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

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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.* $NaBH_4$), ammonia borane (NH_3BH_3), ammonia (NH_3), hydrous hydrazine ($N_2H_4 \cdot H_2O$), and hydrazine borane ($N_2H_4BH_3$), have received much attention as potential chemical hydrogen storage materials because of their high hydrogen contents and the advantage of CO-free H_2 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%), hydrous hydrazine (N$_2$H$_4$·H$_2$O, 8.0 wt%), and hydrazine borane (N$_2$H$_4$BH$_3$, 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.

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Zhang-Hui Lu

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.[16,21,33] 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.

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \qquad (1)$$

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$_3^-$ and M–H intermediate species. Subsequently, M–BH$_3^-$ reacts with OH$^-$ and H$_2$O, possibly *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)$_4^-$ 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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Table 1 Catalytic activities for hydrogen evolution from the hydrolysis of $NaBH_4$ by different catalysts

Catalyst	Synthetic method	Temp. (K)	Activity (mL min^{-1} g^{-1})	E_a (kJ mol^{-1})	Ref.
Intrazeolite Co nanoclusters	Ion-exchange and chemical reduction	298	—	34	62
Co/CCs	Hydrothermal and impregnation–reduction	293	10 400	24.04	66
Co/ACs	Hydrothermal and impregnation–reduction	298	11 220	38.4	67
Co@C-700	Pyrolysis	303	—	56.9	68
Co@NMGC	Pyrolysis	298	3575	35.2	69
Co/IR-120	Wet-chemical reduction	308	200	66.67	70
Co/Fe$_3$O$_4$@C	Impregnation–reduction	298	1403	49.2	71
Fe$_3$O$_4$@C–Co	Solvothermal and impregnation–reduction	298	1746	47.3	72
Co/SiO$_2$	Impregnation–reduction	313	8701	59	32
Cryogel p(AAm)–Co	*In situ* chemical reduction	303	1130.2	39.7	73
Cryogel p(AAm)–Ni	*In situ* chemical reduction	303	579.4	—	73
Ni/graphitic layer	Chemical vapor deposition	298	600	—	74
CoB	Chemical reduction and post-annealing	288	2970	—	77
Co–B thin films	Pulsed laser deposition	298	3300	—	78
Co–B hollow spheres	Chemical reduction and post-annealing	298	2720	45.5	79
CoB/SiO$_2$	Impregnation–reduction	298	10 586	—	80
Mesoporous Co–B	Chemical reduction	303	3350	40	81
Co–Cr–B	Chemical reduction	298	3400	37	85
Co–Mo–B	Chemical reduction	298	2875	39	86
Co–Mo–B/carbon cloth	Two-step electrodeposition	303	1280.9	51	91
Co–Mn–B	Chemical reduction and post-annealing	293	1440	52.1	92
Co–Ti–B	Chemical reduction	323	7760	49.88	93
Co–Ce–B	Chemical reduction and carbonization	303	4760	33.1	94
Co–Zn–B	*In situ* chemical reduction	303	2180	35.92	95
Co–B/carbon	Impregnation–reduction	298	1127.2	57.8	96
CoB/o-CNTs	Impregnation–reduction	298	3041	37.63	98
CoB/TiO$_2$	Impregnation–reduction	293	6738	51	99
Co–B/nickel foam	Electroless plating	298	111	33	103
Ni–B–silica nanocomposite	*In situ* chemical reduction	298	1916	60.7	104
Ni–B/Ni foam	Dipping–chemical reduction	303	—	61.841	105
Multi-shaped Ni–B	Complexing–reduction	303	—	64.9	106
NiB/NiFe$_2$O$_4$	Impregnation–reduction	298	299.88	72.52	107
Fe–B/C cloth	Adsorption–chemical reduction	298	813	—	108
Fe–B/Ni foam	Chemical reduction	323	5487	64.26	109
Cu–B	Complexing–reduction preparation	303	6500	23.79	110
Co–P/Cu substrate	Electroplating	303	954	—	111
Co–P	Electroless deposition	303	3300	60.2	112
Co–P/Cu sheet	Electroless deposition	303	1846	48.1	113
Co–P/Cu sheet	Electroless plating	323	2275.1	27.9	114
CoP/Ti mesh	Phosphidation	298	6100	42.01	115
CoP nanowire array/Ti	Phosphidation	293	6500	41	116
Co–W–P/Cu sheet	Electroless deposition	303	5000	22.8	117
Co–W–P/γ-Al$_2$O$_3$	Electroless deposition	318	11 820	49.58	118
Co–W–P/carbon cloth	Electroless deposition	303	4379	27.18	119
Co–Ni–P/Cu substrates	Electroless deposition	303	2479	—	120
Co–Ni–P/Cu sheet	Electroless plating	303	2172.4	53.5	121
Cu–Co–P/γ-Al$_2$O$_3$	Electroless deposition	298	1115	47.8	122
Fe–CoP/Ti	Phosphidation	298	6060	39.6	123

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.[51,55–58] 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 $NaBH_4$ hydrolysis (Table 1).[31,59–61]

2.1. Metal catalysts

Cobalt catalysts have been reported to be effective in catalytic hydrolysis of $NaBH_4$.[31,59] These are usually deposited on a support material in the form of Co^{2+} 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 Co^{2+} ions with the extra-framework Na^+ ions in zeolite-Y followed by reduction with $NaBH_4$.[62] The obtained intrazeolite Co nanoclusters provided 36 000 turnovers in the hydrolysis of $NaBH_4$ 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 (hydrotalcites, KF/Al$_2$O$_3$, and heteropolyanions) to immobilize Co NPs.[64] Among them, a heteropolyanion supported Co pre-catalyst showed the highest hydrogen generation rate in $NaBH_4$ hydrolysis.

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Various carbon supported Co catalysts have been reported, which have the advantages of relatively low cost and excellent catalytic hydrogen production performance.[65–69] Gou and co-worker found that Co supported on colloidal carbon spheres (Co/CCS) 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}.[66,67] Zhang *et al.* fabricated a Co@C pre-catalyst by using Co-MOF as the starting precursor.[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 *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 ethylenedia-minetetraacetic acid (EDTA).[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.[70–72] Chen *et al.* synthesized a magnetic Co/IR-120 pre-catalyst by a combination of ion-exchange and reduction methods.[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.[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.[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 gene-ration rate.[73–75]

2.2. Metal boride catalysts

Schlesinger and co-workers first found that Co$_2$B was active for hydrogen evolution from the hydrolysis of NaBH$_4$.[54] Afterwards, there have been many reports on the preparation and catalytic activity of Co–B catalysts.[60,61,76–81] It has been reported that the structure and catalytic activity of Co–B cata-lysts were sensitive to their preparation conditions. Jeong and coworkers prepared a Co–B pre-catalyst by the chemical reduction method using NaBH$_4$ as a reductant.[76] The obtained Co–B catalyst was amorphous and showed excellent catalytic performance for hydrogen generation from an aqueous alka-line NaBH$_4$ solution, which was comparable to that of a Ru catalyst. Wu and coworker 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.[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 cata-lyst drastically decreased due to the decomposition of Co–B to form metal Co.

To further obtain efficient Co–B catalysts, the synthesis parameters such the cobalt salt, ratio of NaBH$_4$/Co^{2+}, calcina-tion temperature and solvent type are investigated. Kim and coworkers examined the catalytic activity of a Co–B catalyst pre-pared by using different Co precursors (CoCl$_2$ and CoSO$_4$) and NaBH$_4$/Co^{2+} molar ratios (0.67, 1.5, and 3) at different calcina-tion temperatures (130, 250 and 450 °C).[82] With CoCl$_2$ as the precursor, a NaBH$_4$/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 con-firmed 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$_4$, CoF$_2$, and Co(NO$_3$)$_2$).[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.[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.*).[85–91] These dopant metals, mainly in the form of oxides, act as atomic barriers that are able to sig-nificantly 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 *et al.* conducted a sys-tematic and comparative study on transition metal (Cr, Mo, W, Cu, Ni and Fe) doped Co–B catalysts for hydrogen generation by hydrolysis of NaBH$_4$.[86] They found that the hydrogen gene-ration 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,[92] Ti,[93] Ce[94] and Zn[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,[96–98] Al$_2$O$_3$,[99] CeO$_2$,[99] TiO$_2$,[99–101] and Ni foam.[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 hydro-lysis of NaBH$_4$. Kim and co-workers reported a Ni–B–silica

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nanocomposite pre-catalyst *via* an *in situ* reduction method.[104] The obtained amorphous pre-catalyst was active, providing a hydrogen generation of 1916 mL min^{-1} g^{-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$_4$.[105] Zhang and coworkers prepared an amorphous Ni–B pre-catalyst *via* an ultrasonic complexing reduction route.[106] 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$_2$O$_4$ 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$_2$O$_4$ can be easily separated from the reaction solution using an external magnet.[107]

Lee reported a Fe–B/C cloth pre-catalyst by electrochemical adsorption techniques.[108] The hydrogen generation rate using the Fe–B/C cloth pre-catalyst can achieve 813 mL min^{-1} g^{-1} at room temperature. The Fe–B/Ni foam catalyst was also prepared by the same group for hydrogen generation from NaBH$_4$ in a mixture solution of H$_2$O and CH$_3$OH.[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$_4$.[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$_4$.[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$_2$PO$_2^-$ ions.[111] They found that the amorphous Co–P pre-catalyst with 13 at% P showed the best hydrogen generation rate of 954 mL min^{-1} g^{-1} in a solution of 1 wt% NaOH and 10 wt% NaBH$_4$ 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.[113,114] Chen's group found that the Co–P pre-catalyst formed at a pH value of 12.5, a NaH$_2$PO$_2$ concentration of 0.8 M, and a deposition time no more than 6 min showed the highest catalytic activity for the hydrolysis of NaBH$_4$ solution.[113] By tuning the deposition temperature, nanostructured Co–P/Cu sheets with different morphologies (nanoplatelets, nanospheres, pores and nanoclews) were selectively obtained.[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^{-1} g^{-1} and a low apparent activation energy of 27.9 kJ mol^{-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.[115,116] Sun's group designed 3D cobalt phosphide nanosheet arrays on Ti mesh (CoP/Ti mesh) *via* a topotactical conversion reaction.[115] The obtained 3D monolithic pre-catalyst showed high catalytic activity, providing a maximum hydrogen generation rate of 6100 mL min^{-1} g^{-1} for NaBH$_4$ hydrolysis in alkaline media and an activation energy of 42.01 kJ mol^{-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$_4$ in basic solutions.[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$_4$ alkaline solution.[117–123] Ma and coworkers found that the catalytic activity of the amorphous Co–P pre-catalyst could be markedly improved by incorporating W.[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$_2$O$_3$ and carbon cloth, the catalytic activity and stability of the pre-catalyst can be significantly improved.[118,119] Kim *et al.* synthesized porous Co–Ni–P on Cu substrates by electrodeposition.[120] The three-dimensional Co–Ni–P pre-catalyst formed at a high cathodic current density (>0.5 A cm^{-2}) had a larger surface area than the two-dimensional pre-catalyst formed at a low cathodic current density (0.01 A cm^{-2}), which significantly increased the rate of hydrogen generation in the alkaline NaBH$_4$ 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.[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$_4$ hydrolysis.[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$_4$ hydrolysis, resulting in a hydrogen generation rate of 6060 mL min^{-1} g^{-1} and an activation energy of about 39.6 kJ mol^{-1}.[123]

