

Review Article

Nanocatalysts for Hydrogen Generation from Ammonia Borane and Hydrazine Borane

Zhang-Hui Lu, Qilu Yao, Zhujun Zhang, Yuwen Yang, and Xiangshu Chen

College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, China

Correspondence should be addressed to Zhang-Hui Lu; luzh@jxnu.edu.cn and Xiangshu Chen; cxs66cn@jxnu.edu.cn

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Ammonia borane (denoted as AB, NH_3BH_3) and hydrazine borane (denoted as HB, $\text{N}_2\text{H}_4\text{BH}_3$), having hydrogen content as high as 19.6 wt% and 15.4 wt%, respectively, have been considered as promising hydrogen storage materials. Particularly, the AB and HB hydrolytic dehydrogenation system can ideally release 7.8 wt% and 12.2 wt% hydrogen of the starting materials, respectively, showing their high potential for chemical hydrogen storage. A variety of nanocatalysts have been prepared for catalytic dehydrogenation from aqueous or methanolic solution of AB and HB. In this review, we survey the research progresses in nanocatalysts for hydrogen generation from the hydrolysis or methanolysis of NH_3BH_3 and $\text{N}_2\text{H}_4\text{BH}_3$.

1. Introduction

Hydrogen, as a globally accepted clean and source-independent energy carrier, has a high energy content per mass (120 MJ/kg) compared to petroleum (44 MJ/kg). It can serve as energy source for different end uses, such as hydrogen fuel cell vehicles and portable electronics [1], which will enable a secure and clean energy future. The use of hydrogen fuel cells in portable electronic devices or vehicles requires lightweight hydrogen storage or on-board hydrogen production. For vehicular applications, the US Department of Energy (DOE) has set storage targets; the gravimetric and volumetric system targets for near-ambient temperature and moderate pressure are 9.0 wt% and 81 g/L for 2015, respectively. In order to meet the targets set by the US DOE, various storage solutions have been developed and a large number of studies have been performed on the hydrogen storage materials [2–9], such as metal hydrides [2], organic hydrides [10], and metal organic frameworks [11]. However, big challenges still remain.

Chemical storage materials with low molecular weight and high gravimetric hydrogen density are highly promising as hydrogen sources [12–14]. Particularly, ammonia borane (AB, NH_3BH_3) and hydrazine borane (HB, $\text{N}_2\text{H}_4\text{BH}_3$) have attracted much attention. The simplest B-N compound of ammonia borane, which has a hydrogen capacity as high as

19.6 wt% and a low molecular weight (30.9 g/mol), exceeding that of gasoline and Li/NaBH_4 , has made itself an attractive candidate for chemical hydrogen storage applications [14]. The closely related compound hydrazine borane contains 15.4 wt% of hydrogen, which is greater than the 2015 target of US DOE, and needs to be considered as another B-N compound that can be used for the storage of hydrogen [15].

Ammonia borane and hydrazine borane can release their hydrogen through thermal dehydrogenation in solid state and solvolysis (hydrolysis and methanolysis) in solution [12]. Generally speaking, thermal dehydrogenation process requires high temperature and power consumption. In contrast, ammonia borane and hydrazine borane are able to release hydrogen via a room temperature solvolysis reaction in the presence of a suitable catalyst [5, 12, 15]. Various nanocatalysts have been tested for hydrogen generation from the solvolysis of AB and HB. This review is to serve as an up-to-date account of the recent progress in nanocatalysts for hydrogen generation from AB and HB.

2. Ammonia Borane

Ammonia borane is a colorless molecular crystal under ambient conditions with a density of 0.74 g cm^{-3} and soluble

