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Ceria supported rhodium nanoparticles: Superb catalytic activity in hydrogen generation from the hydrolysis of ammonia borane

Serdar Akbayrak[a], Yalçın Tonbul[a,b], Saim Özkar[a,*]

[a] Department of Chemistry, Middle East Technical University, 06800 Ankara, Turkey
[b] Ziya Gökalp Faculty of Education, Dicle University, 21280 Diyarbakır, Turkey

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ABSTRACT

We investigated the effect of various oxide supports on the catalytic activity of rhodium nanoparticles in hydrogen generation from the hydrolysis of ammonia borane. Among the oxide supports (CeO_2, SiO_2, Al_2O_3, TiO_2, ZrO_2, HfO_2) ceria provides the highest catalytic activity for the rhodium(0) nanoparticles in the hydrolysis of ammonia borane. Rhodium(0) nanoparticles supported on nanoceria (Rh^0/CeO_2) were prepared by the impregnation of rhodium(III) ions on the surface of ceria followed by their reduction with sodium borohydride in aqueous solution at room temperature. They were isolated from the reaction solution by centrifugation and characterized by a combination of advanced analytical techniques. The catalytic activity of Rh^0/CeO_2 samples with various rhodium loading in the range of 0.1–4.0% wt. Rh was also tested in hydrogen generation from the hydrolysis of ammonia borane at room temperature. The highest catalytic activity was achieved by using 0.1% wt. rhodium loaded nanoceria. The resulting Rh^0/CeO_2 with a metal loading of 0.1% wt. Rh show superb catalytic activity in hydrogen generation from the hydrolysis of ammonia borane with a record turnover frequency value (TOF) of 2010 min^{-1} at 25.0 ± 0.1 °C. The superb catalytic activity of Rh^0/CeO_2 is ascribed to the reducible nature of ceria. The reduction of cerium(IV) to cerium(III) leads to a build-up of negative charge on the oxide surface which favors the bonding of rhodium(0) nanoparticles on the surface and, thus, their catalytic activity. Rh^0/CeO_2 are also reusable catalysts preserving 67% of their initial catalytic activity even after the fifth use in hydrogen generation from the hydrolysis of ammonia borane at room temperature ($TOF = 1350\ min^{-1}$. The work reported here also includes the kinetic studies depending on the temperature to determine the activation energy ($E_a = 43 \pm 2$ kJ/mol) and the effect of catalyst concentration on the rate of hydrolysis of ammonia borane.

1. Introduction

Ammonia borane (NH_3BH_3, AB) is one of the most promising solid hydrogen storage materials for on-board hydrogen applications due to its high hydrogen storage capacity (19.6% wt.), non-toxicity, and high stability under ambient conditions [1–6]. Ammonia borane can release 3 equivalent H_2 upon hydrolysis in the presence of suitable catalysts even at ambient temperature according to Eq. (1).

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

Although a large variety of catalysts including noble [7–10] and non-noble [11–14] metal nanoparticles have been tested in hydrogen generation from the hydrolysis of ammonia borane, the development of efficient and stable catalysts is still an important challenge in using ammonia borane as solid hydrogen storage materials for the fuel cell applications under moderate conditions [15]. So far rhodium(0) nanoparticles supported on carbon nanotubes have been reported to be the highest activity catalyst with a turnover frequency of 706 min^{-1} in hydrogen generation from the hydrolysis of ammonia borane at room temperature [16]. Therefore it is quite plausible to give effort for further improving the catalytic activity of rhodium nanoparticles in this industrially important reaction. The catalytic performance of metal nanoparticles depends on the particle size and dispersion of the active sites while the reusability and catalytic lifetime of nanoparticles are affected by their stability against agglomeration [17]. Stable metal nanoparticles catalysts can be obtained by using suitable stabilizer ligands or supporting materials with large surface area [18–20]. Recent studies have shown that metal nanoparticles supported on reducible

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* Corresponding author.
E-mail address: sozkar@metu.edu.tr (S. Özkar).

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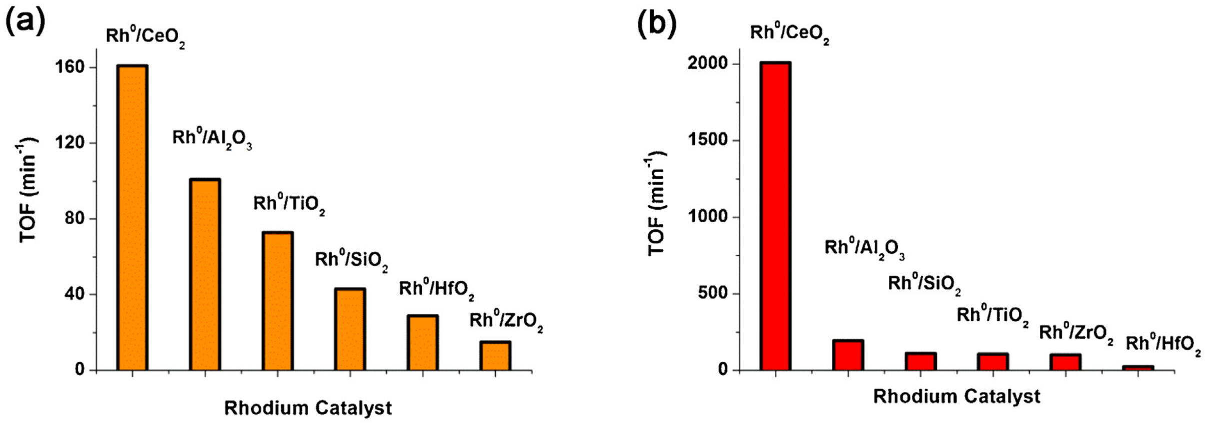

