Rhodium(0) nanoparticles supported on hydroxyapatite nanospheres and further stabilized by dihydrogen phosphate ion: A highly active catalyst in hydrogen generation from the methanolysis of ammonia borane

Derya Özhava, Saim Özkar*

Department of Chemistry, Middle East Technical University, 06800 Ankara, Turkey

ABSTRACT

Rhodium(0) nanoparticles, supported on nanosized hydroxyapatite (Rh(0)/nanoHAP), were prepared by ion exchange of Rh^{+3} ions with Ca^{+2} ions of hydroxyapatite, followed by reduction of the resulting Rh^{+3}/nanoHAP precatalyst during the catalytic methanolysis of ammonia borane (AB) in the presence of tetrabutylammonium dihydrogen phosphate (TBAP) at room temperature. Rh(0)/nanoHAP were characterized by a combination of advance analytical techniques including ICP-OES, XRD, TEM, EDX, XPS, ATR–IR and N_2 adsorption—desorption. Rh(0)/nanoHAP with an average particle size of 4.7 ± 0.8 nm were found to be highly active catalyst in hydrogen generation from the methanolysis of AB liberating 3.0 equivalent H_2 per mole of AB. They provide 26,000 turnovers in hydrogen generation from the methanolysis of AB over 23 h before deactivation and an initial TOF value of 147 min^{-1} which is the highest TOF value ever reported for the methanolysis of AB using rhodium catalyst at 25.0 ± 0.5 °C. Carbon disulfide poisoning experiment demonstrates that Rh(0)/nanoHAP catalyzed methanolysis of AB is a heterogeneous catalysis. This study also covers the detailed kinetics of the methanolysis of AB catalyzed by Rh(0)/nanoHAP depending on stabilizer concentration, catalyst concentration and temperature. The apparent activation energy of the catalytic reaction was calculated from the evaluation of temperature dependent kinetic data: $E_{aapp} = 56 \pm 2$ kJ/mol.

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Introduction

The use of hydrogen as energy carrier is expected to facilitate the transition from fossil fuels to renewable energy sources on the way towards a sustainable energy future [1]. However, the main obstacle on the way to a hydrogen powered society is the storage and release of hydrogen under ambient conditions [2]. Many of recent studies have been devoted to the development of chemical hydrides as potential on-board hydrogen source

[3]. Among these chemical hydrides, ammonia borane (NH_3BH_3, AB) has been considered as potential hydrogen storage material because of its high hydrogen capacity (19.6% wt.), high stability, and non-toxicity [4,5]. AB can release hydrogen *via* different processes including thermolysis [6–8], dehydrogenation in non-aqueous medium [9–11], hydrolysis [12–16] and methanolysis [17]. Although the hydrolysis of AB has been extensively studied and widely accepted, the methanolysis of AB has a series of advantages: *(i)* the solubility of AB in methanol is high, 23% wt. at 23 °C [18], *(ii)* the solution of AB in methanol is highly stable with respect to self-methanolysis at ambient conditions, *(iii)* pure hydrogen can be produced from methanolysis of AB without ammonia contamination [19,20], *(iv)* methanolysis of AB can be initiated at temperatures below 0 °C in the presence of appropriate catalyst, which facilitates portable applications in cold weather [21], *(v)* the methanolysis product of AB, $NH_4B(OCH_3)_4$, can be converted back to AB by a room temperature reaction with $LiAlH_4$ plus NH_4Cl [19]. Methanolysis can release 3.0 equivalents of H_2 per mole of AB only in the presence of a suitable catalyst (eqn. (1)):

