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

Qilu Yao, Yiyue Ding and Zhang-Hui Lu *

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

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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

*Institute of Advanced Materials (IAM), College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, 330022, P.R. China.
E-mail: luzh@jxnu.edu.cn*



Qilu Yao

Qilu Yao received her PhD (2017) degree in chemistry from Jiangxi Normal University under the supervision of Prof. Zhang-Hui Lu. Since 2017, she has been working as a research associate at the Institute of Advanced Materials, Jiangxi Normal University. Her research is centered on the design and preparation of nanostructured materials and their applications in energy-/environment-related catalysis.



Yiyue Ding

Yiyue Ding was born in Hunan, P. R. China in 1999. She received her bachelor's degree in Chemistry from Changchun Normal University (2019), China. She is currently studying for her master's degree at Jiangxi Normal University under the supervision of Prof. Zhang-Hui Lu. Her research is mainly focused on the design and synthesis of nanocatalysts for hydrogen production from chemical hydrogen storage materials.

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. NaBH₄, 10.8 wt%), ammonia borane (NH₃BH₃, 19.6 wt%), ammonia (NH₃, 17.7 wt%), hydrous hydrazine (N₂H₄·H₂O, 8.0 wt%), and hydrazine borane (N₂H₄BH₃, 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.



Zhang-Hui Lu

Zhang-Hui Lu is currently a professor at Jiangxi Normal University. He received his PhD degree in Chemical Science and Engineering in 2011 from Kobe University (Japan) under the supervision of Prof. Qiang Xu. He is the winner of the First Prize in the Natural Science Award of Jiangxi Province in 2019 and has published more than 100 papers with citations >4000. His current research interest is mainly focused on

synthesizing micro/nanostructured materials and exploring their applications in the area of heterogeneous catalysis and electro-catalysis for clean energy and environmental clean-up.

2. Metal borohydrides

Metal borohydrides, such as LiBH₄, NaBH₄, KBH₄ and Mg(BH₄)₂, have received considerable interest as promising hydrogen storage materials due to their high gravimetric hydrogen capacities.^{33–43} Compared to LiBH₄, KBH₄ and Mg(BH₄)₂, NaBH₄ is more widely studied because it provides a safe and low-cost route to produce hydrogen.^{16,21,33} Thus, NaBH₄ is taken as a representative for discussion.

Hydrogen stored in NaBH₄ can be released by either thermolysis or hydrolysis.^{33,44–48} However, the thermolysis of NaBH₄ is not conceivable because it requires high temperature (>500 °C), and it inevitably produces toxic species. Alternatively, hydrolysis can be used to release H₂ from NaBH₄ 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 (NaBO₂) is nontoxic and can be recycled for regeneration, which facilitates its use in fuel cells. In general, NaBH₄ is not stable in aqueous solution and can spontaneously release H₂ without catalysts. However, the self-hydrolysis is too slow and uncontrollable, and only 7–8% of NaBH₄ can be converted. In order to suppress the self-hydrolysis, NaOH is often added into the NaBH₄ solution as a stabilizer. The alkaline NaBH₄ solution can only be hydrolyzed by using suitable catalysts.



Unlike the simple hydrolysis reaction formula shown in eqn (1), the detailed mechanism of the hydrolysis of NaBH₄ 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 NaBH₄.⁴⁹ Firstly, BH₄[−] ions are chemisorbed on a metal active site surface, forming M–BH₃[−] and M–H intermediate species. Subsequently, M–BH₃[−] reacts with OH[−] and H₂O, possibly *via* a BH₃ intermediate, to form BH₃(OH)[−] and M–H intermediate species. Then, the intermediate BH₃(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 H₂ and to regenerate the metal active sites. Peña-Alonso *et al.* suggested that the intermediate M–H directly reacts with H₂O to generate H₂.⁵⁰ Guella *et al.* proposed a mechanism based on ¹¹B NMR measurements, and suggested that the rate-controlling step of the metal catalyzed hydrolysis of NaBH₄ is the cleavage of the O–H bond in water.^{51,52} It is worth noting that the catalytic hydrolysis of NaBH₄ is closely related to the metal active sites, as there is a charge transfer between the metal active sites and NaBH₄ or intermediates. Therefore, the development of efficient metal catalysts is very important.

Schlesinger and coworker first found that adding an acid into aqueous NaBH₄ solution can significantly accelerate the hydrolysis reaction.⁵⁴ Since then, a number of catalysts have been investigated to accelerate the NaBH₄ hydrolysis. Noble-

Table 1 Catalytic activities for hydrogen evolution from the hydrolysis of NaBH₄ 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	<i>In situ</i> chemical reduction	303	1130.2	39.7	73
Cryogel p(AAm)–Ni	<i>In situ</i> 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	<i>In situ</i> 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	<i>In situ</i> 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 NaBH₄ hydrolysis (Table 1).^{31,59–61}

2.1. Metal catalysts

Cobalt catalysts have been reported to be effective in catalytic hydrolysis of NaBH₄.^{31,59} These are usually deposited on a support material in the form of Co²⁺ ions and then reduced to metal Co. Microporous and mesoporous materials are considered as suitable support materials because it can effectively

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

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 NaBH₄ 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 NaBH₄ 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(NO₃)₂·6H₂O and ethylenediaminetetraacetic 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 NaBH₄ 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% NaBH₄ solution. Kim and co-workers reported novel Co NPs supported on magnetic carbon (Co/Fe₃O₄@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 NaBH₄. Ferromagnetic metals Co, Ni, and Fe were supported on porous SiO₂ *via* an incipient wetness impregnation method.³² The catalytic activities of ferromagnetic metal/SiO₂ followed the order Co/SiO₂ > Ni/SiO₂ > Fe/SiO₂. Furthermore, various other Ni-based catalysts have been reported, but Co-based catalysts have been found to be the most superior in terms of the maximum hydrogen generation rate.^{73–75}

2.2. Metal boride catalysts

Schlesinger and co-workers first found that Co₂B was active for hydrogen evolution from the hydrolysis of NaBH₄.⁵⁴ 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 catalysts were sensitive to their preparation conditions. Jeong and co-workers prepared a Co–B pre-catalyst by the chemical reduction method using NaBH₄ as a reductant.⁷⁶ The obtained Co–B catalyst was amorphous and showed excellent catalytic performance for hydrogen generation from an aqueous alkaline NaBH₄ solution, which was comparable to that of a Ru catalyst. Wu and co-worker found that amorphous Co–B after heat treatment showed much higher catalytic activity than the untreated sample, which is attributed to the formation of the crystalline state of Co–B.⁷⁷ In addition, the Co–B catalyst

treated at 500 °C exhibited the best crystallization and showed the highest hydrogen generation performances. When the Co–B catalyst was heated at 700 °C, the catalytic activity of the catalyst drastically decreased due to the decomposition of Co–B to form metal Co.

