



Research Paper

Nanoalumina-supported rhodium(0) nanoparticles as catalyst in hydrogen generation from the methanolysis of ammonia borane

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ARTICLE INFO

Article history:

Received 4 May 2017

Received in revised form 9 June 2017

Accepted 13 June 2017

Keywords:

Hydrogen generation
Ammonia borane
Methanolysis
Alumina nanopowder
Rhodium
Nanoparticles

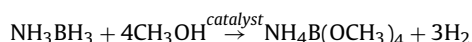
ABSTRACT

Rhodium(0) nanoparticles were *in situ* formed from the reduction of rhodium(II) octanoate and supported on the surface of nanoalumina yielding Rh(0)/nanoAl₂O₃ which is highly active catalyst in hydrogen generation from the methanolysis of ammonia borane at room temperature. The kinetics of nanoparticle formation can be followed just by monitoring the volume of hydrogen gas evolved from the methanolysis of ammonia borane. The evaluation of the kinetic data gives valuable insights to the slow, continuous nucleation and autocatalytic surface growth steps of the formation of rhodium(0) nanoparticles. Rh(0)/nanoAl₂O₃ could be isolated and characterized by a combination of advanced analytical techniques including ATR-IR, PXRD, TEM, XPS, SEM, SEM-EDX and ICP-OES. The results reveal that rhodium(0) nanoparticles are highly dispersed on the surface of nanoalumina. The particle size of Rh(0)/nanoAl₂O₃ increases with the initial rhodium loading of nanoalumina. Rh(0)/nanoAl₂O₃ is highly active catalyst in hydrogen generation from the methanolysis of AB providing an exceptional initial turnover frequency of TOF = 218 min⁻¹ at 25.0 ± 0.5 °C, which is the highest value ever reported for rhodium catalysts in hydrogen generation from the methanolysis of ammonia borane.

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1. Introduction

Ammonia borane (AB) is one of the potential hydrogen storage materials because of its high hydrogen content (19.6 wt%), nontoxicity, and stability under ambient conditions [1]. Although intensive efforts have been devoted to the hydrolysis of AB, methanolysis of AB has been considered as another efficient way of releasing the H₂ gas because of many advantages over the hydrolysis [2]. The most frequently encountered problems in hydrogen generation from hydrolysis of AB are the concomitant release of ammonia gas from concentrated AB solutions [3] and difficulties in recycling process of hydrolysis product, ammonium metaborate (NH₄BO₂). Additionally, AB has not only high solubility in methanol, 23% wt. at 23 °C [4] but also high stability with respect to self methanolysis at ambient conditions. In the presence of a suitable catalyst, methanolysis can release 3.0 equivalents of H₂ per mole of AB (Eq. (1)):



Up to now, methanolysis of AB has been investigated in the presence of many transition metals [5]. Among them, rhodium(0) nanoparticles can be incontestably pronounced the most active transition metal catalyst in the methanolysis of AB. However, rhodium(0) nanoparticles as other metal(0) nanoparticles are prone to agglomerate due to their high surface energy and they need to be stabilized against agglomeration [6]. Porous materials with large surface area have been used as support to obtain stable and catalytically active rhodium(0) nanoparticles [7]. The catalytic activity of nanoparticles depends on the particle size of support. We have recently used nanopowders of silica [8], hydroxyapatite [9], and titania [10] as support to make rhodium(0) nanoparticles highly active and long lived catalyst. Alumina is another widely used oxide support due to favourable combination of its textural properties such as surface area, pore volume and pore size distribution as well as chemical and hydrothermal stability [11]. Alumina has also been used to stabilize rhodium(0) nanoparticles catalyst in the hydrolysis of AB, if not the methanolysis [12]. In our ongoing research on the use of oxide nanopowders as support for rhodium(0) nanoparticles in hydrogen generation from the methanolysis of AB, herein we report the use of nanoalumina with an average particle size of 13 nm for stabilizing rhodium(0) nanoparticles. Nanoalumina supported rhodium(0) nanoparticles, hereafter referred to as Rh(0)/nanoAl₂O₃, were *in situ* generated

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from the reduction of rhodium(II) octanoate, impregnated on the surface of nanoalumina, during the methanolysis of AB in methanol. Rh(0)/nanoAl₂O₃ were isolated from the reaction medium and characterized by a combination of advanced analytical techniques including ATR-IR, PXRD, TEM, XPS, SEM, SEM-EDX and ICP-OES. The results reveal the formation of uniformly dispersed rhodium(0) nanoparticles with a mean particle diameter of 3.6–4.1 nm on the porous nanoalumina. These rhodium(0) nanoparticles were tested as catalyst in hydrogen generation from the methanolysis of AB and the kinetics of the nanoparticle formation and catalytic methanolysis of AB was studied in details.

2. Experimental

2.1. Materials

Rhodium(II) octanoate, ammonia borane (97%), methanol (99%), and nanoalumina (Al₂O₃, particle size ≈ 13 nm) were purchased from Aldrich. Methanol was distilled over Mg metal and kept under nitrogen atmosphere until the use in methanolysis.

2.2. Instrumentation

All the instrumentations used in this work are the same as reported elsewhere [8] with the exception of taking the IR spectra and the SEM images. The ATR-IR spectra of the nanoalumina samples were recorded on a Vartex-70 spectrophotometer. SEM analyses were run on a JEOL JSM-5310LV operating at 15 kV and 33 Pa in a low-vacuum mode without metal coating on the aluminum support.

