

# Dissociation and hydrolysis of ammonia-borane with solid acids and carbon dioxide: An efficient hydrogen generation system

Manish Chandra, Qiang Xu \*

*National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan*

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## Abstract

Pure hydrogen generation under mild conditions in a controllable way is important for portable devices. Recently, we have found that an aq. ammonia-borane ( $\text{NH}_3\text{BH}_3$ ) solution is a potential hydrogen source with noble metal catalysts. For practical use, the development of a low-cost, efficient and safe system is desired. In this study, we found that solid acids such as cation exchange resins and zeolites, which are low-cost and safe, also exhibit high activities for the dissociation and hydrolysis of  $\text{NH}_3\text{BH}_3$  to generate hydrogen with an  $\text{H}_2$  to  $\text{NH}_3\text{BH}_3$  ratio up to 3.0 at room temperature. The reaction rate depends on the type of solid acid. Especially, Dowex and Amberlyst, the two low-cost solid acids often used as catalysts in a variety of reactions, exhibit reaction kinetics higher than the noble metal catalysts. Carbon dioxide is also active as an acid for this reaction. The reaction products in solution have been identified by  $^{11}\text{B}$  NMR, and the evolved gases have been analyzed by mass spectrometry which indicates high purity hydrogen. This new system may have a high potential for application in fuel cells.

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**Keywords:** Hydrolysis; Ammonia-borane; Hydrogen generation; Solid acids; Carbon dioxide

## 1. Introduction

Fuel cells have attracted much attention as a power source to replace lithium ion batteries in response to the increasing demand of portable electronic devices. Among the various types of fuel cells, the polymer electrolyte membrane fuel cell (PEMFC) has been a promising candidate, which has a high efficiency and high power density, while the hydrogen supply has been a bottle-neck to the application of PEMFC as portable power sources. The storage of hydrogen as a compressed gas or as a cryogenic liquid, or by absorption on activated carbon or nanotubes, in alloys or in chemical hydrides has been studied. Liquid hydrocarbons have also been considered as hydrogen sources. However, the existing technologies are far from meeting the requirements for portable applications due to the low volumetric and gravimetric efficiencies of hydrogen storage and the difficulties in operation during the high temperature reforming processes of hydrocarbons as well as the safety issue.

Recently, much attention has been paid to the hydrolysis of sodium borohydride ( $\text{NaBH}_4$ ) [1–9], which shows a number of advantages as a hydrogen source for portable application: non-flammable and stable in air, easy control of hydrogen generation rate, recycling of the side products, and high  $\text{H}_2$  storage efficiency. Strong base-stabilized  $\text{NaBH}_4$  hydrolyses to hydrogen and sodium metaborate in the presence of catalysts, such as fluorinated metals, hydrogen absorbing alloys, Ru, Ni and Pt metals and Co and Ni borides [1–5]. Hydrogen generation by the hydrolysis of  $\text{LiBH}_4$  has also been reported [10].

The ammonia-borane complex contains 19.6 wt.% hydrogen. There have already been a number of reports on the  $\text{H}_2$  release from  $\text{NH}_3\text{BH}_3$  whereas improvements in the reaction control are needed for application to hydrogen sources. The pyrolysis of  $\text{NH}_3\text{BH}_3$  in the pure form [11–14] or infused in nanoporous silica [15] has been widely investigated, whereas high temperatures are required. The rhodium catalyzed dehydrogenation of dimethylaminoboranes has also been studied [16]. Recently, we reported a new catalytic system based on the metal-catalyzed dissociation and hydrolysis of  $\text{NH}_3\text{BH}_3$  at room temperature, which exhibits a fast hydrogen release with an  $\text{H}_2/\text{NH}_3\text{BH}_3 = 3.0$  in the presence of noble metal catalysts such as Pt, Rh and Pd [17]. However, for practical use, the development of a low-cost, effi-

\* Corresponding author. Tel.: +81 72 751 9562; fax: +81 72 751 9629.  
E-mail address: [q.xu@aist.go.jp](mailto:q.xu@aist.go.jp) (Q. Xu).

cient and safe system is desired. In this manuscript, we report that solid acids such as Dowex, Amberlyst, Nafion and H-Zeolites and carbon dioxide, which are low-cost in comparison with the noble metal catalysts and safe, show equal activity to the hydrolysis of ammonia-borane to generate hydrogen.