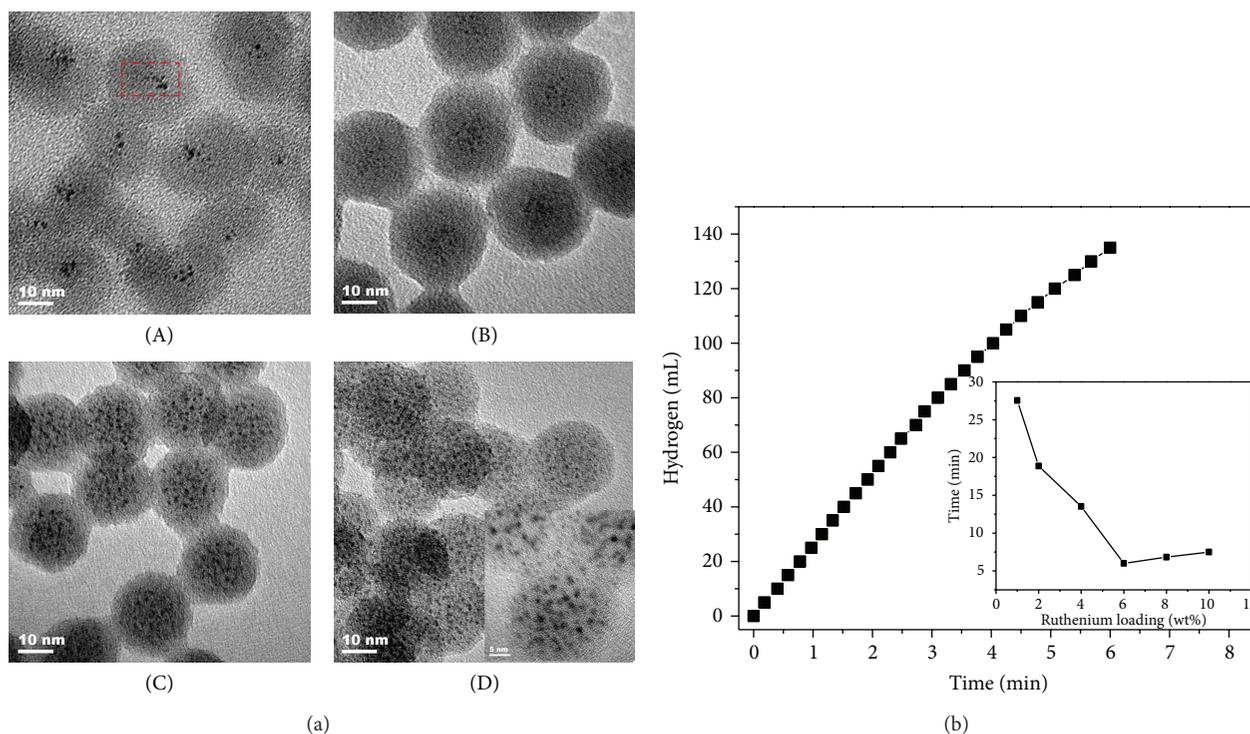


FIGURE 1: (a) Representative TEM images of the core-shell NPs Ru@SiO₂ with different Ru loadings: (A) 1 wt%, (B) 2 wt%, (C) 6 wt%, and (D) 10 wt%. (b) Hydrogen generation from hydrolysis of NH₃BH₃ (200 mM, 10 mL) by Ru@SiO₂ NPs (Ru loading = 6 wt% and (Ru) = 0.5 mM) at 298 K. The inset shows the reaction time versus the loading of ruthenium. Reprinted with the permission from [38]. Copyright: 2014 Elsevier.

in water and other relatively polar solvents. The hydrogen stored in AB can be released either by thermolysis in solid state and nonaqueous medium or metal catalyzed reactions in protic solvents (water and methanol) [14]. About 1 mol H₂ (i.e., 6.5 wt% H) per mol AB is released by thermal decomposition of AB under moderate conditions (<100°C) [14]. However, to maximize the use of hydrogen in AB higher temperature is needed, which also results in the release of the side product borazine. To reduce the threshold temperature and volatile byproducts, a number of approaches have been achieved, including dehydrogenating AB on nanoscaffolding [16], catalytic modifications [17], dispersion in an ionic liquid [18], and the synthesis of derivatives (e.g., metal amidoboranes) [9].

Thermal decomposition of AB usually required high temperature and the reaction was relatively difficult to control. In contrast, the catalytic hydrolysis or methanolysis provides a more convenient strategy for hydrogen generation from AB [19–25]. In the presence of a suitable catalyst, hydrolysis of AB can release as much as 3 mol of hydrogen per mol of AB at room temperature via the following reaction:



In 2006, noble metal (Pt, Ru, and Pd) nanocatalysts were firstly found by Xu's group to have considerable activities toward hydrolytic dehydrogenation of AB [26]. The Al₂O₃, C, and SiO₂ supported noble metals (Ru, Rh, Pd, Pt, and Au) nanoparticles were also investigated for hydrolysis of AB [27].

Among them, Pt-based nanocatalysts were found to be most active. Recently, ultrafine Pt NPs immobilized inside metal organic framework (MIL-101) were synthesized as highly efficient catalysts for hydrolytic dehydrogenation from AB [28]. Metin and coworkers found that the poly(4-styrenesulfonic acid-co-maleic acid) (PSSA-co-MA) stabilized Ru and Pd NPs having average particle size of 1.9 ± 0.5 and 3.5 ± 1.6 nm, respectively [29], were highly active catalysts for hydrolysis of AB. In addition, Ru, Rh, and Pd NPs stabilized by xonotlite [30], zeolite [31], hydroxyapatite [32], aluminum oxide [33], carbon black [34], carbon nanotubes [35], and graphene [36, 37] were also reported to have good catalytic activity in the hydrolytic dehydrogenation of AB. Particularly, the activation energy for the hydrolysis of AB in the presence of Ru/graphene was reported to be 11.7 kJ/mol [37], which is the lowest value ever reported for the same reaction. More recently, Ru NPs embedded in SiO₂ nanospheres (Ru@SiO₂ core-shell NPs) have been synthesized by us and used as catalysts for hydrolysis of AB [38], as shown in Figure 1. The characterized results show that ultrafine Ru nanoparticles (NPs) of around 2 nm are effectively embedded in the center of well-proportioned spherical and porous silica nanospheres (~25 nm in diameter). Interestingly, the number of Ru NPs increases inside the spherical particles of SiO₂ as the increase of Ru loading. The as-synthesized Ru@SiO₂ exhibited high catalytic activity and good durability for hydrogen generation from AB.