Overall, Co-based catalysts are demonstrated to be cost-effective, active and stable catalysts for hydrogen generation from the hydrolysis of NaBH$_4$. In addition, most of the reported metal borides/phosphides are in an amorphous state.[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

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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 (NH_3BH_3, 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.[125] Owing to its high hydrogen content (19.6 wt%), low molecular weight (30.9 g mol^{-1}), and nontoxic and environmentally friendly nature, NH_3BH_3 has been considered as a promising hydrogen storage material.[126–133] Hydrogen stored in NH_3BH_3 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 NH_3BH_3.[134–137] Although pure NH_3BH_3 possesses 3 equivalents of H_2, only 2 equivalents could be released at a temperature of 200 °C. In order to maximize the efficacy of NH_3BH_3, 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 NH_3BH_3 requires high temperature and the reaction is relatively difficult to control. In contrast, the hydrolytic (eqn (2)) or methanolytic (eqn (3)) dehydrogenation of NH_3BH_3 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 NH_3BH_3 hydrolysis system ($NH_3BH_3 \cdot 2H_2O$) is about 8.9 wt%, which is higher than that from NH_3BH_3 methanolysis ($NH_3BH_3 \cdot 4MeOH$, 3.9 wt%).

$$NH_3BH_3 + 2H_2O \rightarrow NH_4BO_2 + 3H_2 \quad (2)$$

$$NH_3BH_3 + 4MeOH \rightarrow NH_4B(OMe)_4 + 3H_2 \quad (3)$$

In 2006, Xu's research group firstly found that a stoichiometric amount of hydrogen could be released from the hydrolysis of NH_3BH_3 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 NH_3BH_3.[143–148] Also, several reviews have been reported on the research progress on the hydrolysis of NH_3BH_3.[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 NH_3BH_3.

3.1.   Monometallic catalysts

Xu's research group reported that non-noble-metals Co, Ni and Cu supported on different supports (Al_2O_3, SiO_2 and C) were catalytically active, whereas supported Fe was inactive in hydrolytic dehydrogenation of NH_3BH_3 at room temperature.[154]

Unexpectedly, amorphous Fe NPs synthesized by in situ reduction (Fe/NH_3BH_3 = 0.12) with NH_3BH_3 and $NaBH_4$ 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 NH_3BH_3, 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(Co_{60})) through the complexation of Co^{2+} cations with the internal tertiary amine of sixth-generation hydroxyl-terminated poly(amidoamine) dendrimers followed by reduction with NH_3BH_3 and $NaBH_4$.[158] The synthesized (G6-OH(Co_{60})) was highly dispersed (1.6 nm) and active for the hydrolysis of NH_3BH_3. Duan et al. constructed a Co@g-C_3N_4 core–shell nanostructure anchored onto the surface of rGO sheets (Co@g-C_3N_4-rGO), where g-C_3N_4 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-C_3N_4-rGO as the pre-catalyst. To further improve the activity of Co-based catalysts for NH_3BH_3 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 NH_3BH_3.[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 NH_3BH_3 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 NH_3BH_3 (Fig. 2).

Table 2 Catalytic activities for hydrogen evolution from the hydrolysis of NH_3BH_3 by different catalysts

Catalyst	Temp. (K)	n_{metal}/n_{AB}	TOF ($mol_{H_2} \, mol_{metal}^{-1} \, min^{-1}$)	E_a (kJ mol^{-1})	Ref.
In situ Fe NPs	RT	0.12	3.12	—	155
Co/γ-Al$_2$O$_3$	RT	0.018	2.27	62	154
In situ Co NPs	RT	0.04	44.1	—	156
G6-OH(Co$_{60}$)	298	0.013	10	50.2	158
Co/PEI-GO	298	0.11	39.9	28.2	160
Co/MIL-101	298	0.02	51.4	31.3	167
Co/CTF	298	0.05	42.3	42.7	169
Co NCs@PCC-2a	298	0.07	90.1	—	170
Co@N–C-700	298	0.057	5.6	31	171
Co/NPCNW	298	0.075	7.29	25.4	172
Co/HPC	323	0.11	2.94	32.8	174
Co-(CeO$_x$)$_{0.91}$/NGH	298	0.04	79.5	31.82	161
Co@C–N@SiO$_2$-800	298	—	8.4	36.1	162
Ni/γ-Al$_2$O$_3$	RT	0.018	2.5	—	154
Ni/C	298	0.0425	8.8	28	175
Ni/SiO$_2$	298	0.0225	13.2	34	180
Ni@MSC-30	RT	0.016	30.7	—	181
Ni/ZIF-8	RT	0.016	14.2	—	182
Ni NPs/ZIF-8[a]	298	0.03	85	42.7	183
Ni/CNT ALD	298	—	26.2	32.3	185
Ni@3D-(N)GFs	RT	0.009	41.7	—	186
NiMo/graphene	298	0.05	66.7	21.8	188
Ni-CeO$_x$/graphene	298	0.08	68.2	28.9	194
Ni/PDA-CoFe$_2$O$_4$	298	0.017	7.6	50.8	178
Ni/Ketjenblack	298	0.13	7.5	66.6	179
Cu/γ-Al$_2$O$_3$	RT	0.018	0.23	—	154
p(AMPS)-Cu	303	0.069	0.72	48.8	197
Zeolite confined Cu	298	0.013	1.25	51.8	201
Cu/CoFe$_2$O$_4$@SiO$_2$	298	0.0031	40	—	202
Cu/RGO	298	0.1	3.61	38.2	203
Cu@SiO$_2$	298	0.08	3.24	36	204
Fe$_{0.5}$Ni$_{0.5}$ alloy	293	0.12	11.1	—	210
Fe$_{0.3}$Co$_{0.7}$ alloy	293	0.12	13.9	16.3	216
Cu$_{0.33}$Fe$_{0.67}$	298	0.04	13.95	43.2	219
CuCo/graphene	293	0.02	9.18	—	220
Cu$_{0.2}$Co$_{0.8}$/PDA-rGO	303	0.05	51.5	54.9	221
Cu$_{0.2}$Co$_{0.8}$/PDA-HNTs	298	0.09	30.8	35.15	222
CuCo/C	298	0.033	45	51.9	223
Cu$_{0.5}$Co$_{0.5}$@SiO$_2$	298	0.08	4.26	24	230
Cu$_{0.3}$Co$_{0.7}$@MIL-101	RT	0.034	19.6	—	231
Cu$_{0.72}$Co$_{0.18}$Mo$_{0.1}$	298	0.04	46.0	45	190
Cu$_{0.72}$Co$_{0.18}$Mo$_{0.1}$[a]	298	0.04	119.0	—	190
CuNi/CMK-1	298	0.072	54.8	—	224
Cu$_{0.2}$Ni$_{0.8}$/MCM-41	298	0.05	10.7	38	228
CuNi/47-SiO$_2$	298	0.165	23.5	34.2	229
Cu$_{0.8}$Co$_{0.2}$O/GO	298	0.024	70	45.5	243
Ni$_2$P	298	0.12	40.4	44.6	255
CoP[a]	298	0.043	72.2	46.7	262
Ni$_{0.7}$Co$_{1.3}$P/GO[a]	298	0.026	109.4	—	263

[a] The reaction was promoted with the addition of NaOH.

Table 3 Catalytic activities for hydrogen evolution from the methanolysis of NH_3BH_3 by different catalysts

| Catalyst	Temp. (K)	n_{metal}/n_{AB}	TOF ($mol_{H_2} \, mol_{metal}^{-1} \, min^{-1}$)	E_a (kJ mol^{-1})	Ref.
Cu$_2$O	298	0.15	0.16	—	198
Nano-Cu@Cu$_2$O	298	0.15	0.12	—	198
Nano-Cu	298	0.15	0.08	—	198
PVP-stabilized Ni	298	0.005	12.1	62	267
Co–Ni–B	RT	0.2	10	—	276
Co–Co$_2$B	RT	0.2	6	—	276
Ni-Ni$_3$B	RT	0.2	3.6	—	276
Flower-like Cu	298	0.15	2.41	34.2	277
Cu–Cu$_2$O–CuO/C	298	0.04	24	67.9	278
b-CuO NA/CF	298	0.018	13.3	34.7	279
CuNi/graphene	298	0.03	49.1	24.4	280
Cu/Co(OH)$_2$	298	0.129	61.63	37.6	281
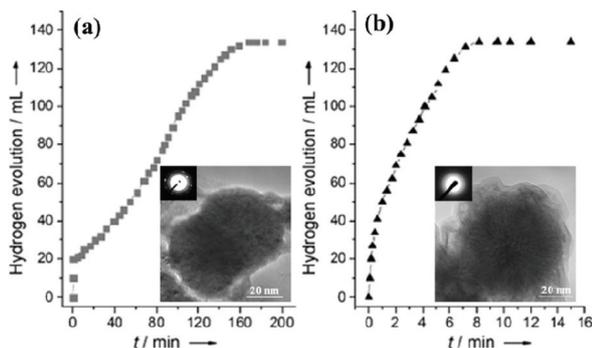
Fig. 1 Hydrogen generation by hydrolysis of aqueous AB (0.16 m, 10 mL) in the presence of (a) the pre-synthesized and (b) *in situ* synthesized Fe catalysts (Fe/AB = 0.12) at room temperature under argon. The inset shows the corresponding TEM images and SAED patterns of the as-synthesized catalysts. Reprinted with permission from ref. 155. Copyright (2008) Wiley-VCH.
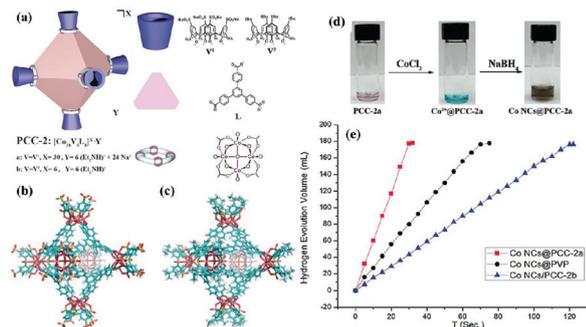

Fig. 2 (a) Cartoon of octahedron cage PCC-2 and the cage components, (b) the crystal structure of PCC-2, and (c) the crystal structure of PCC-2b. (d) The preparation of Co NCs with PCC-2a. (e) Time course plots of H_2 generation for the hydrolysis of AB by Co NCs@PCC-2a, Co NCs/PCC-2b, and Co NCs@PVP. Reprinted with permission from ref. 170. Copyright (2018) Wiley-VCH.