To further obtain efficient Co–B catalysts, the synthesis parameters such the cobalt salt, ratio of NaBH₄/Co²⁺, calcination temperature and solvent type are investigated. Kim and coworkers examined the catalytic activity of a Co–B catalyst prepared by using different Co precursors (CoCl₂ and CoSO₄) and NaBH₄/Co²⁺ molar ratios (0.67, 1.5, and 3) at different calcination temperatures (130, 250 and 450 °C).⁸² With CoCl₂ as the precursor, a NaBH₄/Co²⁺ molar ratio of 1.5, and a calcination temperature of 250 °C, the hydrogen evolution rate of the Co–B catalyst was the highest. Demirci and coworkers further confirmed that CoCl₂ is the best precursor, which showed a four times higher hydrogen generation rate than those of other Co salts (Co(CH₃COO)₂, CoSO₄, CoF₂, and Co(NO₃)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 > H₂O > 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 significantly increase the surface area of the catalyst by avoiding agglomeration. Additionally, these dopant metals can also act as electron donors to increase the electron density on the active metal, which can further improve the catalytic activity of the Co–B catalyst. For instance, Patel *et al.* conducted a systematic and comparative study on transition metal (Cr, Mo, W, Cu, Ni and Fe) doped Co–B catalysts for hydrogen generation by hydrolysis of NaBH₄.⁸⁶ They found that the hydrogen generation rate of Co–B catalysts doped with Cr, W, Mo, and Cu is about 3–4 times higher than that of the undoped catalysts. Ni and Fe are only able to slightly enhance the catalytic activity of the Co–B catalyst. In recent years, Co–B catalysts doped with Mn,⁹² Ti,⁹³ Ce⁹⁴ and Zn⁹⁵ have been investigated and they also showed positive promotion effects on the hydrogen evolution of NaBH₄ hydrolysis. Another efficient route to enhance the catalytic performance is by supporting Co–B NPs in a support material, such as carbon,^{96–98} Al₂O₃,⁹⁹ CeO₂,⁹⁹ TiO₂,^{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 hydrolysis of NaBH₄. Kim and co-workers reported a Ni–B–silica

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 NaBH₄.¹⁰⁵ 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/NiFe₂O₄ magnetic pre-catalyst with a metal loading of 10 wt% retained 85% of its initial activity after the fifth run, and the Ni-B/NiFe₂O₄ 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 NaBH₄ in a mixture solution of H₂O and CH₃OH.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 NaBH₄.¹¹⁰ 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 NaBH₄.^{111,112} Kwon and co-workers first reported a Co-P pre-catalyst electrodeposited on a Cu substrate in a sulfate based solution containing H₂PO₄⁻ 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% NaBH₄ 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 NaH₂PO₂ concentration of 0.8 M, and a deposition time no more than 6 min showed the highest catalytic activity for the hydrolysis of NaBH₄ 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 electro-deposition 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 NaBH₄ 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 NaBH₄ 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 NaBH₄ 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 -Al₂O₃ 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 NaBH₄ 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* NaBH₄ 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 NaBH₄ 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 NaBH₄. 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

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 $112\text{--}114 \text{ }^\circ\text{C}$.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 $200 \text{ }^\circ\text{C}$. 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 thermal decomposition 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 ($\text{NH}_3\text{BH}_3 \cdot 2\text{H}_2\text{O}$) is about 8.9 wt%, which is higher than that from NH_3BH_3 methanolysis ($\text{NH}_3\text{BH}_3 \cdot 4\text{MeOH}$, 3.9 wt%).



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 ($\text{Fe}/\text{NH}_3\text{BH}_3 = 0.12$) 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 ($\text{G6-OH}(\text{Co}_{60})$) 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 ($\text{G6-OH}(\text{Co}_{60})$) was highly dispersed (1.6 nm) and active for the hydrolysis of NH_3BH_3 . Duan *et al.* constructed a $\text{Co}@g\text{-C}_3\text{N}_4$ core-shell nanostructure anchored onto the surface of rGO sheets ($\text{Co}@g\text{-C}_3\text{N}_4\text{-rGO}$), where $g\text{-C}_3\text{N}_4$ 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 $\text{Co}@g\text{-C}_3\text{N}_4\text{-rGO}$ 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 ($\sim 17\%$).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)	$n_{\text{metal}}/n_{\text{AB}}$	TOF ($\text{mol}_{\text{H}_2} \text{mol}_{\text{metal}}^{-1} \text{min}^{-1}$)	E_a (kJ mol^{-1})	Ref.
<i>In situ</i> Fe NPs	RT	0.12	3.12	—	155
Co/ γ - Al_2O_3	RT	0.018	2.27	62	154
<i>In situ</i> 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_2O_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_2O_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

^aThe 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)	$n_{\text{metal}}/n_{\text{AB}}$	TOF ($\text{mol}_{\text{H}_2} \text{mol}_{\text{metal}}^{-1} \text{min}^{-1}$)	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

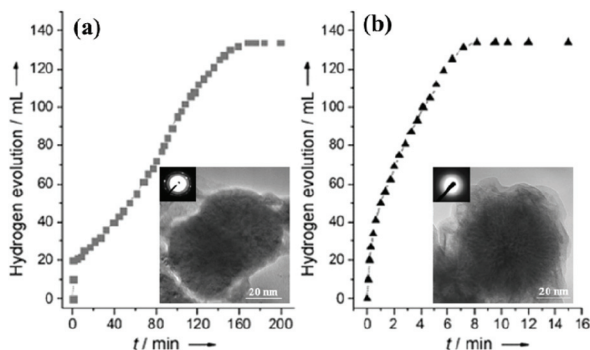


Fig. 1 Hydrogen generation by hydrolysis of aqueous AB (0.16 M, 10 mL) in the presence of (a) the pre-synthesized and (b) *in situ* synthesized Fe catalysts (Fe/AB = 0.12) at room temperature under argon. The inset shows the corresponding TEM images and SAED patterns of the as-synthesized catalysts. Reprinted with permission from ref. 155. Copyright (2008) Wiley-VCH.

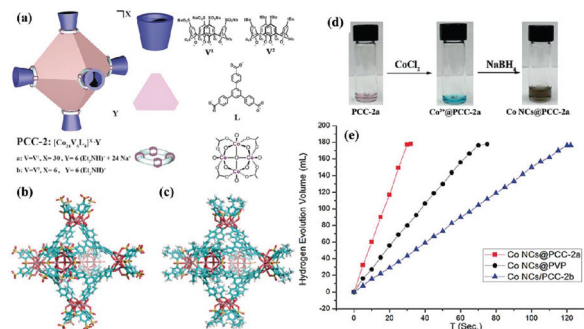


Fig. 2 (a) Cartoon of octahedron cage PCC-2 and the cage components, (b) the crystal structure of PCC-2, and (c) the crystal structure of PCC-2b. (d) The preparation of Co NCs with PCC-2a. (e) Time course plots of H₂ generation for the hydrolysis of AB by Co NCs@PCC-2a, Co NCs/PCC-2b, and Co NCs@PVP. Reprinted with permission from ref. 170. Copyright (2018) Wiley-VCH.

