Due to their tunable porous structures, metal–organic frameworks (MOFs) have been used as supports to control the sizes of metal NPs.¹⁶⁶–¹⁶⁸ Gu and coworkers reported amorphous Co NPs with small particle size (1.6–2.6 nm) immobilized by MIL-101 through an ultrasound-assisted in situ method. The obtained Co/MIL-101 pre-catalyst showed excellent catalytic activity (51.4 min⁻¹) for hydrogen evolution from the hydrolysis of NH₃BH₃.¹⁶⁷ Chen and coworkers adopted a covalent triazine framework (CTF) as a support with the merits of high surface area, a well-defined porous structure and high nitrogen content (~17%).¹⁶⁹ Specifically, the Co/CTF with 3 wt% Co loading showed the highest activity towards NH₃BH₃ hydrolysis, providing a TOF value of 42.3 min⁻¹ at room temperature. Zhou and coworkers developed a new type of metal–organic hybrid material, the porous coordination cage (PCC), which is efficient at stabilizing Co nanoclusters.¹⁷⁰ The obtained Co@PCC-2a exhibited extraordinary catalytic activity (90.1 min⁻¹) in the hydrolysis of NH₃BH₃ (Fig. 2).
Table 2  Catalytic activities for hydrogen evolution from the hydrolysis of NH$_3$BH$_3$ by different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp. (K)</th>
<th>$n_{metal}/n_{AB}$</th>
<th>TOF (molH$<em>2$ mol$</em>{metal}^{-1}$ min$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>In situ Fe NPs</td>
<td>RT</td>
<td>0.12</td>
<td>3.12</td>
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<td>155</td>
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<tr>
<td>Co/γ-Al$_2$O$_3$</td>
<td>RT</td>
<td>0.018</td>
<td>2.27</td>
<td>62</td>
<td>154</td>
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<tr>
<td>In situ Co NPs</td>
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<td>44.1</td>
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<td>156</td>
</tr>
<tr>
<td>G6-OH(Co$_{60}$)</td>
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<td>158</td>
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<td>Co/Pd-GO</td>
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<td>39.9</td>
<td>28.2</td>
<td>160</td>
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<td>31.3</td>
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<td>42.7</td>
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<td>2.5</td>
<td>—</td>
<td>173</td>
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<td>Ni@MSC-30</td>
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<td>7.5</td>
<td>66.6</td>
<td>179</td>
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<td>0.018</td>
<td>0.23</td>
<td>—</td>
<td>182</td>
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<td>0.069</td>
<td>0.72</td>
<td>48.8</td>
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<td>1.25</td>
<td>51.8</td>
<td>201</td>
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<td>0.0031</td>
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<td>202</td>
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<td>0.12</td>
<td>11.1</td>
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<td>0.072</td>
<td>54.8</td>
<td>—</td>
<td>224</td>
</tr>
<tr>
<td>Cu$<em>{0.7}$Ni$</em>{0.3}$/MCM-41</td>
<td>298</td>
<td>0.05</td>
<td>10.7</td>
<td>38</td>
<td>228</td>
</tr>
<tr>
<td>CuNi/47-SiO$_2$</td>
<td>298</td>
<td>0.165</td>
<td>23.5</td>
<td>32.4</td>
<td>229</td>
</tr>
<tr>
<td>Cu$<em>{0.3}$Co$</em>{0.7}$/O/GO</td>
<td>298</td>
<td>0.024</td>
<td>70</td>
<td>45.5</td>
<td>243</td>
</tr>
<tr>
<td>Ni-P</td>
<td>298</td>
<td>0.12</td>
<td>40.4</td>
<td>44.6</td>
<td>255</td>
</tr>
<tr>
<td>Co$^a$</td>
<td>298</td>
<td>0.043</td>
<td>72.2</td>
<td>46.7</td>
<td>262</td>
</tr>
<tr>
<td>Ni$<em>{0.8}$Co$</em>{0.2}$/P/GO$^a$</td>
<td>298</td>
<td>0.026</td>
<td>109.4</td>
<td>—</td>
<td>263</td>
</tr>
</tbody>
</table>

$^a$ The reaction was promoted with the addition of NaOH.

Table 3  Catalytic activities for hydrogen evolution from the methanolysis of NH$_3$BH$_3$ by different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp. (K)</th>
<th>$n_{metal}/n_{AB}$</th>
<th>TOF (molH$<em>2$ mol$</em>{metal}^{-1}$ min$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$O</td>
<td>298</td>
<td>0.15</td>
<td>0.16</td>
<td>—</td>
<td>198</td>
</tr>
<tr>
<td>Nano-Cu@Cu$_2$O</td>
<td>298</td>
<td>0.15</td>
<td>0.12</td>
<td>—</td>
<td>198</td>
</tr>
<tr>
<td>Nano-Cu</td>
<td>298</td>
<td>0.15</td>
<td>0.08</td>
<td>—</td>
<td>198</td>
</tr>
<tr>
<td>PVP-stabilized Ni</td>
<td>298</td>
<td>0.005</td>
<td>12.1</td>
<td>62</td>
<td>267</td>
</tr>
<tr>
<td>Co-Ni-B</td>
<td>RT</td>
<td>0.2</td>
<td>10</td>
<td>—</td>
<td>276</td>
</tr>
<tr>
<td>Co-Co$_{0.9}$</td>
<td>RT</td>
<td>0.2</td>
<td>6</td>
<td>—</td>
<td>276</td>
</tr>
<tr>
<td>Ni-Ni$_{0.8}$B</td>
<td>RT</td>
<td>0.2</td>
<td>3.6</td>
<td>—</td>
<td>276</td>
</tr>
<tr>
<td>Flower-like Cu</td>
<td>298</td>
<td>0.15</td>
<td>2.41</td>
<td>34.2</td>
<td>277</td>
</tr>
<tr>
<td>Cu-Cu$<em>{0.8}$O-Cu$</em>{0.2}$C</td>
<td>298</td>
<td>0.04</td>
<td>24</td>
<td>67.9</td>
<td>278</td>
</tr>
<tr>
<td>b-Cu$_{0.8}$O/CF</td>
<td>298</td>
<td>0.018</td>
<td>13.3</td>
<td>34.7</td>
<td>279</td>
</tr>
<tr>
<td>CuNi/graphene</td>
<td>298</td>
<td>0.03</td>
<td>49.1</td>
<td>24.4</td>
<td>280</td>
</tr>
<tr>
<td>Cu/Co(OH)$_2$</td>
<td>298</td>
<td>0.129</td>
<td>61.63</td>
<td>37.6</td>
<td>281</td>
</tr>
</tbody>
</table>
Recently, carbonization of inorganic/organic composites has been developed to prepared catalysts for the AB hydrolysis reaction due to their excellent chemical and mechanical stabilities, large specific surface areas and various functionalities.\textsuperscript{163,171–174} Chen and coworkers reported the preparation of Co@N–C pre-catalysts through one-step thermolysis of Co [salen, $N,N'$-bis(salicylidene)ethylendiamine] at selected temperatures ($600–800$ °C) under an Ar atmosphere.\textsuperscript{172} They found that Co@N–C obtained at $700$ °C (Co@N–C-700) shows superior catalytic performance (5.6 min$^{-1}$) and high sustainability among the synthesized pre-catalysts. After that, they also synthesized Co NPs (~3.5 nm) supported on nitrogen-doped porous carbon nanowires (Co/NPCNW) by carbonization of a Co–metal organic framework (Co-MOF), which show a TOF of $7.29$ min$^{-1}$ and a relatively low activation energy of $25.4$ kJ mol$^{-1}$.\textsuperscript{172} Later on, Zhang et al. reported a series of highly active and stable nitrogen-doped mesoporous carbon embedded-Co NP pre-catalysts through a thermolysis and etching combined strategy.\textsuperscript{173} More recently, Yang and coworkers employed a selective atom evaporation-isolation strategy with bimetal Co/Zn-MOF-74 as a sacrificial template to obtain a metallic Co/HPC pre-catalyst by direct carbonization and in situ reduction under an Ar atmosphere.\textsuperscript{174} The as-synthesized Co/HPC pre-catalyst exerted higher catalytic activity and showed excellent reusability as compared to the Co/HPC derived from pure Co-MOF-74. The excellent catalytic performance can be attributed to the uniform dispersion and small particle size of metallic Co obtained under the assistance of the dopant Zn.

Ni catalysts are also widely studied as low cost non-noble metal catalysts owing to their exceptional activity in catalytic dehydrogenation of aqueous AB (Table 2).\textsuperscript{175–179} Monodisperse Ni NPs (3.2 nm) supported on Ketjen carbon black (Ni/C) showed high catalytic activity for the hydrolysis of AB with a TOF of $8.8$ min$^{-1}$.\textsuperscript{175} However, Ni/C was not stable during the reusability test due to the agglomeration of Ni NPs on the carbon support. In order to improve the stability of Ni NPs, they used various oxides including SiO$_2$, Al$_2$O$_3$, and CeO$_2$ as support materials.\textsuperscript{180} They found that 3.2 nm Ni NPs supported on SiO$_2$ showed the highest activity (13.2 min$^{-1}$) and durability. Subsequently, the Ni NPs (6.3 ± 1.7 nm) deposited into the nanoporous carbon (MSC-30) synthesized by Xu’s research group showed excellent catalytic activity with a TOF value as high as 30.7 min$^{-1}$, which is the highest one among all of the Ni catalysts ever reported for this hydrolysis reaction at room temperature.\textsuperscript{181} They also reported the synthesis of highly dispersed Ni NPs immobilized on the zeolitic metal–organic framework ZIF-8 (Ni/ZIF-8), which showed high catalytic activity and durability.\textsuperscript{182} They pointed out that this is the first example of water-stable MOF-supported metal NPs for hydrogen generation from hydrolysis of NH$_3$BH$_3$. Using the zeolitic metal–organic framework ZIF-8 as the support, Astruc and coworkers further developed highly dispersed Fe, Co, Ni and Cu NPs, and the highest catalytic performance with a TOF value of 85 min$^{-1}$ was achieved in the presence of Ni/ZIF-8 with the assistance of an additive (NaOH).\textsuperscript{183}

Zhong and coworkers reported a Ni/CNT hybrid pre-catalyst for the hydrolysis of NH$_3$BH$_3$.\textsuperscript{184} Combined with identical high-resolution TEM images, scanning transmission X-ray microscopy (STXM) clearly revealed the existence of a strong interaction between Ni NPs and thin CNTs [C–O–Ni bonds], which favored the tunable electronic structure of Ni NPs and facilitated the catalytic hydrolysis process. Later on, Qin and coworkers presented a facile atomic layer deposition approach (ALD) to synthesize highly dispersed Ni NPs on CNTs.\textsuperscript{185} The resultant Ni/CNT pre-catalyst produced with 200 ALD cycles showed the best catalytic activity (26.2 min$^{-1}$) among all the Ni/CNT pre-catalysts. Mahyari et al. employed a three-dimensional nitrogen-doped graphene-based framework (3D-(N)GF) as a support to immobilized Ni NPs, which showed excellent catalytic activity (41.7 min$^{-1}$) and high stability in NH$_3$BH$_3$ hydrolysis.\textsuperscript{186} Recently, our group reported a facile chemical reduction method to incorporate a small amount of inactive metals (Mo,
Cr, and W) into Ni NPs. The characterization results revealed that the incorporation of Mo (mainly in the oxidation state) can not only reduce the metal particle size and crystallinity of the metal NPs, but also increase the electron density on the metal surface, which can effectively improve the catalytic activity of the catalysts. To further improve the dispersion and activity of the catalyst, Ni NPs modified with a Mo dopant have been synthesized on graphene (Ni–Mo/graphene), and they exhibit a high Pt-like catalytic activity (66.7 min⁻¹) and robust durability in the hydrolysis of NH₃BH₃ at room temperature (Fig. 3). In addition, our synthesis is not limited only to Ni–M (M = Mo, Cr, W), but can also be extended to other transition metal systems (Cu–M, Co–W, etc.), providing a general method for the synthesis of highly efficient catalysts for the hydrogen evolution reaction.

