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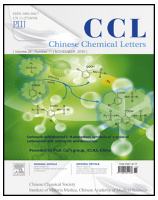

Original article

Ruthenium deposited on MCM-41 as efficient catalyst for hydrolytic dehydrogenation of ammonia borane and methylamine borane

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ABSTRACT

Ultrafine Ru nanoparticles are successfully deposited on MCM-41 by using a simple liquid impregnation-reduction method, and further investigated for catalytic hydrolysis of ammonia borane and methylamine borane. Among all the catalysts tested, 1.12 wt% Ru/MCM-41 exhibits the highest catalytic activity, with turnover frequency value of 288 min^{-1}.

1. Introduction

Hydrogen is considered as one of the most important clean fuel for the sustainable development because of its merit of high efficiency and power density [1]. Safe and controlled storage of hydrogen are the widely known barriers in the fuel cell based hydrogen economy [2]. Recently, ammonia borane (NH_3-BH_3, AB) has been regarded as one of the best potential chemical hydrogen storage candidate because of its 19.6 wt% hydrogen content, highly stability, and environmental benignity [3]. Meanwhile, methylamine borane (CH_3NH_2-BH_3, MeAB), the derivative of AB has also been studied due to its high gravimetric hydrogen content (11.1 wt%). The hydrogen release from hydrolysis of AB/MeAB could be as much as 3 mol of hydrogen per mol of AB/MeAB with an appropriate catalyst according to Eqs. (1) and (2) [4], which seems to be the most convenient way for portable hydrogen storage applications compared with solid phase thermolysis [5], and catalytic dehydrogenation in non-aqueous solvents [6].

$$NH_3\text{-}BH_3 + 2H_2O \xrightarrow{\text{catalyst}} NH_4BO_2 + 3H_2 \tag{1}$$

$$MeNH_2\text{-}BH_3 + 2H_2O \xrightarrow{\text{catalyst}} (MeNH_3)BO_2 + 3H_2 \tag{2}$$

So far, a lot of metal nanoparticles (NPs) based catalysts have been developed for catalytic hydrolysis of AB and MeAB [7–9], among them, the Ru based nanocatalysts have been identified as one of the most effective catalysts. However, their catalytic activities are highly depended on the dispersion of active metal sites [10]. In order to avoid the aggregation, many methods have been employed in their synthesis route. For example, Özkar reported laurate stabilized Ru NPs with TOF of 75 min^{-1} [11], Miele reported γ-Al_2O_3 supported Ru NPs with turnover frequency (TOF) value of 77 min^{-1} toward catalytic hydrolysis of AB [12], and multiwalled carbon nanotube supported Ru NPs with TOF of 329 min^{-1} [13], Ma reported carbon black supported Ru NPs with TOF of 429 min^{-1} [14]. Very recently, our group reported microporous metal-organic frameworks MIL-96 supported Ru NPs with TOF of 231 min^{-1} [15], and MIL-101 immobilized Ru NPs with TOF of 178 min^{-1} [16]. As a continuous work to study the pore size effect to the effect of catalytic activity of Ru NPs, MCM-41 a mesoporous material with high special surface areas, large pore volumes, and homogeneous pore arrays [17], which consists of ordered hexagonal pores has been used as supported material for Ru NPs. Herein, Ru NPs have been firstly deposited on MCM-41, and further tested for catalytic hydrolysis of AB and MeAB.

2. Experimental

2.1. Chemicals and materials

All chemicals were commercial and used without further purification. MCM-41 (Sinopharm Chemical Reagent Co., Ltd.),

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ruthenium chloride hydrate ($RuCl_3 \cdot nH_2O$, Wuhan Greatwall Chemical Co., Ltd., 99%), ammonia borane (NH_3BH_3, AB, United Boron (Zhengzhou) Energy Materials S&T LLC., 98%), methylamine hydrochloride ($CH_3NH_2 \cdot HCl$, Sinopharm Chemical Reagent Co., Ltd., ≥96%), sodium borohydride ($NaBH_4$, Sinopharm Chemical Reagent Co., Ltd., 96%), tetrahydrofuran (C_4H_8O, Sinopharm Chemical Reagent Co., Ltd., ≥99%), diethyl ether anhydrous ($C_4H_{10}O$, Sinopharm Chemical Reagent Co., Ltd., ≥99.7%), ethanol (C_2H_5OH, Sinopharm Chemical Reagent Co., Ltd., >99.8%), ketjen black EC-300J (Triquo Chemical Co., Ltd.), neutral silica power (SiO_2, Branch of Qingdao Haiyang Chemical Co., Ltd.), were used as received. We use ordinary distilled water as the reaction solvent.

2.2. Synthesis of methyl ammonia borane (CH_3NH_2-BH_3, MeAB)

MeAB was synthesized by the method reported in the literature [18]. Methylamine hydrochloride and sodium borohydride were added to a flask. The mixure of contents were vigorously stirred when THF was transferred into the flask. The resultant solution was filtered by suction filtration after the reaction was carried out for 12 h, and the filtrate was concentrated. MeAB was obtained from purification by diethyl ether.

