

Room temperature hydrogen generation from aqueous ammonia-borane using noble metal nano-clusters as highly active catalysts

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Abstract

Nano-clusters of noble metals Ru, Rh, Pd, Pt and Au have been supported on γ -Al₂O₃, C and SiO₂, of which the catalytic activities have been investigated for hydrolysis of NH₃BH₃. Among these catalysts, the Ru, Rh and Pt catalysts exhibit high activities to generate stoichiometric amount of hydrogen with fast kinetics, whereas the Pd and Au catalysts are less active. Support effect has been studied by testing the hydrogen generation reaction in the presence of Pt supported on γ -Al₂O₃, VULCAN[®] carbon and SiO₂, and it is found that Pt on γ -Al₂O₃, which has the smallest particle size, is the most active. Concentration dependence of the hydrogen generation from aqueous NH₃BH₃ solutions has been investigated in the presence of Pt/ γ -Al₂O₃ by keeping the amount of Pt/ γ -Al₂O₃ catalyst unchanged, which exhibits that the hydrogen release versus time (ml H₂ min⁻¹) does not significantly change with increasing the NH₃BH₃ concentration, indicating that the hydrogen release rate is not dependent on the NH₃BH₃ concentration and the high activity of the Pt catalyst can be kept at high NH₃BH₃ concentrations. Activation energies have been measured to be 23, 21 and 21 kJ mol⁻¹ for Ru/ γ -Al₂O₃, Rh/ γ -Al₂O₃ and Pt/ γ -Al₂O₃ catalysts, respectively, which may correspond to the step of B–N bond breaking on the metal surfaces. The particle sizes, surface morphology and surface areas of the catalysts have been obtained by TEM and BET experiments.

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Keywords: Ammonia-borane; Noble metals; Supported catalysts; Hydrogen generation

1. Introduction

Portable polymer electrolyte membrane (PEM) fuel cells are considered as an alternative to traditional batteries. PEM fuel cells require stable, non-flammable and high capacity pure hydrogen generator at ambient condition. Recently, due to high hydrogen contents, chemical hydrides are expected as potential sources for pure hydrogen, which could be directly used in portable PEM fuel cells. NaBH₄ is one of the potential chemical hydrides, which generates hydrogen at room temperature in the presence of metal catalysts and highly basic NaOH solution [1–6].

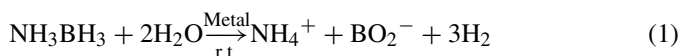
The ammonia-borane complex, NH₃BH₃, which is stable under ordinary storage conditions [7–10], possesses high potential for hydrogen generation for portable fuel cells. It contains

19.6 wt.% of hydrogen. Dehydrogenation by thermal decomposition of solid NH₃BH₃ has been widely investigated [11–15]. Heating acetonitrile and ethereal solutions of NH₃BH₃ above 80 °C releases stepwise hydrogen leading to the formation of cyclotriborazane and borazine along with other minor products [16]. Catalytic dehydrocoupling of NH₃BH₃ in diglyme or tetraglyme results in evolution of hydrogen gas along with the formation of borazine at 45 °C [17]. In situ spectroscopic studies using ¹¹B NMR and X-ray absorption fine structure spectroscopy (XAFS) have been performed to evaluate the rhodium-catalyzed dehydrogenation of dimethylamine borane in toluene solution [18]. Dehydrogenation of ammonia-borane in ionic liquid at 95 °C has been reported, which releases 1.6 equivalent of H₂ along with traces of borazine in 22 h [19].

In our previous reports we have investigated the hydrolysis of NH₃BH₃ in the presence of metals and solid acids at ambient conditions [9,10,20]. Aq. NH₃BH₃ releases stoichiometric amount of hydrogen (H₂/NH₃BH₃ = 3.0), corresponding to 8.9 wt.% of hydrogen relative to the starting materials NH₃BH₃

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and H₂O (Eq. (1)), in the presence of Pt, Rh, Pd [9] and some non-noble metal catalysts [20]. Among these metals Pt was found to be the most active.



Catalytic activity of metals is largely dependent upon the morphology and the support. Our present work is devoted to the study of nano-clusters of Pt and other noble metals on various supports for hydrogen generation from aq. NH₃BH₃. We present that catalytic performance of the noble metals Ru, Rh, Pd, Pt and Au for hydrogen generation from aq. NH₃BH₃ may be improved by modifying the metal catalysts.

2. Experimental

2.1. Preparation of catalysts

Supported metal catalysts used in this study were prepared by a conventional impregnation method. γ -Al₂O₃ (Aluminium Oxide, specific surface area = 43 m² g⁻¹, Aldrich), VULCAN[®] carbon (VULCAN XC-72R, specific surface area = 240 m² g⁻¹, Cabot Corp., USA) and SiO₂ (fumed silica, specific surface area = 390 m² g⁻¹, Aldrich) were used as the catalytic supports. For preparing γ -Al₂O₃ and SiO₂ supported catalysts, impregnation was performed by stirring the supports with known amounts of aqueous solutions of RuCl₃·xH₂O, Rh(NO₃)₃ (Kanto Chemical, Japan), Pd(NO₃)₂·xH₂O, PtCl₄ (Aldrich) and HAuCl₄·4H₂O (Kishida Chemicals, Japan), respectively, at 363 K for 12–16 h. The solvent was evaporated to dryness at 363 K. The Ru, Rh, Pd, Pt and Au samples were calcined in air for 5 h at 573 K. After purging argon in the fixed bed stainless steel reactor containing the calcined samples, a continuous H₂ gas flow was introduced at a rate of 50 ml min⁻¹ at 523 K for 5 h for reduction. For preparing the VULCAN[®] carbon supported platinum catalyst, impregnation was performed by ultrasonically mixing the mixture of PtCl₄ dissolved in methanol and VULCAN[®] carbon for 30 min at room temperature. The ultrasonicated sample was dried at 363 K for 12 h and then the dried sample was reduced by a continuous H₂ gas flow at a rate of 150 ml min⁻¹ at 523 K for 2 h in a similar way. After reduction the catalysts were stored in an argon atmosphere until being used for hydrogen generation.