Ni doped with CeOₓ and supported on graphene (Ni–CeOₓ/graphene) was also fabricated by our research group via a facile chemical reduction route. The combination of CeOₓ, metal, and graphene of the Ni–CeOₓ/graphene pre-catalyst confers remarkably enhanced catalytic activity (68.2 min⁻¹) for the hydrolytic dehydrogenation of NH₃BH₃ (Fig. 4), as well as high stability. In addition, some other rare-earth metal oxides (ReOₓ, Re = La, Dy, Er, Yb, Gd, and Tb) doped Ni/graphene (Ni–ReOₓ/graphene) were also prepared and all showed higher catalytic activities than pure Ni/graphene. The excellent catalytic activities of Ni–ReOₓ/graphene might be attributed to the similar physical and chemical properties of the ReOₓ species, all of which promote the active sites of Ni to electron-rich states that are beneficial for the catalytic reaction. By using a similar approach, Co–CeOₓ/NGH and CuNi–CeOₓ/rGO were prepared and they showed synergistic and superior catalytic activities.

Comparing Co- and Ni-based catalysts, Cu-based catalysts have been reported to show a lower catalytic activity (Table 2). In 2006, Xu and coworkers found that Cu/γ-Al₂O₃ was catalytically active in NH₃BH₃ hydrolysis (0.78 min⁻¹), but it takes nearly 600 minutes to release 2.83 equivalents of hydrogen (nCu/nAB = 0.018). Subsequently, nanostructured Cu, Cu₂O, and Cu₄@Cu₄O NPs were synthesized by Kalindini and co-workers via the solvated metal atom dispersion (SMAD) method. They found that core–shell Cu₄@Cu₂O and Cu₂O NPs are more active than pure Cu NPs for this hydrolysis reaction. After that, Fukuzumi and co-worker synthesized a series of Cu/Co₃O₄ composite pre-catalysts by a conventional impregnation method. The catalytic activities of Cu/Co₃O₄ were significantly dependent on the shape and size of nanosized Co₃O₄, and it was found that Cu₂O₄ with a hexagonal sheet shape showed better catalytic activity than that with a cube or uncontrolled shape. They also found that capping of Cu₂O with Co₃O₄ NPs was an effective way to suppress agglomerate formation, which made the Cu₂O₄–Co₃O₄ composites exhibit high catalytic reactivity in hydrolytic dehydrogenation of NH₃BH₃.

Ozkar and co-worker synthesized zeolite confined Cu NPs by ion-exchange of Cu²⁺ with the extra framework Na⁺ in zeolite-Y followed by the reduction of the Cu²⁺ ions with NaBH₄. The zeolite confined Cu NPs were found to be active in the hydrolysis of NH₃BH₃ with a TOF value of 0.78 min⁻¹. Cu NPs supported on magnetic SiO₂/CoFe₂O₄ (CuNPs@SCF) were reported to have an initial TOF of 40 min⁻¹ for hydrolysis of NH₃BH₃ at 298 K. The authors claimed that this TOF value was higher than those of all the reported non-noble metal catalysts for the same hydrolysis reaction. It should be noted that the support of CoFe₂O₄ was not considered in the TOF calculation. The oxides of Fe and Co are difficult to be reduced by NH₃BH₃; however, they might be reduced by the Cu–H active species or hydrogen released in the hydrolysis reaction.

Our group reported the synthesis of reduced graphene oxide supported Cu NPs (Cu/RGO) via a facile in situ procedure using NH₃BH₃ as a reductant. The obtained Cu/RGO showed a higher catalytic activity than Cu/graphite powder, Cu/activated carbon and free Cu NPs, over which the NH₃BH₃...
hydrolysis reaction is completed in 8.3 min, giving a TOF value of 3.61 min at 298 K. We also found that the ultrafine Cu NPs (∼2 nm) encapsulated in porous silica nanospheres can be simply fabricated via a one-pot synthetic route in a reverse micelle system.204 The outer shell of silica can effectively prevent the Cu NPs from aggregation. The Cu@SiO₂ core–shell nanospheres showed superior activity as compared to Cu/commercial SiO₂, Cu/SiO₂ and free Cu NPs for hydrolysis of NH₃BH₃ (Fig. 5). Furthermore, the Cu@SiO₂ core–shell nanospheres showed long-term stability, retaining 90% of their initial catalytic activity even after 10 runs. Recently, Zhang and coworkers fabricated Cu nanocrystals with different nanostructures (nanocubes, nanowires, nanotetrahedra, etc.) via simply adjusting the addition proportion of the reductant and orientation agent.205 In comparison with the ordinary Cu NPs with extremely low or hardly any catalytic performance activity, all of the regularly shaped Cu nanocrystals showed high catalytic activity, among which the nanocubed Cu nanocrystals exerted the best catalytic performance for hydrolyzing NH₃BH₃ with 3 equiv. of H₂ extracted within 28 min at 298 K. However, the productivity of the hydrolysis reaction over a nanocubed Cu catalyst showed an obvious decrease after 5 runs.

3.2. Heterometallic catalysts

Heterometallic catalysts, including bi-metallic and multi-metallic catalysts, with unique structures may show higher catalytic performance than their monometallic counterparts due to the strong synergistic effects/electronic effects between the metals.23,206–209 A number of heterometallic catalysts, such as Fe–Ni,210–213 Fe–Co,214–216 Ni–Co,217,218 Cu–Fe,219 Cu–Co220–223 and Cu–Ni,224–228 have been reported toward the hydrolysis of NH₃BH₃. For example, our group prepared a series of Cu₁₋ₓFeₓ alloy NPs by a very simple in situ reduction method, and the optimal Cu₀.₃₃Fe₀.₆₇ alloy NPs exhibited superior catalytic activity with a TOF value of 13.95 min⁻¹ (Fig. 6).219 Moreover, these in situ synthesized CuFe alloy NPs can be easily separated from the solution with an external magnet, and they showed good recycling stability.

In subsequent research, various distinct support materials, such as carbon materials, nanotubes, nanofibers, silica spheres, metal–organic frameworks (MOFs), and so on, have been used to fabricate well-dispersed and stable bimetallic NP nanocatalysts.220–224,229–231 Co decorated Cu NPs on graphene (graphene–CuCo) have been synthesized by Yan et al. via a one-step self-catalytic method, which showed high efficiency toward the hydrolytic dehydrogenation of NH₃BH₃.220 Xu’s research group employed diamine-functionalized reduced graphene oxide as a support for CuCo NPs (CuCo/PDDA-rGO), which showed higher catalytic performance (41 min⁻¹) as compared to CuCo/rGO (20.6 min⁻¹).221 Later on, Zhang and coworkers prepared poly(diallyldimethylammonium chloride) functionalized halloysite nanotube supported Cu–Co NPs (CuCo/PDDA-HNTs), in which CuCo NPs were highly dispersed on the surface of halloysite nanotubes and they showed an extraordinary catalytic property (30.8 min⁻¹) in NH₃BH₃ hydrolysis reaction.222 Zahmakin and coworkers reported copper-cobalt alloy NPs supported on activated carbon (CuCo/C) by a surfactant-free deposition-reduction technique. The obtained CuCo/C showed excellent catalytic performance with an initial TOF of 45 min⁻¹.223 Kleitz and coworkers selected mesoporous carbons (CMK-1 and MCNS) and mesoporous silica (MCM-48) as supports for CuNi alloy NPs.224 The catalytic performances of carbon-supported Cu₀.₅Ni₀.₅/CMK-1 and Cu₀.₅Ni₀.₅/MCNS are comparable in the hydrolysis of NH₃BH₃ and are 3-fold higher than that of silica-supported Cu₀.₅Ni₀.₅/MCM-48. Yu and coworkers successfully immobilized CuNi NPs on six differently sized SiO₂ spheres (47, 97, 195, 333, 391 and 485 nm).225 The results showed that the catalytic activity of CuNi/SiO₂ increases with the decrease of SiO₂ particle size, due to which the CuNi NPs supported on the smallest SiO₂ (CuNi/47-SiO₂) exhibit the
highest catalytic activity in the hydrolysis of NH3BH3 at 298 K. However, the stability of CuNi/47-SiO2 showed obvious degradation after seven cycles. Our group successfully encapsulated ultrafine Cu–Co NPs (~2 nm) inside SiO2 nanospheres (CuCo@SiO2) (Fig. 7), which can effectively prevent metal NP aggregation and enhance the pre-catalyst stability.230 The optimized Cu0.5Co0.5@SiO2 pre-catalyst showed excellent catalytic activity in the hydrolysis of NH3BH3 and preserved 93% of its initial catalytic activity even after 10 runs. CuCo alloy NPs confined in the pores of MIL-101 (CuCo@MIL-101) via a double-solvent method combined with the excellent reduction approach also showed high activity and long durability for hydrolysis of NH3BH3.231

Trimetallic CuCoMo NPs without any surfactant or support have been fabricated by our group through a facile co-reduction method.239 Compared to their bi-/mono-metallic counterparts, the obtained optimized trimetallic Cu0.72Co0.18Mo0.1 NPs showed synergistic and superior catalytic activity for hydrogen evolution from the hydrolysis of NH3BH3.232 In addition, H2 generation over Cu1@Co4 NPs is the most active among them, with a TOF value of 46.0 min−1 at 298 K (Fig. 8). Moreover, the catalytic performance of Cu0.72Co0.18Mo0.1 can be further significantly improved by introducing NaOH as a promoter, providing a TOF value as high as 119.0 min−1 at 298 K, which is among the highest values of all the reported non-noble metal catalysts (Table 2) and even higher than that of the commercial Pt/C pre-catalyst for the same reaction.236 However, introducing the NH4+ species (e.g., NH3·H2O, NH4Cl, etc.) into the reaction system is unfavorable for the hydrolysis of AB.

