

A high-performance hydrogen generation system: Transition metal-catalyzed dissociation and hydrolysis of ammonia–borane

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Received 7 April 2005; received in revised form 16 May 2005; accepted 17 May 2005

Available online 7 July 2005

Abstract

A high-performance hydrogen generation system based on transition metal-catalyzed dissociation and hydrolysis of ammonia–borane complex (NH_3BH_3) at room temperature has been achieved. NH_3BH_3 dissolves in water to form a solution stable in the absence of air. The addition of a catalytic amount of suitable metal catalysts such as Pt, Rh, and Pd into the solutions with various concentrations leads to rigorous 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 . The Pt catalysts are the most active and no significant deactivation was observed for the recycled catalysts. This new system possesses high potential to find its application to portable fuel cells.

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Keywords: Ammonia borane; Hydrogen generation; Hydrolysis; Metal catalysts; Platinum

1. Introduction

Hydrogen, H_2 , is a globally accepted clean fuel. The use of hydrogen fuel cells in vehicles or in portable electronic devices requires lightweight H_2 storage or “on-board” hydrogen generation. There have been a large number of reports on H_2 storage [1,2] and on “on-board” reforming of hydrocarbons into H_2 [3]. However, all the methods are not suitable for portable applications due to the low volumetric and gravimetric efficiency of hydrogen storage and the difficulties in operation of high-temperature reforming processes of hydrocarbons as well as to the safety issue. Significant reports dealing with sodium borohydride (NaBH_4) as a potential carbon-free portable hydrogen source are available, whereas this system needs a highly basic solution [4–7]. For portable hydrogen generation systems, in particular, the most important are safety, ease to control and high kinetics of the hydrogen release along with a high hydrogen content.

In this manuscript, we report a new excellent catalytic system suitable for use as a portable hydrogen source from the above points of view, which is based on transition metal-catalyzed dissociation and hydrolysis of ammonia–borane complex (NH_3BH_3) at room temperature.

Ammonia–borane complex contains 19.6 wt.% hydrogen. There have been thus far a number of reports on the H_2 release from NH_3BH_3 whereas improvements of the reaction control are needed for application to portable hydrogen sources. Previous investigations have shown that NH_3BH_3 undergoes acid-catalyzed hydrolysis to produce boric acid along with the H_2 release [8,9]. The pyrolysis of NH_3BH_3 has been widely investigated; when heating it liberates H_2 in a sequence of reactions between 137 and 400 °C that reaches 19.6 wt.% of its initial mass [10–12]. A catalytic dehydrocoupling route to derivatives of aminoborane, $(\text{NH}_2\text{BH}_2)_3$, and borazine, $(\text{NHBH})_3$, from either primary or secondary amine–borane adducts has been recently developed using late transition metal complexes as precatalysts [13–15]. Our present work reveals unprecedented high catalytic activity of transition metals to the dissociation and hydrolysis of NH_3BH_3 at room

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temperature, which is accompanied by a release of H₂ up to 8.9 wt.% of the starting materials, NH₃BH₃ and H₂O.

2. Experimental

Commercial ammonia–borane complex NH₃BH₃ (Tech. 90%, Aldrich) was used without further purification. Metal catalysts and precatalysts, [Rh(1,5-COD)(μ-Cl)]₂, RuO₂, W, (NH₄)₂[TiO(C₂O₄)₂], Au₂O₃, IrO₂ (Aldrich), PtO₂, Pd black (Mitsuwa Pure Chemicals), 20 wt.% Pt/C, 40 wt.% Pt/C, Pt black (Johnson Matthey), Ag₂O and K₂PtCl₄ (Wako Pure Chemicals) were purchased and used as received.

The reactions were carried out at room temperature and under argon atmosphere. A weighed solid metal catalyst or precatalyst was kept in a two-necked round-bottom flask with one of the flask openings connected to a gas burette and another to an addition funnel with a pressure-equalization arm. The reaction was started by stirring the mixture of the metal catalyst and the aqueous 0.33 wt.% NH₃BH₃ solution added from the addition funnel and the evolution of gas was monitored using the gas buret. After the completion of reaction, the solutions were filtered to separate the metal catalysts as residues, which were dried and used for TEM measurements, and the filtrates used for ¹¹B NMR and pH measurements.

