

A portable hydrogen generation system: Catalytic hydrolysis of ammonia–borane

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Abstract

Ammonia–borane, NH_3BH_3 , dissolves in water to form a stable solution, to which the addition of a catalytic amount of suitable metal catalysts leads to hydrogen release with an H_2 to NH_3BH_3 ratio up to 3.0, corresponding to 8.9 wt.% of the starting materials NH_3BH_3 and H_2O . This article presents a brief overview of the hydrogen generation system based on the catalytic dissociation and hydrolysis of ammonia–borane, which possesses high potential to find application to portable fuel cells.

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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 bottleneck to the application of PEMFC as portable power sources. PEM fuel cells require stable and high-capacity hydrogen generator at ambient condition. Recently, due to high hydrogen contents, chemical hydrides are expected as potential sources for hydrogen used in portable PEM fuel cells. Sodium borohydride, NaBH_4 , is one of the potential chemical hydrides, which shows a number of advantages as a hydrogen source for portable application, while it needs highly basic NaOH solution to stabilize the starting material NaBH_4 [1–6]. Hydrogen generation by the hydrolysis of LiBH_4 has also been reported [7].

The ammonia–borane complex, NH_3BH_3 , which is stable under ordinary storage conditions [8–13], contains 19.6 wt.% of hydrogen. Dehydrogenation of NH_3BH_3 has been studied from both solid-state and solution approaches. The pyrolysis of NH_3BH_3 in solid-state has been widely investigated [14–18].

Heating acetonitrile and etheral solutions of NH_3BH_3 releases stepwise hydrogen leading to the formation of cyclotriborazane and borazine along with other minor products [19]. Catalytic dehydrocoupling of NH_3BH_3 and its derivatives in organic solvents along with evolution of hydrogen gas has been reported [20–21]. Dehydrogenation of ammonia–borane in ionic liquid at elevated temperatures results in release of hydrogen up to 1.6 equivalent along with traces of borazine [22].

This paper presents a brief overview focusing on the metal-catalyzed dissociation and hydrolysis of ammonia–borane, of which the detailed experimental procedures and discussions are available from the recent literature [10–13]. This system has the following advantages: (1) it does not need highly basic solution to stabilize the starting material and the solution is close to neutral; (2) the reaction proceeds at room temperature with high kinetics in the presence of suitable catalysts, among which not only noble metal but also non-noble metal catalysts are available; (3) this system has a high hydrogen capacity, which releases hydrogen with an H_2 to NH_3BH_3 ratio up to 3.0, corresponding to 8.9 wt.% of the starting materials NH_3BH_3 and H_2O . A hydrogen generation system for portable fuel cells may be established on the basis of the catalytic hydrolysis of ammonia–borane.

2. Stability of aqueous NH_3BH_3 solution

For a hydrogen generation system, a high stability of starting material is the first important prerequisite. NH_3BH_3 dissolves

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in water to form a colorless solution (pH 9.1), which exhibits a quadruplet centered at $\delta = -23.9$ ppm with $^1J_{B-H} = 91$ Hz in the ^{11}B NMR spectra [10,11]. This ^{11}B resonance remains unchanged for more than 80 days under an argon atmosphere, indicating the high stability of NH_3BH_3 in water. Noteworthy, carbon dioxide, acting as an acid in this case, is active for the hydrolysis of aqueous NH_3BH_3 [11]. This observation suggests avoiding exposure to air for long-term storage of NH_3BH_3 .

3. Metal catalyzed hydrolysis of NH_3BH_3

3.1. Noble metal catalysts

The addition of a catalytic amount of suitable metal catalysts such as Pt, Rh, and Pd into the aqueous NH_3BH_3 solution leads to vigorous release of hydrogen gas with an H_2 to NH_3BH_3 ratio up to 3.0, corresponding to 8.9 wt.% of the starting materials NH_3BH_3 and H_2O (Eq. (1)) [10]. The quadruplet ^{11}B resonance at $\delta = -23.9$ ppm disappears while a single ^{11}B resonance around 8 ppm due to products such as H_2BO_3 , BO_2^- and other borate species in equilibrium in the solution, which undergoes rapid exchange between each other on the NMR time scale, appears instead [10]. The reaction rate significantly depends on the metal catalysts or precatalysts employed (Table 1). Pt black exhibits a high catalytic activity, with which the reaction is completed in 12 min with $\text{H}_2/\text{NH}_3\text{BH}_3 = 3.0$. A slightly lower catalytic activity was observed for $[\text{Rh}(1,5\text{-COD})(\mu\text{-Cl})_2]$; it appears that $[\text{Rh}(1,5\text{-COD})(\mu\text{-Cl})_2]$ is reduced upon NH_3BH_3 addition and Rh clusters and/or colloids may be the active catalytic species. This Rh catalyst has also been used for the hydrolysis of ammonia triborane, a closely related reaction reported very recently [23]. With Pd black, the hydrolysis reaction of NH_3BH_3 needs much longer time to reach the completion. The other noble metal compounds such as RuO_2 , Ag_2O , Au_2O and IrO_2 do not give active catalysts for this reaction.