2.2. Characterization of catalysts

The morphology of the catalysts was observed using a Hitachi H-9000NA transmission electron microscope (TEM) operating with an acceleration voltage of 200 kV using Cu TEM grid as sample holder. Average metal particle sizes were measured from TEM micrographs.

The textural data of catalysts were measured by N₂ adsorption at liquid N₂ temperature with a micromeritics ASAP 2010 BET analyzer. Before the analysis the samples were outgassed at 300 °C for γ -Al₂O₃, SiO₂ and its supported catalysts and at 275 °C for VULCAN[®] carbon and its supported catalyst under vacuum for 4 h.

2.3. Hydrogen generation

Commercial ammonia-borane, NH₃BH₃ (Tech. 90%, Aldrich) was used as purchased. Reaction apparatus for measuring the hydrogen generation rate from the aq. NH₃BH₃ solution is similar to that previously reported [9,10]. In general, the hydrolysis reactions of aq. NH₃BH₃ with prepared catalysts were carried out at room temperature. A weighed catalyst was placed in the three-necked round-bottom flask (50 ml) and the reaction was started by stirring the mixture of the catalyst and the aq. NH₃BH₃ solution added from the addition funnel, and the evolution of gas was monitored using a gas burette to an accuracy of ± 0.5 ml for the 0.33 and 1 wt.% aq. NH₃BH₃ solutions and using a flow-meter (Horiba STEC, SEF 7330) to an accuracy of ± 1% for the 1, 5, 10, 15 and 25 wt.% aq. NH₃BH₃ solutions. For obtaining the activation energy, we carried out the hydrogen generation reaction at 25, 30 and 40 °C. A water jacket was used to keep the solution temperature constant within the range of the set value of ± 1.0 °C.

3. Results and discussion

Generally, the catalytic behavior of catalysts is largely dependent upon the surface morphology, metal particle size, and support. In our previous investigations [9], we have shown that Pt is the most efficient catalyst for the release of stoichiometric hydrogen. This paper reports the activities of supported nano-clusters of Pt and other noble metals, Ru, Rh, Pd and Au, on different supports, γ -Al₂O₃, VULCAN[®] carbon and SiO₂, for hydrogen generation from aq. NH₃BH₃.

The morphology and particle sizes of the Ru/ γ -Al₂O₃, Rh/ γ -Al₂O₃, Pd/ γ -Al₂O₃, Pt/ γ -Al₂O₃, Pt/C, Pt/SiO₂ and Au/ γ -Al₂O₃ catalysts were examined using TEM (Fig. 1). Spherical metal particles are embedded on the edges of the crystalline γ -Al₂O₃ support in the cases of Ru/ γ -Al₂O₃, Rh/ γ -Al₂O₃, Pd/ γ -Al₂O₃, Pt/ γ -Al₂O₃ and Au/ γ -Al₂O₃ catalysts, while in the cases of Pt/C and Pt/SiO₂ catalysts, metal particles are dispersed on the surfaces of amorphous VULCAN[®] carbon and SiO₂ supports, respectively. The average particle sizes are 1.8, 2.5, 3.6, 1.5, 1.9, 5.1 and 2.6 nm for Ru/ γ -Al₂O₃, Rh/ γ -Al₂O₃, Pd/ γ -Al₂O₃, Pt/ γ -Al₂O₃, Pt/C, Pt/SiO₂ and Au/ γ -Al₂O₃ catalysts, respectively. Histograms representing the particle size distributions for the Ru/ γ -Al₂O₃, Rh/ γ -Al₂O₃, Pd/ γ -Al₂O₃, Pt/ γ -Al₂O₃, Pt/C, Pt/SiO₂ and Au/ γ -Al₂O₃ catalysts are shown in Fig. 2.

The specific surface areas of the catalysts determined by using the BET method are summarized in Table 1. There are only small changes in the surface area with loading metals to the supports. We have observed significant increase in pore size and pore volume for metal supported γ -Al₂O₃ and SiO₂ catalysts. During impregnation process in aqueous medium water is dissociatively chemisorbed on Al₂O₃ or SiO₂, which causes reconstruction of surfaces and also changes in pore size and pore volume [21–24]. Our results are in line with the previous investigations. Such a phenomenon was not observed for VULCAN[®] carbon supported catalysts.

