A facile synthesis of nearly monodisperse ruthenium nanoparticles and their catalysis in the hydrolytic dehydrogenation of ammonia borane for chemical hydrogen storage

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ARTICLE INFO

ABSTRACT

A facile method for the preparation of nearly monodisperse Ru nanoparticles (NPs) and their record catalytic activity in the hydrolytic dehydrogenation of ammonia borane (AB) for chemical hydrogen storage are reported herein. Ru NPs were prepared by a novel protocol comprising the thermal decomposition and concomitant reduction of ruthenium(III) acetylacetonate ($Ru(acac)_3$) in the presence of oleylamine (OAm) and benzylether (BE). In the protocol, OAm served as both a stabilizer and reducing agent and BE used as a solvent. Ru NPs were supported on aluminum oxide nanopowder ($Ru@Al_2O_3$) via a simple liquid impregnation method before their use as catalyst for the dehydrogenation of AB in water. Without any special treatment to remove the surfactants, $Ru@Al_2O_3$ showed high catalytic activity in the hydrolytic dehydrogenation of AB providing an initial turnover frequency (TOF) of 39.6 mol H_2 (mol Ru min)$^{-1}$. Their catalytic performance was further enhanced dramatically by the acetic acid treatment and the initial TOF value is increased to 83.3 mol H_2 (mol Ru min)$^{-1}$ that is the highest among the reusable Ru catalysts and even higher than Pt-based catalysts tested in the hydrolysis of AB. Additionally, the work reported here includes a wealth of kinetic data to determine the rate law and apparent activation parameters for the catalytic dehydrogenation of AB in water.

1. Introduction

The use of transition metal nanoparticles (NPs) in catalysis has attracted much attention in all areas of science and technology because of its high activity and selectivity associated with their small particle size and large surface area [1–3]. In recent years, Ru NPs have emerged as one of the most active catalysts among other transition metals due to their high activities under mild conditions in various catalytic reactions [4,5]. Many chemical routes have been reported for the preparation of Ru NPs including alcohol reduction [6] or borohydride reduction [7] either in water or organic solvents in the presence of various stabilizers [8–10]. However, monodisperse Ru NPs with shape and size control are only made by decomposition of organometallic Ru complexes in the presence of surfactants such as long-chain thiols [11,12] or polymers [13,14] that bind strongly to surface of Ru, which forms a hindrance to obtain high catalytic activity. Although there are some reports on the removing those type of surfactants from the NPs surface [15], the aggregation of NPs and catalysis deterioration is

unavoidable in those protocols. In this regard, the preparation of Ru NPs with a narrow size distribution in the presence of weakly binding surfactants is aspired to develop their highly active heterogeneous catalysts. In our recent study, we demonstrated that monodisperse Ni NPs prepared from the reduction of nickel(II) acetylacetonate by borane ter-butylamine in oleylamine (OAm) and oleic acid as surfactants are highly active and stable catalysts in the hydrolytic dehydrogenation of ammonia borane (AB) [16]. Sun et al. also reported highly active catalysis of monodiperse palladium NPs prepared from reduction palladium(II) acetylacetonate by borane ter-butylamine in OAm for the formic acid oxidation [17]. Correlatively, the preparation of monodiperse Ru NPs in the presence of OAm or oleic acid as a weakly binding surfactant will be advantageous for the preparation of highly active and stable Ru nanocatalyst.