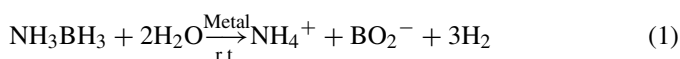


Table 1

Hydrogen generation in the presence of noble metals from aqueous ammonia-borane^a

| Catalyst or catalyst precursor | Maximum $\text{H}_2/\text{NH}_3\text{BH}_3$ ratio ^b | Time for reaction completion (min) |
|--|--|------------------------------------|
| 20 wt.% Pt/C | 3.0 | 2.0 |
| 40 wt.% Pt/C | 3.0 | 3.0 |
| PtO_2 | 3.0 | 8.0 |
| Pt black | 3.0 | 12 |
| K_2PtCl_4 | 3.0 | 19 |
| $[\text{Rh}(1,5\text{-COD})(\mu\text{-Cl})_2]$ | 2.6 | 15 |
| Pd black | 2.6 | 250 |

^a 0.33 wt.% aqueous NH_3BH_3 ; metal/ NH_3BH_3 , 0.018.

^b $\text{H}_2/\text{NH}_3\text{BH}_3$ ratio at the completion of reaction.

Investigation on different Pt catalysts or precatalysts with the Pt contents normalized to the same has illustrated that the catalytic activity remarkably depends on the catalysts or precatalysts used (Table 1) [10]. The catalytic activities are in the order of 20 wt.% Pt/C > 40 wt.% Pt/C > PtO_2 > Pt black > K_2PtCl_4 . It is considered that the precatalysts PtO_2 and K_2PtCl_4 are reduced by NH_3BH_3 during the reaction to produce Pt clusters and/or colloids, similar to the case of $[\text{Rh}(1,5\text{-COD})(\mu\text{-Cl})_2]$. TEM studies after reaction have shown that the activities of these catalysts are correlated to the Pt particle sizes [10]. For example, with the Pt contents normalized to the same, the 20 wt.% Pt/C catalyst has smaller particle size and higher catalytic activity in comparison with the 40 wt.% Pt/C catalyst.

Supporting the noble metals on suitable supports significantly enhances the catalytic activities (Table 2) [13]. The $\gamma\text{-Al}_2\text{O}_3$ supported Ru, Rh, and Pt catalysts are highly active for the hydrolysis of NH_3BH_3 , exhibiting hydrogen release of $\text{H}_2/\text{NH}_3\text{BH}_3 = 3.0$ in 3.0, 1.3 and 0.75 min, respectively. Pd/ $\gamma\text{-Al}_2\text{O}_3$ shows a lower catalytic activity, releasing hydrogen of $\text{H}_2/\text{NH}_3\text{BH}_3 = 2.9$ in 120 min. The Au/ $\gamma\text{-Al}_2\text{O}_3$ catalyst exhibits a much lower catalytic activity for hydrolysis of aq. NH_3BH_3 , releasing hydrogen of $\text{H}_2/\text{NH}_3\text{BH}_3 = 1.9$ in 610 min. It is noted

Table 2

Catalytic activities of supported noble metals for the hydrogen generation from aqueous ammonia-borane^a

| Catalyst | Average particle size ^b (nm) | Maximum $\text{H}_2/\text{NH}_3\text{BH}_3$ ratio ^c | Time for reaction completion (min) |
|--|---|--|------------------------------------|
| $\gamma\text{-Al}_2\text{O}_3$ | - | _d | _d |
| C ^e | - | _d | _d |
| SiO_2 ^f | - | _d | _d |
| 2 wt.% Ru/ $\gamma\text{-Al}_2\text{O}_3$ | 1.8 | 3.0 | 3.0 |
| 2 wt.% Rh/ $\gamma\text{-Al}_2\text{O}_3$ | 2.5 | 3.0 | 1.3 |
| 2 wt.% Rh/ $\gamma\text{-Al}_2\text{O}_3$ ^g | 2.5 | 3.0 | 1.6 |
| 2 wt.% Pd/ $\gamma\text{-Al}_2\text{O}_3$ | 3.6 | 2.9 | 120 |
| 2 wt.% Pt/ $\gamma\text{-Al}_2\text{O}_3$ | 1.5 | 3.0 | 0.75 |
| 2 wt.% Pt/C | 1.9 | 3.0 | 1.5 |
| 2 wt.% Pt/ SiO_2 | 5.1 | 3.0 | 3.0 |
| 2 wt.% Au/ $\gamma\text{-Al}_2\text{O}_3$ | 2.6 | 1.9 | 610 |

^a 1 wt.% aq. NH_3BH_3 ; metal/ NH_3BH_3 , 0.018.