The noble metal-based catalysts provide significant catalytic activities in hydrogen generation from hydrolysis of

AB. For practical use, the development of low-cost and highly efficient catalysts is desired. Therefore, the development of efficient and economical nonnoble catalysts to further improve the kinetic properties is of great importance for the practical application of hydrogen generation/storage systems. The nonnoble metals (i.e., Fe, Co, Ni, and Cu) containing catalysts have been extensively investigated in the past several years [39–51], and among them, Co-based catalysts with similar structure or stabilizer were found to have the highest catalytic activity. The γ -Al₂O₃, SiO₂, and C supported nonnoble metals (Co, Ni, and Cu) NPs were reported to be catalytically active, whereas supported Fe NPs were inactive for catalytic hydrolysis of AB [39]. Unexpectedly, amorphous Fe NPs synthesized by in situ reduction with AB and NaBH₄ exhibited the noble metal-like catalytic activity in the hydrolysis of AB (Fe/AB = 0.12) [40]. And then, the amorphous Co and Ni NPs were also found to have enhanced catalytic performance in comparison to their crystalline counterparts [41–43]. The high activity of the amorphous metal NPs could be attributed to the 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.

Unexpectedly, monodisperse 3.2 nm Ni NPs with a polycrystalline structure, supported on Ketjen carbon black [44], were shown to be a highly active catalyst for the hydrolysis of AB, with the total turnover frequency (TOF) reaching 8.8 mol⁻¹ H₂ mol⁻¹ Ni min⁻¹. But this Ni/C catalyst was not stable during the hydrolysis reaction due to the agglomeration of Ni NPs on the carbon support. 3.2 nm Ni NPs supported on SiO₂ were found by the same group to have the excellent activity and durability [45]. Recently, the Ni NPs (6.3 ± 1.7 nm) deposited into the nanoporous carbon (MSC-30) showed an excellent catalytic activity with a TOF value as high as 30.7 (mol⁻¹ H₂ mol⁻¹ Ni min⁻¹) [46], which is the highest one among all of the Ni nanocatalysts ever reported for this reaction at room temperature.

Compared to the Fe-, Co-, and Ni-based catalysts, the Cu-based catalysts were reported to have a lower catalytic activity [52–57]. Iron, cobalt, and nickel oxides formed from the corresponding metals under atmosphere condition were difficult to be reduced by weak reductants such as AB. Thus, before use to attain an effective catalyst, reductive pretreatment is necessary. However, copper oxides are easily reduced by a milder reductant (such as AB) and are exceptional catalysts working without reductive pretreatment in catalytic hydrolysis of AB. Nanostructured Cu, Cu₂O, and Cu@Cu₂O NPs synthesized by the solvated metal atom dispersion (SMAD) method were tested for the hydrolysis of AB [53]. Cu@Cu₂O showed better catalytic activity than Cu and Cu₂O. A series of Co₃O₄ NPs in which Cu was loaded on the surface were examined as catalysts in the hydrolysis of AB [54]. Their catalytic activity was dependent on the shape and size of nanosized Co₃O₄. Recently, capping of Cu₂O with organic reagents or inorganic materials was performed and tested in AB hydrolysis [55]. It was found that capping of Cu₂O with 50-facet Co₃O₄ NPs was the most active. Cu NPs supported on silica-coated cobalt(II) ferrite SiO₂/CoFe₂O₄

(CuNPs@SCF) were reported to have an initial TOF value of 2400 mol H₂ mol⁻¹ Cu h⁻¹ in air at room temperature [56]. They claimed that the TOF value was the highest one among the first row metal catalysts used in the hydrolysis of AB. It was noted that the CoFe₂O₄ of the support was not considered in the TOF test. Iron and cobalt oxides were difficult to be reduced by AB; however, they might be reduced by the Cu-H active species or H₂ generated in the hydrolysis reaction. In addition, zeolite and hydrogel networks-confined Cu NPs were synthesized and used as catalyst systems [48]. Graphene-supported Cu NPs were synthesized by us via a facile in situ procedure using AB as a reductant, which exerted satisfied catalytic activity (3.61 mol H₂ mol catalyst⁻¹ min⁻¹) [57], appearing to be the best Cu nanocatalysts up to now.