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.[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)ethylenediamine) at selected temperatures (600–800 °C) under an Ar atmosphere.[171] 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}.[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.[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.[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).[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}.[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_2O_3, and CeO_2 as support materials.[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.[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.[182] They pointed out that this is the first example of water-stable MOF-supported metal NPs for hydrogen generation from hydrolysis of NH_3BH_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).[183]

Zhong and coworkers reported a Ni/CNT hybrid pre-catalyst for the hydrolysis of NH_3BH_3.[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.[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_3BH_3 hydrolysis.[186]

Recently, our group reported a facile chemical reduction method to incorporate a small amount of inactive metals (Mo,

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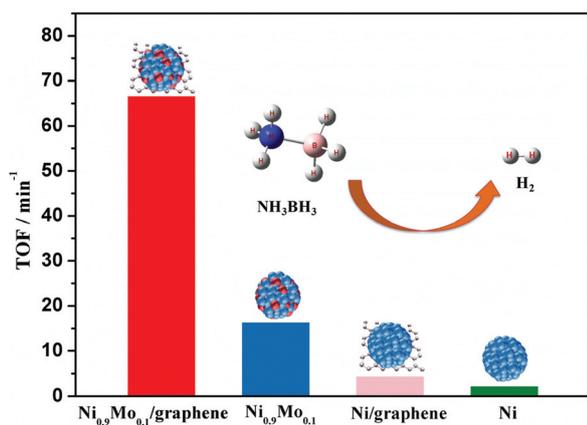This journal is © the Partner Organisations 2020

Fig. 3 Catalytic activities for hydrogen generation from AB aqueous solution (5 mL, 0.2 M) over $Ni_{0.9}Mo_{0.1}$/graphene, $Ni_{0.9}Mo_{0.1}$, Ni/graphene, and Ni at 298 K (metal/AB = 0.05). Reprinted with permission from ref. 188. Copyright (2016) Royal Society of Chemistry.
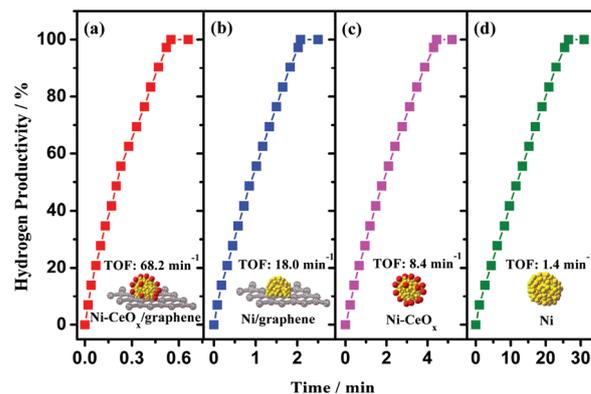

Fig. 4 Hydrogen productivity *vs.* reaction time for hydrogen release from an aqueous AB solution (200 mM, 5 mL) catalyzed by (a) Ni-CeO$_x$/graphene, (b) Ni/graphene, (c) Ni-CeO$_x$, and (d) Ni at 298 K (nNi/nAB = 0.08). Reprinted with the permission from ref. 194. Copyright (2018) Springer Nature.

Cr, and W) into Ni NPs.[187] 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 NH_3BH_3 at room temperature (Fig. 3).[188] 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.[189–193]

Ni doped with CeO$_x$ and supported on graphene (Ni-CeO$_x$/graphene) was also fabricated by our research group *via* a facile chemical reduction route.[194] The combination of CeO$_x$, metal, and graphene of the Ni-CeO$_x$/graphene pre-catalyst confers remarkably enhanced catalytic activity (68.2 min^{-1}) for the hydrolytic dehydrogenation of NH_3BH_3 (Fig. 4), as well as high stability. In addition, some other rare-earth metal oxide (ReOx, Re = La, Dy, Er, Yb, Gd, and Tb) doped Ni/graphene (Ni-ReO$_x$/graphene) were also prepared and all showed higher catalytic activities than pure Ni/graphene. The excellent catalytic activities of Ni-ReO$_x$/graphene might be attributed to the similar physical and chemical properties of the ReO$_x$ 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-CeO$_x$/NGH and CuNi-CeO$_x$/rGO were prepared and they showed synergistic and superior catalytic activities.[161,195]

Comparing Co- and Ni-based catalysts, Cu-based catalysts have been reported to show a lower catalytic activity (Table 2).[196,197] In 2006, Xu and coworkers found that Cu/γ-Al$_2$O$_3$ was catalytically active in NH_3BH_3 hydrolysis

(0.78 min^{-1}), but it takes nearly 600 minutes to release 2.83 equivalents of hydrogen (nCu/nAB = 0.018).[154] Subsequently, nanostructured Cu, Cu$_2$O, and Cu@Cu$_2$O NPs were synthesized by Kalidindi and co-workers *via* the solvated metal atom dispersion (SMAD) method.[198] They found that core–shell Cu@Cu$_2$O and Cu$_2$O NPs are more active than pure Cu NPs for this hydrolysis reaction. After that, Fukuzumi and co-worker synthesized a series of Cu/Co$_3$O$_4$ composite pre-catalysts by a conventional impregnation method.[199] The catalytic activities of Cu/Co$_3$O$_4$ were significantly dependent on the shape and size of nanosized Co$_3$O$_4$, and it was found that Co$_3$O$_4$ with a hexagonal sheet shape showed better catalytic activity than that with a cube or uncontrolled shape. They also found that capping of Cu$_2$O with Co$_3$O$_4$ NPs was an effective way to suppress agglomerate formation, which made the Cu$_2$O–Co$_3$O$_4$ composites exhibit high catalytic reactivity in hydrolytic dehydrogenation of NH_3BH_3.[200]

Özkar and co-worker synthesized zeolite confined Cu NPs by ion-exchange of Cu^{2+} with the extra framework Na$^+$ in zeolite-Y followed by the reduction of the Cu^{2+} ions with NaBH$_4$.[201] The zeolite confined Cu NPs were found to be active in the hydrolysis of NH_3BH_3 with a TOF value of 0.78 min^{-1}. Cu NPs supported on magnetic SiO$_2$/CoFe$_2$O$_4$ (CuNPs@SCF) were reported to have an initial TOF of 40 min^{-1} for hydrolysis of NH_3BH_3 at 298 K.[202] 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 CoFe$_2$O$_4$ was not considered in the TOF calculation. The oxides of Fe and Co are difficult to be reduced by NH_3BH_3; 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 NH_3BH_3 as a reductant.[203] The obtained Cu/RGO showed a higher catalytic activity than Cu/graphite powder, Cu/activated carbon and free Cu NPs, over which the NH_3BH_3

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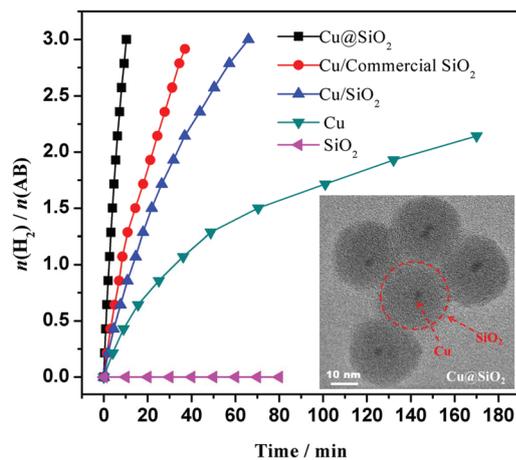*Inorg. Chem. Front.*, 2020, **7**, 3837–3874 | **3845**

Fig. 5 Hydrogen generation from the hydrolysis of AB (0.2 M, 5 mL) in the presence of different catalysts at 298 K (Cu/AB = 0.09). The inset shows the TEM image of the Cu@SiO$_2$ catalyst. Reprinted with permission from ref. 204. Copyright (2014) Springer Nature.
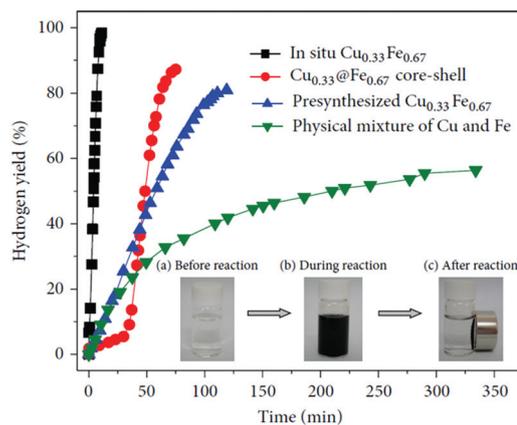

Fig. 6 Hydrogen generation from the hydrolysis of AB in the presence of different catalysts (metal/AB = 0.04). The inset shows photographs of the catalytic hydrolysis of AB via *in situ* synthesized Cu$_{0.33}$Fe$_{0.67}$ alloys. Reprinted with permission from Ref. 219. Copyright (2013) Elsevier.