In addition to alloy NPs, core–shell NPs have also attracted considerable attention due to their unique physical and chemical properties, and they exhibited excellent catalytic performance in hydrolytic dehydrogenation of NH3BH3.232–238 Among them, catalysts with a Cu core are the most attractive. In 2011, Xu’s research group first reported the synthesis of Cu@M (M = Co, Fe, Ni) NPs via a simple one-step seeding-growth route using NH3BH3 as a weak reducing agent, which could selectively reduce Cu2+ first to form the core, and successively reduce M2+ (M = Co, Fe, Ni) to form the shell.233 A relatively stronger reductant NaBH4, instead of NH3BH3, resulted in the formation of CuM alloys. Compared to monometallic and alloy counterparts, the core–shell Cu@M (M = Co, Fe, Ni) NPs showed synergistic and superior catalytic activity for hydrogen evolution from the hydrolysis of NH3BH3. In addition, H2 generation over Cu1@Co4 NPs is the most active among that over all the Cu@M (M = Co, Fe, Ni) NPs, with which the hydrolysis reaction is completed within 10 min at room temperature. By following a similar approach, various core–shell catalysts based on Cu as a core, such as bimetallic Cu@Co234 and tetrametallic Cu@FeNi236 Cu@FeCo237 Cu@CoNi238,239 Cu@CoMo240 and even trimetallic Cu@FeCoNi241 have been synthesized and they showed higher activities than the corresponding monometallic and alloy counterparts toward the hydrolysis of ammonia borane for hydrogen production.

3.3. Other catalysts

Since non-noble metal NPs are very easy to oxidize, the direct use of non-noble metal oxides as catalysts for hydrolytic dehydrogenation of NH3BH3 has attracted much attention in recent years.241–244 Li and coworkers prepared CuCo2O4 pre-catalysts with different shapes (nanoplates, nanosheets, and nanoparticles).241 Among them, the nanoplate-shaped CuCo2O4 pre-catalyst showed the best catalytic activity for hydrogen production from the hydrolysis of NH3BH3, giving a TOF value of 44 min−1 at room temperature. Moreover, the CuCo2O4 nanoplate pre-catalyst almost retained its initial catalytic activity after eight cycles, indicative of its excellent durability and stability. Later on, they developed a series of non-noble metal oxides such as NiCo2O4242 MnCo2O4245 CuMoO4246 CuNiCo2O4247 Co2O4/CuMoO4248 CuO–NiO/CuO249 and Co1−xNi1−xO2@Co3Ni1−xO4,250 which are active in NH3BH3 hydrolysis reaction. Zhong and coworkers reported the synthesis of bimetallic oxide NPs CuCo1−xO deposited on graphene oxide (GO) via a facile route.243 The obtained Cu0.8Co0.2O/GO pre-catalyst exhibits an initial TOF value as high as 70.0 min−1 for the hydrolysis of NH3BH3, owing to the interfacial interaction between CuCoO NPs and GO. Moreover,
they performed the first in situ XAS experiments to study the electronic structure changes of the pre-catalyst during hydrolysis. Recently, Liu and coworkers reported a graphene oxide supported Cu@CuCoOx pre-catalyst, with which superior catalytic activity was achieved toward the hydrolysis of NH₃BH₃ with a TOF of 44.6 min⁻¹ at room temperature.²⁴⁴ With a metal oxide as a pre-catalyst, the catalytically active component of the catalyst is the zero-valent metal because a part of the metal oxide can be reduced by NH₃BH₃. Therefore, such metal oxide catalysts are mainly Cu-based oxides, because Cu oxides can be easily reduced to Cu(0) by NH₃BH₃ at room temperature.

Non-noble-metal catalysts are also easily prone to aggregation in air and under the catalytic reaction conditions, resulting in loss or deactivation of catalytic activity. Recent studies have shown that the catalytic activity and stability of non-noble-metal catalysts could be improved by the introduction of metalloid elements (e.g. B and P).⁶⁰,⁶¹,¹¹⁶,²⁵¹⁻²⁵⁷ A series of Co–B catalysts have been reported to show high catalytic activity and durability for hydrogen generation from NH₃BH₃.²⁵¹,²⁵²,²⁵⁸⁻²⁶¹ For example, Figen and Coskuner synthesized a Co–B pre-catalyst by the sol–gel reaction of boron oxide with cobalt chloride hexahydrate in the presence of citric acid.²⁵² The obtained amorphous Co–B pre-catalyst showed higher catalytic activity than a crystalline Co–B catalyst due to its high specific surface area and it retained 90% of its initial activity after 4 runs. They also found that Co–B supported on mesoporous silica (SBA-15) and a Co–B thin film pre-catalyst deposited by Pulsed Laser Deposition (PLD) were able to decrease the activation energy, thus improving the catalytic activity in NH₃BH₃ hydrolysis.²⁵⁸,²⁵⁹

Fu and coworkers reported the synthesis of Ni₂P NPs by reacting Ni(OH)₂ with solid NaH₂PO₂ in argon at 543 K.²⁵⁴ The obtained Ni₂P NPs (<12 nm) showed excellent catalytic activity and high sustainability toward hydrogen evolution from the hydrolysis of NH₃BH₃ with an initial TOF of 40.4 min⁻¹ at 298 K. In addition, they investigated the reaction mechanism via DFT calculations (Fig. 9), suggesting that the combination of the Ni₂P surface and substrate molecules significantly enhances the hydrolytic dehydrogenation activity by reducing the reaction barrier, making it easy to overcome at room temperature. They also found that the introduction of anions (OH⁻, F⁻, and Cl⁻) during NH₃BH₃ hydrolysis could significantly promote the catalytic activity in NH₃BH₃ hydrolysis reaction over a Co–P pre-catalyst at room temperature.²⁶² Moreover, the effect of OH⁻ was higher than that of F⁻ and Cl⁻ on the TOF, and a high TOF of 72.2 min⁻¹ was achieved at a CoP/NH₃BH₃ molar ratio of 0.041 at 298 K. Recently, a series of Co-doped Ni₂P NPs and their nanohybrid with graphene oxide were also fabricated by Fu and coworkers.²⁶¹ The optimal Ni₂₋₅Co₃₋₅P/GO pre-catalyst shows a high initial TOF of up to 109.4 min⁻¹ in the presence of NaOH at 298 K. The incorporation of Co into Ni₂P can effectively optimize the electronic structures of Ni₂₋₅Co₃₋₅P pre-catalysts, enhance their interaction with NH₃BH₃, and facilitate the hydroxyl activation of NH₃BH₃, thus resulting in a decrease of the reaction energy barrier and improvement of the hydrogen generation rate.

For the transition metal catalyzed hydrolysis of NH₃BH₃, some plausible mechanisms have been proposed. In 2006, Xu’s research group suggested that the formation of an activated complex species between a metal surface and NH₃BH₃ molecules is the rate-determining step.¹⁵⁴ Then, the activated complex species is attacked by H₂O, leading to concerted dissociation of the B–N bond and hydrolysis of the resulting BH₃ intermediate to produce the borate ion along with H₂ release. Jagirdar and Chen assumed that the release of H₂ is due to the attack of H₂O on a transient M–H.¹⁹⁸,²⁶⁴ Fu et al. proposed an almost self-powered process based on DFT calculations, which involves the formation of BH₃OH⁻ and NH₄⁻ species, and then attacking adjacent H₂O to produce H₂.²⁵⁴ Recently, He and Duan proposed that the rate-determining step for NH₃BH₃ is the breaking of the O–H bond in H₂O based on the kinetic isotopic effect measurements.¹⁶⁹,²⁶⁵

### 3.4. Catalysts for NH₃BH₃ methanolysis

As for NH₃BH₃ methanolysis, despite the GHSC of the NH₃BH₃–MeOH system (3.9 wt%) being much lower than that from the hydrolysis system, NH₃BH₃ methanolysis has some advantages that merit its potential applications as a portable hydrogen source.²⁵,¹³⁸,²⁶⁶–²⁷² Firstly, addition of suitable catalysts can initiate the NH₃BH₃ methanolysis reaction below 0 °C, thereby satisfying the applications in cold weather. Secondly, pure H₂ can be released by methanolysis of NH₃BH₃ without the production of NH₃. More importantly, the byproduct of NH₂BH₃ methanolysis (i.e., NH₄B(OMe)₄) can be easily reconverted back to NH₃BH₃ by reaction with NH₄Cl and LiAlH₄ at room temperature.¹³⁸

Compared with the extensive studies of NH₃BH₃ hydrolysis, there are only a few studies regarding NH₃BH₃ methanolysis (Table 3).¹³⁸,²⁶⁷,²⁷⁴–²⁷⁶ In 2007, RuCl₃, RhCl₃, PdCl₂, CoCl₂,
NiCl₂, Pd/C, and RANEY® Ni were firstly reported for the methanolsis of NH₃BH₃. Since then, non-noble metal pre-catalysts such as PVP-stabilized Ni, Co-Co₂B, Ni-Ni₃B, Co-Ni-B, and Co-Ni-P pre-catalysts have been reported for dehydrogenation of NH₃BH₃ in methanol. Later on, mesoporous Cu with diverse morphologies (flower-, nanosheet-, bundle- andandelion-like) have been prepared by our group via a simple wet-chemical method combined with a reduction strategy. Among the four Cu nanostructures, the flower-like Cu nanosucructure was the most active with a TOF of 2.41 min⁻¹ toward the methanolysis of NH₃BH₃. Moreover, the flower-like Cu nanostructures also showed excellent recyclability in the methanolysis of NH₃BH₃. Subsequently, Zahmakiran and coworkers reported Cu–Cu₄O–CuO/C composites to catalyze hydrogen generation from the methanolysis of NH₃BH₃, which showed high activity (24 min⁻¹) in this methanolysis reaction. After that, bunch-like copper oxide nanowire arrays on copper foam (b-CuO NA/CF) were prepared via a simple oxidation process and they behaved as efficient pre-catalysts (13.3 min⁻¹) for methanolytic dehydrogenation of NH₃BH₃. Recently, Sun’s research group found that CuNi alloy NPs deposited on graphene (CuNi/G) showed excellent catalytic activity (49.1 min⁻¹) and recyclability toward the methanolysis of NH₃BH₃. More recently, a noble-metal-free Cu/Co(OH)₂ nanohybrid pre-catalyst was fabricated by Chen and coworkers via a feasible in situ method. By varying the metal/support ratio, a highly efficient catalytic performance (61.63 min⁻¹) for the methanolysis of NH₃BH₃ and long-term stability at ambient temperature were observed. By DFT calculations, they revealed the role of charge transfer in promoting the methanolysis reactions and the metal/support ratio in manipulating the catalytic activity via tuning electrostatic interactions.