## 2. Experimental set-up and procedure

A commercial ammonia-borane complex  $\text{NH}_3\text{BH}_3$  (Tech. 90%, Aldrich) was used as purchased. Dowex 50 W  $\times$  8 (50–100 mesh, 4.8 mequiv.  $\text{g}^{-1}$ ), Amberlyst 15 (16–50 mesh, 4.7 mequiv.  $\text{g}^{-1}$ ) and Nafion NR50 in the hydrogen form (beads,  $\geq 0.8$  mequiv.  $\text{g}^{-1}$ ) were purchased from Aldrich and used as obtained. H-type zeolites, H-BEA (Beta, Zeolyst International,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$ ), and H-MOR (Mordenite, Catalysis Society of Japan,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 15$ ) were used as obtained.

### 2.1. Experimental set-up

Fig. 1 depicts the experimental apparatus devised to measure the hydrogen generation rate from the aq.  $\text{NH}_3\text{BH}_3$  solution, which consists of a three-necked round-bottom flask with one of the flask openings connected to a gas burette, one to an addition funnel with a pressure-equalization arm, and the other one to a thermometer.

### 2.2. Experimental procedure

The reactions with solid acids were carried out at room temperature. A weighed solid acid was placed in the three-necked

round-bottom flask (50 ml) and the reaction was started by stirring the mixture of the solid acid and the aq. 0.33 wt.%  $\text{NH}_3\text{BH}_3$  solution added from the addition funnel, and the evolution of gas was monitored using the gas burette to an accuracy of  $\pm 0.5$  ml. The solution temperature was kept constant ( $25^\circ\text{C}$ ) within the range of the set value of  $\pm 1.0^\circ\text{C}$  using a water jacket. After the completion of the reaction, the solutions were filtered to separate the solid acids as residues, and the filtrates were used for the  $^{11}\text{B}$  NMR and pH measurements.

The reaction with carbon dioxide was also carried out at room temperature. The aq.  $\text{NH}_3\text{BH}_3$  solution (1 wt.%, 30 ml) was kept in a 200 ml two-necked round-bottom flask with one flask opening connected to a 500 ml gas balloon filled with carbon dioxide. The reaction was started by stirring the solution in the carbon dioxide atmosphere. After the completion of the reaction, the solution was analyzed by  $^{11}\text{B}$  NMR and pH measurements and the gas was analyzed by MS spectrometry.

The  $^{11}\text{B}$  NMR spectra were recorded using a JEOL JNM-AL400 spectrometer operating at 128.15 MHz. Liquid samples of the filtrates, in which  $\text{D}_2\text{O}$  was included as a lock, were contained in sample tubes of 5 mm o.d., in which coaxial inserts of  $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$  as an external reference were placed. The  $^{11}\text{B}$  chemical shifts are given in  $\delta$  unit (parts per million) downfield from  $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ . The MS measurements were performed using a Balzers Prisma QMS 200 mass spectrometer.

## 3. Results and discussion

Previous investigations have shown that  $\text{NH}_3\text{BH}_3$  is hydrolyzed in mixed aqueous solvents with strong liquid acids