Fig. 3 shows the hydrogen generation profiles with time for the reactions of aq. NH₃BH₃ (1.0 wt.%) in the presence

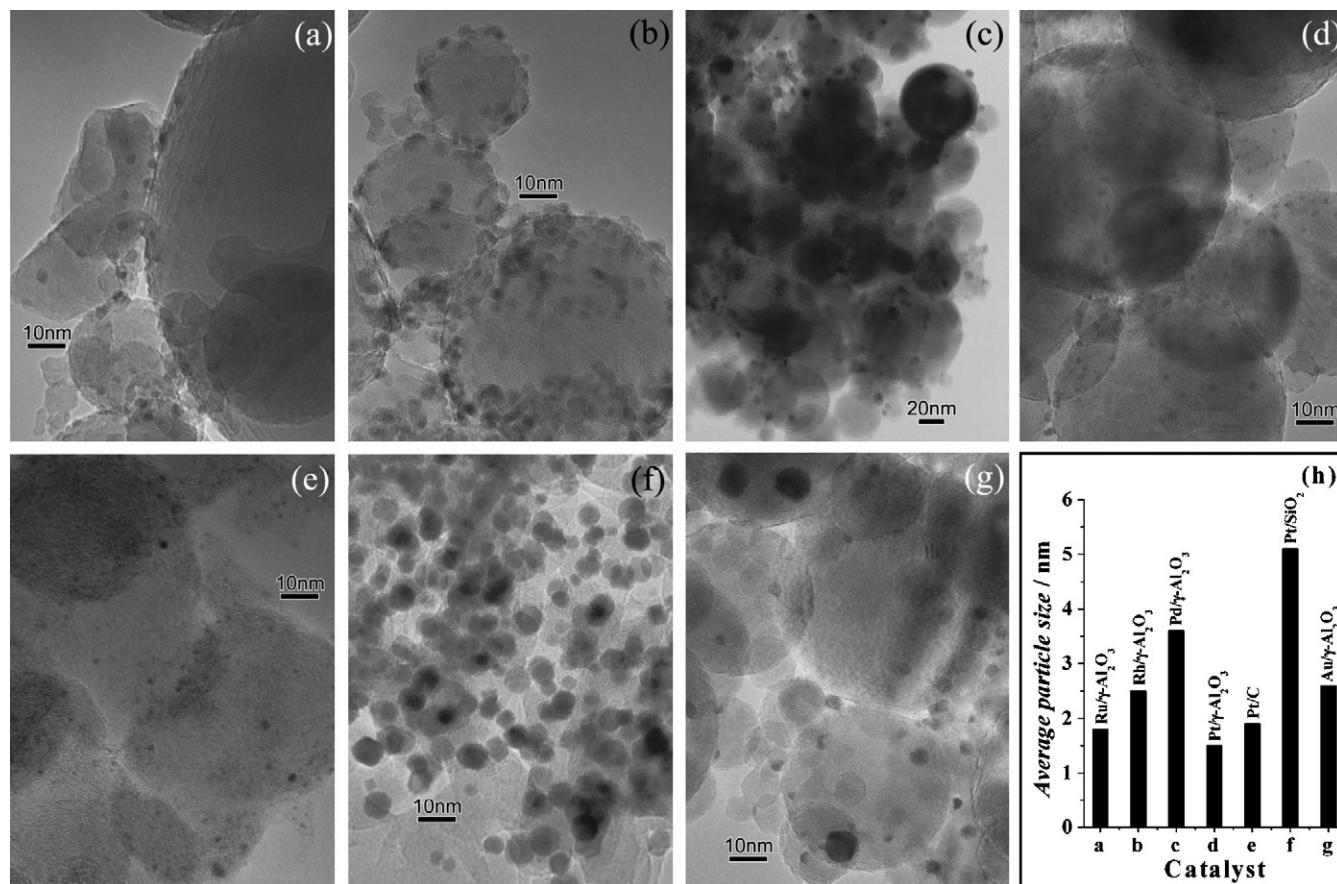


Fig. 1. TEM micrographs for: (a) Ru/ γ -Al₂O₃, (b) Rh/ γ -Al₂O₃, (c) Pd/ γ -Al₂O₃, (d) Pt/ γ -Al₂O₃, (e) Pt/C, (f) Pt/SiO₂ and (g) Au/ γ -Al₂O₃ catalysts (2 wt.%) and (h) a graph representing the average metal particle size (nm) for the above mentioned catalysts (particle sizes are obtained from 60, 172, 65, 137, 51, 217 and 140 metal particles, respectively, on the basis of TEM micrographs).

of the γ -Al₂O₃ supported Ru, Rh, Pd, Pt and Au catalysts (2 wt.%) with the metal contents normalized to the same (metal/NH₃BH₃ = 0.018). It is revealed that the Ru, Rh, and Pt catalysts, of which the average particle sizes are 1.8, 2.5 and 1.5 nm, respectively, are highly active for the hydrolysis of NH₃BH₃, exhibiting hydrogen release of H₂/NH₃BH₃ = 3.0 in 3, 1.3 and 0.75 min, respectively. It has been reported that γ -Al₂O₃ itself (as well as the γ -Al₂O₃ supported Fe catalyst) is inactive to this reaction [20]. It is noted that the bulk RuO₂ precursor

did not show catalytic activity for the hydrolysis of NH₃BH₃ [9], while the supported Ru nano particles show high activity, suggesting that the particle size is an important factor for the catalytic activity. In comparison with the other platinum-group metal catalysts, Pd/ γ -Al₂O₃, which has an average particle size of 3.6 nm, shows a lower catalytic activity, releasing hydrogen of H₂/NH₃BH₃ = 2.9 in 120 min. The Au/ γ -Al₂O₃ catalyst, which has an average particle size of 2.6 nm, exhibits a much lower catalytic activity for hydrolysis of aq. NH₃BH₃, releasing hydrogen