On the other hand, the storage of hydrogen is still a major hurdle for prospective hydrogen economy although the use of hydrogen as an energy carrier in various daily-life applications has been already initiated. Recently, ammonia borane (AB, $H_3N·BH_3$) has been regarded as the most promising entrant for vehicular hydrogen storage applications among all other chemical hydrogen storage materials [18–21] owing to its high hydrogen content of 19.6 wt% that is greater than the 2015 target of the U.S. Department of Energy (9 wt% hydrogen for a material) [22] and stability

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in the solid state under ambient conditions [23,24]. The hydrogen stored in AB can be released through different ways [25–27], but the hydrolytic dehydrogenation of AB (hydrolysis, Eq. (1)) [28–30] seems to be most promising route considering on-board applications [31].

$$H_3NBH_3(aq) + 2H_2O(l) \rightarrow (NH_4)BO_2(aq) + 3H_2(g) \qquad (1)$$
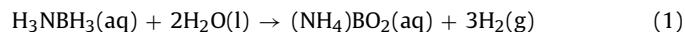
However, a catalyst facilitating the B—N bond cleavage is required to generate hydrogen from the hydrolysis of AB due to the strong B—N bond of AB [32–35]. Because of the advantages of heterogeneous catalysis, current research on finding new catalyst systems that possess high activity with a practical rate of hydrogen generation from the hydrolysis of AB has been directed toward the development of heterogeneous catalysts [36–42].

Herein we report a facile method for the preparation of nearly monodisperse Ru NPs and their superb catalysis in the hydrolytic dehydrogenation of AB under ambient conditions. The Ru NPs were prepared by a facile and novel method comprising the thermal decomposition and concomitant reduction of ruthenium(III) acetylacetonate ($Ru(acac)_3$) in the presence of oleylamine (OAm) and benzylether (BE). In our protocol, OAm served as both a surfactant and reducing agent and BE was used as a solvent. The as-prepared Ru NPs are dispersible and colloidally stable for months in non-polar solvents such as hexane and tetrahydrofuran. Without any special treatment to remove the surfactants, as-prepared Ru NPs were supported on aluminum oxide nanopowder ($Ru@Al_2O_3$) via simple liquid impregnation method and showed high catalytic activity and stability in the hydrolytic dehydrogenation of AB. Their catalytic performance was further enhanced dramatically by the acetic acid treatment and the TOF value is increased from 39.6 to 83.3 mol H_2 (mol Ru min)$^{-1}$ that is the best among the reusable Ru catalyst and even higher than the best Pt-based catalysts tested in the hydrolysis of AB. Kinetics of the $Ru@Al_2O_3$ catalyzed hydrolytic dehydrogenation of AB was also studied depending on the catalyst concentration, substrate concentration and temperature.

2. Experimental

2.1. Chemicals

All commercially obtained chemicals were used as received unless indicated otherwise. Ruthenium(III) acetylacetonate (99%), oleylamine (OAm, >70%), borane ammonia complex (AB, 97%), hexane (99%), benzyl ether (BE, 97%), aluminum oxide nanopowder (γ-Al_2O_3, particle size <50 nm (TEM), surface area >40 m^2/g (BET)), acetic acid (99%), isopropanol, deuterated water and chloroform were purchased from Sigma–Aldrich®. All glassware and Teflon-coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying at 150 °C in oven for overnight.

2.2. Instrumentation

Transmission electron microscope (TEM) and high resolution TEM (HRTEM) images were obtained using a JEM-2100 (JEOL) instrument operating at 200 kV. Samples were examined at magnification between 50 and 800 K. X-ray diffraction pattern (XRD) was recorded on a Rigaku Miniflex diffractometer with Cu Kα (30 kV, 15 mA, λ = 1.54051 Å), over a 2θ range from 10° to 80° at room temperature. Ruthenium content of the catalyst samples were determined by using Leiman series inductively coupled plasma-optical emission spectroscopy (ICP-OES) after each sample was completely dissolved in aqua-regia (HNO$_3$/HCl: 1/3, v/v, ratio). ^{11}B NMR spectrum was measured on a Bruker Avance DPX 400 MHz spectrometer (400.1 MHz for ^{1}H NMR; 100.6 MHz for ^{13}C NMR;