Bimetallic catalysts usually show improved catalytic performance in comparison to their monometallic counterparts; due to that the metal-metal interactions in the bimetallic systems presumably account for the tuning of the bonding pattern of reactants and stabilization of reaction intermediates on the catalyst surface. A number of bimetallic catalysts [58–73], such as Au-Co [58, 59], Au-Ni [60, 61], Ru-Co [62], Ru-Ni [63, 64], Ru-Cu [62], Pt-Ni [65, 66], Pd-Co [67], Cu-Co [68, 69], Cu-Fe [70], Fe-Ni [71], Fe-Co [72], and Co-Ni [73], have been employed in the hydrolysis of AB. For example, small Au-Ni and Au-Co NPs (2–4 nm) embedded in SiO₂ nanospheres (about 15 nm) exhibited superior performance in the hydrolysis of AB [58, 61], in contrast to monometallic counterparts Au@SiO₂, Ni@SiO₂, and Co@SiO₂. After heat treatment in vacuum, multiple Au-Co NPs embedded in SiO₂ nanospheres merged into single Au-Co NPs within SiO₂, resulting in a size increase of the bimetallic core NPs [58], as shown in Figure 2. Unexpectedly, single Au-Co NPs within SiO₂ showed a better catalytic activity than multiple small bimetallic core NPs within SiO₂, which is due to the decrease in the content of basic ammine by the decomposition of metal ammine complexes (precursor) during the heat treatment.

Bimetallic NPs with core-shell architecture have attracted growing attention in recent years due to their unique and novel optical, electrical, and catalytic properties compared with their monometallic counterparts and alloys. Yan and coworkers prepared Au@Co core-shell NPs through the one-step seeding growth route with AB as the reductant [59]. By exposing a mixture of Au³⁺ and Co²⁺ precursors to the aqueous solution of AB at the same time, the core Au NPs can be formed first and then serve as the in situ seeds for successive catalytic reduction leading to the growth of outer shell Co NPs, which is to take advantage of the difference in reduction potentials of the two metal ions. A relative stronger reductant NaBH₄, instead of AB, causes the formation of Au-Co alloys. Therefore, a suitable reductant is essential in this one-step synthesis method. Compared to alloy and monometallic counterparts, the Au@Co NPs exhibited excellent catalytic activity and long-term stability in the hydrolysis of AB. A similar approach was used to synthesize bimetallic Cu@M [74], Pd@M [75], Ag@M [76], and Ru@M (M = Fe, Co, Ni) [77] and trimetallic Au@Co@Fe [78], Cu@FeNi [79], Cu@CoNi [80], Cu@FeCo [81], Cu@CoCr [82], Ag@CoFe