Table 1
Characteristics of supports and catalysts tested for the hydrogen generation reaction

Catalysts	Metal content (wt.%)	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (Å)	Average particle size ^a (nm)
γ -Al ₂ O ₃	–	43	0.091	84	–
C ^b	–	240	0.312	51	–
SiO ₂ ^c	–	390	0.425	55	–
Ru/ γ -Al ₂ O ₃	2	40	0.183	186	1.8
Rh/ γ -Al ₂ O ₃	2	41	0.188	182	2.5
Pd/ γ -Al ₂ O ₃	2	37	0.188	205	3.6
Pt/ γ -Al ₂ O ₃	2	38	0.175	183	1.5
Pt/C	2	239	0.334	56	1.9
Pt/SiO ₂	2	396	1.20	122	5.1
Au/ γ -Al ₂ O ₃	2	35	0.177	200	2.6

^a Calculated from TEM micrographs.

^b VULCAN[®] carbon.

^c Fumed SiO₂.

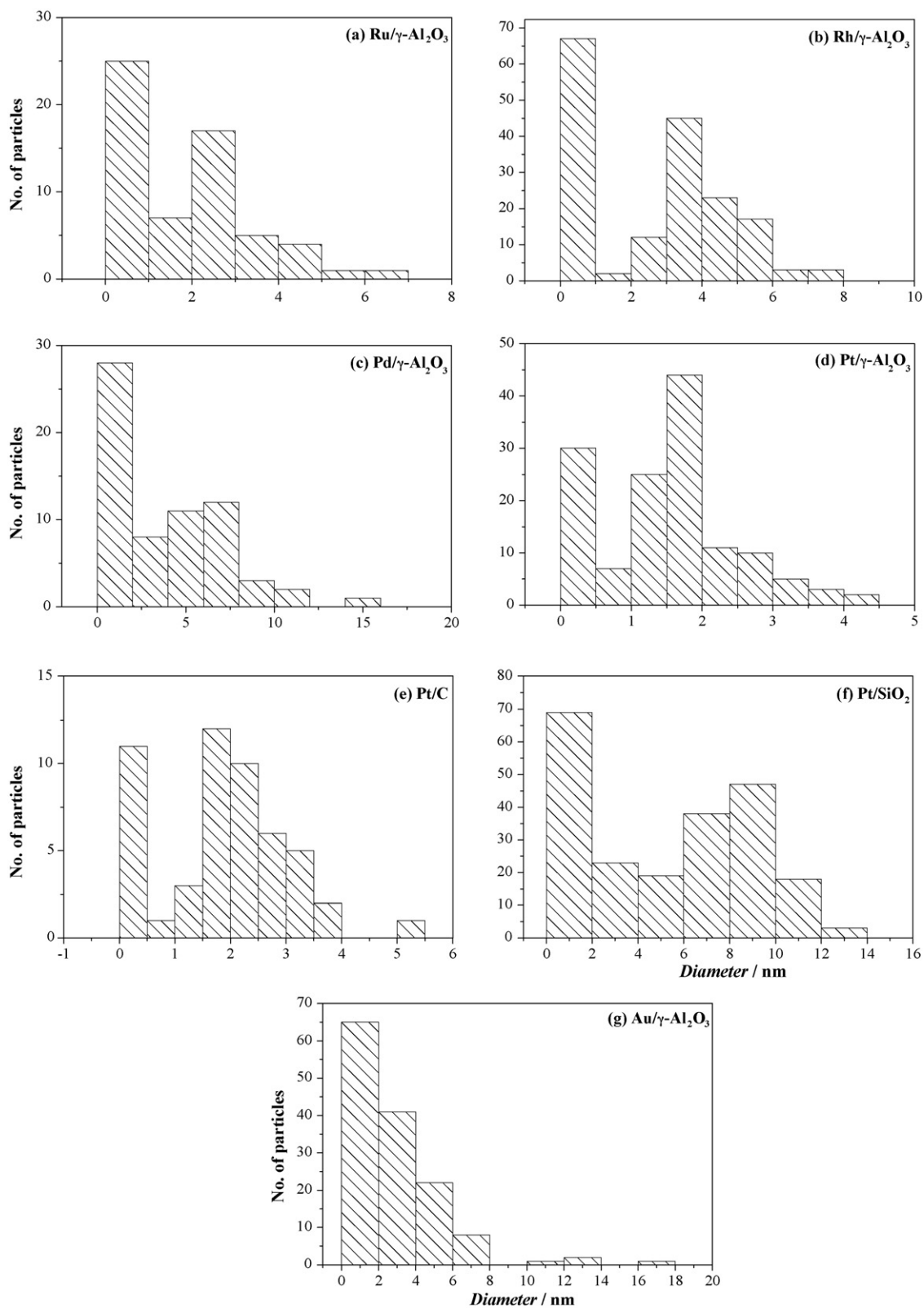


Fig. 2. Metal particle size distributions of: (a) Ru/ γ -Al₂O₃, (b) Rh/ γ -Al₂O₃, (c) Pd/ γ -Al₂O₃, (d) Pt/ γ -Al₂O₃, (e) Pt/C, (f) Pt/SiO₂ and (g) Au/ γ -Al₂O₃ catalysts (2 wt.%).