2.3. In situ preparation of Rh(0)/nanoAl₂O₃ and catalytic methanolysis of AB

The preparation of Rh(II)/nanoAl₂O₃ and the *in situ* generation of Rh(0)/nanoAl₂O₃ during the catalytic methanolysis of ammonia borane were performed in the same medium following the procedure given elsewhere [8]. Briefly an aliquot of the stock solution of 4.9 mM rhodium(II) octanoate is transferred into a jacketed 50 mL flask with a Teflon-coated stir bar, containing alumina nanopowders, thermostated by circulating water through its jacket at 25.0 ± 0.5 °C or at a certain temperature specified. After addition of 6.5 mL methanol, the resulting suspension is stirred for 1 h. Then, 64 mg (2.0 mmol) AB in 3.0 mL methanol is added to the flask and the reaction is launched. The volume of H₂ gas released is recorded by measuring the displacement of water level in the glass tube connected to the reaction flask [8]. Note that all the experiments in this study were performed under stirring at 1000 rpm to ensure that the methanolysis in the presence of Rh(0)/nanoAl₂O₃ catalyst is in the kinetic regime, not under mass transfer limitation [8].

Calculation of the turnover frequency (TOF):

$$\text{TOF} = \frac{\text{mol of H}_2}{\text{mol of Rh} \times \text{time}}$$

Corrected TOF = TOF × percentage of catalytically active Rh atoms
Number of Rh atoms in nanoparticle,

$$n = \frac{N_0 \rho \left(\frac{4}{3}\right) \pi \left(\frac{D}{2}\right)^3}{W}$$

where

n = number of Rh atoms

N₀ = 6.022 × 10²³ mol⁻¹

D = diameter of rhodium nanoparticles

W = atomic weight of rhodium (102.91 g/mol)

ρ = room-temperature density of rhodium (12.41 g/cm³)

Number of Rh atoms on the surface of NP,

$$n_s = \frac{4\pi \left(\frac{D}{2}\right)^2}{(2r)^2}$$

r = atomic radius of rhodium (0.135 nm)"

2.4. Activation parameters for the methanolysis of AB catalyzed by Rh(0)/nanoAl₂O₃

The *in situ* generation of Rh(0)/nanoAl₂O₃ and catalytic methanolysis of AB are performed starting with 200 mM (64 mg) AB and 0.24 mM Rh (50 mg Rh(II)/nanoAl₂O₃, 0.5 wt.% Rh.) at 20, 25, 30 and 35 °C following the procedure given in the previous section.

2.5. Catalytic lifetime of Rh(0)/nanoAl₂O₃ catalyst in the methanolysis of AB

A lifetime experiment is performed starting with 10 mL solution containing 50 mg Rh(II)/nanoAl₂O₃ (0.50 wt.% rhodium, 2.4 mmol Rh) and 400 mM (128 mg) AB at 25.0 ± 0.5 °C following the procedure described elsewhere [8].

2.6. Heterogeneity test for Rh(0)/nanoAl₂O₃ by carbon disulfide poisoning in the methanolysis of AB

Catalyst poisoning experiment is performed by injecting carbon disulfide to reaction solution containing Rh(0)/nanoAl₂O₃ during methanolysis of AB following the procedure described elsewhere [8].

2.7. Leaching test for Rh(0)/nanoAl₂O₃

A leaching test is performed for the Rh(0)/nanoAl₂O₃ in hydrogen generation from the methanolysis of AB by following the procedure described elsewhere [8]. Additionally, the filtrate solution obtained by filtration of the reaction mixture after the catalytic methanolysis reaction is also analyzed by ICP-OES for the rhodium content.

3. RESULTS and DISCUSSION

3.1. Formation of rhodium(0) nanoparticles and concomitant hydrogen generation from the methanolysis of AB

The reduction of rhodium(II) octanoate, impregnated on the porous nanoalumina, Rh(II)/nanoAl₂O₃, provides the *in situ* formation of nanoalumina supported rhodium(0) nanoparticles, Rh(0)/nanoAl₂O₃, during methanolysis of AB. First, the rhodium(II) octanoate solution in methanol was added to the suspension of nanoalumina in methanol solution and stirred for 1 h. Before using this precatalyst mixture in the catalytic methanolysis of AB, a solid sample was isolated for taking the ATR-IR spectrum to check whether rhodium(II) ions are accompanied by the octanoate anion in the impregnation on the surface of nanoalumina. Fig. 1 depicts the ATR-IR spectra of bare nanoalumina and nanoalumina-impregnated Rh(octanoate)₂, Rh(II)/nanoAl₂O₃ with a rhodium loading of 1.0% wt. Both spectra show a broad absorption at 3500 cm⁻¹ and a weak band at 1638 cm⁻¹ for the stretching and bending modes of OH groups on nanoalumina, in addition to the strong framework bands in the range 500–1000 cm⁻¹ (not shown in the spectra to simplify the view) [13]. ATR-IR spectrum of Rh(II)/nanoAl₂O₃ shows additionally two absorption bands at 1570 and 1420 cm⁻¹ due to the asymmetric and symmetric stretching of carboxylate group along with the C–H stretching bands at around 2900 cm⁻¹ indicating the presence of octanoate anion on

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