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@SiO$_2$ core–shell nanospheres showed superior activity as compared to Cu/commercial SiO$_2$, Cu/SiO$_2$ and free Cu NPs for hydrolysis of NH$_3$BH$_3$ (Fig. 5). Furthermore, the Cu@SiO$_2$ 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 NH$_3$BH$_3$ with 3 equiv. of H$_2$ 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–Co,[220–223] and Cu–Ni,[224–228] have been reported toward the hydrolysis of NH$_3$BH$_3$. For example, our group prepared a series of Cu$_{1-x}$Fe$_x$ alloy NPs by a very simple *in situ* reduction method, and the optimal Cu$_{0.33}$Fe$_{0.67}$ 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 NH$_3$BH$_3$.[220] Xu's research group employed diamine-functionalized reduced graphene oxide as a support for CuCo NPs (CuCo/PDA-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 NH$_3$BH$_3$ hydrolysis reaction.[222] Zahmakiran 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 Cu$_{0.5}$Ni$_{0.5}$/CMK-1 and Cu$_{0.5}$Ni$_{0.5}$/MCNS are comparable in the hydrolysis of NH$_3$BH$_3$ and are 3-fold higher than that of silica-supported Cu$_{0.5}$Ni$_{0.5}$/MCM-48. Yu and coworkers successfully immobilized CuNi NPs on six differently sized SiO$_2$ spheres (47, 97, 195, 333, 391 and 485 nm).[229] The results showed that the catalytic activity of CuNi/SiO$_2$ increases with the decrease of SiO$_2$ particle size, due to which the CuNi NPs supported on the smallest SiO$_2$ (CuNi/47-SiO$_2$) exhibit the

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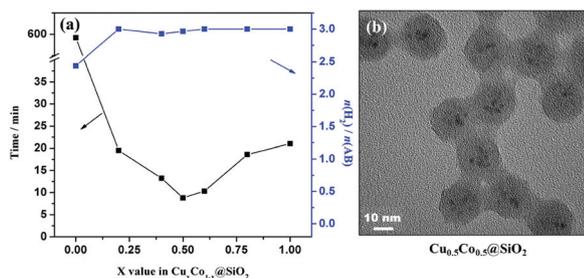This journal is © the Partner Organisations 2020

Fig. 7 (a) $Cu_xCo_{1-x}@SiO_2$ core–shell nanospheres with different x values under an ambient atmosphere at 298 K; (b) TEM image of $Cu_{0.5}Co_{0.5}@SiO_2$. Reprinted with permission from Ref. 209. Copyright (2015) American Chemical Society.

highest catalytic activity in the hydrolysis of NH_3BH_3 at 298 K. However, the stability of CuNi/47-SiO_2 showed obvious degradation after seven cycles. Our group successfully encapsulated ultrafine Cu–Co NPs ($\sim$2 nm) inside SiO_2 nanospheres ($CuCo@SiO_2$) (Fig. 7), which can effectively prevent metal NP aggregation and enhance the pre-catalyst stability.[230] The optimized $Cu_{0.5}Co_{0.5}@SiO_2$ pre-catalyst showed excellent catalytic activity in the hydrolysis of NH_3BH_3 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 NH_3BH_3.[231]

Trimetallic CuCoMo NPs without any surfactant or support have been fabricated by our group through a facile co-reduction method.[190] Compared to their bi-/mono-metallic counterparts, the obtained optimized trimetallic $Cu_{0.72}Co_{0.18}Mo_{0.1}$ pre-catalyst exhibits the highest catalytic activity for AB hydrolysis with a TOF value of 46.0 min^{-1} at 298 K (Fig. 8). Moreover, the catalytic performance of
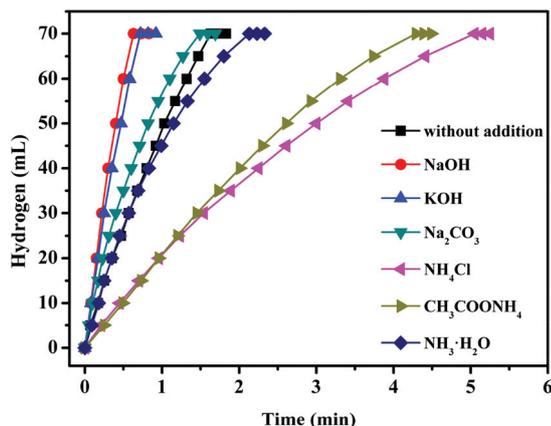
$Cu_{0.72}Co_{0.18}Mo_{0.1}$ can be further significantly improved by introducing NaOH as a promoter, providing a TOF value as high as 119.0 min^{-1} at 298 K, which is among the highest values of all the reported non-noble metal catalysts (Table 2) and even higher than that of the commercial Pt/C pre-catalyst for the same reaction.[126] However, introducing the NH_4^+ species ($e.g.$, $NH_3 \cdot H_2O$, NH_4Cl, $etc.$) 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 NH_3BH_3.[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 NH_3BH_3 as a weak reducing agent, which could selectively reduce Cu^{2+} first to form the core, and successively reduce M^{2+} (M = Co, Fe, Ni) to form the shell.[233] A relatively stronger reductant $NaBH_4$, instead of NH_3BH_3, 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 NH_3BH_3. In addition, H_2 generation over $Cu_1@Co_4$ 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@Co,[234] trimetallic Cu@FeNi,[236] Cu@FeCo,[237] Cu@CoNi,[238,239] Cu@CoMo[240] and even tetrametallic Cu@FeCoNi,[225] 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 NH_3BH_3 has attracted much attention in recent years.[241–244] Li and coworkers prepared $CuCo_2O_4$ pre-catalysts with different shapes (nanoplates, nanosheets, and nanoparticles).[241] Among them, the nanoplate-shaped $CuCo_2O_4$ pre-catalyst showed the best catalytic activity for hydrogen production from the hydrolysis of NH_3BH_3, giving a TOF value of 44 min^{-1} at room temperature. Moreover, the $CuCo_2O_4$ 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 $NiCo_2O_4$,[242] $MnCo_2O_4$,[245] $CuCoMoO_4$,[246] $CuNiCo_2O_4$,[247] $Co_3O_4/CuMoO_4$,[248] $CuO-NiO/Co_3O_4$[249] and $Co_xCu_{1-x}Co_2O_4@Co_yCu_{1-y}Co_2O_4$,[250] which are active in NH_3BH_3 hydrolysis reaction. Zhong and coworker reported the synthesis of bimetallic oxide NPs $Cu_xCo_{1-x}O$ deposited on graphene oxide (GO) via a facile route.[243] The obtained $Cu_{0.8}Co_{0.2}O/GO$ pre-catalyst exhibits an initial TOF value as high as 70.0 min^{-1} for the hydrolysis of NH_3BH_3, owing to the interfacial interaction between CuCoO NPs and GO. Moreover,

Fig. 8 Hydrogen generation from the hydrolysis of AB (0.20 M, 5 mL) with the addition of 1 M NaOH, KOH, Na_2CO_3, NH_4Cl, CH_3COONH_4 and $NH_3 \cdot H_2O$ (2 mL) catalyzed by $Cu_{0.72}Co_{0.18}Mo_{0.1}$ NPs at 298 K (n_{metal} = 0.04 mmol). Reprinted with permission from ref. 190. Copyright (2018) Royal Society of Chemistry.

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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@CuCoO$_x$ pre-catalyst, with which superior catalytic activity was achieved toward the hydrolysis of NH$_3$BH$_3$ 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 NH$_3$BH$_3$. Therefore, such metal oxide catalysts are mainly Cu-based oxides, because Cu oxides can be easily reduced to Cu(0) by NH$_3$BH$_3$ 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 NH$_3$BH$_3$.[251,252,258-261] For example, Figen and Coșkuner 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 NH$_3$BH$_3$ hydrolysis.[258,259]

Fu and coworkers reported the synthesis of Ni$_2$P NPs by reacting Ni(OH)$_2$ with solid NaH$_2$PO$_2$ in argon at 543 K.[254] The obtained Ni$_2$P NPs (<12 nm) showed excellent catalytic activity and high sustainability toward hydrogen evolution from the hydrolysis of NH$_3$BH$_3$ 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 Ni$_2$P 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 NH$_3$BH$_3$ hydrolysis could significantly promote the catalytic activity in NH$_3$BH$_3$ 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/NH$_3$BH$_3$ molar ratio of 0.041 at 298 K. Recently, a series of Co-doped Ni$_2$P NPs and their nanohybrid with graphene oxide were also fabricated by Fu and coworkers.[263] The optimal Ni$_{0.7}$Co$_{1.3}$P/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 Ni$_2$P can effectively optimize the electronic structures of Ni$_{2-x}$Co$_x$P pre-catalysts, enhance their interaction with NH$_3$BH$_3$, and facilitate the hydroxyl activation of NH$_3$BH$_3$, thus resulting in a decrease of the reaction energy barrier and improvement of the hydrogen generation rate.
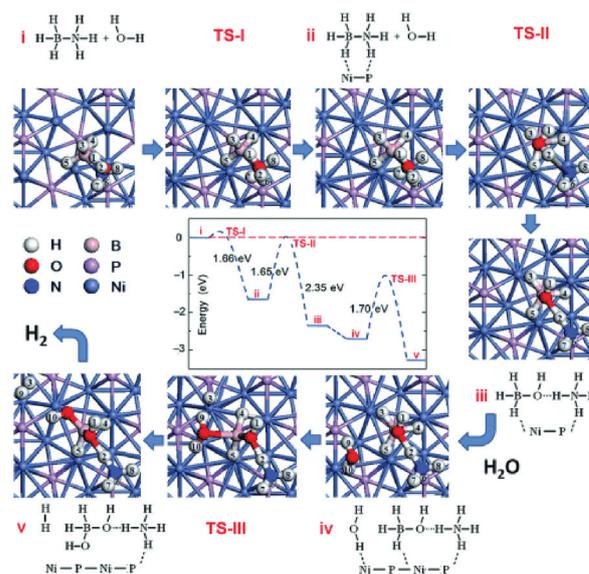

Fig. 9 Plot of energy changes *versus* reaction coordinates calculated for Ni$_2$P-catalyzed hydrolysis of AB. Reprinted with permission from ref. 254. Copyright (2016) Wiley-VCH.