Recently, carbonization of inorganic/organic composites has been developed to prepare 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 SiO₂, Al₂O₃, and CeO₂ as support materials.¹⁸⁰ They found that 3.2 nm Ni NPs supported on SiO₂ 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 NH₃BH₃. 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 NH₃BH₃.¹⁸⁴ 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 immobilize Ni NPs, which showed excellent catalytic activity (41.7 min⁻¹) and high stability in NH₃BH₃ hydrolysis.¹⁸⁶

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

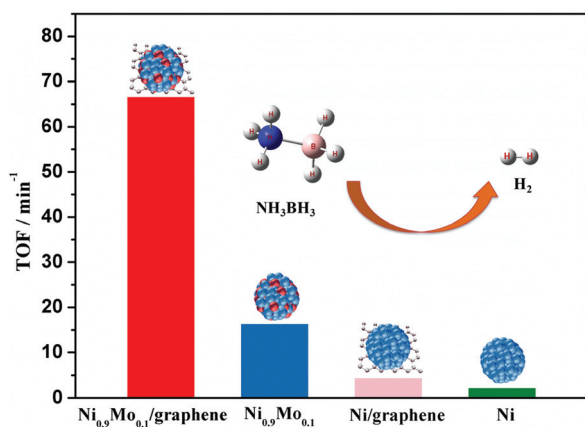


Fig. 3 Catalytic activities for hydrogen generation from AB aqueous solution (5 mL, 0.2 M) over $\text{Ni}_{0.9}\text{Mo}_{0.1}/\text{graphene}$, $\text{Ni}_{0.9}\text{Mo}_{0.1}$, $\text{Ni}/\text{graphene}$, and Ni at 298 K (metal/AB = 0.05). Reprinted with permission from ref. 188. Copyright (2016)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

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 ($\text{Ni-Mo}/\text{graphene}$), 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 ($\text{Ni-CeO}_x/\text{graphene}$) was also fabricated by our research group *via* a facile chemical reduction route.¹⁹⁴ The combination of CeO_x , metal, and graphene of the $\text{Ni-CeO}_x/\text{graphene}$ 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 (ReO_x , Re = La, Dy, Er, Yb, Gd, and Tb) doped $\text{Ni}/\text{graphene}$ ($\text{Ni-ReO}_x/\text{graphene}$) were also prepared and all showed higher catalytic activities than pure $\text{Ni}/\text{graphene}$. The excellent catalytic activities of $\text{Ni-ReO}_x/\text{graphene}$ 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, $\text{Co-CeO}_x/\text{NGH}$ and $\text{CuNi-CeO}_x/\text{rGO}$ 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 $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ was catalytically active in NH_3BH_3 hydrolysis

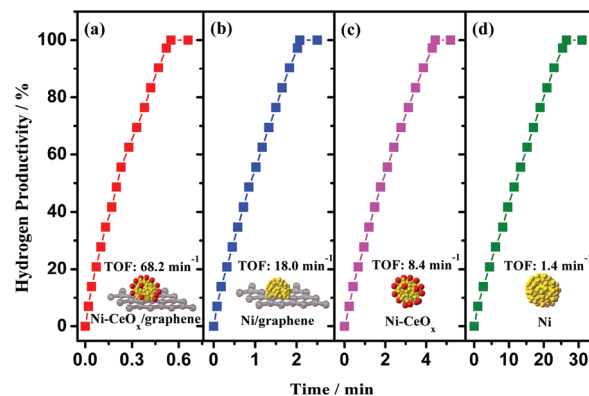


Fig. 4 Hydrogen productivity vs. reaction time for hydrogen release from an aqueous AB solution (200 mM, 5 mL) catalyzed by (a) $\text{Ni-CeO}_x/\text{graphene}$, (b) $\text{Ni}/\text{graphene}$, (c) Ni-CeO_x , and (d) Ni at 298 K ($n\text{Ni}/n\text{AB} = 0.08$). Reprinted with the permission from ref.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

(0.78 min^{-1}), but it takes nearly 600 minutes to release 2.83 equivalents of hydrogen ($n\text{Cu}/n\text{AB} = 0.018$).¹⁵⁴ Subsequently, nanostructured Cu, Cu_2O , and $\text{Cu@Cu}_2\text{O}$ NPs were synthesized by Kalidindi and co-workers *via* the solvated metal atom dispersion (SMAD) method.¹⁹⁸ They found that core-shell $\text{Cu@Cu}_2\text{O}$ and Cu_2O NPs are more active than pure Cu NPs for this hydrolysis reaction. After that, Fukuzumi and co-worker synthesized a series of $\text{Cu}/\text{Co}_3\text{O}_4$ composite pre-catalysts by a conventional impregnation method.¹⁹⁹ The catalytic activities of $\text{Cu}/\text{Co}_3\text{O}_4$ were significantly dependent on the shape and size of nanosized Co_3O_4 , and it was found that Co_3O_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_2O with Co_3O_4 NPs was an effective way to suppress agglomerate formation, which made the $\text{Cu}_2\text{O-Co}_3\text{O}_4$ 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 $\text{SiO}_2/\text{CoFe}_2\text{O}_4$ (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_2O_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 $\text{Cu}/\text{graphite}$ powder, $\text{Cu}/\text{activated carbon}$ and free Cu NPs, over which the NH_3BH_3

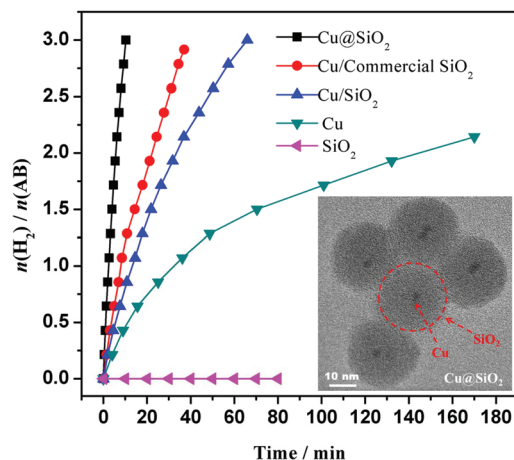


Fig. 5 Hydrogen generation from the hydrolysis of AB (0.2 M, 5 mL) in the presence of different catalysts at 298 K (Cu/AB = 0.09). The inset shows the TEM image of the Cu@SiO₂ catalyst. Reprinted with permission from ref. 204. Copyright (2014) Springer Nature.

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

3.2. Heterometallic catalysts

Heterometallic catalysts, including bi-metallic and multi-metallic catalysts, with unique structures may show higher catalytic performance than their monometallic counterparts due to the strong synergistic effects/electronic effects between the metals.^{23,206–209} A number of heterometallic catalysts, such as Fe–Ni,^{210–213} Fe–Co,^{214–216} Ni–Co,^{217,218} Cu–Fe,²¹⁹ Cu–Co,^{220–223} and Cu–Ni,^{224–228} have been reported toward the hydrolysis of NH₃BH₃. 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

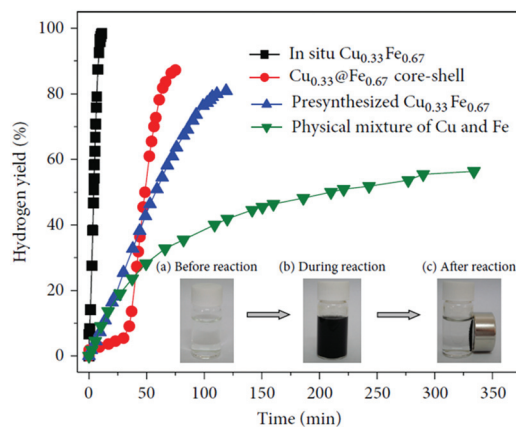


Fig. 6 Hydrogen generation from the hydrolysis of AB in the presence of different catalysts (metal/AB = 0.04). The inset shows photographs of the catalytic hydrolysis of AB *via in situ* synthesized Cu_{0.33}Fe_{0.67} alloys. Reprinted with permission from Ref. 219. Copyright (2013) Elsevier.

(Fig. 6).²¹⁹ Moreover, these *in situ* synthesized CuFe alloy NPs can be easily separated from the solution with an external magnet, and they showed good recycling stability.

