## **RSC Advances**

## PAPER

Cite this: RSC Adv., 2014, 4, 13742

Received 16th January 2014 Accepted 31st January 2014

DOI: 10.1039/c4ra00469h

www.rsc.org/advances

## Introduction

Ammonia-borane (NH<sub>3</sub>BH<sub>3</sub>, AB) has been regarded as one of the leading candidates for 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.<sup>1</sup> Hydrogen stored in the AB complex can be released by either thermolysis<sup>2</sup> or solvolysis.<sup>3</sup> Since high temperature is required for the former,<sup>4</sup> the latter reaction is highly advantageous for hydrogen generation from AB. However, hydrogen stored in AB can be released at an appreciable rate *via* hydrolysis only in the presence of a suitable catalyst (eqn (1)).<sup>5,6</sup> Therefore, the development of efficient and stable catalysts under moderate conditions is vital for practical applications.

$$H_{3}NBH_{3}(aq) + 2H_{2}O(l) \xrightarrow{\text{catalyst}} NH_{4}^{+}(aq) + BO_{2}^{-}(aq) + 3H_{2}(g)$$
(1)

A number of catalysts have been tested in hydrogen generation from the hydrolysis of AB, including transition metal nanoparticles such as platinum, rhodium, ruthenium, palladium, cobalt and nickel.<sup>7,8</sup> Although rhodium, platinum and ruthenium metal nanoparticles have high prices and limited abundance, they are superior to the non-noble metal nanoparticles due to their long life-time and high activity in the hydrolysis of ammonia borane. Therefore the use of noble metal nanoparticles as catalysts has been intensively studied in recent

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

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Rhodium(0) nanoparticles supported on the surface of titanium dioxide (Rh(0)@TiO<sub>2</sub>) were *in situ* generated from the reduction of rhodium(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 show that (i) highly dispersed rhodium(0) nanoparticles with sizes in the range 1.3-3.8 nm were formed on the surface of titanium dioxide, (ii) Rh(0)@TiO<sub>2</sub> shows high catalytic activity in hydrogen generation from the hydrolysis of ammonia borane with a turnover frequency value up to 260 min<sup>-1</sup> at 25.0 ± 0.1 °C, (iii) the results of kinetic studies on the hydrogen generation from the hydrolysis of at activation energy of  $65.5 \pm 2$  kJ mol<sup>-1</sup> for this reaction.

years. Metal nanoparticles exhibit much higher catalytic activity compared to the bulk metal due to the large fraction of atoms on their surface. However, metal nanoparticles tend to aggregate into clumps causing a decrease in catalytic activity.<sup>9,10</sup> Titanium dioxide with a large surface area ranging from 10 to  $300 \text{ m}^2 \text{ g}^{-1}$  can be used as a support to prevent the aggregation of metal nanoparticles. Titanium dioxide is one of the suitable catalysts for environmental applications because of its nontoxicity, strong oxidizing power and the high stability against corrosion.<sup>11</sup> Titanium dioxide has also been extensively studied as a semiconductor material due to its wide band gap and low cost.<sup>12</sup>

Herein we report the in situ generation, characterization, and catalytic use of rhodium(0) nanoparticles supported on titanium dioxide with particle sizes of about 100 nm, hereafter referred to as Rh(0)@TiO<sub>2</sub>. Rhodium(III) ions impregnated on the surface of titania particles were reduced by ammonia borane forming the Rh(0)@TiO<sub>2</sub> without using any additional reducing agents during the hydrolysis of ammonia borane. The use of in situ generation of Rh(0)@TiO2 provides the opportunity to avoid laborious catalyst preparation steps. Rh(0)@TiO<sub>2</sub> was isolated from the reaction solution and characterized using ICP-OES, XRD, TEM, SEM-EDS, XPS and N2 adsorptiondesorption techniques. Our report also includes the following major findings: (i) formation of highly dispersed rhodium(0) nanoparticles on the surface of titanium dioxide with particle sizes in the range 1.3-3.8 nm. (ii) Remarkable catalytic activity of Rh(0)@TiO<sub>2</sub> in hydrogen generation from the hydrolysis of AB with a turnover frequency of 260 min<sup>-1</sup> at 25  $\pm$  0.1 °C. (iii) Reusability of Rh(0)@TiO2 providing the complete hydrolysis of AB generating 3 mole H<sub>2</sub> per mole of AB even in the fifth use of the catalyst.