For the transition metal catalyzed hydrolysis of NH$_3$BH$_3$, 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 NH$_3$BH$_3$ molecules is the rate-determining step.[154] Then, the activated complex species is attacked by H$_2$O, leading to concerted dissociation of the B–N bond and hydrolysis of the resulting BH$_3$ intermediate to produce the borate ion along with H$_2$ release. Jagirdar and Chen assumed that the release of H$_2$ is due to the attack of H$_2$O 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 BH$_3$OH$^-$ and NH$_4^+$ species, and then attacking adjacent H$_2$O to produce H$_2$.[254] Recently, He and Duan proposed that the rate-determining step for NH$_3$BH$_3$ is the breaking of the O–H bond in H$_2$O based on the kinetic isotopic effect measurements.[169,265]

3.4. Catalysts for NH$_3$BH$_3$ methanolysis

As for NH$_3$BH$_3$ methanolysis, despite the GHSC of the NH$_3$BH$_3$–4MeOH system (3.9 wt%) being much lower than that from the hydrolysis system, NH$_3$BH$_3$ methanolysis has some advantages that merit its potential applications as a portable hydrogen source.[25,138,266-273] Firstly, addition of suitable catalysts can initiate the NH$_3$BH$_3$ methanolysis reaction below 0 °C, thereby satisfying the applications in cold weather. Secondly, pure H$_2$ can be released by methanolysis of NH$_3$BH$_3$ without the production of NH$_3$. More importantly, the byproduct of NH$_3$BH$_3$ methanolysis (*i.e.*, NH$_4$B(OMe)$_4$) can be easily reconverted back to NH$_3$BH$_3$ by reaction with NH$_4$Cl and LiAlH$_4$ at room temperature.[138]

Compared with the extensive studies of NH$_3$BH$_3$ hydrolysis, there are only a few studies regarding NH$_3$BH$_3$ methanolysis (Table 3).[138,267,274-276] In 2007, RuCl$_3$, RhCl$_3$, PdCl$_2$, CoCl$_2$,

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NiCl$_2$, Pd/C, and RANEY® Ni were firstly reported for the methanolysis of NH$_3$BH$_3$.[138] Since then, non-noble metal pre-catalysts such as PVP-stabilized Ni, Co-Co$_2$B, Ni-Ni$_3$B, Co–Ni–B, and Co–Ni–P pre-catalysts have been reported for dehydrogenation of NH$_3$BH$_3$ in methanol.[276] Later on, mesoporous Cu with diverse morphologies (flower-, nanosheet-, bundle- and dandelion-like) have been prepared by our group via a simple wet-chemical method combined with a reduction strategy.[277] Among the four Cu nanostructures, the flower-like Cu nanostructure was the most active with a TOF of 2.41 min^{-1} toward the methanolysis of NH$_3$BH$_3$. Moreover, the flower-like Cu nanostructures also showed excellent recyclability in the methanolysis of NH$_3$BH$_3$. Subsequently, Zahmakiran and co-workers reported Cu–Cu$_2$O–CuO/C composites to catalyze hydrogen generation from the methanolysis of NH$_3$BH$_3$, which showed high activity (24 min^{-1}) in this methanolysis reaction.[278] 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 NH$_3$BH$_3$.[279] 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 NH$_3$BH$_3$.[280] 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.[281] By varying the metal/support ratio, a highly efficient catalytic performance (61.63 min^{-1}) for the methanolysis of NH$_3$BH$_3$ 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 NH$_3$BH$_3$ 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 NH$_3$BH$_3$. 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.[282] Ammonia is also considered as a potential hydrogen carrier because of its high gravimetric capacity (17.7 wt% H), low price, and production of inherently CO$_x$-free H$_2$.[24,26,283–286] 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.[287–289] NH$_3$

can be decomposed to release H$_2$ along with N$_2$ by the following reaction (eqn (4)):

$$2NH_3 \rightarrow N_2 + 3H_2 \qquad (4)$$

The NH$_3$ decomposition is an endothermic reaction (ΔH = 92 kJ mol^{-1}) and a high temperature is required for efficient hydrogen generation.[290] Thermal decomposition of NH$_3$ into H$_2$ and N$_2$ has been extensively studied in the past decades.[24,26,284,286] The works before the 1990s on NH$_3$ decomposition were mainly studied to gain insight into the reaction kinetics of NH$_3$ synthesis.[291] Nowadays, the research on NH$_3$ decomposition is mainly focused on the generation of high quality H$_2$. Generally, N$_2$ adsorption is thought to be rate-limiting in NH$_3$ synthesis, while the rate determining step for NH$_3$ 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, N$_2$ 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 NH$_3$.[294–298] However, the high cost and limited availability inhibit the wide scale use of these catalysts. Therefore, much attention has been recently 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]

4.1. Monometallic catalysts

Fe-Based catalysts have been extensively studied in the NH$_3$ decomposition reaction owing to its industrial use in the NH$_3$ synthesis reaction.[299–304] Fe promoted by K$_2$O, CaO, SiO$_2$ and Al$_2$O$_3$ is active for NH$_3$ synthesis at temperatures above 400 °C and was initially considered as a potential pre-catalyst for NH$_3$ decomposition.[299] The overall activity of Fe-based pre-catalysts toward NH$_3$ 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 NH$_3$ 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 CNF morphology. In addition, the pre-catalyst of Fe–CNFs/mica showed a higher catalytic activity and stability than the Fe/CNF pre-catalyst, which could be attributed to the Fe particles isolated by mica and CNFs and the higher degree of graphitization of CNFs. Recently, a series of Fe-based catalysts supported on two-dimensional mica nanosheets (Fe/MS) were synthesized by Yuan and coworkers via three different methods namely homogeneous precipitation (HP), impregnation (IM), and deposition precipitation (DP) methods.[306] The catalytic results show that the Fe/MS prepared by the HP method showed the highest catalytic performance among all the synthesized pre-catalysts with different methods. The excel-

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.[307–309] Highly dispersed γ-Fe_2O_3 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.[307] The obtained γ-Fe_2O_3/CMK-5 pre-catalyst showed the high catalytic activity toward the decomposition of NH_3 at 600 °C. The Fe_2O_3/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.[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, Varisli *et al.* synthesized a robust Fe@mesoporous carbon pre-catalyst by a traditional impregnation procedure, which was very active for microwave-assisted NH_3 decomposition.[309]

Ni-Based catalysts have also been used as alternative catalysts for NH_3 decomposition due to their substantially lower costs compared to Ru and the higher activity compared to Fe.[310–314] Previously, Ganley *et al.* reported an order of activity as Ru > Ni > Rh > Co > Ir > Fe for NH_3 decomposition.[310] Zhang *et al.* reported a co-precipitation method to prepare a series of supported pre-catalysts by depositing Ni NPs on Al_2O_3.[311] The catalytic activity of Ni/Al_2O_3 increased with increasing Ni loading and reached a maximum at a Ni/Al ratio of 1.2. Interestingly, the conversion of NH_3 was further increased after the addition of a La promoter into the Ni/Al_2O_3 pre-catalyst. For example, when the La/Ni molar ratio increased from 0 to 0.2, the conversion of NH_3 progressively increased from 38.2 to 63.9% at 773 K. The characterization results indicated that the Ni/La–Al_2O_3 pre-catalyst with an appropriate amount of La possessed a more open mesoporous structure and higher dispersion of Ni as compared to Ni/Al_2O_3. Later on, Xu and coworker reported that the addition of CeO_2 obviously improved the catalytic activity and stability of Ni/Al_2O_3 for NH_3 decomposition to CO_x-free H_2.[315] The characterization results showed that the addition of CeO_2 could enlarge the pre-catalyst pores, moderate the interaction between the metal and support, suppress Ni NPs from sintering, and improve the recombinative desorption of N adatoms 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 NH_3 decomposition activity, and the highest activity could be achieved when the Ce(La)/Ni ratio was around 0.3.[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 (Y_2O_3, CeO_2, La_2O_3, Sm_2O_3 and Gd_2O_3) for NH_3 decomposition.[317] Among the samples investigated, the Ni/Y_2O_3 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/Y_2O_3 was relatively small at high temperatures. Furthermore, this group also found that the catalytic activity of Ni/Y_2O_3 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.[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.[319] The obtained 3D-printed Ni/CeO_2 pre-catalyst showed higher catalytic performance than the Ni/CeO_2 powder pre-catalyst and the conventional cordierite honeycomb wash coated with Ni/CeO_2 under the same reaction conditions.

Compared with Fe-based and Ni-based catalysts, Co-based catalysts are less studied in NH_3 decomposition reactions.[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 NH_3 decomposition, and the microstructure of the CNTs remained unchanged after the decomposition reaction.[320] After that, Co supported on CNTs was synthesized and studied.[321] The conversion of NH_3 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 (N_2 and H_2).[322] It is found that the catalytic activity of Co/CNT pre-catalyst treatment in N_2 was higher than that of Co/CNT in H_2, and the pretreatment of Co/CNTs at 600 °C showed the highest NH_3 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 NH_3 decomposition as compared to the calcined sample in pure N_2 flow.[323] Podila and coworkers have reported that Co supported on a Mg–La mixed oxide showed high activity for NH_3 decomposition.[324,325] Recently, Jia and coworkers synthesized a high surface area Co–SiO_2 pre-catalyst by a simple two-step procedure with activated carbon as the template for NH_3 decomposition reaction.[326] The presence of SiO_2 can effectively protect active Co species from agglomeration during the calcination and NH_3 decomposition reaction. The obtained Co–SiO_2 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 bimetallic catalysts, such as Co–Mo,[327–329] Fe–Mo,[330] Fe–Co,[331–334] Fe–Ni[335–337] and Co–Ni,[338] 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.[327] 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.[328] The results showed that the CoMo-I/γ-Al_2O_3 pre-catalyst prepared using monocomponent metal amine metallate ($Co(en)_3MoO_4$) as the active phase precursor exhibited higher activity and stability for ammonia decomposition than the CoMo-II/γ-Al_2O_3 pre-catalyst prepared using bicomponent $Co(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}$ 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).[329] The Co–Mo pre-catalyst calcined in air showed higher catalytic activity, and Co_3Mo_3N 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 reaction.[330]

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.[331] 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 ($Co_xFe_{3−x}O_4@mSiO_2$) have been fabricated by Zhang and coworkers.[334] By tuning the chemical stoichiometry of $Co_xFe_{3−x}O_4$ nanosheets, the strength of the M–N bond can reasonably adjust and subsequently greatly optimize the catalytic performance. The optimized $Co_{0.89}Fe_{2.11}O_4@mSiO_2$ 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_2O_3,[335,336] Ni–Fe alloys[337] and NiCo/$Ce_{0.6}Zr_{0.3}Y_{0.1}O_2$ solid solutions[338] 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_x, MoC_x FeC_x, VC_x and TaC_x) and nitrides (MoN_x, VN_x and WN_x) have also been investigated for NH_3 decomposition reaction.[339–344] 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 gas mixture (H_2/CO) before the decomposition reaction.[339] Subsequently, Shi and coworkers synthesized a mesoporous WC pre-catalyst *via* an impregnation–compaction route, which showed high and stable catalytic activity, and complete NH_3 decomposition was achieved at a low temperature (500 °C).[340] Kraupner and coworkers reported mesoporous Fe_3C with high crystallinity and high surface area by a combination of a hard-

templating approach and carbothermal reduction.[341] The obtained Fe_3C pre-catalyst showed good catalytic activity in NH_3 decomposition with conversion above 95% at 700 °C. Choi *et al.* investigated VC and TaC as pre-catalysts for NH_3 decomposition, which showed excellent catalytic performance, higher than that of a Pt/C pre-catalyst.[342,343] Zheng *et al.* synthesized high-surface area Mo_2C from a h-MoO_3 precursor *via* a temperature-programmed reduction–carburization under a flowing atmosphere of H_2 and CH_4.[344] The result showed that Mo_2C undergoes a phase transformation during the NH_3 decomposition reaction, and the active phase is actually MoN.