In short, tremendous progress has been achieved in catalytic dehydrogenation of NH₃BH₃ by noble-metal-free catalysts (Table 2). However, further efforts are still needed to develop efficient and stable catalysts or some new methods (e.g. photocatalytic assisted technology) to promote the hydrolysis of NH₃BH₃. It is worth noting that the convenience of conducting AB hydrolysis reaction enables its use not only in chemical storage/hydrogen production, but also as a model reaction (similar to the CO oxidation reaction) for testing the activity of new catalysts, which will attract the attention of more and more researchers.

4. Ammonia

Ammonia is a second largest chemical in the world (after sulphuric acid) with over 170 megatonne per year being synthesized via the Haber–Bosch process, bulk of which is used as fertilizers. Ammonia is also considered as a potential hydrogen carrier because of its high gravimetric capacity (17.7 wt% H₂), low price, and production of inherently CO₂-free H₂.[1,2] In particular, it can be readily liquefied under mild conditions (~33.4 °C at 1 atm or 20 °C at 8.46 atm), which makes its storage and delivery relatively easy.[217-240] NH₃ can be decomposed to release H₂ along with N₂ by the following reaction (eqn (4)):

\[2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2 \] (4)

The NH₃ decomposition is an endothermic reaction (ΔH = 92 kJ mol⁻¹) and a high temperature is required for efficient hydrogen generation.[240] Thermal decomposition of NH₃ into H₂ and N₂ has been extensively studied in the past decades.[24,26,284,286] The works before the 1990s on NH₃ decomposition were mainly studied to gain insight into the reaction kinetics of NH₃ synthesis.[291] Nowadays, the research on NH₃ decomposition is mainly focused on the generation of high quality H₂. Generally, N₂ adsorption is thought to be rate-limiting in NH₃ synthesis, while the rate determining step for NH₃ decomposition varies. For noble metal (e.g. Ru, Rh, Ir, Pt, or Pd) catalysts, N-H cleavage is the rate-determining step, while, for non-noble metal (e.g. Fe, Co, Ni, etc.) catalysts, N₂ desorption is the rate-determining step.[24,26,292,293]

Up to now, Ru-based catalysts are known to be the most active in catalytic decomposition of NH₃.[294-298] However, the high cost and limited availability inhibit the wide scale use of these catalysts. Therefore, much attention has been recently paid to non-noble metal catalysts, such as Fe, Co, and Ni as well as a series of bimetallic systems, metal carbides, and metal nitrides.[24]

4.1. Monometallic catalysts

Fe-based catalysts have been extensively studied in the NH₃ decomposition reaction owing to its industrial use in the NH₃ synthesis reaction.[299-304] Fe promoted by K₂O, CaO, SiO₂ and Al₂O₃ is active for NH₃ synthesis at temperatures above 400 °C and was initially considered as a potential pre-catalyst for NH₃ decomposition.[299] The overall activity of Fe-based pre-catalysts toward NH₃ decomposition is relatively low. Great efforts have been made to enhance the catalytic performances of Fe-based catalysts by depositing Fe onto supports such as carbon nanotubes, zeolites, and metal oxides, since their properties such as reducibility, particle size and dispersion, thermal stability and electronic structures would be improved after Fe particles are supported.[301-303,305] For example, Duan et al. synthesized a novel Fe-CNF/mica pre-catalyst via a catalytic CVD method and it showed excellent catalytic activity for NH₃ decomposition.[305] They also found that the size and shape of Fe particles on the top of CNFs depended on the Fe particle reconstruction and different methods have been paid to non-noble metal catalysts, such as Fe, Co, and Ni as well as a series of bimetallic systems, metal carbides, and metal nitrides.[24]
lent catalytic performance of the Fe/MS-HP pre-catalyst is attributed to the highly dispersed Fe species, layered structure of mica, and strong metal–support interactions between Fe and mica.

High temperatures easily lead to Fe sintering, but that can be prevented by confining Fe in porous materials or forming a core–shell structure.\textsuperscript{307–309} Highly dispersed γ-Fe₂O₃ NPs (≈6 nm) confined within the porous systems of CMK-5 carbons and a carbon-SBA-15 composite were synthesized by Lu and coworker via a facile wet impregnation method.\textsuperscript{307} The obtained γ-Fe₂O₃/CMK-5 pre-catalyst showed the high catalytic activity toward the decomposition of NH₃ at 600 °C. The Fe₂O₃/carbon-SBA-15 pre-catalysts were much more stable over a long reaction time. The excellent catalytic performance is attributed to the space limitation in the pores and the strong interaction with the composite support, thus preventing the migration and subsequent sintering of nanoparticles. The group of Ji and Au has embedded Fe NPs in microporous and mesoporous silica shells via a sonication-assisted Stöber process.\textsuperscript{308} The core–shell structure of Fe NPs showed higher catalytic activity and more stability than that of naked Fe NPs owing to the stable silica shells that effectively prevent aggregation of Fe NPs. Recently, Varišli et al. synthesized a robust Fe@mesoporous carbon pre-catalyst by a traditional impregnation procedure, which was very active for microwave-assisted NH₃ decomposition.\textsuperscript{309}

Ni-Based catalysts have also been used as alternative catalysts for NH₃ decomposition due to their substantially lower costs compared to Ru and the higher activity compared to Fe.\textsuperscript{310–314} Previously, Ganley et al. reported an order of activity as Ru > Ni > Rh > Co > Ir > Fe for NH₃ decomposition.\textsuperscript{310} Zhang et al. reported a co-precipitation method to prepare a series of supported pre-catalysts by depositing Ni NPs on Al₂O₃.\textsuperscript{311} The catalytic activity of Ni/Al₂O₃ increased with increasing Ni loading and reached a maximum at a Ni/Al ratio of 1.2. Interestingly, the conversion of NH₃ was further increased after the addition of a La promoter into the Ni/Al₂O₃ pre-catalyst. For example, when the La/Ni molar ratio increased from 0 to 0.2, the conversion of NH₃ progressively increased from 38.2 to 63.9% at 773 K. The characterization results indicated that the Ni/La-Al₂O₃ pre-catalyst with an appropriate amount of La possessed a more open mesoporous structure and higher dispersion of Ni as compared to Ni/Al₂O₃. Later on, Xu and coworker reported that the addition of CeO₂ obviously improved the catalytic activity and stability of Ni/Al₂O₃ for NH₃ decomposition to CO₂-free H₂.\textsuperscript{315} The characterization results showed that the addition of CeO₂ could enlarge the pre-catalyst pores, moderate the interaction between the metal and support, suppress Ni NPs from sintering, and improve the recombining desorption of N atoms from the Ni NP surface. After that, the group of Liu has also proved that adding an appropriate amount of Ce and La to Ni/SBA-15 can improve the NH₃ decomposition activity, and the highest activity could be achieved when the Ce/La/Ni ratio was around 0.3.\textsuperscript{316} Rare-earth oxides can not only act as an additive but can also be employed as an efficient support for the synthesis of high performance Ni-based catalysts. Okura and coworkers investigated the catalytic performances over Ni supported on various rare-earth oxides (Y₂O₃, CeO₂, La₂O₃, Sm₂O₃ and Gd₂O₃) for NH₃ decomposition.\textsuperscript{317} Among the samples investigated, the Ni/Y₃O₃ pre-catalyst showed the highest catalytic activity. The kinetics studies revealed that most of the rare-earth oxides could effectively alleviate the inhibition of hydrogen in the decomposition reaction. In addition, the desorption behavior of hydrogen showed that the amount of hydrogen atoms adsorbed on the Ni NP surface of Ni/Y₃O₃ was relatively small at high temperatures. Furthermore, this group also found that the catalytic activity of Ni/Y₃O₃ can be remarkably improved by modifying with a small amount of Sr or Ba species, while the addition of Mg and Ca species was not effective.\textsuperscript{318} Recently, ceria catalytic structures with a woodpile geometry of micro-channels have been prepared by 3D printing and used as a support to disperse Ni NPs.\textsuperscript{319} The obtained 3D-printed Ni/CoO₂ pre-catalyst showed higher catalytic performance than the Ni/CoO₂ powder pre-catalyst and the conventional cordierite honeycomb wash coated with Ni/CoO₂ under the same reaction conditions.

Compared with Fe-based and Ni-based catalysts, Co-based catalysts are less studied in NH₃ decomposition reactions.\textsuperscript{320,321} The roles of supports such as carbon materials and mesoporous silica and various promoters were also investigated on Co as well. Zhang et al. reported that fresh commercial carbon nanotubes (CNTs) containing residual Co or Fe NPs are highly active for NH₃ decomposition, and the microstructure of the CNTs remained unchanged after the decomposition reaction.\textsuperscript{320} After that, Co supported on CNTs was synthesized and studied.\textsuperscript{321} The conversion of NH₃ over Co/CNTs was 60.8%, which was higher as compared to 14.8% for Fe/CNTs and 25.4% for Ni/CNTs at 500 °C. Moreover, the effect of metal–support interactions between Co and CNTs was investigated by varying the pretreatment temperatures (230–700 °C) and gas (N₂ and H₂).\textsuperscript{322} It is found that the catalytic activity of Co/CNT pre-catalyst treatment in N₂ was higher than that of Co/CNT in H₂, and the pretreatment of Co/CNTs at 600 °C showed the highest NH₃ decomposition activity and the lowest activation energy (68.6 kJ mol⁻¹). Furthermore, Li and coworkers found that the Co@C-700-N sample calcined under limited air atmosphere showed a better activity for NH₃ decomposition as compared to the calcined sample in pure N₂ flow.\textsuperscript{323} Podila and coworkers have reported that Co supported on a Mg–La mixed oxide showed high activity for NH₃ decomposition.\textsuperscript{324,325} Recently, Jia and coworkers synthesized a high surface area Co-SiO₂ pre-catalyst by a simple two-step procedure with activated carbon as the template for NH₃ decomposition reaction.\textsuperscript{326} The presence of SiO₂ can effectively protect active Co species from agglomeration during the calcination and NH₃ decomposition reaction. The obtained Co-SiO₂ exerted superior activity to other reported catalysts.