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## **Experimental section**

#### Materials

Rhodium(III) chloride trihydrate (RhCl<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 a 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  $^{\circ}$ C.

#### Characterization

The rhodium content of the Rh(0) (a)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 a mixture of HNO3-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 the 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 Ka radiation of 1486.6 eV, the X-ray tube working at 15 kV, 350 W and pass energy of 23.5 keV. 11B 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 rhodium(III) ions impregnated on TiO<sub>2</sub>

 $TiO_2$  (1000 mg) was added to a solution of  $RhCl_3 \cdot 3H_2O$  (53.97 mg) in 100 mL  $H_2O$  in a beaker. This slurry was stirred at room temperature for 72 h and then the  $Rh^{3+}$ @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 rhodium(0) nanoparticles supported on $TiO_2$ and concomitant catalytic hydrolysis of AB

Rhodium(0) nanoparticles supported on TiO<sub>2</sub> (Rh(0)@TiO<sub>2</sub>) were *in situ* generated from the reduction of Rh<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  $25.0 \pm 0.1$  °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, 20 mg powder of Rh<sup>3+</sup>@TiO<sub>2</sub> (0.24 wt% Rh) was dispersed in 10 mL distilled water in the reaction flask thermostated at  $25.0 \pm 0.1$  °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, rhodium(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 the water level every 30 s at a 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 the metaborate anion was confirmed by comparing the intensity of signals in the <sup>11</sup>B NMR spectra of the filtrates.

## Determination of activation energy for hydrolysis of AB catalyzed by Rh(0) (a)TiO<sub>2</sub>

In a typical experiment, the hydrolysis reaction was performed starting with 10 mL of 100 mM (31.8 mg) AB solution and 20 mg  $Rh^{3+}$ @TiO<sub>2</sub> (0.24 wt% rhodium, [Rh] = 0.046 mM) at various temperatures (25, 30, 35, 40, 45 °C) in order to obtain the activation energy.

#### Reusability of Rh(0)@TiO2 in hydrolysis of AB

After the complete hydrolysis of AB started with 10 mL of 100 mM AB (31.8 mg H<sub>3</sub>NBH<sub>3</sub>), and 100 mg Rh<sup>3+</sup>(a)TiO<sub>2</sub> (0.24 wt% rhodium, [Rh] = 0.233 mM) at 25 ± 0.1 °C, the catalyst was isolated as a powder by centrifugation and dried at 120 °C in an oven after washing with 20 mL of water. The isolated samples of Rh(0)(a)TiO<sub>2</sub> were weighed and redispersed in 10 mL solution of 100 mM AB for a subsequent run of hydrolysis at 25 ± 0.1 °C.

# Determination of the catalytic lifetime of Rh(0) ( $\overline{0}$ ) TiO<sub>2</sub> in the hydrolysis of AB

The catalytic lifetime of Rh(0)@TiO<sub>2</sub> in the hydrolysis of AB was determined by measuring the total turnover number (TTO). Such a lifetime experiment was started with a 50 mL solution containing 0.046 mM Rh(0)@TiO<sub>2</sub> and 30 mM AB at 25.0  $\pm$  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.

### **Results and discussion**

Rhodium(0) nanoparticles supported on titanium dioxide were *in situ* generated from the reduction of  $Rh^{3+}$  (a)TiO<sub>2</sub> during the catalytic hydrolysis of AB. First, rhodium(m) ions were impregnated on titania with particle sizes of 100 nm from an aqueous solution of rhodium(m) chloride yielding  $Rh^{3+}$  (a)TiO<sub>2</sub> and then reduced by AB at room temperature. Both reduction of rhodium(m) to rhodium(0) and hydrogen release from the hydrolysis of AB occur concomitantly when the AB solution is added to a suspension of  $Rh^{3+}$  (a)TiO<sub>2</sub>. The progress of the hydrolysis of AB was followed by monitoring the change in hydrogen pressure which was then converted into the equivalent H<sub>2</sub> per mole of AB, using the known 3 : 1 H<sub>2</sub> : AB stoichiometry (eqn (1)).