Mo-Based nitrides for NH_3 decomposition are the most studied among the metal carbides and nitrides due to their low cost and high activity. Li *et al.* reported that MoN_x/α-Al_2O_3 and $NiMoN_y$/α-Al_2O_3 exhibited excellent catalytic properties for NH_3 decomposition with conversions reaching as high as 98.7% and 99.8%, respectively, at 650 °C.[345] Moreover, the increasing nitride phase content of Ni_2Mo_3N up to 37 wt% doubles the NH_3 conversion at 550 °C.[346] Podila *et al.* found that the addition of Co into γ-Mo_2N can further improve the conversion of NH_3 decomposition, which is due to the formation of the Co_3Mo_3N phase in Co-containing samples.[347] After that, Srifa *et al.* synthesized pure phase Co_3Mo_3N from $CoMoO_4$ *via* a temperature-programmed reaction method, which showed almost 100% of NH_3 conversion at 600 °C.[289] The catalytic activity of the Co_3Mo_3N pre-catalyst for NH_3 decomposition can be significantly improved by the addition of a small amount of Cs species.[348] Furthermore, Mo-based nitrides such as Mo_2N, Ni_2Mo_3N, Ni_3Mo_3N and Fe_3Mo_3N also have been suggested as the highly active species for the NH_3 decomposition reaction.[348–350]

5. Hydrous hydrazine

Anhydrous hydrazine (N_2H_4), a colorless flammable liquid at room temperature, has a high hydrogen capacity as high as 12.5 wt%. Hydrogen stored in N_2H_4 can be catalytically decomposed over supported metals, metal carbides, and metal nitrides in two pathways (eqn (5) and eqn (6)).[351–358] 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.

$$N_2H_4 \rightarrow N_2 + 2H_2 \quad (5)$$

$$3N_2H_4 \rightarrow N_2 + 4NH_3 \quad (6)$$
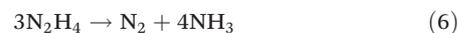
Hydrous hydrazine, such as hydrazine monohydrate ($N_2H_4·H_2O$) which has a hydrogen capacity of 8.0 wt%, is

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believed to be relatively safe.[19,20,22,359–361] Notably, $N_2H_4 \cdot H_2O$ 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 N_2H_4 generates only a by-product of N_2 in addition to H_2, which does not need on-board collection for recycling. These merits have made $N_2H_4 \cdot H_2O$ a promising hydrogen carrier for storage and transportation. Thereby, it is crucial to develop effective and selective catalysts for complete hydrogen generation from $N_2H_4 \cdot H_2O$.[361–367] Xu and co-workers initially investigated various metal (Rh, Co, Ru, Ir, Cu, Ni, Fe, Pt and Pd) NPs as catalysts for N_2H_4 decomposition.[368] Among all the synthesized metal NPs, Rh showed the highest H_2 selectivity (43.8%) for hydrogen evolution from $N_2H_4 \cdot H_2O$ decomposition. Other metal NPs, such as Co, Ru, and Ir, exhibited poor H_2 selectivity (7%), and Fe, Cu, Ni, Pd, and Pt were totally inactive under the same reaction conditions. Up to now, Ni,[369–372] Ni–Pt,[373–377] Ni–Rh,[378–383] Ni–Ir,[384,385] Ni–Pd,[386,387] Co–Pt,[388,389] Co–Ir,[390] Rh–Mo,[191] Rh–P,[391] Ni–Fe,[392–394] Ni–Cu,[224,395,396] and Ni–Co[397] have been reported to be efficient in the decomposition of $N_2H_4 \cdot H_2O$ to H_2. Since noble metals (Pt, Rh, Ir, and Pd) are expensive, noble-metal-free catalysts (Ni, Fe, and Cu) were developed for the economic advantage, which is essential for promoting the potential applications of $N_2H_4 \cdot H_2O$ as a hydrogen storage material. Herein, we categorize noble-metal-free catalysts into three major groups: (a) Ni-based metal NPs, (b) complex oxide supported catalysts, and (c) other supported catalysts for catalytic decomposition of $N_2H_4 \cdot H_2O$ to H_2 under various reaction conditions (Table 4).

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.[392] Although all the synthesized Ni–Fe NPs are inactive in the decomposition reaction of $N_2H_4 \cdot H_2O$ 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 $N_2H_4 \cdot H_2O$ in 190 min with NaOH (0.5 M) at 343 K. However, the addition of a weaker base such as NH_3 and CH_3COONa 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, therefore hindering the decomposition of N_2H_4 to NH_3.

It has been reported that the catalytic activity and H_2 selectivity of Ni–Fe NPs could be improved by introducing a Cu core.[398] The Cu core is not selective for hydrogen evolution from the decomposition of $N_2H_4 \cdot H_2O$, while the NiFe/Cu NPs exhibited high activity, stability, and ~100% H_2 selectivity for hydrogen evolution at 330–340 K. After that, Zhang and co-workers synthesized core–shell $Cu@Fe_5Ni_5$ NPs via an in situ seeding-growth approach and investigated their catalytic performances.[399] The core–shell $Cu@Fe_5Ni_5$ NPs have a small size of about 8.5 nm. The core–shell $Cu@Fe_5Ni_5$ pre-catalyst showed high activity and 100% H_2 selectivity within 70 min

Table 4 Catalytic activities for hydrogen evolution from $N_2H_4 \cdot H_2O$ catalyzed by different catalysts

Catalyst	Temp. (K)	$n_{metal}/n_{N_2H_4 \cdot H_2O}$	H_2 selectivity (%)	TOF ($mol_{H_2}\ mol_{metal}^{-1}\ h^{-1}$)	E_a (kJ mol^{-1})	Ref.
$Ni_{0.5}Fe_{0.5}$ NPs	343	0.1	100	6.3	—	392
NiFe/Cu	343	0.2	100	35.3	44	398
$Cu@Fe_5Ni_5$	353	0.11	100	18.2	79.2	399
$NiMoB–La(OH)_3$	323	0.3	100	13.3	55.1	400
$Ni_{0.6}Fe_{0.4}Mo$	323	0.1	100	28.8	50.7	401
$Cu_{0.4}Ni_{0.6}Mo$	323	0.2	100	38.7	56.6	402
$Ni–Al_2O_3$-HT	303	0.4	93	2.2	49.3	403
RANEY® Ni	303	—	>99	162	44.4	369
$Ni-0.080CeO_2$	303	0.45	99	51.6	47	370
Ni/CeO_2	323	0.1	100	34.0	56.2	404
$Ni_{0.5}Cu_{0.5}/CeO_2$	323	0.2	100	111.7	63.0	395
$Ni_{0.5}Cu_{0.5}/CeO_2$	343	0.2	100	371.1	—	395
$Ni–CeO_2@SiO_2$	343	0.1	100	219.5	59.26	405
2D $Ni_{0.6}Fe_{0.4}/CeO_2$	323	0.1	99	5.76	44.06	406
$NiFe/CeZrO_2$	343	0.1	100	119.2	50.4	407
$NiFe–La(OH)_3$	343	0.2	100	100.6	57.8	408
$Ni_{1.5}Fe_{1.0}/(MgO)_{3.5}$	299	0.21	99	10.3	—	393
$Ni_{0.9}Fe_{0.1}–Cr_2O_3$	343	0.2	100	893.5	86.3	394
$NiCo/NiO–CoO_x$	298	0.2	99	12.8	45.15	397
$Ni_3Fe-(CeO_x)_{0.15}/rGO$	343	0.1	100	126.2	34.3	409
$Ni_3Fe-(CeO_x)_{0.15}/rGO$	328	0.1	100	56.8	—	409
Ni nanofiber	333	0.5	100	6.9	52.07	371
Ni–CNTs-OH	333	—	100	19.4	51.05	410
$Ni@TNTs$	333	0.125	100	96	53.2	411
$Ni_{0.5}Cu_{0.5}/MCNS$	333	0.28	100	21.8	—	224
$Ni_{10}Mo/Ni–Mo–O$	323	0.167	100	54.5	—	412
Ni_{250} NPs	343	0.5	100	11.0	56.3	366

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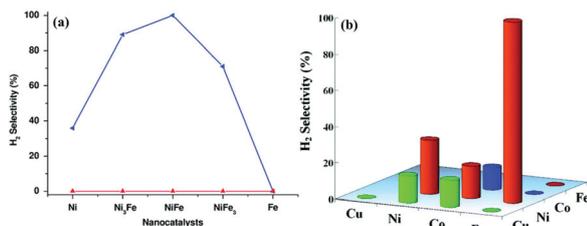This journal is © the Partner Organisations 2020

Fig. 10 (a) Comparison of hydrogen selectivity over Ni, Ni_3Fe, NiFe and Fe nanocatalysts (catalyst/N_2H_4 = 0.1) with NaOH (0.5 M) at (red) 298 K and (blue) 343 K. (b) Comparative hydrogen selectivity in the decomposition of $N_2H_4 \cdot H_2O$ (0.5 M) to hydrogen in the presence of different nanocatalysts. Reprinted with permission from ref. 392. Copyright (2011) American Chemical Society.
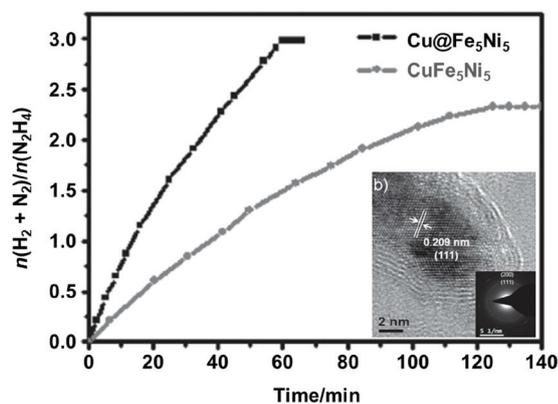

Fig. 11 Time-course plots for the decomposition of $N_2H_4H_2O$ toward H_2 over $Cu@Fe_5Ni_5$ and $CuFe_5Ni_5$NCs in the presence of NaOH at 70 °C. The inset shows an HR-TEM image of the as-synthesized $Cu@Fe_5Ni_5$ NCs. Reprinted with permission from ref. 399. Copyright (2014) Wiley-VCH.

toward the complete decomposition of $N_2H_4 \cdot H_2O$ in the presence of NaOH at 343 K (Fig. 11). In contrast, for the $CuFe_5Ni_5$ alloy NPs, only 2.3 equivalents of gas (H_2 selectivity = 74%) were generated even after 125 min under the same reaction conditions.