^b Calculated from TEM micrographs.

^c $\text{H}_2/\text{NH}_3\text{BH}_3$ ratio at the completion of reaction.

^d No reaction.

^e VULCAN[®] carbon.

^f Fumed SiO_2 .

^g Used catalyst recycled by washing and then dried at 100 °C for one night.

Table 3
Activation energies of hydrolysis of NH_3BH_3 (1 wt.%) on various $\gamma\text{-Al}_2\text{O}_3$ supported catalysts

| Catalyst | Activation energy (kJ mol^{-1}) |
|---|--|
| 2 wt.% Ru/ $\gamma\text{-Al}_2\text{O}_3^{\text{a}}$ | 23 |
| 2 wt.% Rh/ $\gamma\text{-Al}_2\text{O}_3^{\text{a}}$ | 21 |
| 2 wt.% Pt/ $\gamma\text{-Al}_2\text{O}_3^{\text{a}}$ | 21 |
| 10 wt.% Co/ $\gamma\text{-Al}_2\text{O}_3^{\text{b}}$ | 62 |

^a Metal/ NH_3BH_3 , 0.009.

^b Metal/ NH_3BH_3 , 0.018.

that the bulk RuO_2 and Au_2O_3 precursors do not give active catalysts for the hydrolysis of NH_3BH_3 [10], while the supported Ru and Au nano particles are catalytically active, suggesting that the particle size is an important factor for catalytic activity.

The hydrogen release rate is not largely dependent of the NH_3BH_3 concentration and the high activities of the noble-metal catalysts can be kept in a wide range of concentration up to saturation [10,13]. No significant deactivation was observed for the recycled noble metal catalysts. For example, hydrogen of stoichiometric amount ($\text{H}_2/\text{NH}_3\text{BH}_3$ ratio = 3.0) was released in 1.6 min with the recycled 2 wt.% Rh/ $\gamma\text{-Al}_2\text{O}_3$ catalyst, almost the same as observed with the fresh catalyst (Table 2).

The activation energies are 23, 21 and 21 kJ mol^{-1} for the hydrolysis of NH_3BH_3 with the Ru/ $\gamma\text{-Al}_2\text{O}_3$, Rh/ $\gamma\text{-Al}_2\text{O}_3$ and Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalysts, respectively (Table 3) [13]. For comparison, the activation energy is 29 kJ mol^{-1} for the hydrolysis of NaBH_4 with the Ru(0) nanoclusters [5].

3.2. Non-noble metal catalysts

For practical use, the development of low-cost and highly efficient catalysts is desired. Although Co powder does not show catalytic activity to the hydrolysis of NH_3BH_3 [10], supporting Co nanoparticles on supports such as $\gamma\text{-Al}_2\text{O}_3$, SiO_2 and C results in active catalysts, with which hydrogen is released with an almost stoichiometric amount from aqueous NH_3BH_3 and the reaction can be completed in 55–70 min (Table 4) [12]. Among the different supports of $\gamma\text{-Al}_2\text{O}_3$, SiO_2 and C, the C support gives the most active Co catalyst. The supported Ni nanoparticles are almost equally active but the supported Cu nanoparticles show lower activity. The activities of the supported

Table 4
Catalytic activities of supported non-noble metals for the hydrogen generation from aqueous ammonia–borane ^a

| Catalyst | Average metal particle size ^b (nm) | Maximum $\text{H}_2/\text{NH}_3\text{BH}_3$ ratio ^c | Time for reaction completion (min) |
|--|---|--|------------------------------------|
| 10 wt.% Co/ $\gamma\text{-Al}_2\text{O}_3$ | 13 | 2.9 | 70 |
| 10 wt.% Co/ SiO_2^{d} | 12 | 2.9 | 70 |
| 10 wt.% Co/C ^e | 2.5 | 2.9 | 55 |
| 10 wt.% Ni/ $\gamma\text{-Al}_2\text{O}_3$ | 3.8 | 2.9 | 65 |
| 10 wt.% Cu/ $\gamma\text{-Al}_2\text{O}_3$ | 17 | 2.9 | 590 |
| 10 wt.% Fe/ $\gamma\text{-Al}_2\text{O}_3$ | 16 | – ^f | – ^f |

^a 1 wt.% aq. NH_3BH_3 ; metal/ NH_3BH_3 , 0.018.