In subsequent research, various distinct support materials, such as carbon materials, nanotubes, nanofibers, silica spheres, metal-organic frameworks (MOFs), and so on, have been used to fabricate well-dispersed and stable bimetallic NP nanocatalysts.^{220–224,229–231} Co decorated Cu NPs on graphene (graphene–CuCo) have been synthesized by Yan *et al.* *via* a one-step self-catalytic method, which showed high efficiency toward the hydrolytic dehydrogenation of NH₃BH₃.²²⁰ Xu's research group employed diamine-functionalized reduced graphene oxide as a support for CuCo NPs (CuCo/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 NH₃BH₃ 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 NH₃BH₃ 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 SiO₂ spheres (47, 97, 195, 333, 391 and 485 nm).²²⁹ The results showed that the catalytic activity of CuNi/SiO₂ increases with the decrease of SiO₂ particle size, due to which the CuNi NPs supported on the smallest SiO₂ (CuNi/47-SiO₂)₃ exhibit the

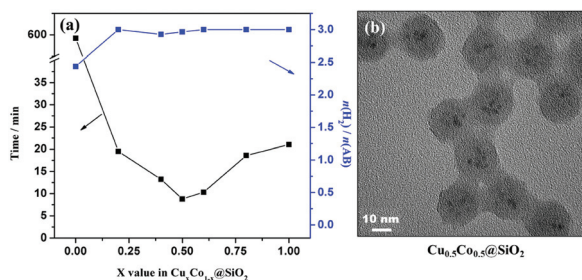


Fig. 7 (a) Cu_xCo_{1-x}@SiO₂ core-shell nanospheres with different x values under an ambient atmosphere at 298 K; (b) TEM image of Cu_{0.5}Co_{0.5}@SiO₂. Reprinted with permission from Ref. 209. Copyright (2015) American Chemical Society.

highest catalytic activity in the hydrolysis of NH₃BH₃ at 298 K. However, the stability of CuNi/47-SiO₂ showed obvious degradation after seven cycles. Our group successfully encapsulated ultrafine Cu-Co NPs (~2 nm) inside SiO₂ nanospheres (CuCo@SiO₂) (Fig. 7), which can effectively prevent metal NP aggregation and enhance the pre-catalyst stability.²³⁰ The optimized Cu_{0.5}Co_{0.5}@SiO₂ pre-catalyst showed excellent catalytic activity in the hydrolysis of NH₃BH₃ and preserved 93% of its initial catalytic activity even after 10 runs. CuCo alloy NPs confined in the pores of MIL-101 (CuCo@MIL-101) *via* a double-solvent method combined with the excellent reduction approach also showed high activity and long durability for hydrolysis of NH₃BH₃.²³¹

Trimetallic CuCoMo NPs without any surfactant or support have been fabricated by our group through a facile co-reduction method.¹⁹⁰ Compared to their bi-/monometallic 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

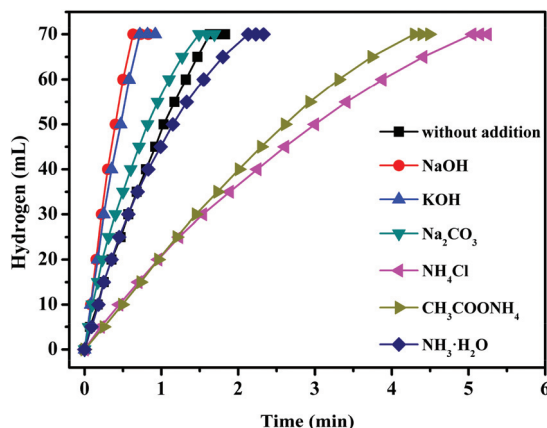


Fig. 8 Hydrogen generation from the hydrolysis of AB (0.20 M, 5 mL) with the addition of 1 M NaOH, KOH, Na₂CO₃, NH₄Cl, CH₃COONH₄ and NH₃·H₂O (2 mL) catalyzed by Cu_{0.72}Co_{0.18}Mo_{0.1} NPs at 298 K ($n_{\text{metal}} = 0.04$ mmol). Reprinted with permission from ref. 190. Copyright (2018) Royal Society of Chemistry.

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 NH₄⁺ species (*e.g.*, NH₃·H₂O, NH₄Cl, *etc.*) into the reaction system is unfavorable for the hydrolysis of AB.

In addition to alloy NPs, core-shell NPs have also attracted considerable attention due to their unique physical and chemical properties, and they exhibited excellent catalytic performance in hydrolytic dehydrogenation of NH₃BH₃.^{232–238} Among them, catalysts with a Cu core are the most attractive. In 2011, Xu's research group first reported the synthesis of Cu@M (M = Co, Fe, Ni) NPs *via* a simple one-step seeding-growth route using NH₃BH₃ as a weak reducing agent, which could selectively reduce Cu²⁺ first to form the core, and successively reduce M²⁺ (M = Co, Fe, Ni) to form the shell.²³³ A relatively stronger reductant NaBH₄, instead of NH₃BH₃, resulted in the formation of CuM alloys. Compared to monometallic and alloy counterparts, the core-shell Cu@M (M = Co, Fe, Ni) NPs showed synergistic and superior catalytic activity for hydrogen evolution from the hydrolysis of NH₃BH₃. In addition, H₂ generation over Cu₁@Co₄ NPs is the most active among that over all the Cu@M (M = Co, Fe, Ni) NPs, with which the hydrolysis reaction is completed within 10 min at room temperature. By following a similar approach, various core-shell catalysts based on Cu as a core, such as bimetallic Cu@Co,²³⁴ trimetallic Cu@FeNi,²³⁶ Cu@FeCo,²³⁷ Cu@CoNi,^{238,239} Cu@CoMo²⁴⁰ 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 NH₃BH₃ has attracted much attention in recent years.^{241–244} Li and coworkers prepared CuCo₂O₄ pre-catalysts with different shapes (nanoplates, nanosheets, and nanoparticles).²⁴¹ Among them, the nanoplate-shaped CuCo₂O₄ pre-catalyst showed the best catalytic activity for hydrogen production from the hydrolysis of NH₃BH₃, giving a TOF value of 44 min⁻¹ at room temperature. Moreover, the CuCo₂O₄ nanoplate pre-catalyst almost retained its initial catalytic activity after eight cycles, indicative of its excellent durability and stability. Later on, they developed a series of non-noble metal oxides such as NiCo₂O₄,²⁴² MnCo₂O₄,²⁴⁵ CuCoMoO₄,²⁴⁶ CuNiCo₂O₄,²⁴⁷ Co₃O₄/CuMoO₄,²⁴⁸ CuO-NiO/Co₃O₄²⁴⁹ and Co_xCu_{1-x}Co₂O₄@Co_yCu_{1-y}Co₂O₄,²⁵⁰ which are active in NH₃BH₃ 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 NH₃BH₃, owing to the interfacial interaction between CuCoO NPs and GO. Moreover,

they performed the first *in situ* XAS experiments to study the electronic structure changes of the pre-catalyst during hydrolysis. Recently, Liu and coworkers reported a graphene oxide supported Cu@CuCoO_x pre-catalyst, with which superior catalytic activity was achieved toward the hydrolysis of NH₃BH₃ with a TOF of 44.6 min⁻¹ at room temperature.²⁴⁴ With a metal oxide as a pre-catalyst, the catalytically active component of the catalyst is the zero-valent metal because a part of the metal oxide can be reduced by NH₃BH₃. Therefore, such metal oxide catalysts are mainly Cu-based oxides, because Cu oxides can be easily reduced to Cu(0) by NH₃BH₃ at room temperature.