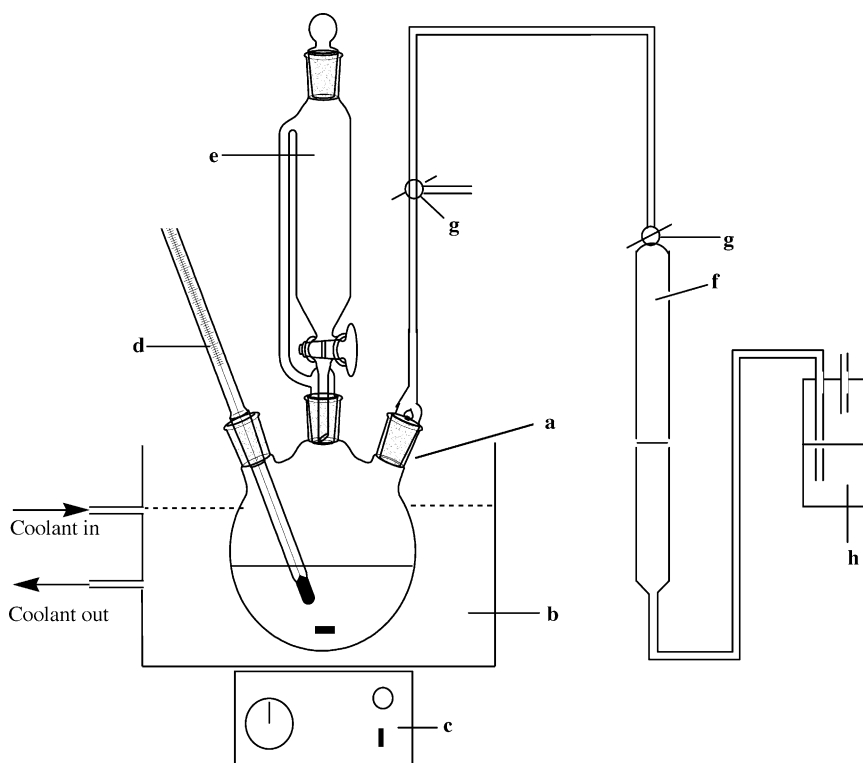


Fig. 1. The reaction apparatus for hydrogen generation from aq.  $\text{NH}_3\text{BH}_3$ . (a) Fifty millilitres three-necked round-bottom flask, (b) water jacket, (c) magnetic stirrer, (d) thermometer, (e) addition funnel with a pressure equalized arm, (f) gas burette, (g) gas cock, (h) leveling bottle.

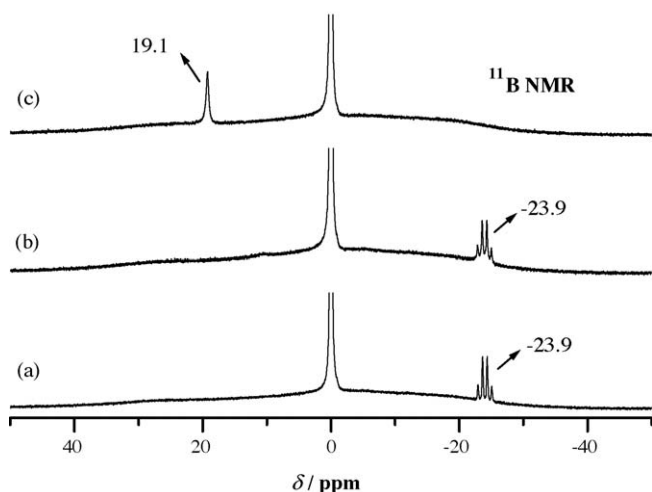
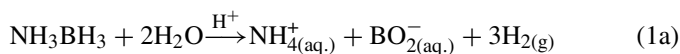


Fig. 2.  $^{11}\text{B}$  NMR spectra of (a) aq.  $\text{NH}_3\text{BH}_3$  solution (0.33 wt.%) freshly prepared, (b) after 80-day storage of (a) under an Ar atmosphere, and (c) after reaction (30 min) of (a) in the presence of Dowex at room temperature. The peak at 0 ppm is due to the external reference,  $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ .

along with the  $\text{H}_2$  release [18,19]. It is obvious that the reactions with strong liquid acids give rise to many problems concerning the safety, handling, health, corrosion, and waste disposal of the liquid acids, which make them less important for the application in fuel cells. Our effort has been devoted to overcome these problems by the application of solid acids and carbon dioxide for the hydrolysis of aq.  $\text{NH}_3\text{BH}_3$ .

$\text{NH}_3\text{BH}_3$  dissolves in water to form a colorless solution (pH 9.1), which exhibits a quadruplet centered at  $\delta = -23.9$  ppm with  $^1J_{\text{B-H}} = 91$  Hz in the  $^{11}\text{B}$  NMR spectra (Fig. 2a), in agreement with the previous reports [20–23]; both the pH and  $\delta$  values are independent of the concentration. The  $^{11}\text{B}$  resonance remains unchanged for more than 80 days under an argon atmosphere (Fig. 2b), indicating the high stability of  $\text{NH}_3\text{BH}_3$  in water. The addition of the solid acid, Dowex, to this solution leads to the vigorous release of  $\text{H}_2$ , which was identified by mass spectrometry, with an  $\text{H}_2$  to  $\text{NH}_3\text{BH}_3$  ratio close to 3.0. After the reaction is completed, the  $^{11}\text{B}$  peak at  $-23.9$  ppm for the aq.  $\text{NH}_3\text{BH}_3$  disappears, whereas the resulting solution produces a low field-shifted single  $^{11}\text{B}$  resonance at 19.1 ppm (Fig. 2c), in contrast with the observation of the  $^{11}\text{B}$  resonance at 8.4 ppm for the hydrolysis reaction with transition metal catalysts. The other solid acids of cation exchange resins and H-type zeolites give the same results. It has previously been shown that an equilibrium process between  $\text{H}_3\text{BO}_3$ ,  $\text{BO}_2^-$  and other borate species, which undergo a rapid change between each other in solution on the NMR time scale, would account for the observed single  $^{11}\text{B}$  resonance and its pH dependence for the resulting solution of the hydrolysis of aq.  $\text{NH}_3\text{BH}_3$  [17]. The overall reactions can be depicted as shown in Eq. (1)