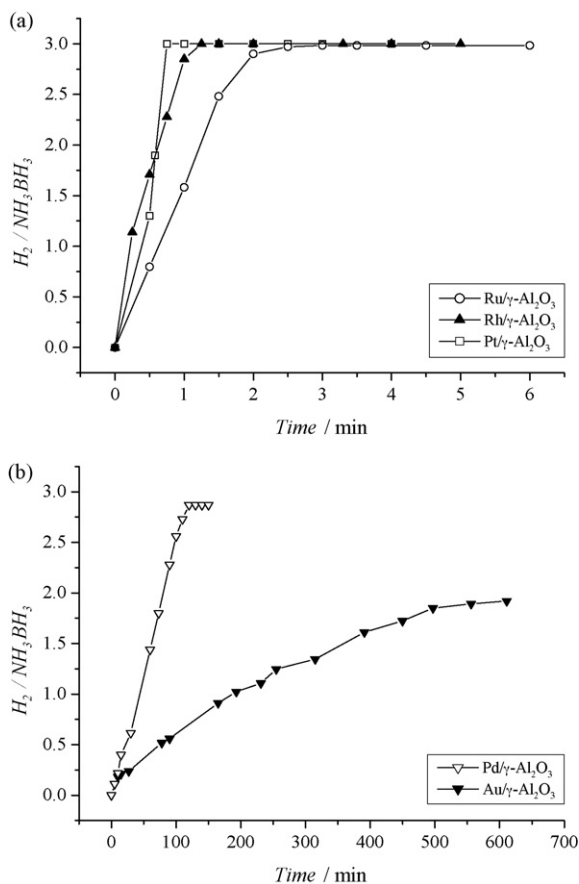


Fig. 3. Hydrogen generation from aq. NH_3BH_3 (1 wt.%, 10 ml) in the presence of: (a) the Ru/ γ - Al_2O_3 , Rh/ γ - Al_2O_3 and Pt/ γ - Al_2O_3 catalysts (2 wt.%) and (b) the Pd/ γ - Al_2O_3 and Au/ γ - Al_2O_3 catalysts (2 wt.%) (metal/ NH_3BH_3 = 0.018).

of $H_2/NH_3BH_3 = 1.9$ in 610 min. It is well known that the particle size is an important factor for the activity of gold catalyst [25]. In the previous work, we found that the Au_2O_3 precursor could not give active gold catalyst for the hydrolysis of NH_3BH_3 [9]. The present supported gold catalyst, Au/ γ - Al_2O_3 , has an average particle size (2.6 nm), which is in the range of active gold catalysts, although its activity is much lower than the platinum-group metal catalysts. Previous studies have reported that gold is a good catalyst for oxidation but not for hydrolysis of sodium borohydride [26]. Noteworthy, the present study also reveals that the catalytic activity of Rh and Pd can be significantly improved, in comparison with $[Rh(1,5-COD)(\mu-Cl)_2]$ and Pd Black in the previous work [9], by supporting the nanoparticles to supports. Furthermore, it is noteworthy that no significant deactivation was observed for the used noble metal catalysts recycled by washing with water and then dried at 100 °C for one night. For example, hydrogen of stoichiometric amount (H_2/NH_3BH_3 ratio = 3.0) was released in 1.6 min with the recycled 2 wt.% Rh/ γ - Al_2O_3 catalyst, close to the observation with the fresh catalyst.

We have studied the effect of NH_3BH_3 concentration on the hydrogen generation rate using Pt/ γ - Al_2O_3 (2 wt.%) catalysts. The amount of Pt/ γ - Al_2O_3 (2 wt.%) catalyst (0.050 g) for hydrogen generation was kept unchanged. As shown in Figs. 4 and 5 it is found that by increasing the NH_3BH_3 concentration

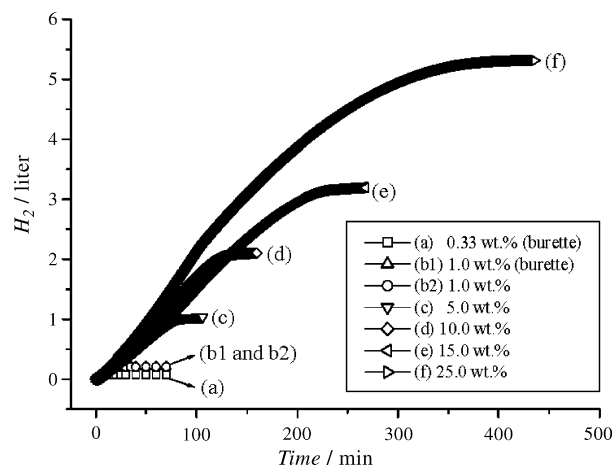


Fig. 4. Volume of hydrogen generated vs. reaction time from aq. NH_3BH_3 solutions with different concentrations in the presence of 2 wt. % Pt/ γ - Al_2O_3 with the catalyst amount kept unchanged: (a) 0.33 wt.% (Pt/ NH_3BH_3 = 0.00534) (monitored by gas burette), (b) 1.0 wt.% (Pt/ NH_3BH_3 = 0.0018) (monitored by both gas burette (b1) and flow-meter (b2)), (c) 5.0 wt.% (Pt/ NH_3BH_3 = 0.00035), (d) 10.0 wt.% (Pt/ NH_3BH_3 = 0.00018), (e) 15.0 wt.% (Pt/ NH_3BH_3 = 0.00012) and (f) 25.0 wt.% (Pt/ NH_3BH_3 = 0.00007) at room temperature. Unless indicated, the volume of hydrogen released was monitored by flow-meter.