4.2. Bimetallic catalysts

Bimetallic catalysts with unique structures may achieve excellent catalytic activity in comparison with their individual...
monometallic components. To date, a series of bimetalllic catalysts, such as Co–Mo, Fe–Mo, Fe–Co, Fe–Ni and Co–Ni, have been prepared and employed as catalysts for NH$_3$ decomposition. For example, Duan et al. reported that the bimetallic Co–Mo/MCM-41 pre-catalyst shows a higher activity in the NH$_3$ decomposition reaction than a monometallic Co/MCM-41 or Mo/MCM-41 pre-catalyst under the same conditions. In addition, Co–Mo/MCM-41 with a Co/Mo molar ratio of 7/3 shows the highest NH$_3$ conversion and exhibits good thermal stability. Later on, they studied the effects of Co–Mo precursors on the catalytic activity. The results showed that the CoMo$_1$/γ-Al$_2$O$_3$ pre-catalyst prepared using monocomponent metal amine metallate (Co(en)$_3$MoO$_4$) as the active phase precursor exhibited higher activity and stability for ammonia decomposition than the CoMo$_2$/γ-Al$_2$O$_3$ pre-catalyst prepared using bicomponent Co(NO$_3$)$_2$ and (NH$_4$)$_2$MoO$_4$ as the active phase precursors. Moreover, they found that the textural and chemical properties of the Co–Mo pre-catalyst were significantly affected by the calcination atmosphere (i.e., Ar and Air). The Co–Mo pre-catalyst calcined in air showed higher catalytic activity, and Co$_3$Mo$_3$N is suggested as the dominant active phase of Co–Mo. In addition, FeMo-based pre-catalysts were also investigated and they were found to be active in NH$_3$ decomposition. 

Zhang et al. successfully encapsulated Fe–Co alloy NPs inside CNTs (FeCo-in-CNTs) on the basis of the capillary phenomenon in the channel of CNTs, which effectively prevented the metal NPs from aggregating even at high temperature. Thus, the resulting FeCo-in-CNT showed remarkable thermal stability in NH$_3$ decomposition reaction. Recently, 2D ultrathin Co–Fe spinel oxide nanosheets confined in mesoporous silica shells (Co$_3$Fe$_{3–x}$O$_x$@mSiO$_2$) have been fabricated by Zhang and coworkers. By tuning the chemical stoichiometry of Co$_3$Fe$_{3–x}$O$_x$ nanosheets, the strength of the M–N bond can reasonably adjust and subsequently greatly optimize the catalytic performance. The optimized Co$_3$Fe$_{2.1}$O$_{0.9}$@mSiO$_2$ pre-catalyst attained 88% conversion of NH$_3$ at 600 °C and a space velocity of 60 000 cm$^3$ g$^{-1}$ h$^{-1}$, even maintained for 48 h without attenuation. Similarly, Ni–Fe/Al$_2$O$_3$, Ni–Fe alloys, and NiCo/Co$_x$Zr$_{6–x}$Y$_x$O$_{2+}$ solid solutions were found to show higher catalytic performance than the single metal pre-catalyst toward the decomposition of NH$_3$.

### 4.3. Metal carbides/nitrides

Transition metal carbides (WC, MoC, FeC, VC, and TaC) and nitrides (MoN, VN, and WN) have also been investigated for NH$_3$ decomposition reaction. Sourabh and coworkers reported that WC can attain complete decomposition of NH$_3$ at 550 °C; however, the WC samples need to be pretreated in a nitrogen flow for 1 h, even maintained for 48 h without attenuation. Similarly, Ni–Fe/Al$_2$O$_3$, Ni–Fe alloys, and NiCo/Co$_x$Zr$_{6–x}$Y$_x$O$_{2+}$ solid solutions were found to show higher catalytic performance than the single metal pre-catalyst toward the decomposition of NH$_3$.

#### 5. Hydrous hydrazine

Anhydrous hydrazine (N$_2$H$_4$), a colorless flammable liquid at room temperature, has a high hydrogen capacity as high as 12.5 wt%. Hydron stored in N$_2$H$_4$ can be catalytically decomposed over supported metals, metal carbides, and metal nitrides in two pathways (eqn (5) and eqn (6)). The reaction decomposition routes are determined by the catalysts used and the reaction conditions. However, most of the reports on hydrazine decomposition showed that ammonia is present as a product, while reports on the selective decomposition of hydrazine exclusively to hydrogen are rare, and high temperatures (>300 °C) are usually required due to the decomposition of NH$_3$. Even worse, the anhydrous hydrazine (>98%) is highly toxic and explosive when exposed to metal catalyst surfaces, making it difficult to use it safely.

$$\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 2\text{H}_2 \quad (5)$$

$$3\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{NH}_3 \quad (6)$$

Hydrous hydrazine, such as hydrazine monohydrate (N$_2$H$_4$·H$_2$O) which has a hydrogen capacity of 8.0 wt%, is...
believed to be relatively safe.\textsuperscript{19,20,22,359–361} Notably, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ is a liquid over a wide range of temperatures (213–392 K), and therefore it is easy to recharge using the current equipment for liquid fuels. Furthermore, the complete decomposition of $\text{N}_2\text{H}_4$ generates only a by-product of $\text{N}_2$ in addition to $\text{H}_2$, which does not need on-board collection for recycling. These merits have made $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ a promising hydrogen carrier for storage and transportation. Thereby, it is crucial to develop effective and selective catalysts for complete hydrogen generation from $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition.\textsuperscript{368} Among all the synthesized metal NPs, Rh showed the highest H2 selectivity (43.8\%) for hydrogen evolution from $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition.

It has been reported that the catalytic activity and H2 selectivity of Ni–Fe NPs could be improved by introducing a Cu core.\textsuperscript{398} The Cu core is not selective for hydrogen evolution from the decomposition of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, while the NiFe/Cu NPs exhibited high activity, stability, and ~100% H2 selectivity for hydrogen evolution at 330–340 K. After that, Zhang and co-workers synthesized core–shell Cu@Fe$_{0.5}$Ni$_{0.5}$ NPs via an in situ seeding-growth approach and investigated their catalytic performances.\textsuperscript{399} The core–shell Cu@Fe$_{0.5}$Ni$_{0.5}$ NPs have a small size of about 8.5 nm. The core–shell Cu@Fe$_{0.5}$Ni$_{0.5}$ pre-catalyst showed high activity and 100% H2 selectivity within 70 min.

### 5.1. Metal NP Catalysts

Xu and co-workers synthesized bimetallic Ni–Fe NPs by co-reduction of an aqueous solution of NiCl$_2$ and FeSO$_4$ in the presence of CTAB.\textsuperscript{392} Although all the synthesized Ni–Fe NPs are inactive in the decomposition reaction of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 298 K, a hydrogen selectivity of 81\% can be achieved with Ni$_{0.5}$Fe$_{0.5}$ NPs with elevation of the reaction temperature at 343 K (Fig. 10). Furthermore, it was found that the hydrogen selectivity could be significantly enhanced by the addition of NaOH into the reaction mixture. The Ni$_{0.5}$Fe$_{0.5}$ NPs released gases in a stoichiometric amount (3.0 equiv.) with 100% H$_2$ selectivity from the decomposition of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in 190 min with NaOH (0.5 M) at 343 K. However, the addition of a weaker base such as NH$_3$ and CH$_3$COONa had no effect on the catalytic performance of the Ni–Fe NPs. The possible reason is that the highly alkaline reaction conditions make the catalyst surface highly basic, which may be unfavorable for the formation of basic NH$_3$, thereby hindering the decomposition of $\text{N}_2\text{H}_4$ to NH$_3$.

