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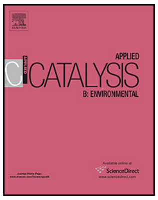

Full Length Article

The highest catalytic activity in the hydrolysis of ammonia borane by poly(*N*-vinyl-2-pyrrolidone)-protected palladium–rhodium nanoparticles for hydrogen generation

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ABSTRACT

The use of poly(*N*-vinyl-2-pyrrolidone)-protected palladium–rhodium nanoparticles (2.5 ± 1.1 nm) as highly efficient catalysts providing a record catalytic activity in the hydrolysis of ammonia borane for hydrogen generation is reported. They are prepared by co-reduction of palladium and rhodium metal ions in ethanol/water mixture by an alcohol reduction method and characterized by TEM-EDX analysis, UV–Vis spectroscopy, and X-ray photoelectron spectroscopy. They are recyclable and highly efficient catalysts for hydrogen generation from the hydrolysis of ammonia borane even at very low concentrations and temperature, providing record average turnover frequency (1333 mol H_2 (mol cat)$^{-1}$ min^{-1}), maximum hydrogen generation rate (36,414 L H_2 min^{-1} (mol cat)$^{-1}$), and total turnovers (171,000). Poly(*N*-vinyl-2-pyrrolidone)-protected palladium-rhodium nanoparticles also provide activation energy of 46.1 ± 2 kJ/mol for the hydrolysis of ammonia borane.

1. Introduction

Ammonia borane (H_3NBH_3, AB) has recently been employed as a solid hydrogen storage material due to its high hydrogen content (19.6 wt%), high solubility and stability in water at room temperature [1,2]. AB is able to release hydrogen upon hydrolysis at room temperature in the presence of suitable catalysts according to Eq. (1):

$$H_3NBH_3(aq) + 2H_2O(l) \xrightarrow{catalyst} NH_4^+(aq) + BO_2^-(aq) + 3H_2(g) \tag{1}$$

Various kinds of catalyst systems have been tested for the hydrolysis of AB so far. Among those, nanoparticle-types were mostly employed catalysts, providing good catalytic activities as expected due to the small particle sizes. Some examples of those are hollow Ni-SiO_2 nanosphere [3], Fe(0) NPs [4], Co(0) NCs [5], polymer-stabilized Ru(0) and Pd(0) NCs [6], Co(0) NPs [7], water/air-stable Ni NPs [8], hollow Co-B nanospindles [9], nanoparticle-assembled Co-B thin film [10], Cu/Co_3O_4 NPs [11], SiO_2 supported monodisperse Ni NPs [12], Co-SiO_2 nanosphere [13], graphene oxide supported Pd NPs [14], Ru NPs [15], HAP-supported Co(0) [16], HAP-supported Pd(0) [17], Pd(0) NPs on $CoFe_2O_4$ [18], and HAP-supported Ru(0) [19].

However, the addition of second element to the monometallic nanoparticles will definitely improve the catalytic properties. Therefore, the employment of highly active bimetallic-type nanoparticles as catalyst for hydrogen generation from the hydrolysis of AB has recently been focused and some bimetallic nanoparticle-type catalysts including Ni@Ru core–shell nanoparticles [20], Ni-Ru alloy nanoparticles [21], RuCo and RuCu on γ-Al_2O_3 [22], RuCu on graphene [23], Ru@Ni core-shell nanoparticles [24], Cu-Ni on MCM-41 [25], Cu@FeCo core–shell nanoparticles [26], Ru@Co on graphene [27], and CoNi on graphene oxide [28] have been employed as catalysts. Additionally, recent articles related to use of poly(*N*-vinyl-2-pyrrolidone) (PVP)-protected ruthenium–palladium [29] and platinum–ruthenium [30] nanoparticles showed that they are highly efficient catalysts for hydrogen generation from boron compounds providing remarkable results. However, there is no reported work on the catalytic activity of PVP-protected palladium-rhodium (Pd-Rh@PVP) nanoparticles in hydrogen production from the hydrolysis of AB, to the knowledge. This study reports the employment of Pd-Rh@PVP nanoparticles as highly efficient catalyst for hydrogen generation from the hydrolysis of AB. The catalysts were prepared by an alcohol reduction method [31], found to be stable as colloidal dispersions, and characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and UV–Vis spectroscopy.

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Although the cost of noble metal catalysts is assumed to be high, the highest catalytic activity of the Pd-Rh@PVP nanoparticles makes them very promising candidates to be used as catalyst in developing efficient portable hydrogen generation systems using AB as solid hydrogen storage material since it would easily compensate the cost concerns.

2. Experimental

2.1. Materials

Potassium tetrachloropalladate (K_2PdCl_4), rhodium (III) chloride trihydrate ($RhCl_3 \cdot 3H_2O$), poly(*N*-vinyl-2-pyrrolidone) (PVP-40), and ammonia borane (H_3NBH_3) were purchased from Aldrich. Ethanol was purchased from Merck. Deionized water was distilled by water purification system (Milli Q-pure WS). All glassware and teflon coated magnetic stir bars were rinsed with acetone, followed by copious washing with distilled water before drying in an oven at 150 °C.

2.2. Preparation of Pd-Rh@PVP nanoparticles

Pd-Rh@PVP nanoparticles were prepared by an alcohol reduction method in which PVP serves as both stabilizer and reducing agent. First, solutions of potassium tetrachloropalladate (0.25 mmol in 25 mL ethanol) and rhodium (III) chloride trihydrate (0.25 mmol in 25 mL water) were mixed and poly(*N*-vinyl-2-pyrrolidone) (PVP-40, 2.5 mmol of monomeric units) was added to this solution. Then, the mixed solution was refluxed at 90 °C for 2 h. Pd-Rh@PVP nanoparticles are brownish black in color and stable at room temperature. The total concentration of both metals was kept as 5.0 mM in 50 mL of the mixed solution.