# Characterization of rhodium(0) nanoparticles supported on $TiO_2$

Rhodium(0) nanoparticles supported on titania (Rh(0)@TiO<sub>2</sub>), in situ formed during the hydrolysis of AB, could be isolated from the reaction solution as a powder by centrifugation and characterized by ICP-OES, XRD, SEM-EDS, TEM, XPS and N2 adsorption-desorption techniques. Rhodium content of Rh(0) (a)TiO2 was determined by ICP-OES and found as 0.24 wt% Rh loading on the titania surface. The N2 adsorption-desorption analysis gave the surface area of titania as 10.71  $m^2 g^{-1}$ . Since the rhodium content of Rh(0)@TiO2 was very low, it is difficult to understand the existence of rhodium(0) nanoparticles on the surface of titania by N2 adsorption-desorption analysis. Comparison of the XRD patterns of TiO<sub>2</sub>, Rh<sup>3+</sup>@TiO<sub>2</sub> and Rh(0)@TiO2 with a rhodium loading of 0.24 wt% Rh, given in Fig. 1a-c, respectively, clearly shows that there is no change in the characteristic diffraction peaks of TiO<sub>2</sub> (PDF card 21-1272). This observation indicates that the host material remains intact after impregnation and reduction of rhodium(m) ions; there is no noticeable alteration in the framework lattice or change in the crystallinity. There is no observable peak attributable to rhodium nanoparticles in Fig. 1b and c, probably because of the low rhodium loading on the TiO<sub>2</sub>.

The SEM image of Rh(0) (a)TiO<sub>2</sub> with a rhodium loading of 0.24 wt% in Fig. 2a shows the presence of nearly monodispersed titania nanoparticles of 100 nm size. The SEM-EDS spectrum of Rh(0) (a)TiO<sub>2</sub> with a rhodium loading of 0.24 wt% in Fig. 2b indicates the presence of the framework elements of TiO<sub>2</sub> (Ti, O). Due to the low rhodium loading on TiO<sub>2</sub>, the presence of rhodium nanoparticles could not be observed in the SEM analysis.

Fig. 3 shows the TEM images of Rh(0) (a)TiO<sub>2</sub> with a rhodium loading of 0.24 wt% taken with different magnifications, which indicate that (i) highly dispersed rhodium(0) nanoparticles are formed on the surface of TiO<sub>2</sub> with particle sizes in the range 1.3–3.8 nm (mean diameter: 2.8 ± 0.7 nm) and (ii) the impregnation of rhodium(m) followed by reduction to rhodium(0) causes no change in the framework lattice of titania in agreement with the XRD results.

The composition of Rh(0) (a)TiO<sub>2</sub> formed *in situ* during the hydrolysis of AB and the oxidation state of rhodium were also



Fig. 1 Powder XRD patterns of (a)  $TiO_2$ , (b)  $Rh^{3+}$ @ $TiO_2$ , (c) Rh(0)@ $TiO_2$  with a 0.24 wt% Rh loading.



Fig. 2 (a) SEM image and (b) SEM-EDS spectrum of Rh(0)@TiO\_2 with a 0.24 wt% Rh loading.

studied by XPS. The survey-scan XPS spectrum of Rh(0)@TiO<sub>2</sub> with a rhodium loading of 0.24 wt%. (Fig. 4) shows that rhodium is the only element detected in addition to the TiO<sub>2</sub> framework elements (Ti, O). High resolution Rh 3d XPS of a Rh(0)@TiO<sub>2</sub> sample given in the inset of Fig. 4 shows two prominent bands at 305.8 eV and 311.4 eV which can readily be assigned to rhodium(0)  $3d_{5/2}$  and  $3d_{3/2}$ , respectively.<sup>13,14</sup> The bands at 309.7 eV and 313.8 eV (colored green in the inset of Fig. 4), might be attributed to rhodium oxides, which might be formed during the XPS sampling.<sup>14</sup>

