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Zeolite confined palladium(0) nanoclusters as effective and reusable catalyst for hydrogen generation from the hydrolysis of ammonia-borane

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ARTICLE INFO

Article history:

Received 28 September 2009

Received in revised form

13 November 2009

Accepted 14 November 2009

Available online 27 November 2009

Keywords:

Zeolite

Palladium

Nanoclusters

Ammonia-borane

Hydrolysis

Hydrogen generation

ABSTRACT

Zeolite confined palladium(0) nanoclusters were prepared by a two step procedure: incorporation of Pd²⁺ ions into the zeolite-Y by ion-exchange followed by the reduction of Pd²⁺ ions in the supercages of zeolite-Y with sodium borohydride at room temperature. Zeolite confined palladium(0) nanoclusters are stable enough to be isolated as solid materials and characterized by ICP-OES, XRD, HRTEM, SEM, X-ray photoelectron spectroscopy and N₂ adsorption technique. These nanoclusters are isolable, redispersible and reusable as an active catalyst in the hydrolysis of ammonia-borane solution. Zeolite confined palladium(0) nanoclusters provide 15,600 turnovers in hydrogen generation from the hydrolysis of ammonia-borane at 25.0 ± 0.1 °C.

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1. Introduction

Fuel cells are attractive and alternative options for producing clean energy for transportation and personal electronic applications [1–3]. Recently, proton exchange membrane fuel cells (PEMFCs) using hydrogen as a fuel have been extensively studied as an energy source due to their high efficiency, high power density, and zero emission of environmental pollutants [4–7]. Development of a safe and convenient hydrogen storage and production system is essential to utilize PEMFCs successfully. Among the new hydrogen storage materials [8,9], ammonia-borane (H₃NBH₃, AB) appears to be the most promising solid hydrogen carrier [10–13] owing to its combined advantages of; (i) the high hydrogen content (19.6% wt) [14,15], (ii) the high solubility in water [10], (iii) the high stability in

aqueous solution with respect to the self-hydrolysis [3], (iv) the ability to generate hydrogen upon hydrolysis (Eq. (1)) at room temperature in the presence of a suitable catalysts [1–3,5].



The catalytic hydrolysis of AB can yield hydrogen gas in a H₂/NH₃BH₃ ratio up to 3.0, corresponding to 8.9 wt.% of the starting materials AB and H₂O. Different types of catalyst systems including various transition metal salts RuCl₃, PdCl₂, and CoCl₂ [16], noble metal nanoclusters and non noble metals supported on γ-Al₂O₃, carbon, and SiO₂ [4,7], solid acid catalysts [3], K₂PtCl₆ [11], Ni_{1-x}Pt_x hollow spheres [17], Ru/C [18], colloidal Rh(0), Ir(0), and Co(0) catalysts [19], Cu@Cu₂O core shell catalysts [20], hollow Ni-SiO₂ nanosphere [21], Pt- and

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doi:10.1016/j.ijhydene.2009.11.056

Ni-based alloys [22], Fe(0) nanoparticles [23], PVP-stabilized nickel catalyst [24], PVP-stabilized cobalt(0) nanoclusters [25], magnetically recyclable Fe-Ni alloy [26], cobalt nanoparticles [27], water/air-stable Ni nanoparticles [28], Pt_xNi_{1-x} nanoparticles [29], and zeolite confined copper(0) nanoclusters [30] were used for hydrogen generation from the hydrolysis of AB. Recently, zeolite confined Rh(0) nanoclusters [31] was also used as catalyst in this hydrolysis reaction. The preparation of Rh(0) nanoclusters in the zeolite cages prevented the aggregation of nanoclusters owing to its confined void spaces. However, the high cost of the rhodium limits the use of such a precious metal as catalyst and stimulated us to use a relatively cheap metal for this reaction. Here, we report the preparation and characterization of zeolite confined palladium(0) nanoclusters and their use as catalyst in the hydrolysis of AB for hydrogen generation. Zeolite confined palladium(0) nanoclusters were easily prepared by a two step procedure recently reported [32]: ion-exchange of Pd^{2+} ions with the extra framework Na^+ ions in zeolite-Y, followed by the reduction of Pd^{2+} ions by sodium borohydride within the cavities of zeolite-Y in aqueous solution all at room temperature. They are stable enough for being isolated as solid materials and characterized by using a combination of advanced analytical techniques including HRTEM, XRD, XPS, SEM, ICP-OES, and N_2 adsorption. These nanoclusters are highly active catalyst in the hydrolysis of ammonia-borane. The reusability and catalytic lifetime experiments showed that zeolite confined palladium(0) nanoclusters can be considered as an efficient and reusable catalyst in the hydrolysis of AB to produce hydrogen.