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

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

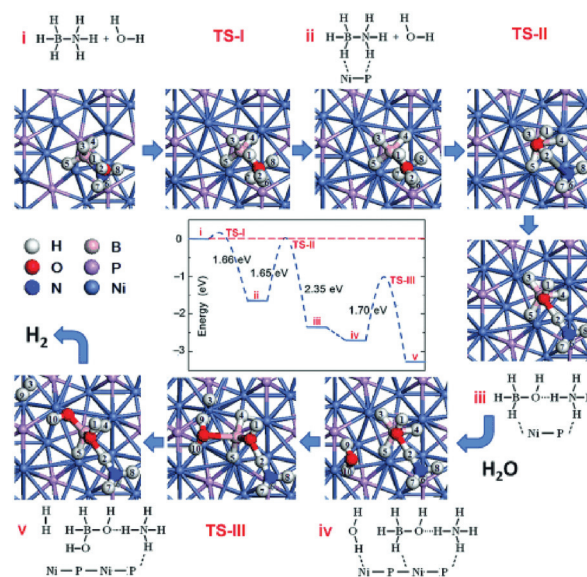


Fig. 9 Plot of energy changes *versus* reaction coordinates calculated for Ni₂P-catalyzed hydrolysis of AB. Reprinted with permission from ref. 254. Copyright (2016) Wiley-VCH.

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

3.4. Catalysts for NH₃BH₃ methanolysis

As for NH₃BH₃ methanolysis, despite the GHSC of the NH₃BH₃-4MeOH system (3.9 wt%) being much lower than that from the hydrolysis system, NH₃BH₃ methanolysis has some advantages that merit its potential applications as a portable hydrogen source.^{25,138,266-273} Firstly, addition of suitable catalysts can initiate the NH₃BH₃ methanolysis reaction below 0 °C, thereby satisfying the applications in cold weather. Secondly, pure H₂ can be released by methanolysis of NH₃BH₃ without the production of NH₃. More importantly, the byproduct of NH₃BH₃ methanolysis (*i.e.*, NH₄B(OMe)₄) can be easily reconverted back to NH₃BH₃ by reaction with NH₄Cl and LiAlH₄ at room temperature.¹³⁸

Compared with the extensive studies of NH₃BH₃ hydrolysis, there are only a few studies regarding NH₃BH₃ methanolysis (Table 3).^{138,267,274-276} In 2007, RuCl₃, RhCl₃, PdCl₂, CoCl₂,

NiCl₂, Pd/C, and RANEY® Ni were firstly reported for the methanolysis of NH₃BH₃.¹³⁸ Since then, non-noble metal pre-catalysts such as PVP-stabilized Ni, Co-Co₂B, Ni-Ni₃B, Co-Ni-B, and Co-Ni-P pre-catalysts have been reported for dehydrogenation of NH₃BH₃ in methanol.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 NH₃BH₃. Moreover, the flower-like Cu nanostructures also showed excellent recyclability in the methanolysis of NH₃BH₃. Subsequently, Zahmakiran and co-workers reported Cu-Cu₂O-CuO/C composites to catalyze hydrogen generation from the methanolysis of NH₃BH₃, 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 NH₃BH₃.²⁷⁹ 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 NH₃BH₃.²⁸⁰ 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 NH₃BH₃ and long-term stability at ambient temperature were observed. By DFT calculations, they revealed the role of charge transfer in promoting the methanolysis reactions and the metal/support ratio in manipulating the catalytic activity *via* tuning electrostatic interactions.

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

4. Ammonia

Ammonia is a second largest chemical in the world (after sulphuric acid) with over 170 megatonne per year being synthesized *via* the Haber-Bosch process, bulk of which is used as fertilizers.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 H₂.^{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 NH₃

can be decomposed to release H₂ along with N₂ by the following reaction (eqn (4)):



The NH₃ decomposition is an endothermic reaction ($\Delta H = 92 \text{ kJ mol}^{-1}$) and a high temperature is required for efficient hydrogen generation.²⁹⁰ Thermal decomposition of NH₃ into H₂ and N₂ has been extensively studied in the past decades.^{24,26,284,286} The works before the 1990s on NH₃ decomposition were mainly studied to gain insight into the reaction kinetics of NH₃ synthesis.²⁹¹ Nowadays, the research on NH₃ decomposition is mainly focused on the generation of high quality H₂. Generally, N₂ adsorption is thought to be rate-limiting in NH₃ synthesis, while the rate determining step for NH₃ decomposition varies. For noble metal (*e.g.* Ru, Rh, Ir, Pt, or Pd) catalysts, N-H cleavage is the rate-determining step, while, for non-noble metal (*e.g.* Fe, Co, Ni, *etc.*) catalysts, N₂ desorption is the rate-determining step.^{24,26,292,293}

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

4.1. Monometallic catalysts

Fe-Based catalysts have been extensively studied in the NH₃ decomposition reaction owing to its industrial use in the NH₃ synthesis reaction.²⁹⁹⁻³⁰⁴ Fe promoted by K₂O, CaO, SiO₂ and Al₂O₃ is active for NH₃ synthesis at temperatures above 400 °C and was initially considered as a potential pre-catalyst for NH₃ decomposition.²⁹⁹ The overall activity of Fe-based pre-catalysts toward NH₃ decomposition is relatively low. Great efforts have been made to enhance the catalytic performances of Fe-based catalysts by depositing Fe onto supports such as carbon nanotubes, zeolites, and metal oxides, since their properties such as reducibility, particle size and dispersion, thermal stability and electronic structures would be improved after Fe particles are supported.^{301-303,305} For example, Duan *et al.* synthesized a novel Fe-CNF/mica pre-catalyst *via* a catalytic CVD method and it showed excellent catalytic activity for NH₃ decomposition.³⁰⁵ They also found that the size and shape of Fe particles on the top of CNFs depended on the Fe particle reconstruction and 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 -Fe₂O₃ NPs (~6 nm) confined within the porous systems of CMK-5 carbons and a carbon-SBA-15 composite were synthesized by Lu and coworker *via* a facile wet impregnation method.³⁰⁷ The obtained γ -Fe₂O₃/CMK-5 pre-catalyst showed the high catalytic activity toward the decomposition of NH₃ at 600 °C. The Fe₂O₃/carbon-SBA-15 pre-catalysts were much more stable over a long reaction time. The excellent catalytic performance is attributed to the space limitation in the pores and the strong interaction with the composite support, thus preventing the migration and subsequent sintering of nanoparticles. The group of Ji and Au has embedded Fe NPs in microporous and mesoporous silica shells *via* a sonication-assisted Stöber process.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 NH₃ decomposition.³⁰⁹

Ni-Based catalysts have also been used as alternative catalysts for NH₃ decomposition due to their substantially lower costs compared to Ru and the higher activity compared to Fe.^{310–314} Previously, Ganley *et al.* reported an order of activity as Ru > Ni > Rh > Co > Ir > Fe for NH₃ decomposition.³¹⁰ Zhang *et al.* reported a co-precipitation method to prepare a series of supported pre-catalysts by depositing Ni NPs on Al₂O₃.³¹¹ The catalytic activity of Ni/Al₂O₃ increased with increasing Ni loading and reached a maximum at a Ni/Al ratio of 1.2. Interestingly, the conversion of NH₃ was further increased after the addition of a La promoter into the Ni/Al₂O₃ pre-catalyst. For example, when the La/Ni molar ratio increased from 0 to 0.2, the conversion of NH₃ progressively increased from 38.2 to 63.9% at 773 K. The characterization results indicated that the Ni/La-Al₂O₃ pre-catalyst with an appropriate amount of La possessed a more open mesoporous structure and higher dispersion of Ni as compared to Ni/Al₂O₃. Later on, Xu and coworker reported that the addition of CeO₂ obviously improved the catalytic activity and stability of Ni/Al₂O₃ for NH₃ decomposition to CO_x-free H₂.³¹⁵ The characterization results showed that the addition of CeO₂ could enlarge the pre-catalyst pores, moderate the interaction between the metal and support, suppress Ni NPs from sintering, and improve the 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 NH₃ 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 (Y₂O₃, CeO₂, La₂O₃, Sm₂O₃ and Gd₂O₃) for NH₃ decomposition.³¹⁷ Among the samples investigated, the Ni/Y₂O₃ 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/Y₂O₃ was relatively small at high temperatures. Furthermore, this group also found that the catalytic activity of Ni/Y₂O₃ 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/CeO₂ pre-catalyst showed higher catalytic performance than the Ni/CeO₂ powder pre-catalyst and the conventional cordierite honeycomb wash coated with Ni/CeO₂ under the same reaction conditions.

