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Review

Catalytic hydrolysis of ammonia borane for chemical hydrogen storage

Hai-Long Jiang, Qiang Xu*

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

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ABSTRACT

Hydrogen storage for vehicular applications requires high gravimetric/volumetric storage capacity. Ammonia borane (NH_3BH_3, AB), having hydrogen content as high as 19.6 wt%, has been considered as a highly potential hydrogen storage medium for on-board applications. The AB hydrolytic dehydrogenation system presents a hydrogen capacity up to 7.8 wt% of the starting materials AB and H_2O, showing its high potential for chemical hydrogen storage. With significant research efforts, the reaction kinetics has been greatly enhanced under ambient conditions and the catalyst cost has been remarkably lowered for the hydrolytic dehydrogenation of AB in recent five years. Herein, we briefly review the research progresses in catalytic hydrolytic dehydrogeneration from ammonia borane for chemical hydrogen storage. Moreover, we also concisely discuss hydrogen release from aqueous hydrazine boranes, derivatives of AB, as new hydrogen storage materials.

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1. Introduction

There is an increasing and impending demand for sufficient energy supply along with the continuously growing population and the rising standards of living in the world. Hydrogen, as a globally accepted clean and source-independent energy carrier [1], has a high energy content per mass compared to petroleum (120 MJ kg^{-1} for hydrogen versus 44 MJ kg^{-1} for petroleum) and can be energy sources for different end uses, such as hydrogen fuel cell vehicles and portable electronics.

For transportation applications, the energy carrier is required to have a small volume and mass, as well as high energy content, so that it can be stored in a small space and used in a high efficiency. In order to meet the targets set by the U.S. Department of Energy (US DOE) [2], different storage solutions have been developed and a large number of publications on hydrogen storage materials, such as metal hydrides [3,4], sorbents [5–7], on-board reforming of hydrocarbon into hydrogen [8], and organic materials [9] have been reported, while big challenges still remain.

Chemical storage materials with high hydrogen contents are highly promising as hydrogen sources for fuel cells. Among them, boron- or nitrogen-based compounds, such as, $LiNH_2$–LiH, Li/$NaBH_4$ and N_2H_4, etc., have attracted much attention [10–14]. The simplest B–N compound of ammonia borane (NH_3BH_3, AB), with low molecular weight (30.9 g mol^{-1}) and a hydrogen capacity as high as 19.6 wt%, exceeding those of gasoline and Li/$NaBH_4$, is today the most promising boron hydride for on-board hydrogen storage applications [6,12,15–24].

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* Corresponding author. Tel.: +86 72 751 9562; fax: +86 72 751 7942.
E-mail address: q.xu@aist.go.jp (Q. Xu).

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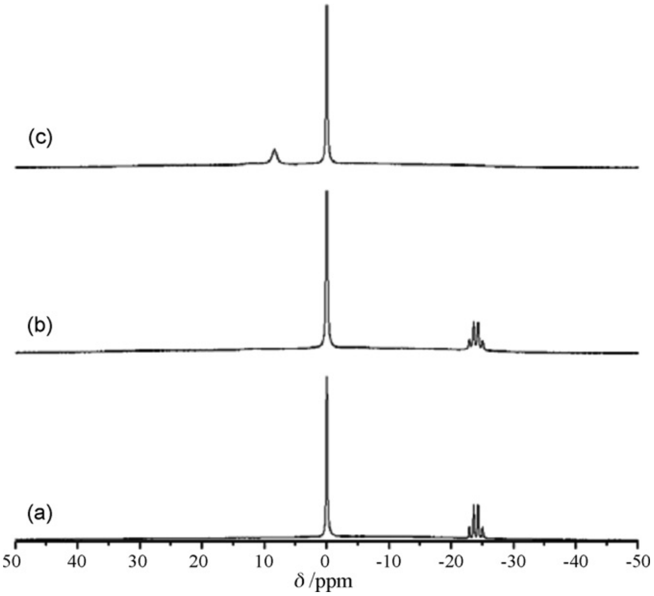

Fig. 1. ^{11}B NMR spectra of (a) aqueous AB solution freshly prepared, (b) after 1 month under Ar atmosphere, and (c) after reaction in the presence of suitable catalyst. The peak at 0 ppm is due to the external reference $BF_3 \cdot (C_2H_5)_2O$.

Ammonia borane is a colorless molecular crystal with tetragonal structure under ambient conditions and soluble in H_2O and other relatively polar solvents (for example, methanol) [18,22]. Pure AB has a density of 0.74 g cm^{-3} and a melting point of 110–125 °C. It is first synthesized in the mid-1950s for developing boron hydride based high-energy fuels for jets and rockets. Presently, several laboratory-scale preparation methods have also been established and one of the most effective method gives high purity ($\geq 98\%$) and high yield ($\geq 95\%$), which involves the reaction of $NaBH_4$ and ammonium formate (HCO_2NH_4) in dioxane [18,25]. Most importantly, AB is nontoxic, stable, environmental benign, and can be safely handled under ambient conditions, which greatly facilitate its application.