128.2 MHz for ^{11}B NMR). BF$_3$·(C$_2$H$_5$)$_2$O was used as the external reference for ^{11}B NMR chemical shifts.

2.3. Synthesis of ruthenium nanoparticles and supporting them on nano γ-Al_2O_3

In a typical synthesis, 200.0 mg ruthenium(III) acetylacetonate (0.5 mmol Ru), 10.0 mL of OAm and 8.0 mL of BE were mixed and stirred at 1000 rpm under continuous nitrogen flow in a special four-necked reactor. Owing to jacketed heater and connected thermocouple placed into the reactor, the mixture was heated up to 120 °C slowly and kept at this temperature for 1 h. Next, the resulted solution was heated to 300 °C (20 °C/min) and maintained at this temperature for 1 h. Then, the mixture was cooled down to 40 °C and centrifuged at 8000 rpm for 10 min after the addition of isopropanol into the each nanoparticle solution separated into four centrifuge tubes. After centrifugation, a very few amount of Ru NPs stacked on the surface of centrifuge tubes was discarded and the supernatant solution was transferred into the 250 mL of erlenmayer. Next, 1.5 g of Al$_2$O$_3$ nanopowder was added into the supernatant solution and stirred for overnight. The resultant mixture was centrifuged at 6000 rpm for 12 min for the separation of Al$_2$O$_3$ nanopowder supported Ru NPs ($Ru@Al_2O_3$). The isolated Ru@Al$_2$O$_3$ catalyst were redispersed in hexane and centrifuged at 6000 rpm for 12 min again to remove the unsupported Ru NPs. Finally, the Ru@Al$_2$O$_3$ catalysts were dispersed in water (20 mL) and treated with 640 mg AB before testing their catalytic activity in the hydrolytic dehydrogenation of AB.

2.4. Hydrolytic dehydrogenation of ammonia borane catalyzed by Ru@Al$_2$O$_3$

A desired amount of as-prepared Ru@Al$_2$O$_3$ catalysts were dispersed in 7.0 mL of water in the jacketed reactor thermostated at 25.0 ± 0.5 °C. Next, 2.0 mmol AB dissolved in 3.0 mL of water was injected into the catalyst solution via gastight syringe under vigorous stirring and hydrogen gas evolution started immediately. The catalytic hydrolysis reaction was followed by measuring the hydrogen generation with time. Hydrogen gas generation from the catalytic reaction solution was followed by using a typical water-filled gas burette system and recording the displacement of water level in the gas burette every minute until no more hydrogen evolution observed. Next, an approximately 0.1 mL aliquot of the reaction solution in the reactor was withdrawn with a glass Pasteur pipette and added to 0.5 mL of D$_2$O in a quartz NMR sample tube (Norell S-500-QTZ), which was subsequently sealed. The ^{11}B NMR spectrum of this solution showed the complete conversion of H$_3$NBH$_3$ (quartet at −23 ppm) to ammonium metaborate giving a peak at 9.1 ppm.

2.5. Kinetics of hydrolytic dehydrogenation of AB catalyzed Ru@Al$_2$O$_3$

In order to establish the rate law and obtain the activation parameters for the hydrolytic dehydrogenation of AB catalyzed by Ru@Al$_2$O$_3$, three different sets of experiment were performed in the same ways described in Section 2.4. In the first set of experiments, the concentration of AB was kept constant at 200.0 mM and the amount of Ru@Al$_2$O$_3$ catalyst (1 wt% Ru) was varied in the range of 50, 75, 100, 125 and 150 mg at 25 ± 0.5 °C. In the second set of experiments, the amount of Ru@Al$_2$O$_3$ catalyst (1 wt% Ru) was held constant at 100 mg while AB concentration was varied in the range of 100, 200, 300, 400 and 500 mM at 25 ± 0.5 °C. Finally, the catalytic dehydrogenation of AB was performed at constant AB concentration (200.0 mM) and amount of Ru@Al$_2$O$_3$ catalyst (75 mg, 1 wt% Ru) at various temperatures in the range of 20–40 °C in order to