### Table 4 Catalytic activities for hydrogen evolution from $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ catalyzed by different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp. (K)</th>
<th>$n_{\text{metal}}/n_{\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}}$</th>
<th>H$_2$ selectivity (%)</th>
<th>TOF (mol$_{\text{H}<em>2}$mol$</em>{\text{metal}}^{-1}$ h$^{-1}$)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{0.5}$Fe$</em>{0.5}$ NPs</td>
<td>343</td>
<td>0.1</td>
<td>100</td>
<td>6.3</td>
<td>—</td>
<td>392</td>
</tr>
<tr>
<td>NiFe/Cu</td>
<td>343</td>
<td>0.2</td>
<td>100</td>
<td>35.3</td>
<td>44</td>
<td>398</td>
</tr>
<tr>
<td>Cu@Fe$<em>{0.5}$Ni$</em>{0.5}$</td>
<td>353</td>
<td>0.11</td>
<td>100</td>
<td>18.2</td>
<td>79.2</td>
<td>399</td>
</tr>
<tr>
<td>NiMo–La(OH)$_3$</td>
<td>323</td>
<td>0.3</td>
<td>100</td>
<td>13.3</td>
<td>55.1</td>
<td>400</td>
</tr>
<tr>
<td>Ni$<em>{0.5}$Fe$</em>{0.5}$Mo</td>
<td>323</td>
<td>0.1</td>
<td>100</td>
<td>28.8</td>
<td>50.7</td>
<td>401</td>
</tr>
<tr>
<td>Cu$<em>{0.4}$Ni$</em>{0.6}$Mo</td>
<td>323</td>
<td>0.2</td>
<td>100</td>
<td>38.7</td>
<td>56.6</td>
<td>402</td>
</tr>
<tr>
<td>Ni–Al$_2$O$_3$–HT</td>
<td>303</td>
<td>0.4</td>
<td>93</td>
<td>2.2</td>
<td>49.3</td>
<td>403</td>
</tr>
<tr>
<td>RANEY® Ni</td>
<td>303</td>
<td>—</td>
<td>&gt;99</td>
<td>162</td>
<td>44.4</td>
<td>369</td>
</tr>
<tr>
<td>Ni–0.80CuCeO$_2$</td>
<td>303</td>
<td>0.45</td>
<td>99</td>
<td>51.6</td>
<td>47</td>
<td>370</td>
</tr>
<tr>
<td>Ni/Co</td>
<td>323</td>
<td>0.1</td>
<td>100</td>
<td>34.0</td>
<td>56.2</td>
<td>404</td>
</tr>
<tr>
<td>Ni$<em>{0.5}$Cu$</em>{0.5}$/CeO$_2$</td>
<td>323</td>
<td>0.2</td>
<td>100</td>
<td>111.7</td>
<td>63.0</td>
<td>395</td>
</tr>
<tr>
<td>Ni$<em>{0.5}$Cu$</em>{0.5}$/CeO$_2$</td>
<td>343</td>
<td>0.2</td>
<td>100</td>
<td>371.1</td>
<td>395</td>
<td></td>
</tr>
<tr>
<td>Ni–CeO$_2$–SiO$_2$</td>
<td>343</td>
<td>0.1</td>
<td>100</td>
<td>219.5</td>
<td>59.26</td>
<td>405</td>
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<tr>
<td>2D Ni$<em>{0.5}$Fe$</em>{0.5}$CeO$_2$</td>
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<td>0.1</td>
<td>99</td>
<td>5.76</td>
<td>44.06</td>
<td>406</td>
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<tr>
<td>NiFe/CoZrO$_2$</td>
<td>343</td>
<td>0.1</td>
<td>100</td>
<td>119.2</td>
<td>50.4</td>
<td>407</td>
</tr>
<tr>
<td>NiFe–La(OH)$_3$</td>
<td>343</td>
<td>0.2</td>
<td>100</td>
<td>100.6</td>
<td>57.8</td>
<td>408</td>
</tr>
<tr>
<td>Ni$<em>{0.5}$Fe$</em>{1.0}$/(MgO)$_{1.5}$</td>
<td>299</td>
<td>0.21</td>
<td>99</td>
<td>10.3</td>
<td>—</td>
<td>393</td>
</tr>
<tr>
<td>Ni$<em>{0.5}$Fe$</em>{0.5}$–Cr$_2$O$_3$</td>
<td>343</td>
<td>0.2</td>
<td>100</td>
<td>893.5</td>
<td>86.3</td>
<td>394</td>
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<tr>
<td>NiCo/NiO–CeO$_2$</td>
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<td>0.2</td>
<td>99</td>
<td>12.8</td>
<td>45.15</td>
<td>397</td>
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<tr>
<td>Ni$_{0.5}$Fe–CeO$_2$–12/rGO</td>
<td>343</td>
<td>0.1</td>
<td>100</td>
<td>126.2</td>
<td>34.3</td>
<td>409</td>
</tr>
<tr>
<td>Ni$_{0.5}$Fe–CeO$_2$–12/rGO</td>
<td>328</td>
<td>0.1</td>
<td>100</td>
<td>56.8</td>
<td>—</td>
<td>409</td>
</tr>
<tr>
<td>Ni nanoﬁber</td>
<td>333</td>
<td>0.5</td>
<td>100</td>
<td>6.9</td>
<td>52.07</td>
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<tr>
<td>Ni–CNTs–OH</td>
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<td>—</td>
<td>100</td>
<td>19.4</td>
<td>51.05</td>
<td>410</td>
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<tr>
<td>Ni@TNTs</td>
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<td>0.125</td>
<td>100</td>
<td>96</td>
<td>53.2</td>
<td>411</td>
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<tr>
<td>Ni$<em>{0.5}$Cu$</em>{0.5}$/MCNS</td>
<td>333</td>
<td>0.28</td>
<td>100</td>
<td>21.8</td>
<td>224</td>
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<tr>
<td>Ni$<em>{0.5}$Cu$</em>{0.5}$/Ni–Mo–O</td>
<td>323</td>
<td>0.167</td>
<td>100</td>
<td>54.5</td>
<td>—</td>
<td>412</td>
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<tr>
<td>Ni$_{0.5}$NPs</td>
<td>343</td>
<td>0.5</td>
<td>100</td>
<td>11.0</td>
<td>56.3</td>
<td>366</td>
</tr>
</tbody>
</table>
also showed excellent catalytic activity toward N$_2$H$_4$·H$_2$O decomposition for hydrogen production. It was found that the catalytic activity and H$_2$ selectivity from ref. 370. Copyright (2015) American Chemical Society.

5.2. Complex oxide supported catalysts

Using a Ni-Al hydrotalcite-like compound (Ni-Al-HT) as the precursor, He et al. obtained a highly dispersed Ni-Al$_2$O$_3$-HT pre-catalyst after reduction of Ni-Al-HT under a H$_2$ atmosphere at 773 K. The obtained Ni-Al$_2$O$_3$-HT pre-catalyst showed a high catalytic activity and 93% H$_2$ selectivity towards H$_2$ for N$_2$H$_4$·H$_2$O decomposition within 70 min at 303 K. In contrast, the impregnated counterpart Ni/Al$_2$O$_3$-IMP pre-catalyst exhibited a much lower H$_2$ selectivity (67%) and catalytic activity with a total reaction time of 440 min. The high catalytic performance of Ni-Al$_2$O$_3$-HT could be attributed to a much stronger interaction of the Ni component with Al$_2$O$_3$ and the strongly basic sites. This is the first report that supported a base metal pre-catalyst showing such high H$_2$ selectivity towards the decomposition of N$_2$H$_4$ aqueous solution. They also found that RANEY® Ni was active and exhibited >99% selectivity towards H$_2$ for the decomposition of N$_2$H$_4$·H$_2$O in the presence of NaOH at 303 K. Compared with RANEY® Ni-40, RANEY® Ni-300 showed higher catalytic and H$_2$ selectivity in this decomposition reaction, which was probably due to a relatively low content of remaining aluminum. In addition, RANEY® Ni-300 could be easily collected and reused after the catalytic reaction, as RANEY® Ni has excellent magnetic properties. This convenient route provides great potential for industrial applications.

He et al. developed a facile coprecipitation approach to synthesize CeO$_2$-modified Ni RANEY® Ni-300. The obtained Ni-0.08CeO$_2$ pre-catalyst (Fig. 12) showed a 99% H$_2$ selectivity and a 3-fold higher TOF value than bare Ni NPs and the impregnated counterpart Ni/Al$_2$O$_3$-IMP for N$_2$H$_4$·H$_2$O decomposition reaction. This improvement was caused by the modification of Ni with CeO$_2$ nearby through strong metal-support interactions (e.g., Ni-O-Ce structure). Although the Ni-O-Ce structure itself is inactive for N$_2$H$_4$·H$_2$O decomposition, it could alter the chemical properties of surface Ni and make it both active and selective for N$_2$H$_4$·H$_2$O. Furthermore, this promoting effect could be extended to other oxides which can also form strong metal-support interactions with Ni, such as ZrO$_2$, MgO, and La$_2$O$_3$. Later on, a series of Ni/CeO$_2$ were prepared by solution combustion synthesis (SCS) in a one-step process and used as efficient catalysts for decomposition of N$_2$H$_4$·H$_2$O. It was found that the catalytic activity and H$_2$
selectivity for hydrogen evolution from \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) significantly depended on the SCS synthesis parameters (ratio of precursor oxidizers, fuel-to-oxidizer ratio and fuel type). The tailored 6 wt% Ni/CeO\(_2\) pre-catalyst prepared with a fuel-to-oxidizer ratio of 2 and \( \text{N}_2\text{H}_4 \) fuel showed the highest catalytic and 100% hydrogen selectivity, for which the decomposition reaction took 17.7 min for 50% conversion of \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) in the presence of NaOH, corresponding to a TOF value of 34.0 h\(^{-1}\) at 323 K. The characterization results confirmed the interaction between Ni and CeO\(_2\), namely the existence of Ni–O–Ce solid solution. In addition, the oxygen vacancy in the Ni–O–Ce solid solution of the Ni/CeO\(_2\) pre-catalyst modifies the electronic ability of Ni as an electron donor and alters the interaction between Ni and \( \text{N}_2\text{H}_4 \), which promotes N–H bond dissociation rather than N–N bond dissociation and makes the \( \text{H}_2 \) generation easier. Inspired by this effective method, they also found that the addition of Cu to Ni/CeO\(_2\) exhibited a synergistic effect to enhance the catalytic activity for the reaction.\(^{395}\)

The above results showed that the catalytic properties of Ni-based catalysts can be significantly enhanced by introducing a certain amount of CeO\(_2\). To further maximize the active interface and the stability of catalysts, our group designed and synthesized ultrafine Ni NPs self-assembled on CeO\(_2\) nanowires embedded in a microporous silica shell (Ni–CeO\(_2\)@SiO\(_2\)) via a one-pot facile strategy (Fig. 13).\(^{395}\) The resulting wormlike core–shell-structured Ni–CeO\(_2\)@SiO\(_2\) pre-catalyst showed high performance and robust durability with 100% hydrogen selectivity for \( \text{H}_2 \) production from \( \text{N}_2\text{H}_4 \) aqueous solution. The excellent catalytic properties of Ni–CeO\(_2\)@SiO\(_2\) can be attributed to the synergistic electronic effect and strong interactions between Ni NPs and CeO\(_2\) NWS with plenty of oxygen vacancies, as well as the unique structure effect.

Wen and co-workers synthesized a two-dimensional NiFe/CeO\(_2\) pre-catalyst via a dynamics controlling coprecipitation reduction (DCCR) process followed by calcination.\(^{406}\) Small NiFe NPs (~5 nm) were uniformly anchored on the surface of CeO\(_2\) nanosheets. The optimal Ni\(_0.25\)Fe\(_{0.75}\)/CeO\(_2\) pre-catalyst displayed over 99% selectivity towards \( \text{H}_2 \) evolution from \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) without using an alkali additive at 323 K. Besides CeO\(_2\), recently we adopted nano CeZrO\(_2\) solid solution as a support to disperse NiFe NPs well, leading to the complete decomposition of \( \text{N}_2\text{H}_4 \) to \( \text{H}_2 \).\(^{407}\) Later, we prepared a NiFe–La (OH)\(_3\) pre-catalyst for \( \text{N}_2\text{H}_4 \) dehydrogenation, in which metal NPs were highly dispersed with smaller particle size and low crystallinity.\(^{408}\) Importantly, 100% hydrogen selectivity from \( \text{N}_2\text{H}_4 \) aqueous solution was achieved in 6.5 min, providing a rather high TOF value of 100.6 h\(^{-1}\) at 334 K, which is about 35-fold higher than that of pure NiFe NPs (2.8 h\(^{-1}\)).

