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Editor's choice paper

Ruthenium(0) nanoparticles supported on nanohafnia: A highly active and long-lived catalyst in hydrolytic dehydrogenation of ammonia borane

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ABSTRACT

Ruthenium(0) nanoparticles supported on nanohafnia (Ru^0/HfO_2) were prepared by impregnation of ruthenium(III) cations on the surface of hafnia followed by their reduction with sodium borohydride at room temperature. Ru^0/HfO_2 samples were isolated from the reaction solution by centrifugation and characterized by a combination of advanced analytical techniques including ICP-OES, BET, XRD, SEM-EDS, TEM, XPS. The catalytic activity of Ru^0/HfO_2 samples with various ruthenium loading in the range 0.5–5.0% wt Ru was tested in hydrogen generation from the hydrolysis of ammonia borane (AB) at room temperature. The highest catalytic activity was achieved by using 4.0% wt ruthenium loaded nanohafnia providing a turnover frequency of 170 min^{-1} and an unprecedented catalytic life time (175,600 turnovers) in hydrogen generation from the hydrolysis of AB at $25.0 \pm 0.1\,^\circ C$. Ru^0/HfO_2 is reusable catalyst preserving 75% of the initial catalytic activity even after the fifth reuse in hydrogen generation from the hydrolysis of AB at room temperature. Our report also includes the results of kinetic studies depending on the catalyst concentration and temperature to determine the activation energy ($E_a = 65 \pm 3$ kJ/mol) for hydrolytic dehydrogenation of AB.

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1. Introduction

Hydrogen has been regarded as a clean and sustainable energy carrier in the transition from fossil fuels to the renewable energy sources [1–3]. However, the safe storage and efficient release of hydrogen under ambient condition still remains a big obstacle to widespread use of hydrogen [4–6]. Over the past few years, increasing efforts have been made to search for suitable hydrogen storage materials [7–9]. Ammonia borane (NH_3BH_3, AB) has recently been considered as an attractive candidate for solid hydrogen storage materials due to its high hydrogen content (19.6% wt H), nontoxicity, and high stability in solid state and solution [10,11]. Ammonia borane can release hydrogen by either thermolysis [12] or solvolysis [13]. Since the former process requires high temperature [14], the hydrolysis of ammonia borane has been preferentially used for hydrogen generation from AB on the account of rapid hydrogen release and controlled kinetics (Eq. (1)) [15,16].

$$NH_3BH_3(aq) + 2H_2O(l) \rightarrow NH_4^+(aq) + BO_2^-(aq) + 3H_2(g) \qquad (1)$$

Regarding the nature of boron containing product of hydrolysis, we adopted the use $BO_2^-(aq)$ ion as hydrolysis product [17]. When dissolved in aqueous solution, BO_2^- ion will be converted first to $B(OH)_4^-$ ion [18] which can undergo condensation to polyborate species as confirmed by ^{11}B NMR spectroscopy [16]. The hydrolysis of ammonia borane occurs only in the presence of a suitable catalyst at room temperature. Recently many transition metal catalysts including noble [19] and non-noble [20] metal nanoparticles have been employed in hydrogen generation from the hydrolysis of ammonia borane. However, it is still a big challenge to develop catalysts with high catalytic activity, reusability, and long life-time for hydrogen generation from the hydrolysis of ammonia borane. To this end, catalytic activity and stability of metal nanoparticles have been improved by supporting them on suitable materials including oxides such as silica (SiO_2) [21], alumina (Al_2O_3) [18], ceria (CeO_2) [22,23], titania (TiO_2) [24], and zirconia (ZrO_2) [25]. Among the oxides of group 4 metals, hafnium dioxide (HfO_2, hafnia) is widely used in the field of electronics due to its relatively high dielectric constant, making it a suitable alternative to silicon dioxide as insulating layers for the improvement of integrated circuits [26,27]. Hafnia has also high chemical and thermal stability [28,29], which make it an alternative supporting material for metal nanoparticle catalysts.

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Herein we report the preparation, characterization, and catalytic use of ruthenium(0) nanoparticles supported on nanohafnia, Ru^0/HfO_2. Ruthenium(III) ions impregnated on the surface of nanohafnia were reduced by sodium borohydride forming Ru^0/HfO_2 which was used in catalyzing the H_2 generation of from ammonia borane. Ru^0/HfO_2 was characterized by ICP-OES, BET, XRD, SEM-EDS, TEM and XPS techniques. Our report includes the following major findings: (i) Highly dispersed ruthenium(0) nanoparticles with particle size in the range 2.4–5.0 nm were formed on the surface of nanohafnia. (ii) Ru^0/HfO_2 is long lived catalyst with an unprecedented total turnover number (TTO = 175,600) in hydrogen generation from the hydrolysis of ammonia borane at room temperature. (iii) Ru^0/HfO_2 is also reusable catalyst as it retains 75% of the initial catalytic activity in the hydrolysis of ammonia borane even after the fifth use.

2. Experimental

2.1. Materials

Ruthenium(III) chloride trihydrate ($RuCl_3{\cdot}3H_2O$), hafnia (HfO_2, particle size ≈100 nm), and ammonia borane (H_3NBH_3, 97%) were purchased from Aldrich. Sodium borohydride ($NaBH_4$, 98%) was purchased from Merck. Deionized water was distilled by water purification system (Milli-Q System).

