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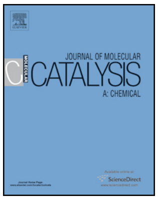

Ruthenium(0) nanoparticles supported on magnetic silica coated cobalt ferrite: Reusable catalyst in hydrogen generation from the hydrolysis of ammonia-borane

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Ruthenium(0) nanoparticles supported on magnetic silica-coated cobalt ferrite ($Ru(0)/SiO_2\text{-}CoFe_2O_4$) were *in situ* generated from the reduction of $Ru^{3+}/SiO_2\text{-}CoFe_2O_4$ during the catalytic hydrolysis of ammonia-borane (AB). Ruthenium(III) ions were impregnated on $SiO_2\text{-}CoFe_2O_4$ from the aqueous solution of ruthenium(III) chloride and then reduced by AB at room temperature yielding $Ru(0)/SiO_2\text{-}CoFe_2O_4$ which were isolated from the reaction solution by using a permanent magnet and characterized by ICP-OES, XRD, TEM, TEM-EDX and XPS techniques. The resulting magnetically isolable $Ru(0)/SiO_2\text{-}CoFe_2O_4$ were found to be highly reusable catalyst in hydrolysis of AB retaining 94% of their initial catalytic activity even after tenth run. $Ru(0)/SiO_2\text{-}CoFe_2O_4$ provide the highest catalytic activity after the tenth use in hydrolysis of AB as compared to the other ruthenium catalysts. The work reported here also includes the formation kinetics of ruthenium(0) nanoparticles. The evaluation of rate constants for the nucleation and autocatalytic surface growth of ruthenium(0) nanoparticles at various temperatures provides the estimation of activation energy for both reactions; $E_a = 116 \pm 7$ kJ/mol for the nucleation and $E_a = 51 \pm 2$ kJ/mol for the autocatalytic surface growth of ruthenium(0) nanoparticles. The report also includes the activation energy of the catalytic hydrogen generation from the hydrolysis of AB ($E_a = 45 \pm 2$ kJ/mol) determined from the evaluation of temperature dependent kinetic data and the effect of catalyst concentration on the rate of hydrolysis of AB.

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1. Introduction

Hydrogen is regarded as one of the best alternative energy carriers to satisfy the increasing demand for a sustainable and clean energy supply [1–3]. A great deal of research efforts has been devoted to find suitable hydrogen storage materials ensuring the safe and economical way [4,5]. Ammonia-borane (NH_3BH_3, AB) has been identified as one of the most attractive candidates for chemical hydrogen storage due to its high hydrogen content, nontoxicity and high stability at room temperature [6–11]. AB can release H_2 by thermolysis [12] or solvolysis [13,14]. However, the search for suitable catalysts for the release of hydrogen from the hydrolysis of AB at an appreciable rate is crucial (Eq. (1)). Therefore, a large number of studies have been published using transition metal nanoparticles as catalysts for the hydrogen generation from AB [15,16].

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

Among the transition metal nanoparticles, ruthenium is one of the most active catalysts for the hydrogen generation from the hydrolysis of AB under mild conditions. Although there exist a wealth of reports on the hydrogenation of AB using ruthenium catalysts such as Ru(0)NP/PSSA-co-MA [17], Ru(0)@Hap [18], Ru/Carbon [19], RuNPs@ZK-4 [20], $Ru@Al_2O_3$ [21], Ru(0)NP/laurate [22], Ru(0)@MWCNTs [23] and Ru/C [24], there is no example of magnetically recoverable ruthenium catalyst for the hydrogen release from AB. Recently, much attention has been paid to the magnetically recoverable catalysts in liquid phase reactions due to their easy magnetic separation making the recovery of catalysts much easier than by filtration and centrifugation [25].

Herein, we report ruthenium(0) nanoparticles supported on silica-coated cobalt ferrite ($SiO_2\text{-}CoFe_2O_4$) as magnetically isolable and recyclable catalyst for the hydrolysis of ammonia-borane.

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Ruthenium(0) nanoparticles supported on magnetic silica-coated cobalt ferrite were *in situ* generated from the reduction of $Ru^{3+}/SiO_2\text{-}CoFe_2O_4$ during the catalytic hydrolysis of AB. Cobalt ferrite ($CoFe_2O_4$) nanoparticles were preferred as magnetic core materials due to the easy preparation procedure as compared to the other magnetic core materials such as Fe_3O_4 [26]. SiO_2 was used to protect the magnetic core material against leaching and agglomeration and it also provides high surface area to stabilize the ruthenium nanoparticles. $Ru(0)/SiO_2\text{-}CoFe_2O_4$ were isolated from the reaction solution by using a permanent magnet and characterized by ICP-OES, XRD, TEM, TEM-EDX and XPS techniques. The results reveal that highly dispersed ruthenium(0) nanoparticles were successfully supported on $SiO_2\text{-}CoFe_2O_4$. The formation kinetics of ruthenium(0) nanoparticles was studied by using the hydrogen evolution from the hydrolysis of AB as reporter reaction. The work reported here also includes the results of kinetic study of the hydrolytic dehydrogenation of AB depending on the temperature and catalyst concentration.

2. Experimental

2.1. Materials

Iron(III) chloride ($FeCl_3$), tetraethylorthosilicate (TEOS), ammonium hydroxide (NH_4OH), sodium hydroxide (NaOH), cobalt(II) chloride ($CoCl_2$), Ruthenium(III) chloride trihydrate ($RuCl_3{\cdot}3H_2O$) and ammonia-borane (H_3NBH_3, 97%) were purchased from Aldrich. 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 150 °C.