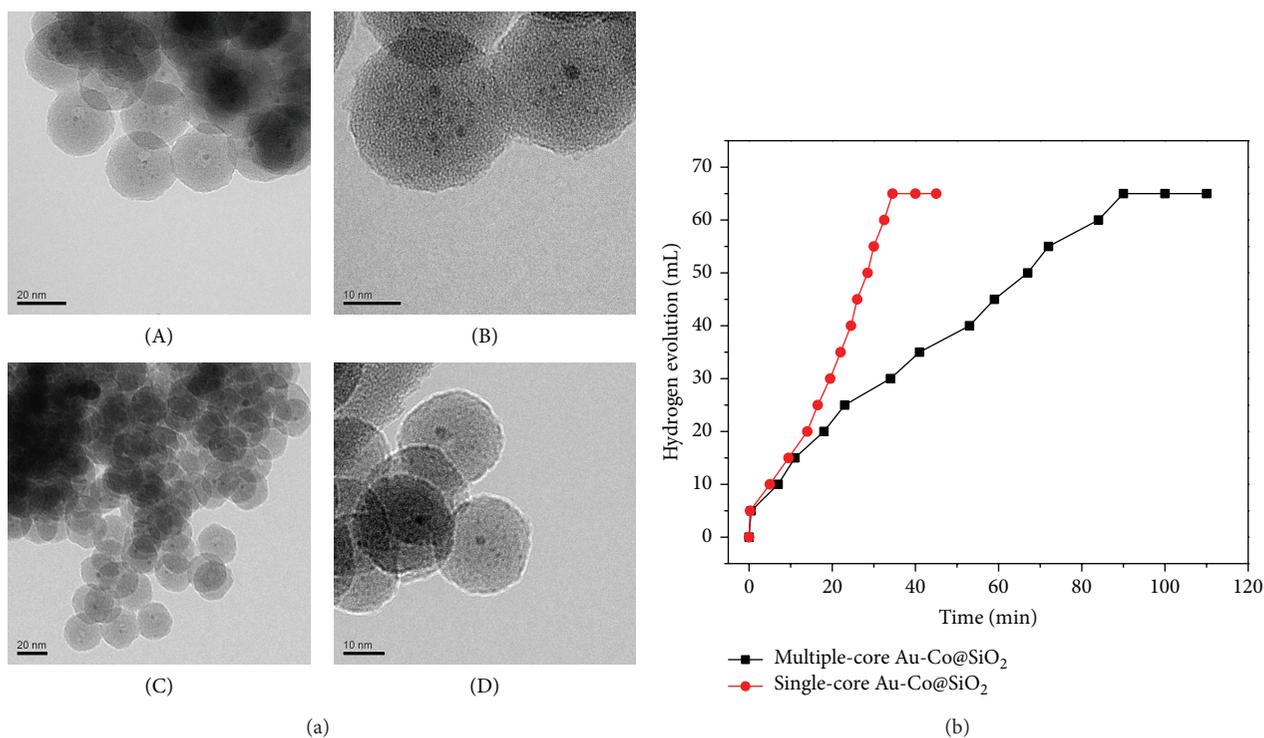


FIGURE 2: (a) Representative TEM images of the core-shell NPs Au-Cu@SiO₂ with multiple- (A-B) and single-core (C-D) NPs. (b) Hydrogen generation from hydrolysis of NH₃BH₃ (160 mM, 5 mL) by different catalysts at 298 K. Reprinted with the permission from [58]. Copyright: 2012 Royal Society of Chemistry.

[83], Ag@NiFe [83], Ag@CoNi [84], and Ag@Co@Ni [85] core shell NPs. It was found that all the obtained bimetallic or trimetallic core-shell NPs showed higher activities than the corresponding monometallic counterparts in the hydrolysis of AB. However, the Cu-Fe bimetallic nanoalloys synthesized by in situ reduction of Cu²⁺ and Fe²⁺ with AB and NaBH₄ as the reductant exhibited excellent catalytic activity, especially for Cu_{0.33}Fe_{0.67} alloy NPs outperforming the activity of monometallic counterparts and even of Cu_{0.33}@Fe_{0.67} core-shell NPs [70], as shown in Figure 3.

Besides the hydrolysis of AB, the methanolysis reaction has also taken place in the presence of suitable catalysts and has been developed to generate hydrogen. This catalytic methanolysis reaction can be expressed as follows:



The hydrogen capacity from this methanolysis reaction is estimated to be about 3.9 wt%, lower than that from the hydrolysis reaction (8.9 wt%). However, the hydrolytic system with high-concentration AB solution can lead to the release of small quantities of NH₃ along with H₂, whereas the methanolysis of AB can overcome this problem. What is more, the methanolysis product of NH₄B(OMe)₄ can be converted back to AB by treatment of lithium aluminium hydride with ammonium chloride. In 2007, RuCl₃, RhCl₃, PdCl₂, CoCl₂, NiCl₂, Pd/C, and Raney-Ni were firstly reported for the methanolysis of AB [86]. Since then, various catalysts have been examined in hydrogen generation from

the methanolysis of AB, such as PVP-stabilized Pd and Ru NPs [87, 88], Ru NPs immobilized in montmorillonite [89], Co-Co₂B, Ni-Ni₃B, Co-Ni-B [90], zeolite stabilized Rh NPs [91], and Cu@Cu₂O [53]. Recently, monodisperse 7 nm CoPd NPs with controlled compositions were synthesized and used for catalytic methanolysis of AB [92]. The CoPd NPs showed the composition-dependent methanolysis at room temperature, with Co₄₈Pd₅₂/C being the most active. More recently, various mesoporous Cu nanostructures with diverse morphologies have been synthesized by us via a facile and scaleable wet-chemical method and applied as catalyst for hydrogen generation from the methanolysis of AB [93]. Among them, the flower-like mesoporous Cu showed the highest catalytic activity.

Catalytic hydrolysis or methanolysis reaction of AB proceeds with rapid kinetics in the presence of suitable metal nanocatalysts at ambient temperatures. A portable hydrogen generation system is expected to be established on the basis of the metal-catalyzed dehydrogenation of AB. A significant drawback of the hydrolysis system is that B-H bonds are converted to much stronger B-O bonds. These byproducts with B-O bonds generated during the hydrolysis reaction will be energetically costly to regenerate. Further experimental and theoretical researches toward the practical application, including the highly efficient catalyst with the low cost and long-time stability, and the regeneration of AB are highly desired. Notably, the convenience and reliability of performing AB hydrolysis reaction make it suitable for application. Like CO oxidation, the hydrolysis of AB has