2.2. Characterization

This section is identical to our recent report [30].

2.3. Preparation of ruthenium(0) nanoparticles supported on hafnia (Ru^0/HfO_2)

Hafnia (400 mg) was added to a solution of $RuCl_3{\cdot}3H_2O$ (in the amount required for the desired ruthenium loading) in 50 mL H_2O in a 100 mL beaker. This slurry was first ultrasonicated for 30 min. After stirring for 24 h at room temperature, 10 mL of sodium borohydride solution (mol ratio of $NaBH_4/Ru = 10$) was added drop wise into the suspension. When the H_2 evolution from the reaction solution ended (~1 h), the solid powders were isolated by centrifugation and washed five times with 50 mL of deionized water to remove metaborate anions and dried under vacuum (10^{-3} Torr) at 60 °C for 12 h. The samples of Ru^0/HfO_2 were bottled as grey powders. Ruthenium content of the Ru^0/HfO_2 samples was determined by ICP-OES analysis.

2.4. Catalytic hydrolysis of ammonia borane using ruthenium(0) nanoparticles supported on hafnia

The catalytic hydrolysis of AB using desired amount of Ru^0/HfO_2 (4.0% wt Ru) was performed by following our well established procedure given in the recent report [30].

2.5. Determination of the most active ruthenium loading for Ru^0/HfO_2 in the hydrolysis of ammonia borane

Ru^0/HfO_2 samples with different Ru contents (0.5–5.0% wt) were tested in hydrolysis of AB (100 mM) in 10 mL of H_2O at 25.0 ± 0.1 °C. For all tests ruthenium concentration was kept constant (0.4 mM Ru) and the most active ruthenium loading for Ru^0/HfO_2 used in hydrolysis of AB was found as 4.0% wt. Therefore, Ru^0/HfO_2 with a ruthenium content of 4.0% wt was used for all characterizations and the other catalytic tests.

2.6. Determination of activation energy for hydrolysis of ammonia borane catalyzed by Ru^0/HfO_2

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^0/HfO_2 ([Ru] = 0.4 mM) at various temperatures (25, 30, 35, 40 °C) in order to obtain the activation energy.

2.7. Reusability of Ru^0/HfO_2 in hydrogen generation from the hydrolysis of ammonia borane

The reusability of Ru^0/HfO_2 (40 mg catalyst, [Ru] = 1.58 mM) was tested in hydrolysis of ammonia borane at 25.0 ± 0.1 °C following the procedure described elsewhere [30].

2.8. Determination of the catalytic lifetime of Ru^0/HfO_2 in hydrogen generation from the hydrolysis of ammonia borane

The catalytic lifetime of Ru^0/HfO_2 in the hydrolysis of AB was determined by measuring the total turnover number (TTO). Catalyst lifetime experiment was performed starting with 3.4 mg Ru^0/HfO_2 ([Ru] = 0.067 mM) in 50 mL solution of AB at 25.0 ± 0.1 °C. When all the ammonia-borane present in the solution was completely hydrolyzed, more AB was added and the reaction was continued in this way until no hydrogen gas evolution was observed.

3. Results and discussion

Ruthenium(0) nanoparticles supported on hafnia (Ru^0/HfO_2) were prepared by impregnation of ruthenium(III) ions on the surface of nanohafnia followed by their reduction with sodium borohydride at room temperature. Ru^0/HfO_2 was isolated from the reaction solution by centrifugation and characterized by ICP-OES, BET, XRD, SEM, SEM-EDS, TEM and XPS.

The BET nitrogen adsorption-desorption analysis gave the surface area of 6.1 m^2/g for nanohafnia and 15.8 m^2/g for Ru^0/HfO_2 (4.0% wt Ru). The increase in the surface area of hafnia upon ruthenium loading implies the existence of ruthenium nanoparticles on the surface of nanohafnia. The increase in the surface area upon ruthenium loading by 4.0% wt Ru can be ascribed to the formation of small ruthenium nanoparticles, which are not tightly bound on the hafnia surface (*vide infra*). Thus, the formation of ruthenium nanoparticles does not cause a significant coverage of the hafnia surface but creates additional surface area.

The powder XRD patterns of hafnia nanopowders and Ru^0/HfO_2 with a 4.0% wt ruthenium loading (Fig. 1) exhibit peaks at 24.18,

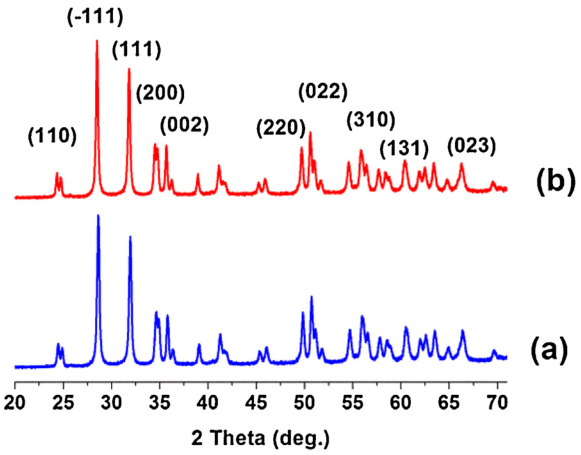

Fig. 1. Powder XRD patterns of (a) HfO_2 and (b) Ru^0/HfO_2 (4.0% wt Ru).

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