In the present case, because of the presence of the acidic sites on the solid acids, Eq. (1b) shifts to the right side, giving the

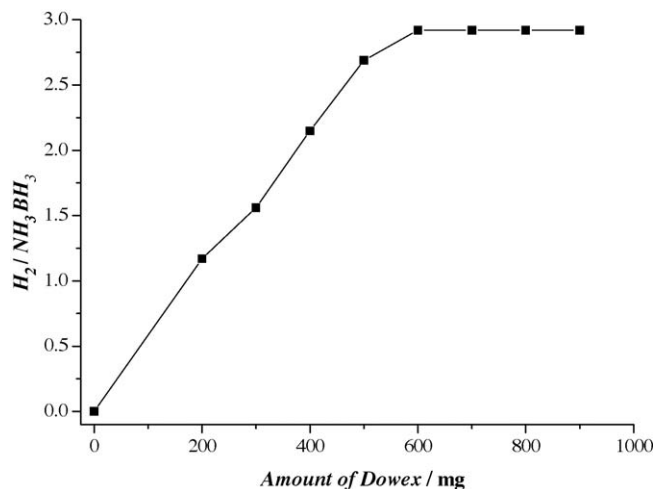


Fig. 3. Hydrogen release from aq.  $\text{NH}_3\text{BH}_3$  solution (0.33 wt.%, 15 ml) with various amounts of Dowex at room temperature.

$^{11}\text{B}$  resonance at 19.1 ppm, in accordance with the value for an aq.  $\text{H}_3\text{BO}_3$  solution [17]. It is known that the activity of a solid acid depends upon the acidity as well as the reaction medium [24–29]. The cationic exchange resins having sulfonic acid groups are typical of insoluble solid acids and their activity is expected to be parallel to that of homogenous strong acids in aqueous medium [28,29].

Hydrogen is readily released from aq.  $\text{NH}_3\text{BH}_3$  upon contacting the cation exchange resins, Dowex, Amberlyst and Nafion-H, to the solution. As shown in Fig. 3, the  $\text{H}_2/\text{NH}_3\text{BH}_3$  ratio increases with the increasing amount of Dowex used; it reaches 3.0 when 600 mg of Dowex is used in this reaction (0.33 wt.%  $\text{NH}_3\text{BH}_3$ , 15 ml) and then remains unchanged when using further increasing amounts of Dowex. The results suggest that the acidic sites of the solid acid are decreased during the reaction as the result of the reaction of  $\text{H}^+$  with borate ion to form the weaker acid, boric acid, as observed by the NMR measurements. All the results shown hereafter are obtained with minimum amounts of solid acids necessary for completing the reaction. Fig. 4 shows the volume of hydrogen released from the aq.  $\text{NH}_3\text{BH}_3$  solution in the presence of Dowex, Amberlyst and Nafion at room temperature versus the reaction time, and Fig. 5 shows the corresponding  $\text{H}_2/\text{NH}_3\text{BH}_3$  ratio versus the reaction time. It is found that the reaction rate depends on the type of solid acid. Dowex and Amberlyst exhibit higher activities, with which the reaction is completed in about 4 min with the  $\text{H}_2/\text{NH}_3\text{BH}_3$  ratio close to 3.0; this reaction rate is much higher than that of the reaction with the Pt catalysts. Nafion-H exhibits a relatively low reaction rate, probably due to its large granule sizes and therefore the difficulty for the reactant to diffuse to the inside acidic sites, while the  $\text{H}_2/\text{NH}_3\text{BH}_3$  ratio reaches the same value. It is noted that in the previous reports on the  $\text{NaBH}_4$  system with the Ru, Co, metallic Co and Ni catalysts, the generated hydrogen volume was almost linearly proportional to the reaction time [5]. In contrast, in the present work, the observed reaction rate decreased with the reaction time because of the consumption of the starting material,  $\text{NH}_3\text{BH}_3$ , which was present in a limited amount for the reaction.

