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# Ruthenium(0) nanoparticles supported on nanotitania as highly active and reusable catalyst in hydrogen generation from the hydrolysis of ammonia borane

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## ABSTRACT

Ruthenium(0) nanoparticles supported on the surface of titania nanospheres (Ru(0)/TiO<sub>2</sub>) were *in situ* generated from the reduction of ruthenium(III) ions impregnated on nanotitania during the hydrolysis of ammonia borane. They were isolated from the reaction solution by centrifugation and characterized by a combination of advanced analytical techniques. The results reveal that highly dispersed ruthenium(0) nanoparticles of size in the range 1.5–3.3 nm were formed on the surface of titania nanospheres. Ru(0)/TiO<sub>2</sub> show high catalytic activity in hydrogen generation from the hydrolysis of ammonia borane with a turnover frequency value up to 241 min<sup>-1</sup> at 25.0 ± 0.1 °C. They provide unprecedented catalytic lifetime measured by total turnover number (TTO = 71,500) in hydrogen generation from the hydrolysis of ammonia borane at 25.0 ± 0.1 °C. The report also includes the results of kinetic study on the catalytic hydrolysis of ammonia borane depending on the temperature to determine the activation energy of the reaction ( $E_a = 70 \pm 2$  kJ/mol) and the catalyst concentration to establish the rate law of the reaction.

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## Introduction

The use of hydrogen as energy carrier is expected to facilitate the transition from fossil fuels to the renewable energy sources, on the way towards a sustainable energy future [1]. However, the lack of safe and efficient hydrogen storage is the major obstacle for its applications [2]. Therefore the development of an efficient hydrogen storage method is needed in

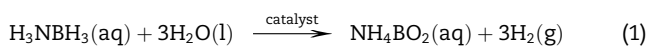
hydrogen economy. Recently, boron containing compounds such as sodium borohydride [3,4], ammonia borane [5,6], hydrazine borane [7,8], methylamine borane [9] and dimethylamine borane [10] have attracted much attention as hydrogen storage materials. Ammonia borane (NH<sub>3</sub>BH<sub>3</sub>, AB) has been recognized as the most promising candidate for on-board applications because of its high hydrogen storage capacity (19.6 wt.%), nontoxicity and high stability under ambient conditions [11,12]. Hydrogen stored in AB can be released at

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appreciable rate via hydrolysis only in the presence of a suitable catalyst (eq. (1)) [13].



Nobel metal nanoparticles supported on carbon nanotubes [14], graphenes [15,16], hydroxyapatites [17], zeolites [18], aluminum oxides [19] have been reported to have high catalytic activity in hydrogen generation from the hydrolysis of AB. However, porous materials such as zeolites, aluminum oxides and SBA-15 as stabilizing agents have some drawbacks. The metal nanoparticles within the cavities of porous materials can easily migrate and, hence, block the entrance of pores after several uses which can limit the use of porous materials as support. The nonporous titanium dioxide with large surface area ranging from 10 to 300 m<sup>2</sup>/g can be used as support to avoid the problems arising from the diffusion in porous materials. There has been growing interest on titanium dioxides as support materials for noble metals. There exist many extensive reports on titanium dioxide due to its chemical stability, interesting optical, antimicrobial and catalytic properties which lead to industrial applications such as gas sensors, solar cells, electrochemical devices, fillers, catalyst supports and photocatalyst [20–22]. Titanium dioxide has been widely used as photocatalyst in the solar energy utilization [23] and environmental cleaning up for the photocatalytic degradation of several organic pollutants [24,25]. However, there are few reports related to titanium dioxide as catalyst support used in dehydrogenation of AB [26,27] and sodium borohydride [28–32].

Herein we report the *in situ* generation, characterization and catalytic use of ruthenium(0) nanoparticles supported on titanium dioxide with particles size of about 100 nm, Ru(0)/TiO<sub>2</sub>. Ruthenium(III) ions impregnated on the surface of nanotitania was reduced by ammonia borane forming the Ru(0)/TiO<sub>2</sub> during the hydrolysis of ammonia borane. Ru(0)/TiO<sub>2</sub> could be isolated from the reaction solution by filtration and characterized by ICP-OES, XRD, TEM, SEM-EDS and XPS techniques. All the results reveal the formation of well dispersed ruthenium nanoparticles of 1.5–3.3 nm size supported on the surface of titanium dioxide. The ruthenium(0) nanoparticles supported on nanotitania have remarkable catalytic activity in hydrogen generation from the hydrolysis of AB with a turnover frequency of 241 min<sup>-1</sup> at 25 ± 0.1 °C. We also report that Ru(0)/TiO<sub>2</sub> are reusable and long-lived catalysts with a total turnover number of 71,500 in hydrogen generation from the hydrolysis of AB at room temperature.