Wang and coworkers found that the NiB NP pre-catalyst showed poor catalytic activity for $N_2H_4 \cdot H_2O$ decomposition.[400] But upon incorporation of Mo and La elements into NiB NPs, the catalytic properties of the $NiMoB$–$La(OH)_3$ pre-catalyst was obviously enhanced for both catalytic activity (13.3 h^{-1}) and H_2 selectivity. Later on, noble-metal-free NiFeMo NPs have been synthesized *via* a simple one-step synthetic route at room temperature.[401] The optimized $Ni_{0.6}Fe_{0.4}Mo$ NPs lead to the complete decomposition of $N_2H_4 \cdot H_2O$ and superior catalytic activity (28.8 h^{-1}) within 15 min at 323 K. Mo acted as an electron donor for Ni and Fe atoms, and it has the potential to endow itself with high catalytic activity for hydrogen generation from the decomposition of $N_2H_4 \cdot H_2O$. Recently, our group reported the synthesis of a CuNiMo pre-catalyst, which also showed excellent catalytic activity toward $N_2H_4 \cdot H_2O$ decomposition for hydrogen production.[402]

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_2O_3-HT pre-catalyst after reduction of Ni–Al-HT under a H_2 atmosphere at 773 K.[403] The obtained Ni–Al_2O_3-HT pre-catalyst showed a high catalytic activity and 93% H_2 selectivity towards H_2 for $N_2H_4 \cdot H_2O$ decomposition within 70 min at 303 K. In contrast, the impregnated counterpart Ni/Al_2O_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_2O_3-HT could be attributed to a much stronger interaction of the Ni component with Al_2O_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_2H_4 aqueous solution. They also found that RANEY® Ni was active and exhibited >99% selectivity towards H_2 for the decomposition of $N_2H_4 \cdot H_2O$ in the presence of NaOH at 303 K.[369] 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/CeO_2–IMP for $N_2H_4 \cdot H_2O$ decomposition reaction.[370] 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 $N_2H_4 \cdot H_2O$ decomposition, it could alter the chemical properties of surface Ni and make it both active and selective for $N_2H_4 \cdot H_2O$. 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_2O_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 $N_2H_4 \cdot H_2O$.[404] It was found that the catalytic activity and H_2
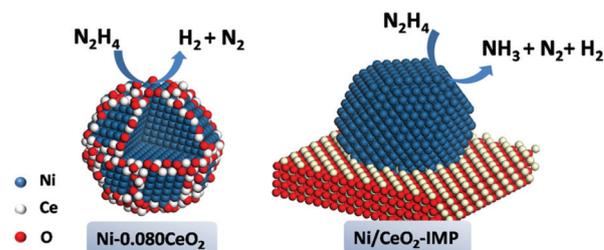

Fig. 12 Structure model of Ni-$0.080CeO_2$ and Ni/CeO_2–IMPcatalysts and the scheme of $N_2H_4 \cdot H_2O$ decomposition. Reprinted with permission from ref. 370. Copyright (2015) American Chemical Society.

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selectivity for hydrogen evolution from $N_2H_4 \cdot H_2O$ 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 N_2H_4 fuel showed the highest catalytic and 100% hydrogen selectivity, for which the decomposition reaction took 17.7 min for 50% conversion of $N_2H_4 \cdot H_2O$ 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 N_2H_4, which promotes N–H bond dissociation rather than N–N bond dissociation and makes the 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).[405] The resulting wormlike core–shell-structured $Ni–CeO_2@SiO_2$ pre-catalyst showed high performance and robust durability with 100% hydrogen selectivity for H_2 production from N_2H_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 $Ni_{0.6}Fe_{0.4}/CeO_2$ pre-catalyst displayed over 99% selectivity towards H_2 evolution from $N_2H_4 \cdot H_2O$ without using an alkali additive at 323 K. Besides

Fig. 13 (a) Synthetic scheme for the preparation of $Ni–CeO_2@SiO_2$. (b) The TEM image of the $Ni–CeO_2@SiO_2$ catalyst. (c) The hydrogen selectivity and TOF value over different catalysts (nNi/nHH = 0.1) for gas generation from $N_2H_4 \cdot H_2O$ (200 mM, 5 mL) at 343 K. Reprinted with permission from ref. 405. Copyright (2020) American Chemical Society.

CeO_2, recently we adopted nano $CeZrO_2$ solid solution as a support to disperse NiFe NPs well, leading to the complete decomposition of N_2H_4 to H_2.[407] Later, we prepared a NiFe–La(OH)$_3$ pre-catalyst for N_2H_4 dehydrogenation, in which metal NPs were highly dispersed with smaller particle size and low crystallinity.[408] Importantly, 100% hydrogen selectivity from N_2H_4 aqueous solution was achieved in 6.5 min, providing a rather high TOF value of 100.6 h^{-1} at 343 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–CoO$_x$ ultrathin layered nanocomposites with NiCo NPs (~4 nm) uniformly anchored on the NiO–CoO$_x$ ultrathin layered nanosheets.[397] The obtained $Ni_{70}Co_{30}/NiO–CoO_x$ pre-catalyst exhibited optimal catalytic performance and 99% hydrogen selectivity for H_2 evolution from the decomposition of $N_2H_4 \cdot H_2O$ 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 $Ni_{1.5}Fe_{1.0}/(MgO)_z$ can be easily tuned by changing the amount of the Mg precursor. The optimized $Ni_{1.5}Fe_{1.0}/(MgO)_{3.5}$ pre-catalyst showed a high catalytic performance with 100% conversion and 99% H_2 selectivity for $N_2H_4 \cdot H_2O$ 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_2O_3 pre-catalyst, which displayed an extraordinary catalytic activity (893.5 h^{-1}) for the complete decomposition of $N_2H_4 \cdot H_2O$ at 343 K.[394]

5.3. Other supported metal catalysts

Various support materials, such as graphene, carbon nanotubes, titanate 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_x-modified NiFe nano-dendrites supported on reduced graphene oxide (NiFe–CeO_x/rGO).[409] The optimal Ni_3Fe-($CeO_x)_{0.15}$/rGO exhibited superior catalytic activity toward H_2 evolution from $N_2H_4 \cdot H_2O$ under alkaline conditions with a TOF value of 126.2 h^{-1} at 343 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 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}
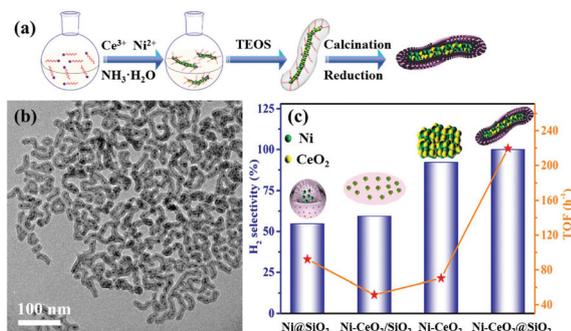
toward the $N_2H_4 \cdot H_2O$ decomposition reaction in the presence of NaOH at 333 K.

Wang and co-workers successfully confined Ni NPs inside a titanate nanotube (Ni@TNT) channel by using the capillary force under ultrasonic treatment.[411] The obtained Ni@TNT pre-catalyst exhibited high activity and 100% hydrogen selectivity, completing the $N_2H_4 \cdot H_2O$ 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.[224] Interestingly, all the bimetallic CuNi/MCNS pre-catalysts showed 100% selectivity to H_2 from the $N_2H_4 \cdot H_2O$ 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 H_2 atmosphere.[412] The obtained nanocomposite enabled the complete decomposition of $N_2H_4 \cdot H_2O$ 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% H_2 selectivity and rapid dynamic response after 5 start/stop cycles.[412] Using a similar method, they also synthesized a series of Ni–W–O-derived nanocomposites.[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 $Ni_4W/WO_2/NiWO_4$ exhibited remarkably distinct catalytic performance, nearly 100% selectivity, and high stability in catalyzing $N_2H_4 \cdot H_2O$ decomposition for hydrogen production.
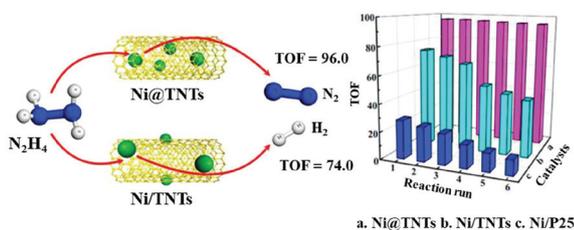

Fig. 14 (Left) Schematic illustration of the formation processes of Ni@TNTs and Ni/TNTs and $N_2H_4 \cdot H_2O$ decomposition. (Right) The tests of re-usability of (a) Ni@TNTs, (b) Ni/TNTs and (c) Ni/P25 for hydrogen generation from $N_2H_4 \cdot H_2O$. Reprinted with permission from ref. 411. Copyright (2018) Elsevier.

Furthermore, they also reported a first-principles study of the elementary steps of N_2H_4 decomposition over a Ni pre-catalyst.[372] The calculation results indicated that the decomposition behaviors of N_2H_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 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 N_2 and H_2 are finally released.

Overall, Ni and Ni-based noble-metal-free catalysts can efficiently catalyze the complete decomposition of $N_2H_4 \cdot H_2O$ 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 $N_2H_4 \cdot H_2O$ as a safe and effective hydrogen storage material, it is necessary to further develop more effective noble-metal-free catalysts for complete conversion of $N_2H_4 \cdot H_2O$ to H_2 at low temperature without additives.