Fig. 1. Comparison of TOF (turnover frequency in mol H_2/(mol Rh × min)) values of rhodium nanoparticles supported on different oxides at (a) high and (b) low rhodium loadings of catalysts used in hydrogen generation from the hydrolysis of ammonia borane (10 mL,100 mM) at 25.0 ± 0.1 °C. For all the tests Rh/AB molar ratio of 0.0008 was used and no correction has been made for the initial TOF values by the fraction of catalytically active surface sites.

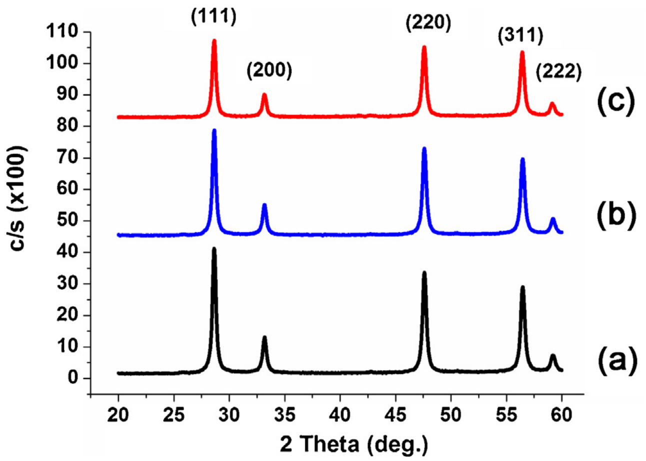

Fig. 2. Powder XRD patterns of (a) CeO_2, (b) Rh^0/CeO_2 with a 0.1% wt. Rh loading, (c) Rh^{00}/CeO_2 with a 3.42% wt. Rh loading.

oxides such as ceria (CeO_2) provide high catalytic activity in many reactions [21]. Cerium oxides have cerium(III) defects which can readily be formed because of the favorable large positive standard reduction potential of $Ce^{4+} \rightarrow Ce^{3+}$ (1.76 V in acidic solution [22]). It is conceivable that the interconversion of two oxidation states cerium(IV) and cerium(III) can occur under the catalytic reaction conditions, that is, ceria can undergo redox cycling in aqueous solution [23]. The formation of cerium(III) causes an excess negative charge to build up on the oxide surface which enhances the coordination of metal(0) nanoparticles to the oxide surface and, thus, the catalytic activity through a more favorable substrate-metal interaction [24]. Therefore, ceria has been used to improve the catalytic performance of transition metals through strong metal–support interaction, in particular, of the electron rich late-transition metal nanoparticles [25–27]. Although the mechanism of the promoting effect of cerium oxides has not been well understood yet, ceria has found broad applications in the field of catalysis such as in water splitting reactions [28,29], water–gas shift reactions [30,31], hydrogen generation from ammonia borane [32], decomposition of hydrazine [33], methanol synthesis from carbon dioxide [34], removal of nitrogen oxides from exhaust gases [35,36], and formic acid oxidation [37].

Herein we report the preparation, characterization, and catalytic use of rhodium(0) nanoparticles supported on nanoceria, Rh^0/CeO_2. For comparison, nanopowders of silica (SiO_2), alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO_2), and hafnia (HfO_2) were also employed as support for the rhodium(0) nanoparticles catalyst in hydrolysis of ammonia borane under the same conditions. The comparative study shows that Rh^0/CeO_2 has superior catalytic activity with a turnover frequency of TOF = 2010 min^{-1} in hydrogen generation from the hydrolysis of ammonia borane at 25.0 ± 0.1 °C. Our report also shows that the nanoceria supported rhodium(0) nanoparticles are reusable catalyst providing a TOF value of 1350 min^{-1} after the fifth run of hydrogen generation from the complete hydrolysis of ammonia borane at 25.0 ± 0.1 °C.

2. Experimental

2.1. Materials

Rhodium(III) chloride hydrate ($RhCl_3 \cdot 3H_2O$), ammonia borane (AB, 97%), nanoceria (CeO_2, particle size ≈ 25 nm), nanotitania (TiO_2, particle size ≈ 25 nm), nanozirconia (ZrO_2, particle size ≈ 100 nm), hafnia (HfO_2, particle size ≈ 100 nm), nanoalumina (Al_2O_3, particle size ≈ 13 nm), and nanosilica (SiO_2, particle size ≈ 12 nm) were purchased from Aldrich. Deionized water was distilled by water purification system (Milli-QSystem). 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 rhodium content of Rh^0/CeO_2 samples was determined by the Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Leeman-Direct Reading Echelle) after each sample was completely dissolved in the mixture of HNO_3/HCl (1/3 ratio). Transmission electron microscopy (TEM) was performed on a JEM-2100F (JEOL) microscope operating at 200 kV. Samples were examined at magnification between 400 K and 700 K. Scanning electron microscope (SEM) images were taken using a JEOL JSM-5310LVat 15 kV and 33 Pa in a low-vacuum mode without metal coating on aluminum support. 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.