from 0.33 to 25.0 wt.%, the change of the H_2/NH_3BH_3 ratio against time decreases but the actual rate of hydrogen release ($ml H_2 min^{-1}$) does not change significantly, indicating that the hydrogen release rate is not largely dependent of the NH_3BH_3 concentration and the high activity of the Pt catalyst can be kept at high NH_3BH_3 concentrations. We found that after completion of hydrogen generation reactions from high concentration NH_3BH_3 some solid residue was observed, which was completely soluble in excess water. It has been reported that the resulting solution after hydrogen release from aq. NH_3BH_3 exhibits a single ¹¹B resonance around 8 ppm due to products such as H_3BO_3 , BO_2^- and other borate species in equilibrium in the solution, which undergoes rapid exchange between each other on the NMR time scale [9], and the present solid residue formed from the high concentration NH_3BH_3 solution may be

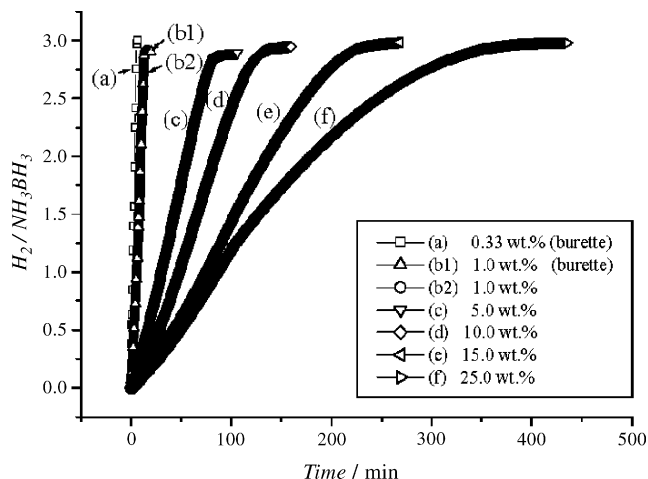


Fig. 5. The H_2/NH_3BH_3 ratio vs. reaction time corresponding to the results shown in Fig. 4.

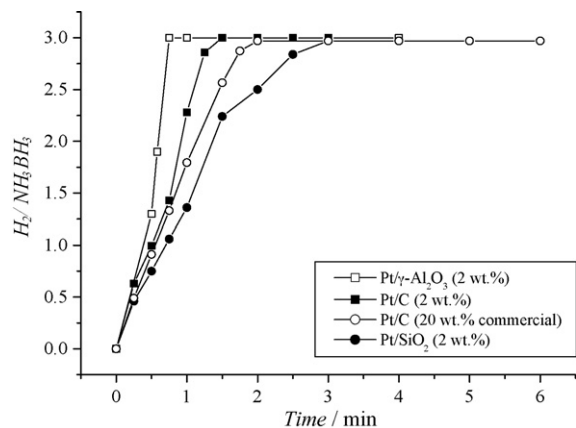


Fig. 6. Hydrogen generation from aq. NH₃BH₃ (1 wt.%, 10 ml) in the presence of Pt/γ-Al₂O₃ (2 wt.%), Pt/C (2 wt.%), Pt/C (20 wt.%) and Pt/SiO₂ (2 wt.%) (Pt/NH₃BH₃ = 0.018).

considered to be the precipitation of some borates due to the limited solubility. It is noted that upon the completion of reaction the H₂/NH₃BH₃ ratio reaches the same value, 3.0, at different concentrations, independent of the weight of H₂O.

We have tested the catalytic activities of Pt on different supports with the Pt content kept unchanged (Pt/NH₃BH₃ = 0.018).

As shown in Fig. 6 the hydrogen generation rates from aq. NH₃BH₃ are in the order of Pt/γ-Al₂O₃ > Pt/C > Pt/SiO₂ with the same Pt loading on support (2 wt.%) while the particle sizes of these catalysts are in the order of Pt/γ-Al₂O₃ (1.5 nm) < Pt/C (1.9 nm) < Pt/SiO₂ (5.1 nm). With Pt/γ-Al₂O₃, Pt/C and Pt/SiO₂ hydrogen is released with H₂/NH₃BH₃ = 3.0 in 0.75, 1.5 and 3 min, respectively. Comparing the catalytic activity of commercial Pt/C (20 wt.%, Johnson Matthey; 2.5 nm) catalyst with the prepared Pt/C (2 wt.%, 1.9 nm) catalyst, it is found that the one with low loading Pt has a little higher activity.