Using the DCCR method, Wen and co-workers synthesized NiCo/NiO–CeO\(_2\) ultrathin layered nanocomposites with NiCo NPs (~4 nm) uniformly anchored on the NiO–CeO\(_2\) ultrathin layered nanosheets.\(^{397}\) The obtained Ni\(_{0.25}\)Co\(_{0.75}\)/NiO–CeO\(_2\) pre-catalyst exhibited optimal catalytic performance and 99% hydrogen selectivity for \( \text{H}_2 \) evolution from the decomposition of \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) without the assistance of NaOH at 298 K. Wu et al. fabricated a bifunctional NiFe/MgO pre-catalyst containing both the NiFe-alloy active center and a solid base via a calcination–reduction of a NiFeMg-layered double hydroxide (LDH) precursor.\(^{393}\) Moreover, the basicity of Ni\(_1\)Fe\(_{1-w}\)(MgO)\(_w\) can be easily tuned by changing the amount of the Mg precursor. The optimized Ni\(_{1.2} Fe_{0.8}(MgO)_{3.5}\) pre-catalyst showed a high catalytic performance with 100% conversion and 99% \( \text{H}_2 \) selectivity for \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) decomposition at 299 K. Notably, there was no obvious correlation between the catalytic performance and surface area, which further confirms that the basicity of the MgO support has a more pronounced effect on the catalytic behavior. Recently, our group reported the synthesis of a NiFe–Cr\(_2\)O\(_3\) pre-catalyst, which displayed an extraordinary catalytic activity (893.5 h\(^{-1}\)) for the complete decomposition of \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) at 343 K.\(^{394}\)

5.3. Other supported metal catalysts

Various support materials, such as graphene, carbon nanotubes, titane nanotubes, mesoporous carbons, and so on, have also been used to fabricate well-dispersed noble-metal NPs with controllable size and morphology. Luo and co-workers reported the synthesis of CeO\(_2\)-modified NiFe nanodendrites supported on reduced graphene oxide (NiFe–CeO\(_2\)/rGO).\(^{409}\) The optimal NiFe–(CeO\(_2\))\(_{0.15}\)/rGO exhibited superior catalytic activity toward \( \text{H}_2 \) evolution from \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) under alkaline conditions with a TOF value of 126.2 h\(^{-1}\) at 334 K. Zhao and coworkers prepared Ni nanofibers via an electrospinning and vacuum thermal reduction method.\(^{371}\) The catalytic performance of the prepared Ni nanofibers significantly depended on the morphologies and Ni grain sizes. The Ni nanofibers with PVP: EC mass ratios of 7:3, and having a high specific surface area and small crystal size, showed nearly 100% hydrogen selectivity to \( \text{H}_2 \) generation and a TOF of 6.9 h\(^{-1}\) in NaOH solution at 333 K. Recently, they have grown carbon nanotubes (CNTs) on Ni nanofibers (Ni–CNTs) and then subjected them to a hydroxylation treatment (Ni–CNTs–OH).\(^{410}\) They found that the introduced CNTs and the hydroxyl groups on the CNTs significantly improved the catalytic performance of the active Ni nanofibers. The Ni–CNTs–OH showed excellent catalytic performance with a TOF of 19.4 h\(^{-1}\).
toward the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition reaction in the presence of NaOH at 333 K.

Wang and co-workers successfully confined Ni NPs inside a titanate nanotube (Ni@TNT) channel by using the capillary force under ultrasonic treatment.\textsuperscript{411} The obtained Ni@TNT pre-catalyst exhibited high activity and 100% hydrogen selectivity, completing the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition in only 5 min in the presence of NaOH at 333 K, which is higher than that of Ni/TNTs. In addition, owing to the good stability of the Ni@TNT pre-catalyst, no significant decrease in catalytic performance was observed, while the Ni/TNTs showed an obvious decrease during the reuse (Fig. 14). The excellent catalytic performance of the Ni@TNT pre-catalyst is attributed to the small size and high dispersion of Ni NPs after encapsulation in the channel of TNTs. The Kleitz group prepared highly dispersed CuNi alloy NPs supported on mesoporous carbons (CuNi/MCNS) by a simple incipient wetness method.\textsuperscript{422} Interestingly, all the bimetallic CuNi/MCNS pre-catalysts showed 100% selectivity to $\text{H}_2$ from the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition and the reaction was complete within 50 min over Cu$_{0.5}$Ni$_{0.5}$/MCNS in the presence of NaOH at 333 K.

Recently, Wang and coworkers reported the synthesis of Ni$_{10}$Mo NPs on a Ni–W–O matrix (Ni$_{10}$Mo NPs/Ni–W–O) through a simple hydrothermal method followed by annealing treatment under a $\text{H}_2$ atmosphere.\textsuperscript{412} The obtained nanocomposite enabled the complete decomposition of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in 7 min at 323 K, providing a TOF value of 54.5 h$^{-1}$. They also synthesized a monolithic Ni$_{10}$Mo/Ni–Mo–O/Ni foam pre-catalyst and showed a high hydrogen generation rate with 98% $\text{H}_2$ selectivity and rapid dynamic response after 5 start/stop cycles.\textsuperscript{412} Using a similar method, they also synthesized a series of Ni–W–O–derived nanocomposites.\textsuperscript{413} It was found that the catalytic properties of the resulting pre-catalyst depended significantly upon the annealing temperature. On the basis of a combination of experimental and DFT theoretical calculations, the observed changes in catalytic properties are related to the changes in the phase structure and microstructural features with temperature during the reductive annealing process. Specifically, the as-synthesized Ni$_x$W/WO$_3$/NiWO$_4$ exhibited remarkably distinct catalytic performance, nearly 100% selectivity, and high stability in catalyzing $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition for hydrogen production. Furthermore, they also reported a first-principles study of the elementary steps of $\text{N}_2\text{H}_4$ decomposition over a Ni pre-catalyst.\textsuperscript{372} The calculation results indicated that the decomposition behaviors of $\text{N}_2\text{H}_4$ strongly depend on the surface coverage. At a lower coverage, the cleavage of the N–N bond is dominant, resulting in the formation of $\text{NH}_3$. In contrast, at a higher coverage, the cleavage of the N–H bond is in competition with that of the N–N bond, and $\text{N}_2$ and $\text{H}_2$ are finally released.

Overall, Ni and Ni-based noble-metal-free catalysts can efficiently catalyze the complete decomposition of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ to produce hydrogen, but the catalytic activity is still not satisfactory at room temperature or without additives (e.g. NaOH). Therefore, for the practical use of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ as a safe and effective hydrogen storage material, it is necessary to further develop more effective noble-metal-free catalysts for complete conversion of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ to $\text{H}_2$ at low temperature without additives.

### 6. Hydrazine borane

Hydrazine borane ($\text{N}_2\text{H}_4\text{BH}_3$, HB, 15.4 wt%) is a derivative of NH$_3$BH$_3$ where an N$_2$H$_4$ group substituted the NH$_3$ group, has been regarded as a competitive candidate for chemical hydrogen storage.\textsuperscript{22,150,151,414–420} $\text{N}_2\text{H}_4\text{BH}_3$ can be easily synthesized through the reaction of (N$_2$H$_3$)$_2$SO$_4$ with NaBH$_4$ in dioxane at room temperature.\textsuperscript{421} The hydrogen in $\text{N}_2\text{H}_4\text{BH}_3$ can be released through either thermolysis or solvolysis.\textsuperscript{421–428} The thermal decomposition of $\text{N}_2\text{H}_4\text{BH}_3$ was firstly reported by Goubeau and Ricker.\textsuperscript{421} $\text{N}_2\text{H}_4\text{BH}_3$ begins to decompose slowly at around 60 °C. It was found that $\text{N}_2\text{H}_4\text{BH}_3$ released 6.5 wt% $\text{H}_2$ within 16 h at 140 °C, while more than 11 wt% $\text{H}_2$ can be released from $\text{N}_2\text{H}_4\text{BH}_3$ in the presence of LiH at 150 °C in less than an hour.\textsuperscript{422}

Like for NH$_3$BH$_3$, the BH$_3$ group in $\text{N}_2\text{H}_4\text{BH}_3$ is readily hydrolyzed in the presence of a suitable catalyst (eqn (7)) at room temperature.\textsuperscript{427–431} The hydrolysis of $\text{N}_2\text{H}_4\text{BH}_3$ over noble-metal-free catalysts was firstly reported by Özkar and co-workers.\textsuperscript{430} They found that highly dispersed Ni(0) and Co(0) NPs stabilized by poly(4-styrenesulfonic acid-co-maleic acid (PSSMA-Ni and PSSMA-Co) could be facilely prepared by in situ reduction of NiCl$_2$ and CoCl$_2$ during the hydrolytic dehydrogenation of $\text{N}_2\text{H}_4\text{BH}_3$.\textsuperscript{430,431} The in situ formed PSSMA-Ni and PSSMA-Co NPs were highly active in the hydrolysis of $\text{N}_2\text{H}_4\text{BH}_3$ with the release of nearly 3 equiv. $\text{H}_2$ per $\text{N}_2\text{H}_4\text{BH}_3$. Moreover, the obtained PSSMA-Co (TOF = 370 h$^{-1}$) showed much higher catalytic performance than PSSMA-Ni (TOF = 183 h$^{-1}$) for this hydrolysis reaction at 298 K.\textsuperscript{430,431} The Cu@SiO$_2$ core–shell pre-catalyst developed by our research group also showed excellent catalytic activity (TOF = 454.8 h$^{-1}$) in the hydrolytic dehydrogenation of $\text{N}_2\text{H}_4\text{BH}_3$.\textsuperscript{429} Due to the protection of the porous silica shell, the stability of the pre-catalyst is effectively improved, because of which the Cu@SiO$_2$ nanospheres preserved 82% of their initial catalytic activity even in the tenth run. Recently, we found that transition metal (Cr, Mo, and W)
modified Ni NPs showed high activity toward hydrogen generation from the hydrolysis of N$_2$H$_4$BH$_3$ at 298 K.$^{187}$

$$\text{N}_2\text{H}_4\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow \text{N}_2\text{H}_2\text{BO}_2 + 3\text{H}_2 \quad (7)$$