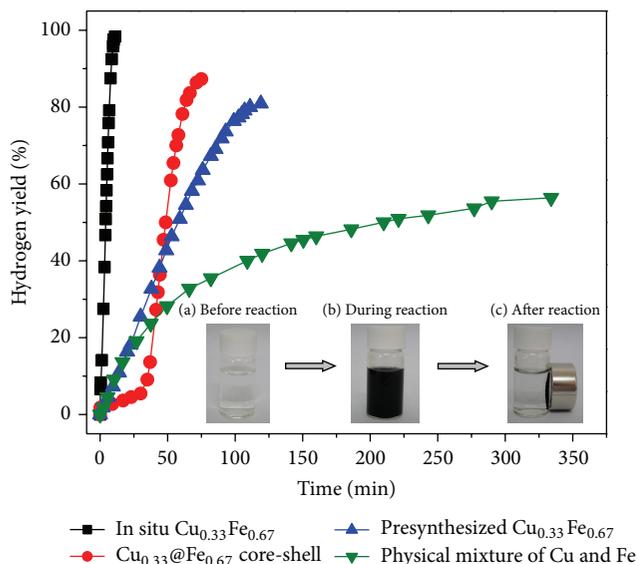


FIGURE 3: Hydrogen generation from the hydrolysis of AB in the presence of different metal nanocatalysts (metal/AB = 0.04). The insert shows photographs of the catalytic hydrolysis of AB via in situ synthesized $\text{Cu}_{0.33}\text{Fe}_{0.67}$ nanoalloy. Reprinted with the permission from [70]. Copyright: 2013 Elsevier.

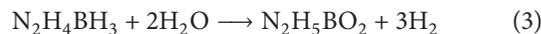
already been widely used as a test (model) reaction for examining the catalytic activity of new nanomaterials.

3. Hydrazine Borane

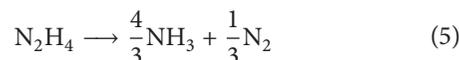
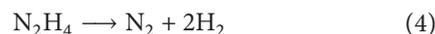
Hydrazine borane ($\text{N}_2\text{H}_4\text{BH}_3$, HB) is one of the hydrogen-dense derivatives of ammonia borane and has a gravimetric hydrogen capacity of 15.4 wt%, with 4 $\text{H}^{\delta+}$ and 3 $\text{H}^{\delta-}$. The first report concerning HB dates back to 1961 when Goubeau and Ricker published the synthesis HB by reaction of $(\text{N}_2\text{H}_5)_2\text{SO}_4$ with NaBH_4 in dioxane at room temperature [94]. Since then several studies were conducted [95–97], focusing on synthesis, decomposition, and hydrogen generating systems. Experimental spectroscopy and DFT calculation were performed to understand the structure of HB [98–100]. The release of hydrogen from HB can be obtained through either thermolysis or solvolysis. The thermal decomposition of solid HB was firstly studied by Goubeau and Ricker [94]. Hydrogen is released from HB in a controlled manner even at temperatures as high as 200 °C. In the presence of LiH, 11 wt% H_2 can be released from HB at 150 °C in less than an hour [15].

The hydrolysis of HB was firstly reported by Karahan and coworkers [4]. In the presence of RhCl_3 precatalyst, the aqueous solution of HB undergoes fast hydrolysis to release nearly 3.0 equivalent of H_2 with TOF = 1200 h^{-1} by hydrolysis of the BH_3 group. They also reported the preparation and characterization of the Rh NPs supported on hydroxylapatite ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$, HAP) and their catalytic hydrolysis of HB with a TOF value of 6700 h^{-1} at room temperature [101]. The poly(4-styrenesulfonic acid-co-maleic acid) (PSSMA) stabilized Ni NPs formed during the hydrolysis of HB were found to be highly active catalyst releasing 2.6–3.0 mol H_2

per mol HB with an initial TOF value of 3.05 min^{-1} [102]. However, only about 3/7 of its hydrogen was released by the hydrolysis of the BH_3 group of HB and the N_2H_4 group was not decomposed:



Like the BH_3 group of AB, the BH_3 group in HB is easy to hydrolyze in the presence of a suitable catalyst. However, unlike the NH_3 group of AB, the N_2H_4 group of HB can also be dehydrogenated in the presence of a selective catalyst (4), although this reaction is in competition with NH_3 release (5). Therefore, HB is of great interest in hydrolysis because the H atoms stored in the N_2H_4 moiety can be recovered as H_2 . The real grand challenge is to dehydrogenate the N_2H_4 group in HB under mild conditions. The key point is to find a suitable reactive and selective catalyst, active in dehydrogenating both BH_3 and N_2H_4 (6), while avoiding the occurrence of the side reaction producing NH_3 . Hence, HB could be ideally dehydrogenated into 5 mol H_2 per mol HB. Great efforts were devoted to synthesize a highly selective catalyst that can achieve the completely dehydrogenated HB [5, 104–107]. Different catalysts for catalytic dehydrogenation from HB are summarized in Table 1:



Singh and coworkers have studied the hydrogen evolution reaction from a mixture of N_2H_4 and NH_3BH_3 ($\text{N}_2\text{H}_4/\text{NH}_3\text{BH}_3 = 1:1$) in the presence of the $\text{Ni}_{0.99}\text{Pt}_{0.01}$ nanocatalysts at 25 and 50 °C and proposed that the Ni-based bimetallic catalysts can be used to release five equivalents of H_2 and one equivalent of N_2 from an aqueous solution of HB [7]. Following researches confirmed this proposal [5, 104]. Hannauer and coworkers have investigated various transition metal chlorides as precursors of in situ forming catalysts by reduction in the presence of HB at 50 °C [105]. They concluded that the dehydrogenation of HB is a two-step metal-catalyzed process, where first the hydrolysis of the BH_3 moiety occurs and second the decomposition of the N_2H_4 moiety takes place. The metals studied can be classified into 3 groups: (1) Fe- and Re-based catalysts, showing an incomplete conversion (<3 mol H_2) in the hydrolysis of the BH_3 group; (2) Co-, Ni-, Cu-, Pd-, Pt-, and Au-based catalysts, only active in the hydrolysis of BH_3 group (3 mol H_2 per mol BH_3 of HB); (3) Ru-, Rh-, and Ir-based catalysts, being also active in the decomposition of N_2H_4 group. With the in situ formed Rh(0) nanorods (10 × 4 nm), 4.1 mol ($\text{H}_2 + \text{N}_2$) per mol HB can be produced at 50 °C [105]. It was found that most of the Ni-based bimetallic systems, with Pt, Ru, Rh, or Ir as the second metal, outperform the monometallic Ni, Pt, Ru, Rh, and Ir catalysts at 50 °C [104]. The performance achieved is 5.1 ± 0.05 mol ($\text{N}_2 + \text{H}_2$) per mol (HB) with $\text{Ni}_{0.89}\text{Rh}_{0.11}$ (reductant: NaBH_4) and $\text{Ni}_{0.89}\text{Ir}_{0.11}$ (reductant: NH_3BH_3) nanocatalysts. Particularly, the hydrogen selectivity reaching $93 \pm 1\%$ and 5.79 ± 0.05 equiv. ($\text{H}_2 + \text{N}_2$) per

TABLE I: Catalytic performance of metal nanocatalysts for hydrogen generation from hydrazine borane (HB).

Catalysts	Temperature ($^{\circ}\text{C}$)	$n(\text{H}_2 + \text{N}_2)/n\text{HB}$	Reference
RhCl ₃ precatalyst	25	2.93	[4]
RuCl ₃ precatalyst	25	~2.9	[4]
Rh NPs/Al ₂ O ₃	25	~2.6	[4]
Ru NPs/Al ₂ O ₃	25	~2.7	[4]
Rh NPs/hydroxyapatite	25	3	[101]
Ni NPs/PSSMA	25	2.6~3	[102]
NiCl ₂ precatalyst	25	3	[103]
Ni NPs/CTAB	50	~3.1	[5]
Pt NPs/CTAB	50	3	[5]
Ru NPs/CTAB	50	3.30 ± 0.05	[104]
Rh NPs/CTAB	50	3.30 ± 0.05	[104]
Ir NPs/CTAB	50	2.25 ± 0.05	[104]
Ni _{0.97} Pt _{0.03} NPs/CTAB	50	5.07 ± 0.05	[5]
Ni _{0.89} Pt _{0.11} NPs/CTAB	50	5.79 ± 0.05	[5]
Ni _{0.77} Pt _{0.23} NPs/CTAB	50	5.29 ± 0.05	[5]
Ni _{0.89} Rh _{0.11} NPs/CTAB	50	5.1 ± 0.05	[104]
Ni _{0.89} Ir _{0.11} NPs/CTAB	50		[104]
Ni _{0.77} Ru _{0.23} NPs/CTAB	50	4 ± 0.05	[104]
RhCl ₃ precatalyst	50	4.1	[105]
RuCl ₃ precatalyst	50	3.3	[105]
IrCl ₃ precatalyst	50		[105]
Rh NPs/CTAB	50	4.4 ± 0.2	[106]
Ni NPs/CTAB	50	3.5 ± 0.1	[106]
Rh ₄ Ni NPs/CTAB	50	5.8 ± 0.2	[106]
Ni@(RhNi-alloy)/Al ₂ O ₃	50	5.74 ± 0.2	[107]
Ni ₁₅ Rh-alloy/Al ₂ O ₃	50	~4.15	[107]

HB could be released in the presence of Ni_{0.89}Pt_{0.11} NPs (reductant: NaBH₄), suggesting that 9.7 wt% of H₂ of the system HB-3H₂O is recovered [5]. More recently, Zhang and coworkers reported that the Rh₄Ni nanocatalyst exhibits high efficiency in dehydrogenation reaction of HB [106], as shown in Figure 4. The hydrogen selectivity reaches almost 100% at 50 $^{\circ}\text{C}$. Interestingly, the dehydrogenation of aqueous hydrazine borane catalyzed by the Rh₄Ni alloy cannot be simply divided into two steps. Moreover, well-dispersed core-shell Ni@(RhNi-alloy) NPs supported on Al₂O₃ exhibited high hydrogen production rate with complete hydrogen generation of HB, that is, 5.74 ± 0.2 equiv. (H₂ + N₂) per HB within 40 min at 50 $^{\circ}\text{C}$ [107].