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

4.2. Bimetallic catalysts

Bimetallic catalysts with unique structures may achieve excellent catalytic activity in comparison with their individual

monometallic components. To date, a series of 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 NH₃ decomposition. For example, Duan *et al.* reported that the bimetallic Co–Mo/MCM-41 pre-catalyst shows a higher activity in the NH₃ 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 NH₃ 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 -Al₂O₃ pre-catalyst prepared using monocomponent metal amine metallate (Co(en)₃MoO₄) as the active phase precursor exhibited higher activity and stability for ammonia decomposition than the CoMo-II/ γ -Al₂O₃ pre-catalyst prepared using bicomponent Co(NO₃)₂ and (NH₄)₆Mo₇O₂₄ 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 Co₃Mo₃N 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 NH₃ 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 NH₃ decomposition reaction. Recently, 2D ultrathin Co–Fe spinel oxide nanosheets confined in mesoporous silica shells (Co_xFe_{3–x}O₄@mSiO₂) have been fabricated by Zhang and coworkers.³³⁴ By tuning the chemical stoichiometry of Co_xFe_{3–x}O₄ 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}O₄@mSiO₂ pre-catalyst attained 88% conversion of NH₃ at 600 °C and a space velocity of 60 000 cm³ g^{–1} h^{–1}, even maintained for 48 h without attenuation. Similarly, Ni–Fe/Al₂O₃,^{335,336} Ni–Fe alloys³³⁷ and NiCo/Ce_{0.6}Zr_{0.3}Y_{0.1}O₂ solid solutions³³⁸ were found to show higher catalytic performance than the single metal pre-catalyst toward the decomposition of NH₃.

4.3. Metal carbides/nitrides

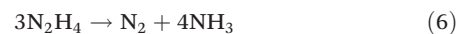
Transition metal carbides (WC_x, MoC_x, FeC_x, VC_x and TaC_x) and nitrides (MoN_x, VN_x and WN_x) have also been investigated for NH₃ decomposition reaction.^{339–344} Sourabh and coworkers reported that WC can attain complete decomposition of NH₃ at 550 °C; however, the WC samples need to be pretreated in a gas mixture (H₂/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 NH₃ decomposition was achieved at a low temperature (500 °C).³⁴⁰ Kraupner and coworkers reported mesoporous Fe₃C with high crystallinity and high surface area by a combination of a hard-

templating approach and carbothermal reduction.³⁴¹ The obtained Fe₃C pre-catalyst showed good catalytic activity in NH₃ decomposition with conversion above 95% at 700 °C. Choi *et al.* investigated VC and TaC as pre-catalysts for NH₃ decomposition, which showed excellent catalytic performance, higher than that of a Pt/C pre-catalyst.^{342,343} Zheng *et al.* synthesized high-surface area Mo₂C from a h-MoO₃ precursor *via* a temperature-programmed reduction–carburization under a flowing atmosphere of H₂ and CH₄.³⁴⁴ The result showed that Mo₂C undergoes a phase transformation during the NH₃ decomposition reaction, and the active phase is actually MoN.

Mo-Based nitrides for NH₃ 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 -Al₂O₃ and NiMoN_y/ α -Al₂O₃ exhibited excellent catalytic properties for NH₃ decomposition with conversions reaching as high as 98.7% and 99.8%, respectively, at 650 °C.³⁴⁵ Moreover, the increasing nitride phase content of Ni₂Mo₃N up to 37 wt% doubles the NH₃ conversion at 550 °C.³⁴⁶ Podila *et al.* found that the addition of Co into γ -Mo₂N can further improve the conversion of NH₃ decomposition, which is due to the formation of the Co₃Mo₃N phase in Co-containing samples.³⁴⁷ After that, Srifa *et al.* synthesized pure phase Co₃Mo₃N from CoMoO₄ *via* a temperature-programmed reaction method, which showed almost 100% of NH₃ conversion at 600 °C.²⁸⁹ The catalytic activity of the Co₃Mo₃N pre-catalyst for NH₃ decomposition can be significantly improved by the addition of a small amount of Cs species.³⁴⁸ Furthermore, Mo-based nitrides such as Mo₂N, Ni₂Mo₃N, Ni₃Mo₃N and Fe₃Mo₃N also have been suggested as the highly active species for the NH₃ decomposition reaction.^{348–350}

5. Hydrous hydrazine

Anhydrous hydrazine (N₂H₄), a colorless flammable liquid at room temperature, has a high hydrogen capacity as high as 12.5 wt%. Hydrogen stored in N₂H₄ 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 NH₃. Even worse, the anhydrous hydrazine (>98%) is highly toxic and explosive when exposed to metal catalyst surfaces, making it difficult to use it safely.



Hydrous hydrazine, such as hydrazine monohydrate (N₂H₄·H₂O) which has a hydrogen capacity of 8.0 wt%, is

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–Co³⁹⁷ 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 ₂ O 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

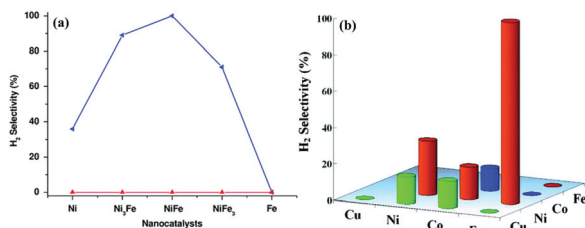


Fig. 10 (a) Comparison of hydrogen selectivity over Ni, Ni₃Fe, NiFe and Fe nanocatalysts (catalyst/N₂H₄ = 0.1) with NaOH (0.5 M) at (red) 298 K and (blue) 343 K. (b) Comparative hydrogen selectivity in the decomposition of N₂H₄·H₂O (0.5 M) to hydrogen in the presence of different nanocatalysts. Reprinted with permission from ref. 392. Copyright (2011) American Chemical Society.