$$NH_3BH_3 + 4CH_3OH \xrightarrow{\text{catalyst}} NH_4B(OCH_3)_4 + 3H_2 \qquad (1)$$
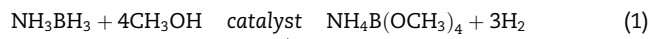
Many transition metal catalysts have been tested in the methanolysis of AB such as $RuCl_3$, $RhCl_3$, $PdCl_2$, $CoCl_2$, $NiCl_2$ [19], copper nanoparticles [22], polymer stabilized-nickel(0) [23], -palladium(0) [24] and -ruthenium(0) nanoparticles [25], silica supported ruthenium(0) nanoparticles [26], $Co–Co_2B$, $Ni–Ni_3B$, $Co–Ni–B$ [27], zeolite confined rhodium(0) nanoparticles [28], MMT-immobilized ruthenium(0) nanoparticles [29], cobalt-palladium nanoparticles [30], mesoporous CuO nanostructures [31], $Cu–Cu_2O–CuO/C$ [32]. Although transition metal nanoparticles are highly active catalyst in methanolysis of AB, they are kinetically unstable against agglomeration and, therefore, have relatively short lifetime [33]. Metal nanoparticles have been stabilized by using microporous or mesoporous materials [34–36] as well as oxide supports with large surface area, such as hydroxyapatite ($Ca_{10}(OH)_2(PO_4)_6$, HAP) [33,37]. HAP appears to be a support of choice as *(i)* having nonporous structure which eliminates the mass transfer limitation, *(ii)* showing high ion-exchange ability and adsorption capacity, and *(iii)* owing to the low surface acidity, which eliminates side reactions derived from support [38]. In addition, reducing the particle size of support from the microcrystalline to the nanocrystalline regime (from > 1 μm to <100 nm) can enhance the activity due to a higher external surface area and a large number of exchange sites [39]. Using nanotitania as support, for example, has provided a high catalytic activity of TOF = 260 min^{-1} for the rhodium(0) nanoparticles in the hydrolysis of ammonia borane [40]. Our two recent papers have shown that reducing the particle size of support increases the catalytic activity of ruthenium(0) nanoparticles in hydrogen generation from the hydrolysis of ammonia borane at 25.0 ± 0.5 °C from TOF = 137 min^{-1} for micron size HAP [41] to TOF = 205 min^{-1} for nanometer size nanoHAP [42]. This significant achievement in catalytic activity of metal(0) nanoparticles on reducing the particle size of support stimulated us to test the catalytic activity of rhodium(0) nanoparticles supported on the surface of nanoHAP in a slightly different reaction, methanolysis of ammonia borane.

Herein, we report the *in-situ* preparation of rhodium(0) nanoparticles supported on hydroxyapatite nanospheres with particle size of smaller than 75 nm, hereafter referred to as Rh(0)/nanoHAP. Rh^{+3} ions were impregnated on the surface of hydroxyapatite nanospheres by the ion-exchange of Rh^{+3} ions with Ca^{+2} ions in the lattice of hydroxyapatite, then reduced to rhodium(0) nanoparticles by AB in the presence of tetra-buthylammonium dihydrogen phosphate as further stabilizer at room temperature. Rh(0)/nanoHAP were isolated from the reaction solution by centrifugation and characterized by ICP-OES, XRD, TEM, EDX, XPS, ATR–IR and N_2-adsorption/desorption techniques. The work presented here also includes i) formation of well dispersed rhodium(0) nanoparticles on the surface of hydroxyapatite nanospheres with particle size in the range of 3.6–6.4 nm, ii) their use as catalyst in hydrogen generation from the methanolysis of AB, iii) kinetics of hydrogen generation, iv) the investigation of temperature effect on the hydrogen generation rate and determination of activation parameters (E_a^{app}, $\Delta H^{\neq}$, and $\Delta S^{\neq}$) for the catalytic methanolysis of AB, v) remarkable catalytic activity of Rh(0)/nanoHAP in hydrogen generation from the methanolysis of AB with an initial turnover frequency of 147 min^{-1} at 25.0 ± 0.5 °C.

Experimental

Materials

Rhodium(III) chloride trihydrate ($RhCl_3 \cdot 3H_2O$), ammonia borane (H_3NBH_3, 97%), methanol (99%) and hydroxyapatite nanopowder ($Ca_{10}(OH)_2(PO_4)_6$, particle size <75 nm) were purchased from Aldrich. Tetrabutylammonium dihydrogen phosphate monobasic (TBAP, 97%) was purchased from Fluka. Methanol were distilled over metallic magnesium and stored under inert gas atmosphere. Distilled methanol was used in all methanolysis reactions under inert gas atmosphere unless otherwise specified. All glassware was cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 120 °C.

Instrumentation

Rhodium content of the Rh^{+3}-exchanged nanosized hydroxyapatite (Rh^{+3}/nanoHAP) samples was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Leeman-Direct Reading Echelle) after each sample was completely dissolved in 0.1 M HNO_3. UV–vis electronic absorption spectra were recorded on Varian-Carry100 double beam instrument. Samples used for taking the UV-vis electronic absorption spectra were harvested from reaction solution after the complete methanolysis of AB and dried under vacuum while the vacuum dried Rh^{+3}/nanoHAP sample was used after ion-exchange process. Transmission electron microscopy (TEM) was performed on a JEM-2100F (JEOL) microscope operating at 200 kV. TEM samples were harvested from *in-situ* generated Rh(0)/nanoHAP solution at the end of catalytic methanolysis of AB. A 0.2 mL aliquot of nanoparticle solution was diluted in 2 mL acetone and ultrasonicated for