In addition, the hydrogen of HB can be released through the catalytic methanolysis at room temperature (7). Karahan and coworkers firstly reported the metal-catalyzed methanolysis of HB using a NiCl₂ precatalyst at room temperature [103]. The methanolic solution of HB (HB/Ni ≥ 200) can release 3 equiv. of H₂ with a rate of 24 mol H₂ (mol Ni min)⁻¹ at room temperature. The catalytic methanolysis of HB can enable rapid and controllable hydrogen generation at ambient temperatures. The hydrogen capacity of this methanolysis reaction of HB is estimated to be only 3.5 wt%, lower than that of the hydrolysis reaction of HB or AB. This then makes this methanolysis reaction of HB less attractive than

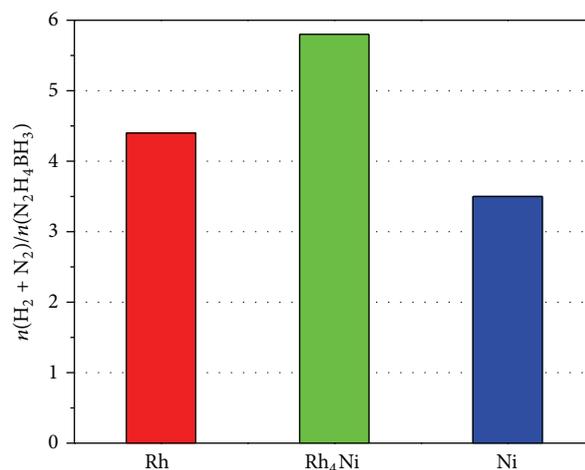
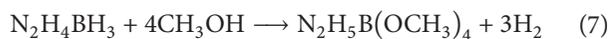


FIGURE 4: Evolution of the mol number of (H₂ + N₂) per mol of N₂H₄BH₃ in the presence of Rh, Rh₄Ni, and Ni nanocatalysts. The data are from [106].

the hydrolysis reaction. Very recently, Thoms and coworkers reported a study of the full dehydrogenation of HB to give H₂ and N₂ catalysed by a variety of group 4 metallocene alkyne complexes in THF at 25 and 50 $^{\circ}\text{C}$ [108]. It was observed

that the amount of hydrogen released is strongly dependent on both the metal and the cyclopentadienyl ligands. This work is the first example for a transition metal-catalysed homogenous process for the dehydrogenation of HB:



Hydrazine borane is a promising novel chemical hydrogen storage material because it stores 15.3 wt% (H) and can dehydrogenate in mild conditions. It can release 5 mol H₂ and 1 mol N₂ per mol HB via the hydrolysis of BH₃ moiety and the decomposition of N₂H₄ moiety in the presence of a suitable catalyst. The hydrolysis reaction system (HB-2H₂O) can ideally release 12.2 wt% H (excess GHSC) and the byproduct gas N₂ is inert towards fuel cells. Similar to AB hydrolysis, byproducts with strong B–O bonds are produced during the hydrolysis reaction, which are difficult to regenerate the B–O bonds to B–H bonds due to the stability of B–O bonds. Compared to AB, it has a higher potential owing to a superior excess gravimetric hydrogen storage capacity and the possibility to decompose the N₂H₄ moiety without liberation of NH₃. The current challenge is to find suitable reactive and selective catalysts to get a conversion of 100% while having selectivity in hydrogen of 100%.

4. Conclusion

Ammonia borane and hydrazine borane store 19.6 wt% and 15.3 wt% hydrogen, respectively, whose dehydrogenation can be approached by either pyrolysis or solvolysis. They have the potential to be used as hydrogen sources suitable for portable fuel cells. This review has summarized some recent progresses on the nanocatalysts for hydrogen generation from catalytic solvolysis of ammonia borane and hydrazine borane. Significant progresses have been obtained in the development of nanocatalysts with high efficiency and low cost, which makes AB and HB promising candidates for some specialized applications of power generation (e.g., emergency or portable power). However, big challenges still remain for practical application of nanocatalysts, such as catalyst cost, deactivation, and control of the reaction kinetics. We are looking forward to the further progress of nanocatalysts for catalytic dehydrogenation of AB and HB in the future.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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