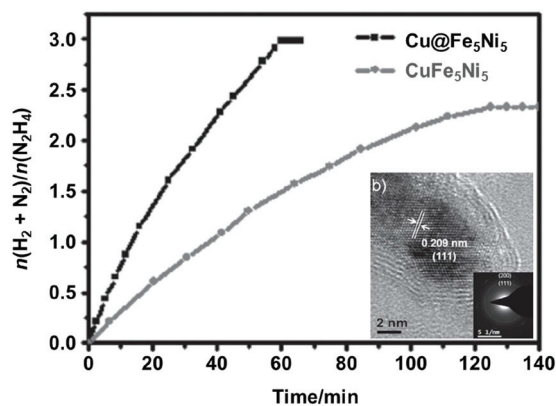


Fig. 11 Time-course plots for the decomposition of N₂H₄·H₂O toward H₂ over Cu@Fe₅Ni₅ and CuFe₅Ni₅NCs in the presence of NaOH at 70 °C. The inset shows an HR-TEM image of the as-synthesized Cu@Fe₅Ni₅ NCs. Reprinted with permission from ref. 399. Copyright (2014) Wiley-VCH.

toward the complete decomposition of N₂H₄·H₂O in the presence of NaOH at 343 K (Fig. 11). In contrast, for the CuFe₅Ni₅ alloy NPs, only 2.3 equivalents of gas (H₂ 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 N₂H₄·H₂O 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 H₂ 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 N₂H₄·H₂O 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 N₂H₄·H₂O. Recently, our group reported the synthesis of a CuNiMo pre-catalyst, which also showed excellent catalytic activity toward N₂H₄·H₂O 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–Al₂O₃-HT pre-catalyst after reduction of Ni–Al-HT under a H₂ atmosphere at 773 K.⁴⁰³ The obtained Ni–Al₂O₃-HT pre-catalyst showed a high catalytic activity and 93% H₂ selectivity towards H₂ for N₂H₄·H₂O decomposition within 70 min at 303 K. In contrast, the impregnated counterpart Ni/Al₂O₃-IMP pre-catalyst exhibited a much lower H₂ selectivity (67%) and catalytic activity with a total reaction time of 440 min. The high catalytic performance of Ni–Al₂O₃-HT could be attributed to a much stronger interaction of the Ni component with Al₂O₃ and the strongly basic sites. This is the first report that supported a base metal pre-catalyst showing such high H₂ selectivity towards the decomposition of N₂H₄ aqueous solution. They also found that RANEY® Ni was active and exhibited >99% selectivity towards H₂ for the decomposition of N₂H₄·H₂O in the presence of NaOH at 303 K.³⁶⁹ Compared with RANEY® Ni-40, RANEY® Ni-300 showed higher catalytic and H₂ 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 CeO₂-modified Ni RANEY® Ni-300. The obtained Ni-0.08CeO₂ pre-catalyst (Fig. 12) showed a 99% H₂ selectivity and a 3-fold higher TOF value than bare Ni NPs and the impregnated counterpart Ni/CeO₂-IMP for N₂H₄·H₂O decomposition reaction.³⁷⁰ This improvement was caused by the modification of Ni with CeO₂ nearby through strong metal–support interactions (*e.g.*, Ni–O–Ce structure). Although the Ni–O–Ce structure itself is inactive for N₂H₄·H₂O decomposition, it could alter the chemical properties of surface Ni and make it both active and selective for N₂H₄·H₂O. Furthermore, this promoting effect could be extended to other oxides which can also form strong metal–support interactions with Ni, such as ZrO₂, MgO, and La₂O₃. Later on, a series of Ni/CeO₂ were prepared by solution combustion synthesis (SCS) in a one-step process and used as efficient catalysts for decomposition of N₂H₄·H₂O.⁴⁰⁴ It was found that the catalytic activity and H₂

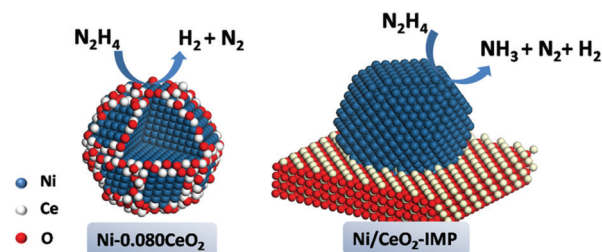


Fig. 12 Structure model of Ni-0.080CeO₂ and Ni/CeO₂-IMP catalysts and the scheme of N₂H₄·H₂O decomposition. Reprinted with permission from ref. 370. Copyright (2015) American Chemical Society.

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/CeO₂ 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 CeO₂, namely the existence of Ni–O–Ce solid solution. In addition, the oxygen vacancy in the Ni–O–Ce solid solution of the Ni/CeO₂ 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 H₂ generation easier. Inspired by this effective method, they also found that the addition of Cu to Ni/CeO₂ 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 CeO₂. To further maximize the active interface and the stability of catalysts, our group designed and synthesized ultrafine Ni NPs self-assembled on CeO₂ nanowires embedded in a microporous silica shell (Ni–CeO₂@SiO₂) *via* a one-pot facile strategy (Fig. 13).⁴⁰⁵ The resulting wormlike core–shell-structured Ni–CeO₂@SiO₂ pre-catalyst showed high performance and robust durability with 100% hydrogen selectivity for H₂ production from N_2H_4 aqueous solution. The excellent catalytic properties of Ni–CeO₂@SiO₂ can be attributed to the synergistic electronic effect and strong interactions between Ni NPs and CeO₂ NWs with plenty of oxygen vacancies, as well as the unique structure effect.

Wen and co-workers synthesized a two-dimensional NiFe/CeO₂ 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 CeO₂ nanosheets. The optimal Ni_{0.6}Fe_{0.4}/CeO₂ pre-catalyst displayed over 99% selectivity towards H₂ evolution from $N_2H_4 \cdot H_2O$ without using an alkali additive at 323 K. Besides

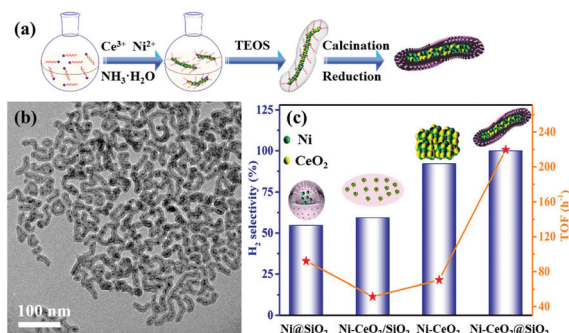


Fig. 13 (a) Synthetic scheme for the preparation of Ni–CeO₂@SiO₂. (b) The TEM image of the Ni–CeO₂@SiO₂ catalyst. (c) The hydrogen selectivity and TOF value over different catalysts ($nNi/nHH = 0.1$) for gas generation from $N_2H_4 \cdot H_2O$ (200 mM, 5 mL) at 343 K. Reprinted with permission from ref. 405. Copyright (2020) American Chemical Society.

CeO₂, recently we adopted nano CeZrO₂ solid solution as a support to disperse NiFe NPs well, leading to the complete decomposition of N_2H_4 to H₂.⁴⁰⁷ 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 Ni₇₀Co₃₀/NiO–CoO_x pre-catalyst exhibited optimal catalytic performance and 99% hydrogen selectivity for H₂ 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% H₂ 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–Cr₂O₃ 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 nanodendrites supported on reduced graphene oxide (NiFe–CeO_x/rGO).⁴⁰⁹ The optimal Ni₃Fe–(CeO_x)_{0.15}/rGO exhibited superior catalytic activity toward H₂ 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 H₂ generation and a TOF of 6.9 h⁻¹ in NaOH solution at 333 K. Recently, they have grown carbon nanotubes (CNTs) on Ni nanofibers (Ni–CNTs) and then subjected them to a hydroxylation treatment (Ni–CNTs–OH).⁴¹⁰ They found that the introduced CNTs and the hydroxyl groups on the CNTs significantly improved the catalytic performance of the active Ni nanofibers. The Ni–CNTs–OH showed excellent catalytic performance with a TOF of 19.4 h⁻¹

toward the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition reaction in the presence of NaOH at 333 K.