#### Catalytic activity of Rh(0)@TiO2 in hydrolysis of AB

Before starting with the investigation of the catalytic activity of Rh(0)@TiO<sub>2</sub> in the hydrolysis of AB, a control experiment was performed to check whether titanium dioxide shows any catalytic activity in the hydrolysis of AB at the same temperature used in this study. In a control experiment starting with 1.0 mmol of AB and 20 mg of powdered TiO<sub>2</sub> (the same amount as used in catalytic activity tests) in 10 mL of water at  $25.0 \pm 0.1$  °C or  $45.0 \pm 0.1$  °C, no hydrogen evolution was observed over 1 h at both temperatures. This observation indicates that the hydrolysis of AB does not occur in the presence of TiO<sub>2</sub> in the temperature range used in this study. However, Rh(0)@TiO<sub>2</sub> is found to be a highly active catalyst in the hydrolysis of AB generating 3.0 equivalents of H<sub>2</sub> gas per mole of AB in the same temperature range.

Fig. 5a shows the evolution of equivalent hydrogen per mole of AB *versus* time plot for the hydrolysis of AB (100 mM) using Rh(0)@TiO<sub>2</sub> as the catalyst in different rhodium concentrations at 25.0  $\pm$  0.1 °C. The hydrogen generation rate was determined from the linear portion of each plot. For all tests a complete hydrogen release (mol H<sub>2</sub>/mol H<sub>3</sub>NBH<sub>3</sub> = 3) was observed. Fig. 5b shows the plot of hydrogen generation rate *versus* initial



Fig. 3 TEM image of Rh(0)@TiO<sub>2</sub> with a rhodium loading of 0.24 wt% at (a) 100 nm, (b) 50 nm, (c) 20 nm, (d) 10 nm, (e) histogram of Rh(0) @TiO<sub>2</sub> showing particle size distribution.

concentration of rhodium, both in logarithmic scale, which gives a straight line with a slope of 1.12 indicating that hydrolysis of AB is first order with respect to the rhodium concentration. The turnover frequency (TOF), mol of H<sub>2</sub> per mol of rhodium per minute, for hydrogen generation from the hydrolysis of AB (100 mM) at  $25.0 \pm 0.1$  °C was determined from the hydrogen generation rate in the linear portion of the plots given in Fig. 5a for experiments starting with 100 mM AB plus Rh(0)



Fig. 4 X-ray photoelectron (XPS) spectrum of Rh(0)@TiO<sub>2</sub> sample with a rhodium loading of 0.24 wt% Rh. The inset gives the high resolution scan and deconvolution of Rh 3d bands.



Fig. 5 (a) mol H<sub>2</sub> per mol H<sub>3</sub>N·BH<sub>3</sub> versus time graph for various rhodium concentrations in Rh(0)@TiO<sub>2</sub> for the hydrolysis of AB (100 mM) at 25.0  $\pm$  0.1 °C; (b) the logarithmic plot of hydrogen generation rate versus the concentration of Rh; ln(rate) = 1.12 ln[Rh] + 4.34.

(a)TiO<sub>2</sub> with a loading of 0.24 wt% Rh. The TOF value of the Rh(0)(a)TiO<sub>2</sub> catalyst is as high as 260 min<sup>-1</sup> (mol H<sub>2</sub> per mol Rh min) in hydrolysis of AB at 25.0  $\pm$  0.1 °C. TOF values of the reported catalysts used in the hydrolysis of AB are listed in Table 1 for comparison. As clearly seen from the comparison of values listed in Table 1, Rh(0)(a)TiO<sub>2</sub> provides a remarkable TOF value in the hydrolysis of AB as compared to the other ruthenium, rhodium and palladium catalysts.