¹¹B NMR spectra were recorded on a JEOL JNM-AL400 spectrometer operating at 128.15 MHz. Liquid samples of the filtrates, in which D₂O was included as a lock, were contained in sample tubes of 5 mm o. d., in which coaxial inserts of BF₃·(C₂H₅)₂O as an external reference were placed. ¹¹B chemical shifts are given in δ unit (parts per million) downfield from BF₃·(C₂H₅)₂O. TEM images were recorded using a Hitachi H-9000NA transmission electron microscope. Identification of H₂ was performed using a Balzers Prisma QMS 200 mass spectrometer.

3. Results and discussion

NH₃BH₃ dissolves in water to form a colorless solution (pH=9.1), which exhibits a quadruplet centered at δ = -23.9 ppm with ¹J_{B-H} = 91 Hz in the ¹¹B NMR spectra (Fig. 1a), in agreement with the previous reports [16–19]; both the pH and δ values are independent of concentration. The ¹¹B resonance keeps unchanged for 30 days under an Ar atmosphere (Fig. 1b), indicating the high stability of NH₃BH₃ in water. Surprisingly, the addition of a catalytic amount of suitable metal catalysts such as platinum black or precatalysts into this solution leads to rigorous release of H₂, which is identified by mass spectrometry, with an H₂ to NH₃BH₃ ratio up to 3.0. After the reaction is completed, the ¹¹B peak at -23.9 ppm for aqueous NH₃BH₃ disappears, whereas the resulting solution gives a low field-shifted single ¹¹B resonance (Fig. 1c). The resulting solutions after the reactions of 0.33, 1.0 and 5.0 wt.% NH₃BH₃ in the presence of Pt black

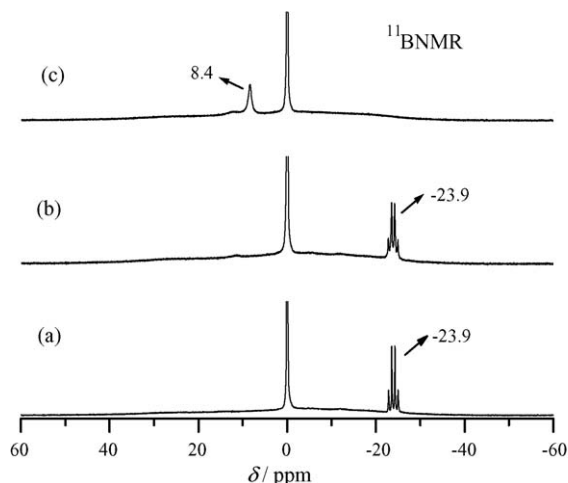
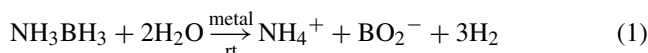


Fig. 1. ¹¹B NMR spectra of (a) aqueous NH₃BH₃ solution (0.33 wt.%) freshly prepared, (b) after 30 days following (a) under Ar atmosphere, and (c) after reaction (25 min) of (a) in the presence of Pt black. The peak at 0 ppm is due to the external reference BF₃·(C₂H₅)₂O.

exhibit pH values of 9.5, 9.7 and 10.0 and single ¹¹B resonances at 8.4, 7.8 and 6.8 ppm, respectively. We measured the ¹¹B NMR spectra of an aqueous H₃BO₃ solution (pH 5.5) and two aqueous solutions of NH₄OH/H₃BO₃ with different ratios (pH 9.6 and 11.4), which exhibited single ¹¹B peaks at 19.0, 7.4 and 1.9 ppm, respectively. An equilibrium process between H₃BO₃, BO₂⁻ and other borate species, which undergo rapid change between each other in the solution on the NMR time scale, would account for the observed low field-shifted single ¹¹B resonance and its pH dependence. Therefore, the reaction can be formulated as shown in Eq. (1):



As shown in Fig. 2, the reaction rate significantly depends on the metal catalysts or precatalysts employed. The Pt catalyst exhibits the highest catalytic activity, with which the reaction is completed in about 10 min with H₂/NH₃BH₃ = 3.0. A similar high catalytic activity was observed for [Rh(1,5-COD)(μ-Cl)]₂, whereas with Pd black it needs 250 min to reach the completion of reaction. The other metals and metal compounds tested show much lower activities or are almost catalytically inactive, with which the ¹¹B resonance at -23.9 ppm due to the starting material NH₃BH₃ remains almost unchanged after 200 min reactions.