2.2. Characterization

The ruthenium contents of the $Ru(0)/SiO_2\text{-}CoFe_2O_4$ samples were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Leeman-Direct Reading Echelle). Transmission electron microscopy (TEM) was performed on a JEM-2100F (JEOL) microscope operating at 200 kV. A small amount of powder sample was placed on a copper grid of the transmission electron microscope. Samples were examined at magnification between 100 and 400 K. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al Kα radiation of 1486.6 eV, the X-ray tube working at 15 kV, 350 W and pass energy of 23.5 keV. ^{11}B NMR spectra were recorded on a Bruker Avance DPX 400 with an operating frequency of 128.15 MHz for ^{11}B.

2.3. Preparation of magnetic silica-coated cobalt ferrite ($SiO_2\text{-}CoFe_2O_4$)

The preparation of magnetic cobalt ferrite nanoparticles was carried out by modification of previously established procedure [27]. The detailed information on the preparation and characterization of silica-coated cobalt ferrite can be found elsewhere [28]. In a typical experiment 25 mL of 0.4 M iron(III) chloride and 25 mL of 0.2 M of cobalt(II) chloride solutions were mixed at room temperature. Then, in a separate vessel 25 mL of 3.0 M sodium hydroxide solution was prepared and slowly added to the salt solution. After complete addition of NaOH solution, a black suspension was obtained. The mechanical stirring was continued for 1 h at 80 °C. Then the solution was cooled to room temperature and the black precipitates were collected by using an external magnet. The supernatant was removed and the particles were washed 3 times with deionized water–ethanol solution and then the particles were dispersed in 50 mL of water. Silica coating was applied by using a modified version of Stober method [29]. For the preparation of silica coating, 200 mL ethanol, 1 mL TEOS and 0.5 mL of NH_4OH were added to the reaction mixture and subsequently 50 mL cobalt ferrite colloid was added to the mixture and the mixture was stirred for 4 h at room temperature. After the formation of the thick silica shell, particles were collected with a magnet and washed 3 times with deionized water. The resulting silica-coated cobalt ferrite nanoparticles ($SiO_2\text{-}CoFe_2O_4$) were separated by using a permanent magnet and washed with excess ethanol and dried at 120 °C for 12 h in the oven.

2.4. Impregnation of ruthenium(III) ions on magnetic silica-coated cobalt ferrite [$Ru^{3+}/SiO_2\text{-}CoFe_2O_4$]

$SiO_2\text{-}CoFe_2O_4$ (100 mg) was added to a solution of $RuCl_3{\cdot}3H_2O$ (5.65 mg) in 20 mL H_2O in a 50 mL beaker. This slurry was stirred at room temperature for 12 h and then, all supernatant solution was removed by using a permanent magnet. Next, the resulting particles $Ru^{3+}/SiO_2\text{-}CoFe_2O_4$ were washed with 20 mL of deionized water and isolated by using a permanent magnet and the remnant was dried at 120 °C for 12 h in the oven.

2.5. In situ formation of ruthenium(0) nanoparticles supported on magnetic silica-coated cobalt ferrite [$Ru(0)/SiO_2\text{-}CoFe_2O_4$] and concomitant catalytic hydrolysis of AB

Ruthenium(0) nanoparticles supported on magnetic silica-coated cobalt ferrite were *in situ* generated from the reduction of $Ru^{3+}/SiO_2\text{-}CoFe_2O_4$ during the catalytic hydrolysis of AB. Before starting the catalyst formation and concomitant catalytic hydrolysis of AB, a jacketed reaction flask (20 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 (60 cm in height and 3.0 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, 10 mg powder of $Ru^{3+}/SiO_2\text{-}CoFe_2O_4$ (1.96 wt.% Ru) was dispersed in 10 mL distilled water in the reaction flask thermostated at 25.0 ± 0.1 °C. Then, 31.8 mg AB (1.0 mmol H_3NBH_3) was added into the flask and the reaction medium was stirred at 1000 rpm. After adding ammonia-borane, ruthenium(0) nanoparticles were formed and the catalytic hydrolysis of AB started immediately. The volume of hydrogen gas evolved was measured by recording the displacement of water level every 30 s at constant atmospheric pressure of 693 Torr. The reaction was stopped when no more hydrogen evolution was observed. In each experiment, the resulting solutions were filtered and the filtrates were analyzed by ^{11}B NMR and conversion of AB to metaborate anion was confirmed by comparing the intensity of signals in the ^{11}B NMR spectra of the filtrates.

2.6. Determination of activation energy for hydrolysis of AB catalyzed by $Ru(0)/SiO_2\text{-}CoFe_2O_4$

In a typical experiment, the hydrolysis reaction was performed starting with 10 mL of 100 mM (31.8 mg) AB solution and 10 mg $Ru^{3+}/SiO_2\text{-}CoFe_2O_4$ (1.96 wt.% ruthenium, [Ru] = 0.186 mM) at various temperatures (25, 30, 35, 40 °C) in order to obtain the activation energy.

2.7. Reusability of $Ru(0)/SiO_2\text{-}CoFe_2O_4$ in hydrolysis of AB

After the complete hydrolysis of AB started with 10 mL of 100 mM AB (31.8 mg H_3NBH_3), and 60 mg $Ru(0)/(SiO_2\text{-}CoFe_2O_4)$

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