The catalytic hydrolysis of AB was carried out at various temperatures in the range of 25–45 °C starting with  $Rh(0)@TiO_2$  (loading = 0.24 wt% Rh and [Rh] = 0.116 mM) plus 100 mM AB in 10 mL of water. The rate constants for the hydrogen

 Table 1
 Catalytic activity of various reported catalysts used in the hydrolysis of AB

Entry	Catalyst	TOF $(\min^{-1})$	$E_{\rm a}$ (kJ mol <sup>-1</sup> )	TTO	Ref.
1	Ru@MWCNT	329	33	26 400	15
2	$Rh(0)$ (a) $TiO_2$	260	65.5	37 350	This study
3	Laurate-stabilized Rh(0)	200	43.6	80 000	16
4	Ru(0)PSSA-co-MA	172	54	51 720	17
5	Ru(0)@hap	137	58	87 000	18
6	Ni@Ru	114	44	_	19
7	Ru/carbon	113	76	_	20
8	Ru/graphene	100	11.7	_	21
9	ZFS Rh(0)	92	66.9	47 200	22
10	RuNPs@ZK-4	90.2	28	36 700	23
11	Ru(0)NP/laurate	75	47	5900	24
12	Pd@Co/graphene	37.5		_	25
13	$Co_{35}Pd_{65}/C$ annealed	35.7	_	_	26
14	2.1 wt% RGO@Pd	26.3	40	_	27
15	Rh/γ-Al <sub>2</sub> O <sub>3</sub>	_	21	_	28

generation at different temperatures were calculated from the slope of the linear part of each plot given in Fig. 6a and used for the calculation of activation energy ( $E_a = 65 \pm 2$  kJ mol<sup>-1</sup>) from the Arrhenius plot in Fig. 6b. The activation energy for hydrolysis of AB catalyzed by Rh(0)@TiO<sub>2</sub> is comparable to the literature values reported for the same reaction using other catalysts (see Table 1).

Reusability of the Rh(0) (a)TiO<sub>2</sub> catalyst was tested in successive experiments performed using the catalyst isolated



from the reaction solution after a previous run of hydrolysis of AB. After the completion of hydrogen generation from the hydrolysis of AB starting with 0.233 mM Rh<sup>3+</sup>(a)TiO<sub>2</sub> plus 100 mM AB in 10 mL aqueous solution at  $25.0 \pm 0.1$  °C, the catalyst was isolated by centrifugation and washed with 10 mL of water. After washing, the isolated sample of Rh(0)(a)TiO<sub>2</sub> was redispersed in 10 mL solution containing 100 mM AB and a second run of hydrolysis was started immediately and continued until the completion of hydrogen evolution. The hydrogen generation process was repeated five times. After the fifth use in the hydrolysis of AB, Rh(0)(a)TiO<sub>2</sub> preserved only 7.0% of the initial catalytic activity. The reusability tests reveal that Rh(0)(a)TiO<sub>2</sub> is still active in the subsequent runs of hydrolysis of AB providing a release of 3.0 equivalent H<sub>2</sub> per mole of NH<sub>3</sub>BH<sub>3</sub> (Fig. 7).

The catalytic activity of the filtrate solution obtained by centrifugation of the solid materials after the first run of the hydrolysis was also tested in the hydrolysis of AB (100 mM) under the same conditions. As shown in Fig. 8, the filtrate solution shows no catalytic activity in the hydrolysis of AB. This observation supports the conclusion that there is no leaching of rhodium into the solution during the hydrolysis and suggests that the rhodium(0) nanoparticles supported on TiO<sub>2</sub> are kinetically competent and a heterogeneous catalyst in the hydrolysis of ammonia borane.



**Fig. 6** (a) The evolution of equivalent hydrogen per mole of AB *versus* time plot for the hydrolysis of AB starting with Rh(0)@TiO<sub>2</sub> (0.116 mM Rh) and 100 mM AB at various temperatures. (b) The Arrhenius plot for the Rh(0)@TiO<sub>2</sub> catalyzed hydrolysis of AB. In  $k = -7883.5(T^{-1}) + 27.27$ .