## Experimental section

### Materials

Ruthenium(III) chloride trihydrate (RuCl<sub>3</sub>·3H<sub>2</sub>O), titanium(IV) oxide (anatase), and ammonia-borane (AB, 97%) were purchased from Aldrich. Deionized water was distilled by water purification system (Milli-Q System). 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.

### Characterization

The ruthenium content of the Ru(0)/TiO<sub>2</sub> sample was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Leeman-Direct Reading Echelle) after the sample was completely dissolved in the mixture of HNO<sub>3</sub>/HCl (1/3 ratio). Transmission electron microscopy (TEM) was performed on a JEM-2100F (JEOL) microscope operating at 200 kV. A small amount of powder sample was placed on the holey carbon grid of the transmission electron microscope. Samples were examined at magnification between 100 and 400 K. Scanning electron microscope (SEM) images were taken using a JEOL JSM-5310LV at 15 kV and 33 Pa in a high-vacuum mode without metal coating on carbon 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 K $\alpha$  radiation of 1486.6 eV, the X-ray tube working at 15 kV, 350 W and pass energy of 23.5 keV. <sup>11</sup>B NMR spectra were recorded on a Bruker Avance DPX 400 with an operating frequency of 128.15 MHz for <sup>11</sup>B.

### Preparation of ruthenium(III) ions impregnated on TiO<sub>2</sub> (Ru<sup>3+</sup>/TiO<sub>2</sub>)

TiO<sub>2</sub> (500 mg) was added to a solution of RuCl<sub>3</sub>·3H<sub>2</sub>O (27.3 mg) in 50 mL H<sub>2</sub>O in a 100 mL beaker. This slurry was stirred at room temperature for 72 h and then Ru<sup>3+</sup>/TiO<sub>2</sub> sample was isolated by centrifugation and washed with 100 mL of distilled water and the remnant was dried at 120 °C for 12 h in the oven.

### *In situ* formation of ruthenium(0) nanoparticles supported on TiO<sub>2</sub> (Ru(0)/TiO<sub>2</sub>) and concomitant catalytic hydrolysis of AB

Ruthenium(0) nanoparticles supported on TiO<sub>2</sub> (Ru(0)/TiO<sub>2</sub>) were *in situ* generated from the reduction of Ru<sup>3+</sup>/TiO<sub>2</sub> during the catalytic hydrolysis of AB. Before starting the catalyst formation and concomitant catalytic hydrolysis of AB, a jacketed reaction flask (20 mL) containing a Teflon-coated stir bar was placed on a magnetic stirrer (Heidolph MR-301) and thermostated to 25.0 ± 0.1 °C by circulating water through its jacket from a constant temperature bath. Then, a graduated glass tube (60 cm in height and 3.0 cm in diameter) filled with water was connected to the reaction flask to measure the volume of the hydrogen gas to be evolved from the reaction. Next, 10 mg powder of Ru<sup>3+</sup>/TiO<sub>2</sub> (1.2 wt.% Ru) was dispersed in 10 mL distilled water in the reaction flask thermostated at 25.0 ± 0.1 °C. Then, 31.8 mg AB (1.0 mmol H<sub>3</sub>N·BH<sub>3</sub>) was added into the flask and the reaction medium was stirred at 1000 rpm. After adding ammonia borane, ruthenium(0) nanoparticles were formed and the catalytic hydrolysis of AB started immediately. The volume of hydrogen gas evolved was measured by recording the displacement of water level every 30 s at constant atmospheric pressure of 693 Torr. The reaction was stopped when no more hydrogen evolution was observed. In each experiment, the resulting solutions were filtered and the filtrates were analyzed by <sup>11</sup>B NMR and conversion of AB to metaborate anion was confirmed by

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