We have tested the catalytic activities on different Pt catalysts or precatalysts with the Pt contents normalized to the same (Pt/NH₃BH₃ = 0.018) and found that the catalytic activity remarkably depends on the catalysts or precatalysts used. As shown in Fig. 3, the catalytic activities are in the order of 20 wt.% Pt/C > 40 wt.% Pt/C > PtO₂ > Pt black > K₂PtCl₄. The carbon supported Pt catalysts exhibit the highest activities, among which a lower loading corresponds to a higher catalytic activity, suggesting that the high

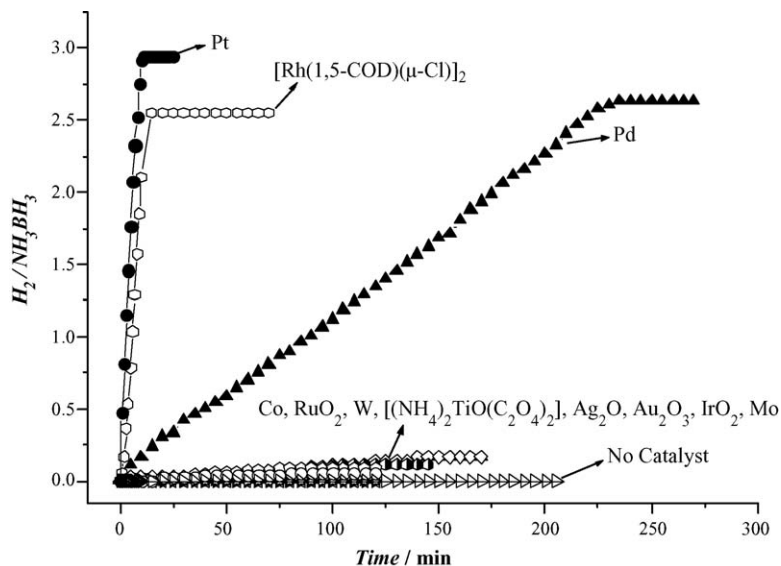


Fig. 2. Hydrogen release from aqueous NH_3BH_3 (0.33 wt.%) solution in the presence of various metal catalysts (metal/ $\text{NH}_3\text{BH}_3 = 0.018$).

activity of the carbon supported Pt catalysts may be due to their high dispersion. Note that the reaction is completed in less than 2 min with the 20 wt.% Pt/C catalyst. The pre-catalyst PtO_2 is more catalytically active than the Pt black, whereas the pre-catalyst K_2PtCl_4 exhibits a lower activity.

We carried out TEM studies on the five Pt catalysts after reaction for investigating the effect of the catalyst structure on the catalytic activity. As shown in Fig. 4, the carbon supported Pt catalysts are the most highly dispersed, among which the one with 20 wt.% loading has smaller particle sizes, corresponding to its higher catalytic activity observed, than the one with 40 wt.% loading. The Pt catalyst formed in situ from PtO_2 exhibits sheet- and needle-like structures, probably due to the peeling off along with the loss of O atoms

during the reduction by ammonia borane, which has been used as an excellent reducing agent in organic syntheses [20,21]; such structures may account for its observed catalytic activity higher than the Pt black although the latter has smaller particle sizes. In contrast, the Pt catalyst formed in situ from the aqueous K_2PtCl_4 solution under the reductive condition during reaction is somewhat spherical with large sizes, which exhibits the lowest catalytic activity.