^b Calculated on the basis of the width of the strongest X-Ray diffraction peak (1 1 1) for Co, Ni and Cu catalysts, and (1 1 0) for Fe catalysts.

^c $\text{H}_2/\text{NH}_3\text{BH}_3$ ratio at the completion of reaction.

^d Fumed SiO_2 .

^e VULCAN[®] carbon.

^f No reaction.

Table 5
Hydrogen generation by hydrolysis of chemical hydrides for fuel cells

| Reaction | H_2 Yield (g H_2/g hydride) | Capacity ^a (Wh/g hydride) |
|--|---|---|
| $\text{LiH} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2$ | 0.25 | 4.7 |
| $\text{NaH} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2$ | 0.084 | 1.6 |
| $\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2$ | 0.21 | 4.0 |
| $\text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{BO}_2^- + 3\text{H}_2$ | 0.19 | 3.7 |

^a Assuming a standard PEM fuel cell operates at 0.7 V, the generation of 1.0 g $\text{H}_2 \text{ s}^{-1}$ corresponds to $96.5 \text{ kA} \times 0.7 = 68 \text{ kW}$.

Co and Ni catalysts are lower than the Pt, Rh, and Ru catalysts, but higher than the Pd catalysts. These non-noble metal catalysts are remarkably valuable from the viewpoint of practical use to fuel cell systems. In contrast with Co, Ni and Cu, supported Fe nanoparticles are catalytically inactive for this reaction [12].

The activation energy is 62 kJ mol^{-1} for the hydrolysis of NH_3BH_3 with the Co/ $\gamma\text{-Al}_2\text{O}_3$ catalyst, higher than the activation energies of 21–23 kJ mol^{-1} for the $\gamma\text{-Al}_2\text{O}_3$ supported Ru, Rh and Pt catalysts [12,13]. This is consistent with the observation of the hydrogen release rates with these catalysts; a higher catalytic activity corresponds to smaller activation energy.

4. Comparison with other chemical hydrides

At 25 °C, the standard-state enthalpy change for Eq. (1) is -156 kJ mol^{-1} from the standard enthalpies of -178 kJ mol^{-1} (NH_3BH_3), -572 kJ mol^{-1} ($2\text{H}_2\text{O}$), -133 kJ mol^{-1} (NH_4^+), -772 kJ mol^{-1} (BO_2^-), and 0 (3H_2) [24] and this reaction is exothermic. In comparison, the standard-state enthalpy change for the hydrolysis of sodium borohydride $\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2$ is -217 kJ mol^{-1} [3]. From the catalytic hydrolysis reaction 0.19 g of hydrogen is liberated per 1.0 g of the NH_3BH_3 , whereas 0.25 g of hydrogen per 1 g of LiH, 0.084 g of hydrogen per 1 g of NaH, and 0.21 g of hydrogen per 1 g of NaBH_4 are released in the respective hydrolysis reactions under appropriate conditions (Table 5) [25]. We can analyze the feasibility of using the chemical hydrides by hydrolysis as potential H_2 source for fuel cells. The generation of 1.0 g $\text{H}_2 \text{ s}^{-1}$ corresponds to $96.5 \text{ kA} \times 0.7 = 68 \text{ kW}$, assuming a standard PEM fuel cell operates at 0.7 V [25]. For supplying

hydrogen to such a PEMFC system to produce 1 kW of electric power for 1 h, the amounts of LiH, NaH, NaBH₄, and NH₃BH₃ needed are 0.21, 0.63, 0.25, and 0.27 kg, respectively.

5. Summary and future prospects

A portable hydrogen generation system is expected to be established on the basis of the metal-catalyzed dissociation and hydrolysis of ammonia–borane. This system does not need highly basic solution to stabilize the starting material. The reaction proceeds at room temperature with high kinetics in the presence of suitable catalysts; not only noble metal but also non-noble metal catalysts are available. A high hydrogen capacity up to 8.9 wt.% of the starting materials NH₃BH₃ and H₂O can be achieved. The mechanism of this reaction and the regeneration of ammonia–borane will be the focuses in future experimental and theoretical studies. For the practical use to portable fuel cells, the development of a high-performance system consisting of a reactor, solution supplier and reaction controller is expected.

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