Fig. 7 Percentage of initial catalytic activity of Rh(0)@TiO<sub>2</sub> ([Rh] = 0.233 mM) in successive runs after reuse for the hydrolysis of ammonia borane (100 mM).



Fig. 8 The evolution of equivalent hydrogen per mole of AB versus time plot for the hydrolysis of AB (100 mM) starting with Rh(0)@TiO<sub>2</sub> (0.233 mM Rh) (black  $\triangle$ ), and the filtrate solution obtained by centrifugation of the solid materials after the first run, (red  $\triangle$ ), at room temperature.

The catalytic lifetime of Rh(0)@TiO<sub>2</sub> was determined by measuring the total turnover number (TTO) in the hydrolysis of ammonia borane. A catalyst lifetime experiment was performed starting with 20 mg Rh<sup>3+</sup>@TiO<sub>2</sub> (rhodium loading = 0.24 wt% Rh, and [Rh] = 0.0466 mM) in 100 mL solution of AB at 25.0 ± 0.1 °C. Fig. 9 shows the variation in turnover number (TON) and turnover frequency (TOF) in the course of reaction. The TOF value decreases expectedly as the rhodium(0) nanoparticles catalysts are deactivated during the lifetime experiment because of the increasing concentration of metaborate ion. Rhodium(0) nanoparticles supported on TiO<sub>2</sub> provide 37 350 turnovers over 20 h in the hydrolysis of AB at 25.0 ± 0.1 °C before deactivation. As shown in Table 1, the TTO value of Rh(0)@TiO<sub>2</sub> for the hydrolysis of ammonia borane is comparable to the literature values reported for the same reaction using other catalysts.

### Conclusions

In summary, rhodium(0) nanoparticles supported on titania were reproducibly prepared from the reduction of  $Rh^{3+}$  (a)TiO<sub>2</sub> during the catalytic hydrolysis of ammonia borane. Rhodium(III) ions were impregnated on titanium dioxide from the aqueous solution of rhodium(III) chloride and then reduced by



Fig. 9 The variation in turnover number (TON) and turnover frequency (TOF) during the catalytic lifetime experiment performed starting with 20 mg Rh(0)@TiO<sub>2</sub> (rhodium loading = 0.24 wt% Rh, and [Rh] = 0.0466 mM) in 100 mL solution of AB at 25.0  $\pm$  0.1 °C.

ammonia borane at room temperature. Highly dispersed rhodium(0) nanoparticles with particle sizes in the range 1.3-3.8 nm on titanium dioxide were prepared and characterized by a combination of advanced analytical techniques. Rh(0) (a) TiO<sub>2</sub> shows high catalytic activity in hydrogen generation from the hydrolysis of ammonia borane providing a turnover frequency value up to 260 min<sup>-1</sup> at 25.0  $\pm$  0.1 °C. Rh(0)@TiO<sub>2</sub> is a longlived catalyst providing 37 350 turnovers in hydrogen generation from the hydrolysis of ammonia borane at 25.0  $\pm$  0.1 °C. Rh(0) (a) TiO<sub>2</sub> is a reusable catalyst as it provides the complete hydrolysis of ammonia borane generating 3 mole H<sub>2</sub> per mole of AB even in the fifth use. The results of quantitative kinetic studies on the hydrogen generation from the hydrolysis of ammonia borane show that the hydrolysis reaction is first order in rhodium concentration and the activation energy is  $65.5 \pm 2$ kJ mol<sup>-1</sup> for the hydrogen generation catalyzed by Rh(0)@TiO<sub>2</sub>. High catalytic activity and simple preparation procedures make Rh(0) (a) TiO<sub>2</sub> a very attractive catalyst for the hydrolysis of ammonia borane.

### Acknowledgements

Partial support by Turkish Academy of Sciences is gratefully acknowledged. We would like to thank Emrah Yıldırım, Seçkin Öztürk and İlker Yıldız for ICP-OES, TEM and XPS analyses, respectively.

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Paper

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