Fig. 5 shows the concentration dependence of the hydrogen release from aqueous NH_3BH_3 solutions in the presence of 20 wt.% Pt/C with the catalyst amount kept unchanged. It is found that by increasing the NH_3BH_3 concentration from 0.33 to 5.0 wt.%, the change of the $\text{H}_2/\text{NH}_3\text{BH}_3$ ratio against time slightly decreases, but the actual rate of hydrogen release ($\text{ml H}_2/\text{min}$) increases, indicating that the turn-over frequency (TOF) of the catalyst increases with increasing the NH_3BH_3 concentration and the high activity of the Pt catalyst can be kept at high NH_3BH_3 concentrations. The same was observed for more concentrated solutions. It is noted that upon the completion of reaction the $\text{H}_2/\text{NH}_3\text{BH}_3$ ratio reaches the same value, 3.0, at different concentrations, independent of the weight of H_2O . Furthermore, it is noteworthy that no significant deactivation was observed for recycled Pt catalysts.

What role the transition metal catalysts play in the reaction is of particular interest. For the present transition metal-catalyzed reaction, there seems no doubt that the activation process takes place on the metal catalyst surfaces. As a plausible mechanism, it is reasonable to consider that there should be interactions between the NH_3BH_3 molecule and the metal particle surface to form some activated complex species, to which attack by a H_2O molecule readily leads to concerted dissociation of the B–N bonding and hydrolysis of the resulting BH_3 intermediate to produce the boric acid product along

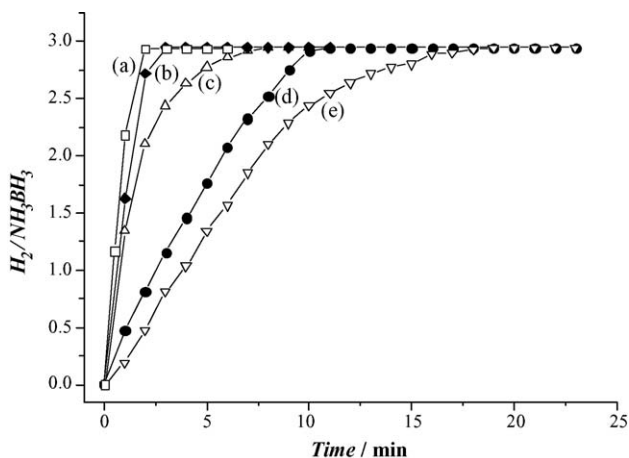


Fig. 3. Hydrogen release from aqueous NH_3BH_3 solution (0.33 wt.%) in the presence of (a) 20 wt.% Pt/C, (b) 40 wt.% Pt/C, (c) PtO_2 , (d) Pt black and (e) K_2PtCl_4 . The amount of Pt is normalized to $\text{Pt}/\text{NH}_3\text{BH}_3 = 0.018$.