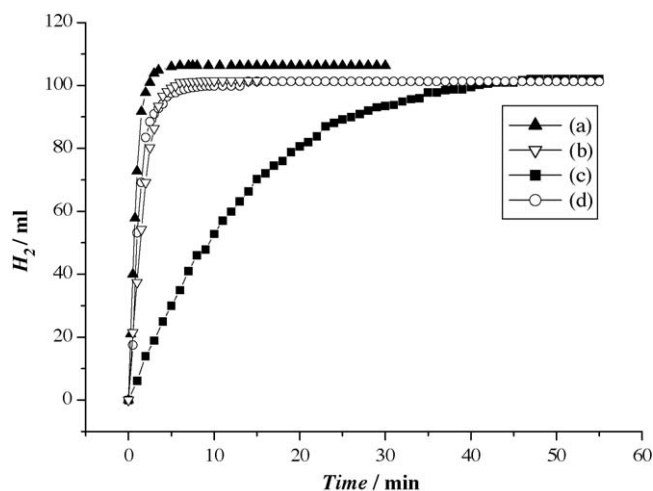


Fig. 4. Volume of hydrogen generated from aq.  $\text{NH}_3\text{BH}_3$  solution (0.33 wt.%, 15 ml) vs. reaction time in the presence of the solid acids of (a) Dowex (600 mg), (b) Amberlyst (600 mg), and (c) Nafion-H (1800 mg) at room temperature, and (d) hydrogen released from the aq.  $\text{NH}_3\text{BH}_3$  (0.33 wt.%, 15 ml) solution that have been preserved in Ar for 80 days before the reaction in the presence of Dowex (600 mg) at room temperature.

Interestingly, the acidic sites of the solid acids decreased during the reaction can be completely recovered by the treatment with acid solution. As shown in Fig. 6, the Dowex sample that has been used one time in this reaction and reused without further treatment exhibits almost no activity during this reaction. However, the treatment with 1 M  $\text{H}_2\text{SO}_4$  leads to the recovery of the acidic sites on the recycled Dowex sample, which shows almost the same activity as the pristine Dowex for the dissociation and hydrolysis of aq.  $\text{NH}_3\text{BH}_3$ .

Fig. 7 shows hydrogen release from aq.  $\text{NH}_3\text{BH}_3$  in the presence of the H-zeolites, H-BEA and H-MOR, with which the reaction is completed in 20–60 min and the  $\text{H}_2/\text{NH}_3\text{BH}_3$  ratio is close to 2.8. The activities of the H-zeolites are lower than those of the sulfonic acid resins, Dowex, Amberlyst and Nafion-H. Due to the hydrophilic nature, the surface of the H-zeolites is covered by water that reduces the acid strength and H-zeolites are generally considered to be less active or inactive in aqueous solutions at relatively low temperature ( $\sim 100^\circ\text{C}$ ) [25,28]. In contrast, the sulfonic acid resins retain the acidity of the sulfonic acid groups in water and are highly active for reactions in aqueous solutions such as the hydrolysis of esters [28]. Both the sulfonic acid resins and H-zeolites are stable in air, non-corrosive and safe, and therefore the use of solid acids instead of liquid acids has a significant advantage for the hydrolysis of  $\text{NH}_3\text{BH}_3$ . Further efforts are needed to raise the ion exchange capacity of the solid acids in order to lower the weight.

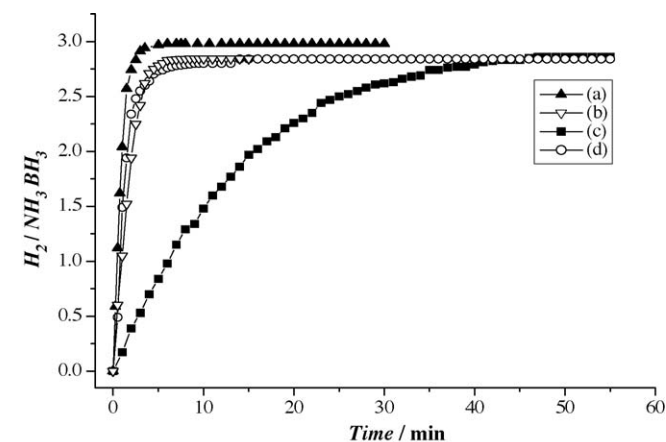


Fig. 5. The  $\text{H}_2/\text{NH}_3\text{BH}_3$  ratio of hydrogen release from aq.  $\text{NH}_3\text{BH}_3$  solution vs. reaction time corresponding to Fig. 4.