2.3. Characterization of Pd-Rh@PVP nanoparticles

Transmission Electron Microscopy analysis was carried out using a JEOL-2010 microscope operating at 200 kV, fitted with a LaB_6 filament and has lattice and theoretical point resolutions of 0.14 nm and 0.23 nm, respectively. Samples were examined at magnification between 100 and 400 K. One drop of dilute suspension of sample was deposited on the TEM grids and the solvent was then evaporated. The diameter of each particle was determined from the enlarged photographs. X-ray photoelectron spectrum of the nanoparticles was taken by using SPECS spectrometer equipped with a hemispherical analyzer and using monochromatic Mg-Kα radiation (1250 eV, the X-ray tube working at 15 kV and 350 W). UV–Vis spectra were recorded on a Cary 5000 (Varian) UV–Vis spectrophotometer. A quartz cell with a part length of 1 cm was used and spectra were collected over the range of 200–900 nm. ^{11}B NMR spectra were recorded on a Bruker Avance DPX 400 with an operating frequency of 128.15 MHz for ^{11}B. D_2O and $BF_3 \cdot (C_2H_5)_2O$ were used as a lock and external reference, respectively. At the end of the hydrolysis reaction, the resulting solutions were filtered and the filtrates used for taking ^{11}B NMR spectra.

2.4. Catalytic evaluation of Pd-Rh@PVP nanoparticles in the hydrolysis of AB

The catalytic activity of Pd-Rh@PVP nanoparticles in the hydrolysis of AB in aqueous solution was determined by measuring the rate of hydrogen generation. In all the experiments, a jacketed reaction flask (50 mL) containing a Teflon-coated stir bar was placed on a magnetic stirrer (Heidolph MR-301) and thermostated to 25.0 ± 0.1 °C by circulating water through its jacket from a constant temperature bath. Then, a graduated glass tube (50 cm in height and 4.0 cm in diameter) filled with water was connected to the reaction flask to measure the volume of the hydrogen gas to be evolved from the reaction. In a typical experiment, 63.6 mg (2 mmol) of H_3NBH_3 was dissolved in 20 mL of water. The solution was transferred with a glass pipet into the reaction flask thermostated at 25.0 ± 0.1 °C. Then, aliquots of Pd-Rh@PVP nanoparticles from the stock solution (5.0 mM) were added into the reaction flask. The experiment was started by closing the flask and the volume of hydrogen gas evolved was measured by recording the displacement of water level at the stirring speed of 1000 rpm. In addition to the volumetric measurement of the hydrogen evolution, the conversion of AB ($\delta = -23.9$ ppm) [32] to metaborate ($\delta = 9$ ppm) [33] was also checked by ^{11}B NMR spectroscopy.

2.5. The effect of stirring speed on hydrogen generation rate

The same experiment described in the Section 2.4 for the hydrogen generation from the hydrolysis of AB was performed at 25 ± 0.1 °C by varying the stirring speed (0, 200, 400, 600, 800, 1000, and 1200 rpm) to check how hydrogen generation rate from the hydrolysis of AB system was affected by stirring speed. The hydrogen generation rate was found to be independent of the stirring speed when it is higher than 800 rpm. This indicates that the system is in a non-mass transfer limitation regime since the present kinetic study was performed at the stirring speed of 1000 rpm.

2.6. The effect of PVP concentration on the catalytic activity of Pd-Rh@PVP nanoparticles in the hydrolysis of AB

In order to study the effect of PVP concentration on the catalytic activity of Pd-Rh@PVP nanoparticles in the hydrolysis of AB (100 mM), hydrolysis reactions were conducted in the presence of catalysts prepared with different [PVP/Cat.] ratios (2, 4, 6, 8, 10, 12, 14, 16). All the experiments were conducted in the same way described in Section 2.4. The optimum [PVP/Cat.] ratio was found to be 10. When this ratio is lower than 10, the catalytic activity of the catalyst is relatively low because PVP molecules do not cover the surface of nanoparticles effectively, leading to decreased catalytic activity by not preventing the agglomeration of nanoparticles. When it is higher than 10, catalytic activity of the catalyst starts to decrease since the surface of the nanoparticles may be wholly covered by PVP, blocking the active sites to be reached by substrate molecules. Therefore, optimum [PVP/Cat.] ratio was determined as 10 for further kinetic studies.

2.7. Determination of activation energy of Pd-Rh@PVP nanoparticles in the hydrolysis of AB

In a typical experiment, the hydrolysis of AB (100 mM) catalyzed by Pd-Rh@PVP nanoparticles (0.3 mM) was performed by following the same procedure described in Section 2.4 at various temperatures (5, 10, 15, 20, and 25 °C) to obtain the activation energy (E_a).

2.8. Determination of catalytic lifetime of Pd-Rh@PVP nanoparticles in the hydrolysis of AB

Catalytic lifetime of Pd-Rh@PVP nanoparticles in the hydrolysis of AB was determined by measuring the total turnover number (TTON). Such a lifetime experiment was started with a 20 mL aqueous solution containing Pd-Rh@PVP nanoparticles (0.3 mM) and H_3NBH_3 (600 mM) at 25.0 ± 0.1 °C. Once complete conversion is achieved, another equivalent of H_3NBH_3 was added and