It is well known that the reaction rate generally increases with the reaction temperature. The values of rate constants *k* have been determined for hydrogen generation from aq. NH₃BH₃ in the presence of γ-Al₂O₃ supported Ru, Rh and Pt catalysts (metal/NH₃BH₃ = 0.009) at different temperatures (25–40 °C) as shown in Figs. 7–9, respectively. The NH₃BH₃ concentration decreases as the reaction proceeds and H₂ volume generated by the catalysts increases nearly linearly with time. Under our experimental conditions, the reaction rate constant, *k*, is nearly constant for a given temperature, implying zero order kinetics for the NH₃BH₃ hydrolysis reaction. This suggests that the hydrogen generation rate is controlled within surface reaction. Thus the rate law for the catalytic hydrolysis of NH₃BH₃ can be given

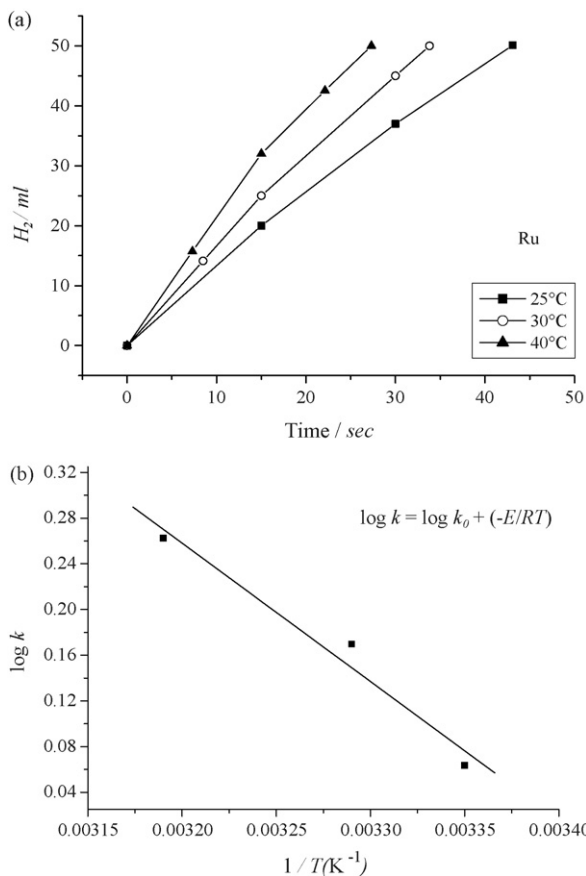


Fig. 7. (a) Hydrogen generation from aq. NH₃BH₃ (1 wt.%, 10 ml) in the presence of Ru/γ-Al₂O₃ (2 wt.%) (Ru/NH₃BH₃ = 0.009) at 25, 30 and 40 °C and (b) the corresponding log *k* vs. 1/*T* plot calculated from (a). Calculated activation energy is 23 kJ mol⁻¹.

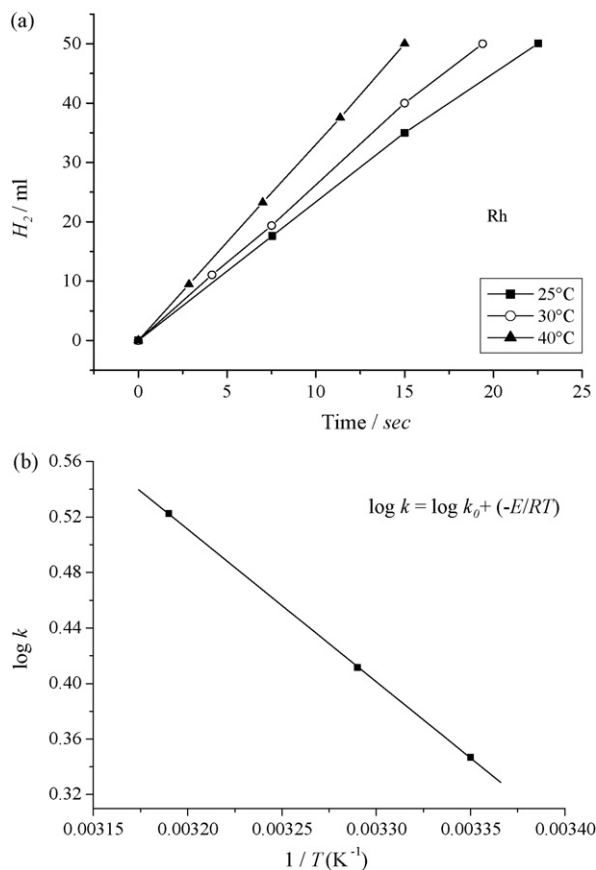


Fig. 8. (a) Hydrogen generation from aq. NH₃BH₃ (1 wt.%, 10 ml) in the presence of Rh/γ-Al₂O₃ (2 wt.%) (Rh/NH₃BH₃ = 0.009) at 25, 30 and 40 °C and (b) the corresponding log *k* vs. 1/*T* plot calculated from (a). Calculated activation energy is 21 kJ mol⁻¹.