Wang and co-workers successfully confined Ni NPs inside a titanate nanotube (Ni@TNT) channel by using the capillary force under ultrasonic treatment.⁴¹¹ The obtained Ni@TNT pre-catalyst exhibited high activity and 100% hydrogen selectivity, completing the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition in only 5 min in the presence of NaOH at 333 K, which is higher than that of Ni/TNTs. In addition, owing to the good stability of the Ni@TNT pre-catalyst, no significant decrease in catalytic performance was observed, while the Ni/TNTs showed an obvious decrease during the reuse (Fig. 14). The excellent catalytic performance of the Ni@TNT pre-catalyst is attributed to the small size and high dispersion of Ni NPs after encapsulation in the channel of TNTs. The Kleitz group prepared highly dispersed CuNi alloy NPs supported on mesoporous carbons (CuNi/MCNS) by a simple incipient wetness method.²²⁴ Interestingly, all the bimetallic CuNi/MCNS pre-catalysts showed 100% selectivity to H_2 from the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition and the reaction was complete within 50 min over $\text{Cu}_{0.5}\text{Ni}_{0.5}/\text{MCNS}$ 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 $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in 7 min at 323 K, providing a TOF value of 54.5 h^{-1} . They also synthesized a monolithic $\text{Ni}_{10}\text{Mo}/\text{Ni–Mo–O}/\text{Ni}$ 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 $\text{Ni}_4\text{W}/\text{WO}_2/\text{NiWO}_4$ exhibited remarkably distinct catalytic performance, nearly 100% selectivity, and high stability in catalyzing $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition for hydrogen production.

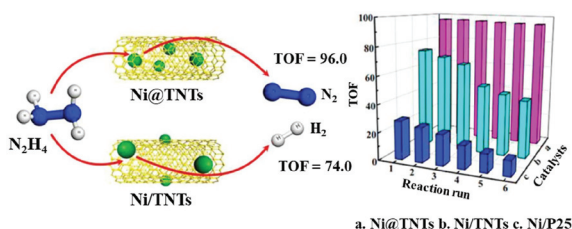


Fig. 14 (Left) Schematic illustration of the formation processes of Ni@TNTs and Ni/TNTs and $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ decomposition. (Right) The tests of re-usability of (a) Ni@TNTs, (b) Ni/TNTs and (c) Ni/P25 for hydrogen generation from $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. 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.

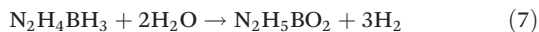
Overall, Ni and Ni-based noble-metal-free catalysts can efficiently catalyze the complete decomposition of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ to produce hydrogen, but the catalytic activity is still not satisfactory at room temperature or without additives (*e.g.* NaOH). Therefore, for the practical use of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ as a safe and effective hydrogen storage material, it is necessary to further develop more effective noble-metal-free catalysts for complete conversion of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ to H_2 at low temperature without additives.

6. Hydrazine borane

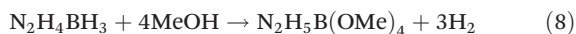
Hydrazine borane ($\text{N}_2\text{H}_4\text{BH}_3$, HB, 15.4 wt%), a derivative of NH_3BH_3 where an N_2H_4 group substituted the NH_3 group, has been regarded as a competitive candidate for chemical hydrogen storage.^{22,150,151,414–420} $\text{N}_2\text{H}_4\text{BH}_3$ can be easily synthesized by the reaction of $(\text{N}_2\text{H}_5)_2\text{SO}_4$ with NaBH_4 in dioxane at room temperature.⁴²¹ The hydrogen in $\text{N}_2\text{H}_4\text{BH}_3$ can be released through either thermolysis or solvolysis.^{421–428} The thermal decomposition of $\text{N}_2\text{H}_4\text{BH}_3$ was firstly reported by Goubeau and Ricker.⁴²¹ $\text{N}_2\text{H}_4\text{BH}_3$ begins to decompose slowly at around 60 °C. It was found that $\text{N}_2\text{H}_4\text{BH}_3$ released 6.5 wt% H_2 within 16 h at 140 °C, while more than 11 wt% H_2 can be released from $\text{N}_2\text{H}_4\text{BH}_3$ in the presence of LiH at 150 °C in less than an hour.⁴²²

Like for NH_3BH_3 , the BH_3 group in $\text{N}_2\text{H}_4\text{BH}_3$ is readily hydrolyzed in the presence of a suitable catalyst (eqn (7)) at room temperature.^{427–432} The hydrolysis of $\text{N}_2\text{H}_4\text{BH}_3$ over noble-metal-free catalysts was firstly reported by Özkar and co-workers.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 readily prepared by *in situ* reduction of NiCl_2 and CoCl_2 during the hydrolytic dehydrogenation of $\text{N}_2\text{H}_4\text{BH}_3$.^{430,431} The *in situ* formed PSSMA-Ni and PSSMA-Co NPs were highly active in the hydrolysis of $\text{N}_2\text{H}_4\text{BH}_3$ with the release of nearly 3 equiv. H_2 per $\text{N}_2\text{H}_4\text{BH}_3$. Moreover, the obtained PSSMA-Co (TOF = 370 h^{-1}) showed much higher catalytic performance than PSSMA-Ni (TOF = 183 h^{-1}) for this hydrolysis reaction at 298 K.^{430,431} The Cu@ SiO_2 core-shell pre-catalyst developed by our research group also showed excellent catalytic activity (TOF = 454.8 h^{-1}) in the hydrolytic dehydrogenation of $\text{N}_2\text{H}_4\text{BH}_3$.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)

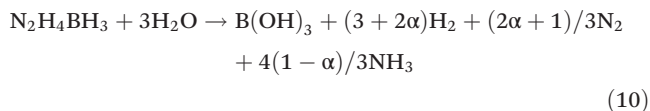
modified Ni NPs showed high activity toward hydrogen generation from the hydrolysis of $N_2H_4BH_3$ at 298 K.¹⁸⁷



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.



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 .



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-

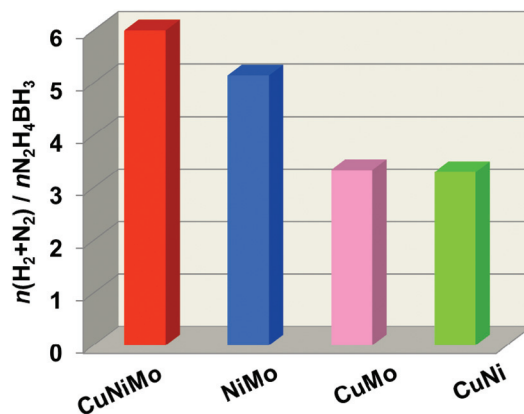


Fig. 15 $n(H_2 + N_2)/n(N_2H_4BH_3)$ for dehydrogenation of $N_2H_4BH_3$ catalyzed by CuNiMo, NiMo, CuMo, and CuNi nanocatalysts in the presence of NaOH (2.0 M) at 323 K. Reprinted with permission from ref. 402. Copyright (2018) Royal Society of Chemistry.

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-CeO₂@SiO₂ 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®

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

Catalyst	Temp. (K)	$n_{\text{metal}}/nN_2H_4BH_3$	$n(H_2 + N_2)/nN_2H_4BH_3$	TOF ($\text{mol}_{H_2} \text{mol}_{\text{metal}}^{-1} \text{h}^{-1}$)	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 BH₃ group of HB only. ^b Hydrogen release from the methanolysis of the BH₃ 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 BH₃ group hydrolysis. Therefore, the current challenges include finding a catalyst that can catalyze both BH₃ 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.

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