2. Experimental

2.1. Materials

Palladium(II) nitrate (98+%), sodium borohydride (99%), sodium zeolite-Y, ammonia-borane complex (97%), D_2O and $BF_3 \cdot (C_2H_5)_2O$ were purchased from Aldrich. All chemicals were used as received. Deionized water was distilled by water purification system (Milli-Q System). All glassware and Teflon-coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 100 °C.

2.2. Preparation of zeolite confined palladium(0) nanoclusters

The sodium form of zeolite-Y (1 g) was added to a solution of palladium(II) nitrate in 100 mL H_2O in a 250 mL round bottom flask. This slurry was stirred at room temperature for three days until the supernatant solution became colorless. The Pd^{2+} -exchanged zeolite-Y samples were filtered by using Whatman-1 filter paper, washed with 20 mL deionized water three times, and dried in the oven at 80 °C. Then, the Pd^{2+} -exchanged zeolite-Y samples were added into 50 mL of 150 mM (284 mg) of aqueous sodium borohydride solution at room temperature. Palladium(II) ions were reduced forming the palladium(0) nanoclusters within the cavities of zeolite-Y. The zeolite confined palladium(0) nanoclusters samples were filtered again, washed thoroughly with deionized water, and

dried in the oven at 80 °C. The palladium content of the samples was determined by ICP-OES analysis.

2.3. Method to test the catalytic activity of zeolite confined palladium(0) nanoclusters in the hydrolysis of ammonia-borane

The catalytic activity of zeolite confined palladium(0) nanoclusters in the hydrolysis of AB was determined by measuring the rate of hydrogen generation. In all the experiments, a jacketed reaction flask (75 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 5.0 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. Next, 63.6 mg (2 mmol) AB was dissolved in 20 mL water, (corresponding to 6 mmol H_2 at 25.0 ± 0.1 °C). This solution was transferred with a 50 mL glass-pipette into the reaction flask thermostated at 25.0 ± 0.1 °C. Then, 520 mg powder of zeolite confined palladium(0) nanoclusters (from 0.82 wt.% loaded Pd(0)Y) was added into the reaction flask. The reaction was started by closing the flask and the volume of hydrogen gas evolved was measured by recording the displacement of water level. The quantity of ammonia liberated during the hydrolysis of ammonia-borane has been found to be negligible when the catalyst concentration is less than 0.06 mol% and the substrate concentration is lower than 6 wt.% [33,34]. The control tests using acid/base indicator showed no ammonia evolution in detectable amount in the experiments performed in this study. ICP-OES analysis of the catalyst sample after catalytic reaction gave the same palladium content (0.82 wt.% Pd) for the zeolite confined palladium(0) nanoclusters as before the reaction.

2.4. Self-hydrolysis of ammonia-borane

In order to determine the rate of hydrogen generation from the self-hydrolysis of AB in the absence of catalyst, 2 mmol (63.6 mg) AB was dissolved in 20 mL water and the solution was transferred with a 50 mL pipette into the reaction flask thermostated at 25.0 ± 0.1 °C. The reaction flask was closed and the reaction was started. The volume of hydrogen gas generated was measured with time. It was found that in the self-hydrolysis of AB after one day, there is no hydrogen gas generation and additionally ^{11}B NMR spectrum of the resulting solution showed only a signal at $\delta = -23.9$ ppm due to the unreacted AB [33].

2.5. Effect of palladium loading on hydrogen generation rate

In a series of experiments, the catalytic activities of zeolite confined palladium(0) nanoclusters ($[Pd] = 2$ mM) with 0.20, 0.40, 0.82, 1.26, 1.66, 2.08, 2.46, 2.84, 3.24, 3.62, 4.04 wt.% palladium loading were tested in the hydrolysis of 20 mL of 100 mM (63.6 mg) aqueous AB solution in order to determine the effect of palladium loading on the hydrogen generation rate. All the experiments were performed in the same way as described in

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