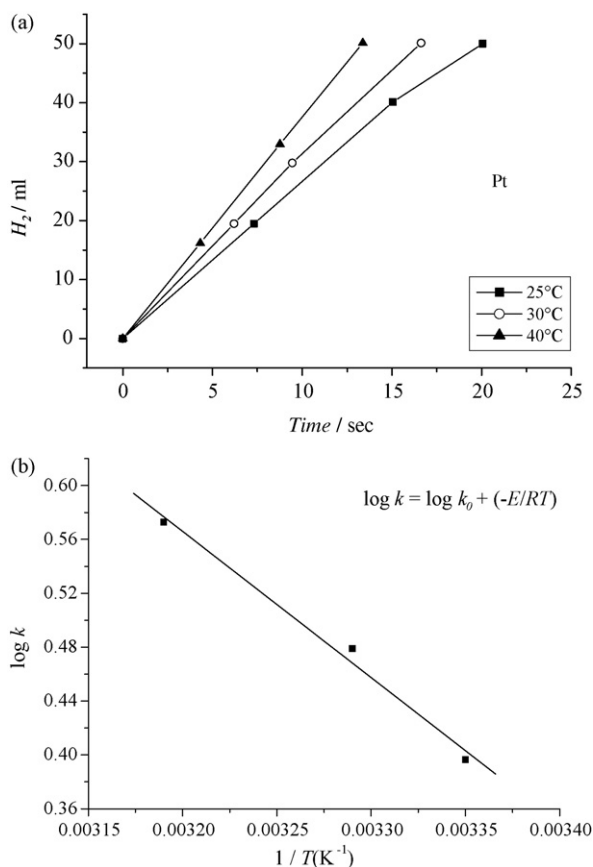


Fig. 9. (a) Hydrogen generation from aq. NH_3BH_3 (1 wt.%, 10 ml) in the presence of $Pt/\gamma-Al_2O_3$ (2 wt.%) ($Pt/NH_3BH_3 = 0.009$) at 25, 30 and 40 °C and (b) the corresponding $\log k$ vs. $1/T$ plot calculated from (a). Calculated activation energy is 21 $kJ\ mol^{-1}$.

as

$$\frac{-1/3d[NH_3BH_3]}{dt} = \frac{d[H_2]}{dt} = k \quad (2)$$

The reaction rate equation can be written as follows:

$$k = k_0 \exp^{-E/RT} \quad (3)$$

where k_0 is reaction constant, E the activation energy for the reaction, R the gas constant and T is the reaction temperature. Following Eq. (3), Figs. 7b–9b show the Arrhenius plots, $\log k$ versus the reciprocal absolute temperature. The slopes of the straight lines give activation energies of 23, 21 and 21 $kJ\ mol^{-1}$ for the $Ru/\gamma-Al_2O_3$, $Rh/\gamma-Al_2O_3$ and $Pt/\gamma-Al_2O_3$ catalysts, respectively. For comparison, in case of hydrogen generation from aq. $NaBH_4$ in the presence of Ru catalyst supported on IRA-400 [2] and $Ru(0)$ nanoclusters [5], the activation energies are 47 and 29 $kJ\ mol^{-1}$, respectively.

It is proposed as one of the plausible mechanisms in our previous reports that the activation process for catalytic hydrolysis reaction takes place on the surface of metal catalysts [9,10,20]. The metal particle surface and NH_3BH_3 molecule form activated complex species, to which attack by a H_2O molecule leads to dissociation of B–N bond which is most likely the rate-determining step and hydrolysis of the resulting BH_3 intermediate to borate species along with hydrogen generation. At 25 °C, the

standard-state enthalpy change for the Eq. (1) can be calculated to be $-156\ kJ\ mol^{-1}$ from the standard enthalpies of $-178\ kJ\ mol^{-1}$ (NH_3BH_3), $-572\ kJ\ mol^{-1}$ ($2H_2O$), $-133\ kJ\ mol^{-1}$ (NH_4^+), $-772\ kJ\ mol^{-1}$ (BO_2^-), and 0 ($3H_2$) [27] and this reaction is exothermic. In comparison, the standard-state enthalpy change for the hydrogen generation reaction of sodium borohydride $NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$ is $-217\ kJ\ mol^{-1}$ [3]. From the present catalytic hydrolysis reaction 0.195 g of hydrogen is liberated per 1 g of the NH_3BH_3 . The generation of 1 g $H_2\ s^{-1}$ corresponds to $96.5\ kA \times 0.7 = 68\ kW$, assuming a standard PEM fuel cell operates at 0.7 V. The amount of NH_3BH_3 needed is 0.27 kg for supplying hydrogen to such a PEMFC system to produce 1 kW of electric power for 1 h.

4. Conclusion

Supported Ru , Rh , Pd , Pt and Au nano-clusters have been developed as catalysts for hydrogen generation from aq. NH_3BH_3 . The Ru , Rh , Pd and Pt catalysts were found to be active for release of stoichiometric hydrogen from aq. NH_3BH_3 . Support effect has been investigated for Pt on different supports ($\gamma-Al_2O_3$, VULCAN[®] carbon and SiO_2) and $Pt/\gamma-Al_2O_3$ is found to be the most active. Activation energies for hydrogen generation in the presence of the $\gamma-Al_2O_3$ supported Ru , Rh and Pt catalysts are 23, 21 and 21 $kJ\ mol^{-1}$, respectively. High concentration NH_3BH_3 solutions also release the stoichiometric amounts of hydrogen ($H_2/NH_3BH_3 = 3.0$) at low catalyst/ NH_3BH_3 ratios. The high performance of the noble metal catalysts makes them a promising candidate to develop highly efficient portable hydrogen generation systems.

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