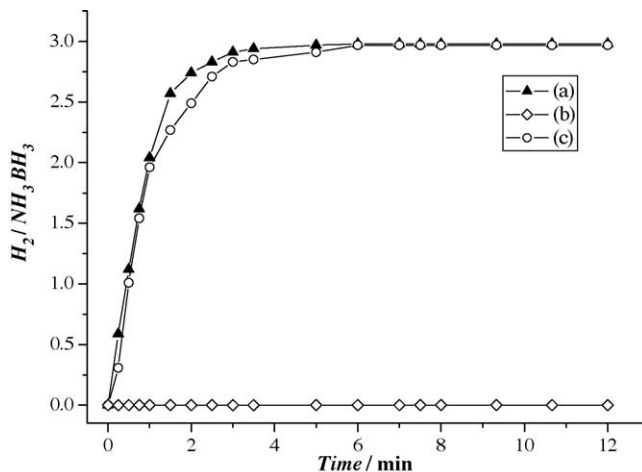


Fig. 6. Hydrogen release from aq.  $\text{NH}_3\text{BH}_3$  solution (0.33 wt.%, 15 ml) at room temperature in the presence of (a) pristine Dowex (600 mg), (b) recycled Dowex (600 mg) without treatment with acid, and (c) recycled Dowex (600 mg) after treatment with 1 M  $\text{H}_2\text{SO}_4$ .

Interestingly, we have found for the first time that carbon dioxide,  $\text{CO}_2$ , is also active as an acid for the hydrolysis of  $\text{NH}_3\text{BH}_3$ .  $\text{CO}_2$  is known as one of the major greenhouse gases; it circulates in the environment through a variety of processes known as the *carbon cycle*. We have found that after dissolution in water [30], carbon dioxide reacts with  $\text{NH}_3\text{BH}_3$  to release hydrogen and form boric acid. After the 7-day continu-

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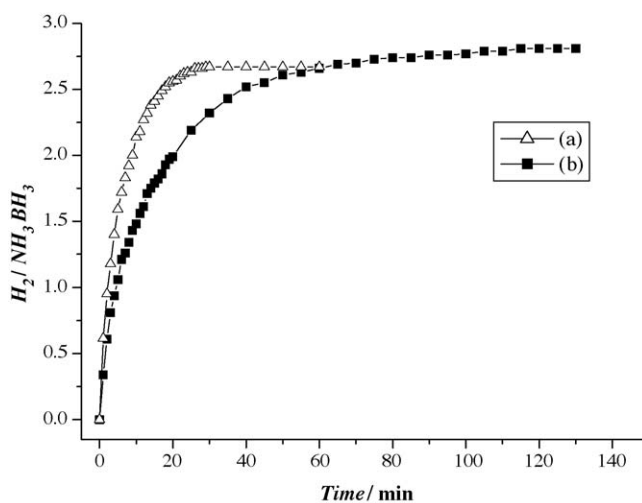


Fig. 7. Hydrogen release from aq.  $\text{NH}_3\text{BH}_3$  solution (0.33 wt.%, 15 ml) in the presence of (a) H-BEA (8.0 g), and (b) H-MOR (6.0 g) zeolites at room temperature.

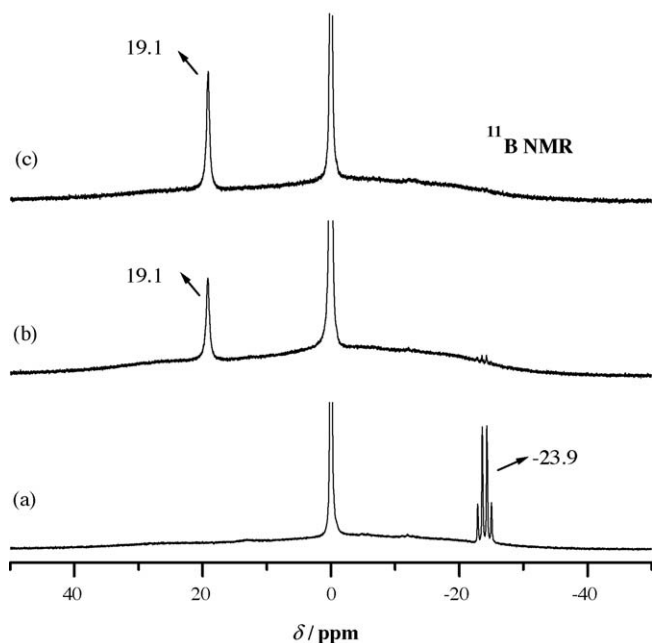


Fig. 8.  $^{11}\text{B}$  NMR spectra of aq.  $\text{NH}_3\text{BH}_3$  solution (1.0 wt.%) (a) freshly prepared, (b) after 5-day stirring, and (c) after 7-day stirring in the presence of carbon dioxide at room temperature. The peak at 0 ppm is due to the external reference,  $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ .

ous stirring of aq.  $\text{NH}_3\text{BH}_3$  in carbon dioxide, the NMR spectra (Fig. 8) exhibited no peak corresponding to the starting material,  $\text{NH}_3\text{BH}_3$ , at  $-23.9$  ppm, whereas a new peak appeared at  $19.1$  ppm, indicating the formation of boric acid as observed in the reactions with solid acids (vide supra). No precipitate was observed during the reaction and the pH value of the solution was found to be 6.0. Mass spectral analyses of the released gases confirmed the hydrogen generation from the aq.  $\text{NH}_3\text{BH}_3$  solution. As shown in Fig. 9, the ion peaks at  $m/z=2$ , 18 and 44 corresponding to  $\text{H}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  were observed along with

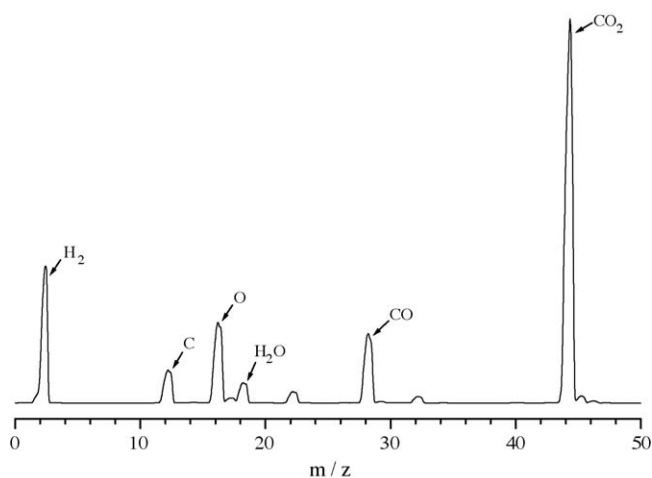


Fig. 9. Mass analysis of released gases from aq.  $\text{NH}_3\text{BH}_3$  solution (1.0 wt.%) stirred in carbon dioxide at room temperature. Peaks at  $m/z=2$ , 18 and 44 are due to  $\text{H}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Fragment ion peaks at  $m/z=12$ , 16 and 28 are due to C, O and CO.

the fragment ion peaks at  $m/z=12$ , 16 and 28 corresponding to C, O and CO. It is obvious that  $\text{H}_2$  has a high concentration in the gas phase.

As far as the reaction mechanism for hydrogen generation from the aq.  $\text{NH}_3\text{BH}_3$  solution with solid acids is concerned, it is reasonable to consider that the activation process takes place due to the acidic protons from the solid acids in aqueous medium, which promote the dissociation of the B–N bond and the hydrolysis of  $\text{BH}_3$  species to produce borate ion species along with the hydrogen release (Eq. (1a)). Because the acidity of the solid acids is higher than that of boric acid, the resulting borate ion species reacts with  $\text{H}^+$  to produce boric acid as the equilibrium in Eq. (1b) shifts to the right side. During the reaction, the acidic sites of the solid acids are decreased as the used solid acids exhibit a much lower activity in this reaction, whereas the acidity can be recovered by treatment with acid solution (Fig. 6). In the case of the reaction with carbon dioxide, carbonic acid is first formed by the dissolution of carbon dioxide in water ( $\text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$ ) [30], which has an acidity higher than boric acid [31] and behaves as an acid during the dissociation and hydrolysis of  $\text{NH}_3\text{BH}_3$  similar to the solid acids.