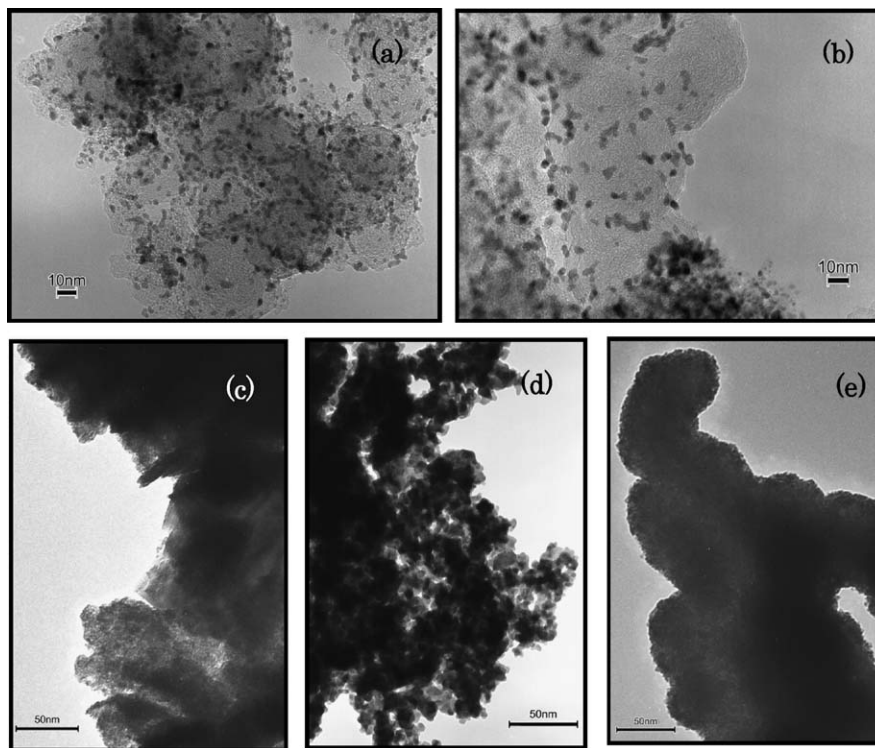


Fig. 4. TEM micrographs for (a) 20 wt.% Pt/C, (b) 40 wt.% Pt/C, (c) PtO₂, (d) Pt black and (e) K₂PtCl₄ after reaction with aqueous NH₃BH₃ (0.33 wt.%). Scales indicate 10 nm in (a) and (b), and 50 nm in (c)–(e).

with the H₂ release. Interestingly, in the absence of H₂O, dehydrocoupling between NH₃BH₃ molecules to form new B–N bonds occurs, probably via a closely related intermediate, on the metal surface [13–15]. To elucidate the reaction mechanism, further kinetics, spectroscopic and theoretical studies are planned.

With respect to the application as a portable hydrogen source, notable advantages of this system are the safety

(the safe reactant, ammonia–borane, and the safe products, ammonium borates), high kinetics of H₂ release at room temperature, ease to control (reaction started by contacting the highly active metal catalysts to and stopped by removing it from the solution) and high H₂ content (up to 8.9 wt.% of the starting materials). In comparison with the aqueous alkaline borohydride system which needs a highly basic solution, it is noteworthy that the NH₃BH₃ system has an advantage that the present solution has a low basicity (pH 9.0–10.0). The present system can release hydrogen up to 8.9 wt.%, close to the corresponding value for the NaBH₄/NaOH system (10.4 wt.%), although the three hydrogen atoms bonded to the N atom are kept unreleased. Searching for new metal catalysts and optimizing their catalytic activities for the present system are in progress.

4. Conclusions

In summary, we have successfully demonstrated for the first time that transition metals such as Pt, Rh and Pd exhibit high catalytic activity to the dissociation and hydrolysis of NH₃BH₃ at room temperature, which is accompanied by a quick release of a large amount of H₂. This catalytic system possesses high potential to find its application as a high-performance hydrogen source to portable fuel cells where liquid or solid fuel storage is essential and systems should be small, simple and robust.

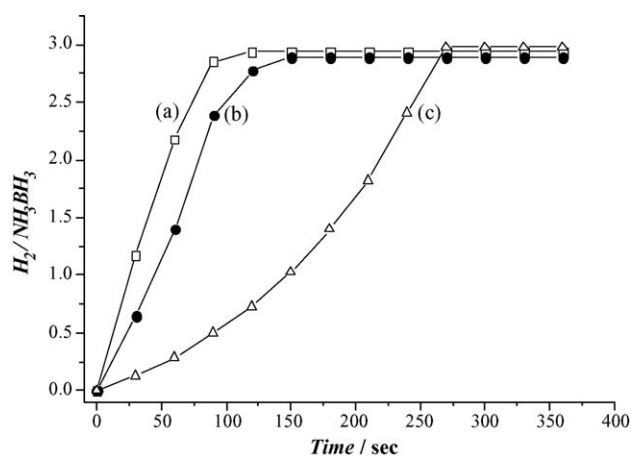


Fig. 5. Hydrogen release from aqueous NH₃BH₃ solutions with different concentrations in the presence of 20 wt.% Pt/C with the catalyst amount kept unchanged: (a) 0.33 wt.% (Pt/NH₃BH₃ = 0.018), (b) 1.0 wt.% Pt/NH₃BH₃ = 0.0059 and (c) 5.0 wt.% (Pt/NH₃BH₃ = 0.0012).

Acknowledgement

The authors would like to express sincere thanks to Dr. Nobuko Tsumori for valuable help, to Ms. Michiko Makino for TEM measurements, and to AIST and JSPS for financial support. M.C. thanks JSPS for a fellowship.

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