6. Hydrazine borane

Hydrazine borane ($N_2H_4BH_3$, HB, 15.4 wt%), a derivative of NH_3BH_3 where an N_2H_4 group substituted the NH_3 group, has been regarded as a competitive candidate for chemical hydrogen storage.[22,150,151,414–420] $N_2H_4BH_3$ can be easily synthesized by the reaction of $(N_2H_5)_2SO_4$ with $NaBH_4$ in dioxane at room temperature.[421] The hydrogen in $N_2H_4BH_3$ can be released through either thermolysis or solvolysis.[421–428] The thermal decomposition of $N_2H_4BH_3$ was firstly reported by Goubeau and Ricker.[421] $N_2H_4BH_3$ begins to decompose slowly at around 60 °C. It was found that $N_2H_4BH_3$ released 6.5 wt% H_2 within 16 h at 140 °C, while more than 11 wt% H_2 can be released from $N_2H_4BH_3$ in the presence of LiH at 150 °C in less than an hour.[422]

Like for NH_3BH_3, the BH_3 group in $N_2H_4BH_3$ is readily hydrolyzed in the presence of a suitable catalyst (eqn (7)) at room temperature.[427–432] The hydrolysis of $N_2H_4BH_3$ over noble-metal-free catalysts was firstly reported by Özkar and coworkers.[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 $N_2H_4BH_3$.[430,431] The *in situ* formed PSSMA-Ni and PSSMA-Co NPs were highly active in the hydrolysis of $N_2H_4BH_3$ with the release of nearly 3 equiv. H_2 per $N_2H_4BH_3$. 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.[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 $N_2H_4BH_3$.[204] 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 85% of their initial catalytic activity even in the tenth run. Recently, we found that transition metal (Cr, Mo, and W)
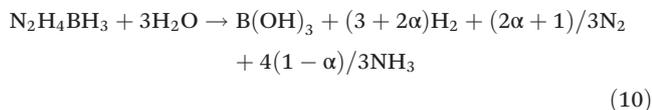
modified Ni NPs showed high activity toward hydrogen generation from the hydrolysis of $N_2H_4BH_3$ at 298 K.[187]

$$N_2H_4BH_3 + 2H_2O \rightarrow N_2H_5BO_2 + 3H_2 \qquad (7)$$
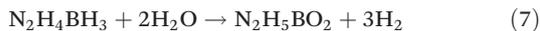
By the hydrolysis of the BH_3 group of $N_2H_4BH_3$, the liberation of H_2 with good kinetics can be achieved with the catalysts reported above. However, the effective GHSC of the $N_2H_4BH_3 \cdot 3H_2O$ system (6.0 wt%) is not high because H in N_2H_4 is not released. Similar to hydrolysis, 1 mol $N_2H_4BH_3$ can also produce 3 mol of H_2 by methanolysis in a suitable catalyst (eqn (8)).[267,366,425] *In situ* formed bulk Ni and PVP-stabilized Ni NPs were developed by Özkar and co-worker for hydrogen evolution from the methanolysis of $N_2H_4BH_3$.[267,425] Since the weight of methanol is much higher than that of water, the GHSC of an $N_2H_4BH_3 \cdot 4MeOH$ (3.5 wt%) system is much lower than that of an $N_2H_4BH_3 \cdot 2H_2O$ (7.4 wt%) system. However, the methanolysis reaction of $N_2H_4BH_3$ can be initiated even below 0 °C, thereby satisfying the cold start requirements of vehicular and portable applications in cold weather.

$$N_2H_4BH_3 + 4MeOH \rightarrow N_2H_5B(OMe)_4 + 3H_2 \qquad (8)$$
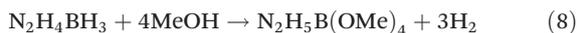
Unlike the NH_3 moiety of NH_3BH_3, the N_2H_4 moiety in $N_2H_4BH_3$ can also be dehydrogenated to H_2 and N_2 over a selective catalyst (eqn (5)).[433–442] Theoretically, 1 mol $N_2H_4BH_3$ can be completely dehydrogenated into 5 mol H_2 and 1 mol N_2 (eqn (9)). This corresponds to an effective GHSC of 10.0 wt% for the $N_2H_4BH_3 \cdot 3H_2O$ system, which is much higher than those of $NaBH_4 \cdot 4H_2O$ (7.3 wt%), $NH_3BH_3 \cdot 2H_2O$ (8.9 wt%) and $N_2H_4 \cdot H_2O$ (8.0 wt%).[22,416] 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_2H_4 group.[443] The optimized $Ni_{0.7}Fe_{0.3}$ NPs can release 3.9 equiv. ($H_2 + N_2$) per $N_2H_4BH_3$ (21% H_2 selectivity) in 180 min at 323 K, indicating an activity in the decomposition of the N_2H_4 moiety NH_3BH_3. However, the conversion of $N_2H_4BH_3$ is incomplete and the reaction kinetics is slow. Therefore, great efforts were devoted to synthesize a highly selective catalyst that could achieve complete dehydrogenation of NH_3BH_3 to H_2.

$$N_2H_4BH_3 + 3H_2O \rightarrow B(OH)_3 + 5H_2 + N_2 \qquad (9)$$

$$N_2H_4BH_3 + 3H_2O \rightarrow B(OH)_3 + (3 + 2\alpha)H_2 + (2\alpha + 1)/3N_2 \\ + 4(1 - \alpha)/3NH_3 \qquad (10)$$

In 2018, our group reported highly active and selective noble-metal-free CuNiMo NPs by using a facile chemical reduction approach.[402] 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 $N_2H_4BH_3$ in an alkaline solution, with which 6 equiv. ($H_2 + N_2$) per $N_2H_4BH_3$ (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 con-
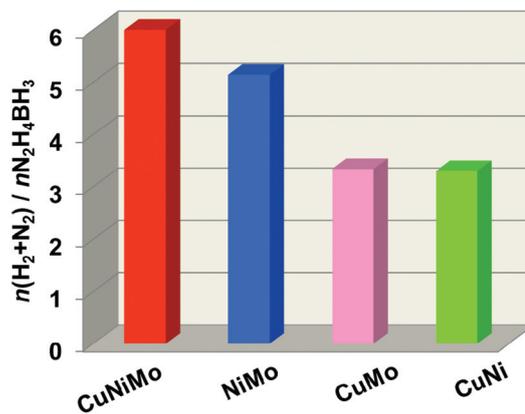

Fig. 15 $n(H_2 + N_2)/n(N_2H_4BH_3)$ for dehydrogenation of $N_2H_4BH_3$ catalyzed by CuNiMo, NiMo, CuMo, and CuNi nanocatalysts in the presence of NaOH (2.0 M) at 323 K. Reprinted with permission from ref. 402. Copyright (2018) Royal Society of Chemistry.

version of $N_2H_4BH_3$ to H_2 (Table 5). Later on, Yan and co-workers reported the synthesis of a boron nitride (BN) supported Ni-MoO$_x$ (Ni-MoO$_x$/BN) pre-catalyst without the help of a surfactant by a sequential impregnation reduction approach.[444] The resultant Ni-MoO$_x$/BN showed excellent catalytic performance with 100% H_2 selectivity for hydrogen generation from $N_2H_4BH_3$ 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$_x$ NPs supported on a MOF substrate, and the obtained NiFe–CeO$_x$/MOF pre-catalyst can also show 100% H_2 selectivity and record good catalytic performance for $N_2H_4BH_3$ decomposition at 343 K.[445]

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 $N_2H_4BH_3$ aqueous solution at 343 K.[405] In addition, we proposed a plausible mechanism for metal catalyzed dehydrogenation of $N_2H_4BH_3$, which involves the chemisorption of $N_2H_4BH_3$ molecules on the metal active surface and generates the activated intermediate species.[405] Subsequently, the activated intermediate species is attacked by H_2O molecules, leading to the dissociation of the B–N bond in $N_2H_4BH_3$. Then, the BH_3 moiety of $N_2H_4BH_3$ is catalytically hydrolyzed by metal active sites; meanwhile, the resulting N_2H_4 group is decomposed to produce H_2 and N_2.

Despite much progress having been made in recent years, the noble-metal-free catalysts reported above for complete hydrogen evolution from NH_3BH_3 required a relatively high reaction temperature (≥323 K). Therefore, the development of non-noble-metal catalysts for the complete dehydrogenation of $N_2H_4BH_3$ at room temperature is highly desired. We found that the RANEY® Ni pre-catalyst exhibited an outstanding catalytic performance with 6.0 equiv. ($H_2 + N_2$) per $N_2H_4BH_3$ being released at 298 K, which is the first report of a noble-metal-free pre-catalyst achieving a complete dehydrogenation of $N_2H_4BH_3$ at room temperature (Table 5).[446] The TOF value over RANEY®

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Table 5 Catalytic activities for hydrogen evolution from $N_2H_4BH_3$ by different catalysts

Catalyst	Temp. (K)	$n_{metal}/nN_2H_4BH_3$	$n(H_2 + N_2)/nN_2H_4BH_3$	TOF ($mol_{H_2} \, mol_{metal}^{-1} \, h^{-1}$)	Ref.
Ni/PSSMA[a]	298	0.01	3	183	430
Co/PSSMA[a]	298	0.01	3	370	431
Cu@SiO$_2$[a]	298	0.09	3	454.8	204
Ni$_{0.9}$Mo$_{0.1}$[a]	298	0.05	3	2400	187
Bulk Ni NPs[b]	298	0.006	3	1440	425
PVP-stabilized Ni[b]	298	0.005	3	2136	267
Ni$_{0.7}$Fe$_{0.3}$ NPs	323	0.35	3.9	3.3	443
Cu$_{0.4}$Ni$_{0.6}$Mo	323	0.1	6	108	402
Ni-MoO$_x$/BN	323	0.1	6	600	444
Ni$_{0.5}$Fe$_{0.5}$-CeO$_x$/MIL-101	343	0.2	6	351.3	445
Ni$_{0.5}$Fe$_{0.5}$-CeO$_x$/ZIF-67	343	0.2	6	361.5	445
Ni-CeO$_2$@SiO$_2$	343	0.1	6	442.5	405
NiFe-La(OH)$_3$	343	0.2	6	251.4	408
RANEY® Ni[c]	298	—	6	892	446

[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.

Ni for the complete dehydrogenation of $N_2H_4BH_3$ at room temperature was calculated to be 892 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 $N_2H_4BH_3$. However, there are still only a handful of catalysts that can catalyze the complete hydrogen evolution from $N_2H_4BH_3$ (Table 5). Moreover, the kinetics of the N_2H_4 moiety decomposition is much sluggish than that of the BH_3 group hydrolysis. Therefore, the current challenges include finding a catalyst that can catalyze both BH_3 group hydrolysis and N_2H_4 moiety decomposition reactions with similar kinetics.

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

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