The stability of the aq.  $\text{NH}_3\text{BH}_3$  solution is essential for its application. Previous investigations have shown significant hydrogen loss from an aq.  $\text{NH}_3\text{BH}_3$  solution stored in air [14]. In the present study, we have found that the  $^{11}\text{B}$  resonance remains unchanged for 80 days under an Ar atmosphere, indicating the high stability of the aq.  $\text{NH}_3\text{BH}_3$  solution in an inert atmosphere (Fig. 2a and b). In addition, our present observations have indicated that an aq.  $\text{NH}_3\text{BH}_3$  solution stored under an Ar atmosphere for 80 days (Fig. 4d) can release hydrogen in almost the same amount as a fresh aq.  $\text{NH}_3\text{BH}_3$  solution (Fig. 4a), confirming the stability of aq.  $\text{NH}_3\text{BH}_3$  solutions in an inert atmosphere. The reactivity of aq.  $\text{NH}_3\text{BH}_3$  towards carbon dioxide, as observed in the present study, may account for its instability in air.

At  $25^\circ\text{C}$ , the standard-state enthalpy change for the reaction  $\text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4^+(\text{aq.}) + \text{BO}_2^-(\text{aq.}) + 3\text{H}_2$  can be calculated to be  $-155.97 \text{ kJ mol}^{-1}$  from the standard enthalpies of  $-178 \text{ kJ mol}^{-1}$  ( $\text{NH}_3\text{BH}_3$ ),  $-571.66 \text{ kJ mol}^{-1}$  ( $2\text{H}_2\text{O}$ ),  $-133.26 \text{ kJ mol}^{-1}$  ( $\text{NH}_4^+$ ),  $-772.37 \text{ kJ mol}^{-1}$  ( $\text{BO}_2^-$ ), and 0 ( $3\text{H}_2$ ) [14,31] and this reaction is exothermic. In comparison, the standard-state enthalpy change for the hydrogen generation reaction of sodium borohydride  $\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2$  is  $-217 \text{ kJ mol}^{-1}$  [3]. In the present  $\text{NH}_3\text{BH}_3$  system, 0.195 g of hydrogen is liberated per 1 g of the  $\text{NH}_3\text{BH}_3$ . In comparison, 0.084 g of hydrogen per 1 g of NaH, 0.213 g of hydrogen per 1 g of  $\text{NaBH}_4$ , and 0.254 g of hydrogen per 1 g of LiH are released in the respective hydrolysis reactions under appropriate conditions [3]. We can analyze the feasibility of using the chemical hydrides by hydrolysis as potential  $\text{H}_2$  source for fuel cell applications. Assume a standard PEM fuel cell operates at 0.7 V, the generation of  $1 \text{ g H}_2 \text{ s}^{-1}$  corresponds to  $96.5 \text{ kA} \times 0.7 = 68 \text{ kW}$  [3]. For supplying hydrogen to such a PEMFC system producing 1 kW of electric power for 8 h, the amounts of  $\text{NH}_3\text{BH}_3$ , NaH,  $\text{NaBH}_4$ , and LiH needed are 2.17, 5.04, 1.99, and 1.67 kg, respectively.

NaBH<sub>4</sub> has been extensively studied as a hydrogen storage material, which is a good candidate for hydrogen generation under ambient conditions. Similar to the excellent hydrogen generation system by NaBH<sub>4</sub>, the present aq. NH<sub>3</sub>BH<sub>3</sub> system also has advantages such as high stability and safety, easy control and high kinetics of hydrogen release. In comparison with the aqueous alkaline borohydride system, which requires a highly basic NaOH solution to stabilize the starting material NaBH<sub>4</sub>, it is noteworthy that the present NH<sub>3</sub>BH<sub>3</sub> system has an advantage that the present aqueous solution is close to neutral. The product of the present reaction, borate ion or boric acid, is environmentally benign and the generated H<sub>2</sub> gas is sufficiently pure, which can be used directly in PEM fuel cells.

#### 4. Conclusions

In summary, an efficient, pure-hydrogen generation system based on the hydrolysis of aq. NH<sub>3</sub>BH<sub>3</sub> in the presence of low-cost solid acids has been revealed. Solid acids and carbon dioxide exhibit significant activity for the dissociation and hydrolysis of aq. NH<sub>3</sub>BH<sub>3</sub> at room temperature to generate hydrogen with an H<sub>2</sub>/NH<sub>3</sub>BH<sub>3</sub> ratio up to 3.0. The reaction rate depends on the type of solid acid. Especially, Dowex and Amberlyst, the two low-cost solid acids often used as catalysts in a variety of reactions, exhibit reaction kinetics higher than the noble metal catalysts. This NH<sub>3</sub>BH<sub>3</sub> system has an advantage that the present aqueous solution is close to neutral. The present system may have potential to find its application in various hydrogen-operated devices.

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