

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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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].

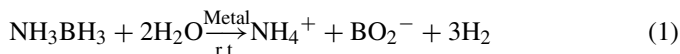
The ammonia-borane complex, NH₃BH₃, which is stable under ordinary storage conditions [7–10], possesses high potential for hydrogen generation for portable fuel cells. It contains

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

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