2.3. Synthesis of Ru/MCM-41

MCM-41 (100 mg) was mixed with 0.01, 0.02, 0.03, 0.04 mmol $RuCl_3$ solution (0.01 mol L^{-1}) in a two-necked round-bottom flask containing 10 mL deionized water for 24 h at room temperature. The resulting mixture was then reduced with AB (30.8 mg, 1 mmol) at 293 K to yield Ru/MCM-41.

2.4. Hydrolysis of AB by Ru/MCM-41

50 mg Ru/MCM-41 with different loadings was kept in a two-necked round-bottom flask containing 10 mL de-ionized water. A pressure-equalization funnel was connected to one neck to introduce aqueous solution of AB (30.8 mg, 1 mmol) and a gas buret was connected to the other neck to record the volume of the gas evolution. As soon as the aqueous solution was added to the catalyst, the volume of the gas evolution was monitored immediately. All the reactions were carried out at 298 K in air.

2.5. Hydrolysis of MeAB by Ru/MCM-41

50 mg Ru/MCM-41 was kept in a two-necked round-bottom flask containing 10 mL de-ionized water. A pressure-equalization funnel was connected to one neck to introduce aqueous solution of MeAB (45 mg, 1 mmol), and the other neck was to record the volume of the gas evolution. As soon as the aqueous solution was added to the catalyst, the volume of the gas evolution was monitored immediately. All the reactions were carried out at 298 K in air.

2.6. In situ synthesis of Ru supported on different materials and their application toward hydrolysis of ammonia borane

50 mg different supported materials (carbon black, SiO_2) were mixed separately with 0.0055 mmol $RuCl_3$ solution (0.01 mol L^{-1}) and kept in a two-necked round-bottom flask containing 10 mL deionized water. After aqueous solution of AB (30.8 mg, 1 mmol) was introduced, Ru^{3+} was reduced to Ru^0. Then the new fresh aqueous solution of AB (30.8 mg, 1 mmol) was added when the hydrogen generation reaction was completed. All the reactions were carried out at 298 K in air.

2.7. Hydrolysis of AB catalyzed by MCM-41

50 mg Ru/MCM-41 was substituted by 50 mg MCM-41, the experiment procedures were similar to that 2.4 procedure. In order to determine the rate law of the catalytic hydrolysis of the AB or MeAB, the concentration was kept unchanged (1 mmol). Also the reactions were carried out at 25 °C, 30 °C, 35 °C and 40 °C, while 50 mg Ru/MCM-41 and AB or MeAB (1 mmol) were kept the same to obtain the activation energy (E_a).

2.8. Cycle stability test

AB or MeAB (1 mmol) solution was introduced to 5 mL of water dispersed 50 mg Ru/MCM-41, the evolution of gas was recorded as described above. As soon as the hydrogen generation reaction was completed, another new fresh equivalent of AB or MeAB (1 mmol) was added to the mixure. Such cycle stability tests of the catalyst were carried out five times at 298 K in air.

2.9. Characterization

The morphologies and sizes of different samples were characterized by using a Tecnai G20 U-Twin transmission electron microscope (TEM) equipped with an energy dispersive X-ray detector (EDX) at an acceleration voltage of 200 kV. The surface area measurements were performed with N_2 adsorption/desorption isotherms at liquid nitrogen temperature (77 K) after dehydration under vacuum at 150 °C for 18 h using Quantachrome NOVA 4200e. The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on IRIS Intrepid II XSP (Thermo Fisher Scientific, USA). Powder X-ray diffraction (XRD) patterns were measured by a Bruker D8-Advance X-ray diffractometer using Cu Ka radiation source ($\lambda = 0.154178$ nm) with a velocity of 1° min^{-1}.

3. Results and discussion

The MCM-41 supported Ru catalyst was synthesized through a simple liquid impregnation-reduction method. The loading values of Ru deposited on MCM-41 of different samples were determined as 0.52, 0.70, 0.90 and 1.12 wt% performed on the inductively coupled plasma atomic emission spectroscopic (ICP-AES). In order to verify the integrity and regularity of the mesoporous structure, MCM-41, Ru/MCM-41 characterized by the powder X-ray diffractions (PXRD) show no loss of crystallinity (Fig. 1), which corresponds to the reported MCM-41 zeolite [19], demonstrating that the integrity and regularity of MCM-41 structure maintained perfect and intact during the catalyst preparation and catalytic process. Furthermore, no obvious diffraction peaks of Ru were observed from the wide-angle PXRD (Fig. 1b), which might be caused by the traps of Ru NPs into the pores of MCM-41 and the ultrafine Ru NPs (*vide infra*). The adsorption–desorption isotherms of MCM-41 and Ru/MCM-41 were shown in Fig. 2a. The specific areas of MCM-41 and Ru/MCM-41 were 900 and 779 $m^2 g^{-1}$, respectively. The decrease in the amount of N_2 adsorption and the pore volume (Fig. 2a, Table 1) of Ru/MCM-41 indicates that the pores of MCM-41 were either occupied by the well dispersed Ru

Table 1
Pore volume and surface area of MCM-41 and Ru/MCM-41.

Sample	Average pore diameter (nm)	Surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)
Ru/MCM-41	3.182	779	0.498
MCM-41	3.407	900	0.879