By the hydrolysis of the BH$_3$ group of N$_2$H$_4$BH$_3$, the liberation of H$_2$ with good kinetics can be achieved with the catalysts reported above. However, the effective GHSC of the N$_2$H$_4$BH$_3$-3H$_2$O system (6.0 wt%) is not high because H in N$_2$H$_4$ is not released. Similar to hydrolysis, 1 mol N$_2$H$_4$BH$_3$ can also produce 3 mol of H$_2$ by methanolysis in a suitable catalyst (eqn (8)). In situ formed bulk Ni and PVP-stabilized Ni NPs were developed by Özkar and co-worker for hydrogen evolution from the methanolysis of N$_2$H$_3$BH$_2$. Since the weight of methanol is much higher than that of water, the GHSC of an N$_2$H$_4$BH$_3$-4MeOH (3.5 wt%) system is much lower than that of an N$_2$H$_4$BH$_2$-2H$_2$O (7.4 wt%) system. However, the methanolysis reaction of N$_2$H$_4$BH$_3$ can be initiated even below 0 °C, thereby satisfying the cold start requirements of vehicular and portable applications in cold weather.

$$\text{N}_2\text{H}_4\text{BH}_3 + 4\text{MeOH} \rightarrow \text{N}_2\text{H}_2\text{B(MeO)}_4 + 3\text{H}_2 \quad (8)$$

Unlike the NH$_3$ moiety of NH$_3$BH$_3$, the N$_2$H$_4$ moiety in N$_2$H$_4$BH$_3$ can also be dehydrogenated to H$_2$ and N$_2$ over a selective catalyst (eqn (5)). Theoretically, 1 mol N$_2$H$_4$BH$_3$ can be completely dehydrogenated into 5 mol H$_2$ and 1 mol N$_2$ (eqn (9)). This corresponds to an effective GHSC of 10.0 wt% for the N$_2$H$_4$BH$_3$-3H$_2$O system, which is much higher than those of NaBH$_4$-4H$_2$O (7.3 wt%), NH$_3$BH$_3$-2H$_2$O (8.9 wt%) and N$_2$H$_4$-H$_2$O (8.0 wt%). However, the dehydrogenation reaction is in competition with NH$_3$ release (eqn (10)). In 2014, Demirci and co-worker synthesized a series of Ni-based bimetallic pre-catalysts for the hydrolysis of the BH$_3$ group and then decomposition of the N$_2$H$_4$ group. The optimized Ni$_{0.7}$Fe$_{0.3}$ NPs can release 3.9 equiv. (H$_2$ + N$_2$) per N$_2$H$_4$BH$_3$ (Fig. 15) can be released within 13.9 min. To the best of our knowledge, this is the first report that a noble-metal-free pre-catalyst can achieve a complete conversion of N$_2$H$_4$BH$_3$ to H$_2$ (Table 5). Later on, Yan and co-workers reported the synthesis of a boron nitride (BN) supported Ni-MoO$_2$ (Ni-MoO$_2$/BN) pre-catalyst without the help of a surfactant by a sequential impregnation reduction approach. The resultant Ni-MoO$_2$/BN showed excellent catalytic performance with 100% H$_2$ selectivity for hydrogen generation from N$_2$H$_4$BH$_3$ alkaline conditions at 323 K, giving a TOF value of 600.0 h$^{-1}$. They also developed a facile and universal methodology for the synthesis of amorphous/poorly crystallized noble-metal-free NiFe-CeO$_2$ NPs supported on a MOF substrate, and the obtained NiFe-CeO$_2$/MOF pre-catalyst can also show 100% H$_2$ selectivity and record good catalytic performance for N$_2$H$_4$BH$_3$ decomposition at 343 K. Recently, our group reported a wormlike Ni–CeO$_2$@SiO$_2$ core–shell pre-catalyst with high performance [442.5 h$^{-1}$] and 100% hydrogen selectivity for hydrogen evolution from N$_2$H$_4$BH$_3$ aqueous solution at 343 K. In addition, we proposed a plausible mechanism for metal catalyzed dehydrogenation of N$_2$H$_4$BH$_3$, which involves the chemisorption of N$_2$H$_4$BH$_3$ molecules on the metal active surface and generates the activated intermediate species. Subsequently, the activated intermediate species is attacked by H$_2$O molecules, leading to the dissociation of the B–N bond in N$_2$H$_4$BH$_3$. Then, the BH$_3$ moiety of N$_2$H$_4$BH$_3$ is catalytically hydrolyzed by metal active sites; meanwhile, the resulting N$_2$H$_4$ group is decomposed to produce H$_2$ and N$_2$.

In 2018, our group reported highly active and selective noble-metal-free CuNiMo NPs by using a facile chemical reduction approach. Among all the synthesized pre-catalysts, the optimized Cu$_{0.4}$Ni$_{0.6}$Mo exhibited the highest catalytic activity and 100% H$_2$ selectivity toward hydrogen generation from N$_2$H$_4$BH$_3$ in an alkaline solution, with which 6 equiv. (H$_2$ + N$_2$) per N$_2$H$_4$BH$_3$ (Fig. 15) can be released within 13.9 min. To the best of our knowledge, this is the first report that a noble-metal-free pre-catalyst can achieve a complete dehydrogenation of N$_2$H$_4$BH$_3$ at room temperature (Table 5). The TOF value over RANEY® Ni pre-catalyst exhibited an outstanding catalytic performance with 6.0 equiv. (H$_2$ + N$_2$) per N$_2$H$_4$BH$_3$ being released at 298 K, which is the first report of a noble-metal-free pre-catalyst achieving a complete dehydrogenation of N$_2$H$_4$BH$_3$ at room temperature.
Ni for the complete dehydrogenation of $\text{N}_2\text{H}_4\text{BH}_3$ at room temperature was calculated to be $892\text{ h}^{-1}$ based on surface Ni atoms.

Up to now, preliminary progress has been made in noble-metal-free catalysts for complete hydrogen generation from $\text{N}_2\text{H}_4\text{BH}_3$. However, there are still only a handful of catalysts that can catalyze the complete hydrogen evolution from $\text{N}_2\text{H}_4\text{BH}_3$ (Table 5). Additionally, to maximize the use of metal atoms, highly dispersed catalysts (e.g., metal single-atom) can be designed and synthesized for further improving the catalytic activity of the catalyst. We are looking forward to new breakthroughs in noble-metal-free catalysts for hydrogen generation from boron- and nitrogen-based chemical hydrides and their practical applications.

### Table 5  Catalytic activities for hydrogen evolution from $\text{N}_2\text{H}_4\text{BH}_3$ by different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temp. (K)</th>
<th>$n_{\text{metal}}/n\text{N}_2\text{H}_4\text{BH}_3$</th>
<th>$n(\text{H}_2 + \text{N}_2)/n\text{N}_2\text{H}_4\text{BH}_3$</th>
<th>TOF (mol$_{\text{H}<em>2}$ mol$</em>{\text{metal}}^{-1}$ h$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/PSSMA$^a$</td>
<td>298</td>
<td>0.01</td>
<td>3</td>
<td>183</td>
<td>430</td>
</tr>
<tr>
<td>Co/PSSMA$^a$</td>
<td>298</td>
<td>0.01</td>
<td>3</td>
<td>370</td>
<td>431</td>
</tr>
<tr>
<td>Cu@SiO$_2$$^{a, b}$</td>
<td>298</td>
<td>0.09</td>
<td>3</td>
<td>454.8</td>
<td>204</td>
</tr>
<tr>
<td>Ni$<em>{0.7}$Mo$</em>{0.3}$</td>
<td>298</td>
<td>0.05</td>
<td>3</td>
<td>2400</td>
<td>187</td>
</tr>
<tr>
<td>Bulk Ni NPs$^b$</td>
<td>298</td>
<td>0.006</td>
<td>3</td>
<td>1440</td>
<td>425</td>
</tr>
<tr>
<td>Ni$<em>{0.5}$Fe$</em>{0.5}$–CeO$_2$/MIL-101</td>
<td>343</td>
<td>0.2</td>
<td>6</td>
<td>2136</td>
<td>267</td>
</tr>
<tr>
<td>Ni$<em>{0.5}$Fe$</em>{0.5}$–CeO$_2$/ZIF-67</td>
<td>343</td>
<td>0.2</td>
<td>6</td>
<td>2136</td>
<td>267</td>
</tr>
<tr>
<td>Ni–CeO$_2$/SiO$_2$</td>
<td>343</td>
<td>0.1</td>
<td>6</td>
<td>442.5</td>
<td>405</td>
</tr>
<tr>
<td>NiFe–La(OH)$_3$</td>
<td>343</td>
<td>0.2</td>
<td>6</td>
<td>251.4</td>
<td>408</td>
</tr>
<tr>
<td>RANEY® Ni$^c$</td>
<td>298</td>
<td>—</td>
<td>6</td>
<td>892</td>
<td>446</td>
</tr>
</tbody>
</table>

$^a$ Hydrogen release from the hydrolysis of the BH$_3$ group of HB only. $^b$ Hydrogen release from the methanolysis of the BH$_3$ group of HB only. $^c$ The TOF reported here was calculated based on the surface Ni atoms in the catalyst.

7. Summary

Safe and efficient storage and delivery of hydrogen are essential for the development of a hydrogen-based energy infrastructure. Boron- and nitrogen-based hydrogen storage materials reviewed above have a relatively high hydrogen content and have tremendous potential to be used as hydrogen sources for portable fuel cells. Overall, each of these materials has its own merits and drawbacks. The catalytic performances for hydrogen evolution from these systems have been greatly improved. Non-noble metal catalysts with low cost and relatively high catalytic activity can make boron- and nitrogen-based hydrides potential candidates for portable fuel cells. However, there is still a certain gap in the catalytic activity between non-noble metal catalysts and noble metal catalysts. In addition, the stability of non-noble metal catalysts is generally low, mainly because of their easy oxidation and agglomeration. Therefore, the development of high-activity and high-stability non-noble metal catalysts still requires further efforts.

Besides, the mechanism of nucleation and growth of metal NPs and the active sites of multi-component catalysts are not clear. Theoretical calculations and modern characterization technologies (e.g., in situ X-ray absorption spectroscopy (XAS), transmission electron microscopy (TEM), Raman spectroscopy, etc.) could be helpful in understanding the structure–catalysis relationship, thus providing an effective method to guide the design of metal catalysts at the molecular level. Furthermore, some new methods (e.g. photocatalysis assisted technology) can be developed to promote the hydrogen generation rate from boron- and nitrogen-based chemical hydrides. Additionally, to maximize the use of metal atoms, highly dispersed catalysts (e.g. metal single-atom) can be designed and synthesized for further improving the catalytic activity of the catalyst. We are looking forward to new breakthroughs in noble-metal-free catalysts for hydrogen generation from boron- and nitrogen-based chemical hydrides and their practical applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21763012 and 21802056), the Natural Science Foundation of Jiangxi Province of China (No. 20192BAB203009), and the Sponsored Program for Cultivating Youths of Outstanding Ability in Jiangxi Normal University.

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