To data, considerable works involving the hydrogen release from the thermal dehydrogeneration of AB have been reported [15,16,26–29]. The thermal dehydrogeneration temperature can be lowered in an organic solution or ionic liquid [26]. In contrast to neat AB, the threshold temperature can be reduced and volatile byproducts can be effectively suppressed by loading AB into different scaffolds (such as, SBA-15 [15], CMK-3 [27], and porous metal-organic framework [16]) or doping with Li [27]. In addition, reaction of AB with metal hydrides (such as, LiH, NaH [28], or CaH_2 [29]) yields metal amidoboranes of $M(NH_2BH_3)_n$ (M = Na, $n = 1$; M = Ca, $n = 2$), which can release hydrogen at lower temperatures with much lower propensity for borazine formation. Generally speaking, thermal decomposition of AB needs high temperature and power consumption. In contrast, the catalytic hydrolysis provides a more promising method for hydrogen generation from AB. Colorless aqueous solution of AB is highly stable (over 1 month) in an argon atmosphere, exhibiting a quadruplet centered at $\delta = -23.9$ ppm with $^1J_{B-H} = 91$ Hz in the ^{11}B NMR spectra (Fig. 1) whereas it undergoes very slow hydrolysis reaction in air due to the catalytic activity of carbon dioxide [30,31]. The hydrolysis reaction (Eq. (1)) can be significantly accelerated in the presence of suitable catalysts, as evidenced by the decrease until the disappearance of the ^{11}B peak at −23.9 ppm for aqueous NH_3BH_3 and the appearance of an additional low field-shifted single ^{11}B resonance due to the production of borate species (Fig. 1). Therefore, one of the major obstacles for the practical application of the catalytic hydrolysis dehydrogenation of AB is to develop efficient and economical catalysts to improve the kinetic properties under moderate reaction conditions.

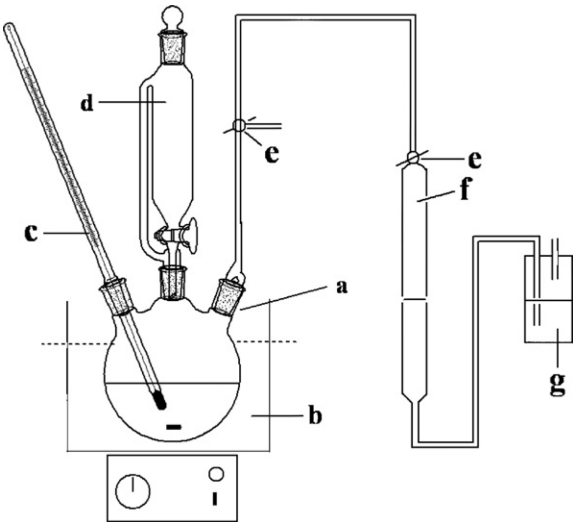

Fig. 2. The reaction apparatus for monitoring hydrogen generation from aq. AB. (a) three-necked flask, (b) water-bath stirrer, (c) thermometer/pH meter, (d) additional funnel with a pressure equalized arm, (e) gas valve, (f) gas burette and (g) reservoir.

$$NH_3BH_3 + 2H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2 \qquad (1)$$

In this review, we briefly survey the research progresses in catalytic hydrogen generation from hydrolysis of AB under ambient conditions in recent five years since the first work was published by our group in 2006 [30].

2. Experimental set-up and procedure

2.1. Experimental set-up

As illustrated in Fig. 2, an experimental apparatus is devised for monitoring the hydrogen generation amount/rate from the AB aqueous 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 or pH meter.

2.2. Experimental procedure

The AB powder is placed in the three-necked flask and the reaction is started by stirring the mixture of the AB and the catalyst aqueous solution added from the additional funnel (for liquid catalysts or catalyst precursors); or the AB powder and catalyst are placed in the flask and distilled water added from the funnel to trigger the reaction (for solid catalysts). The evolution of gas was monitored using the gas burette (the water levels are adjusted to equal height by moving the reservoir during hydrogen evolution). The solution temperature can be controlled by a water-bath stirrer (coolant can be changed with water for cooling if necessary). After the completion of the reaction, the solutions can be filtered to separate the catalyst as residue. The filtrates and the catalyst are used for further characterizations (such as, ^{11}B NMR, powder XRD, TEM, etc.).

3. Catalysts

Through five years of exploration and efforts, it has been found that almost all of active catalysts toward hydrolysis of AB are highly