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Hydrogen generation from the methanolysis of ammonia borane catalyzed by in situ generated, polymer stabilized ruthenium(0) nanoclusters

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ABSTRACT

Addressed herein is the detailed study on in situ generation of poly(N-vinyl-2-pyrrolidone) (PVP) stabilized ruthenium(0) nanoclusters and their catalysis in the methanolysis of ammonia borane (AB). PVP-stabilized ruthenium(0) nanoclusters with an average particle size of 2.4 ± 1.2 nm were generated in situ from the reduction of ruthenium(III) chloride during the methanolysis of AB in the presence of PVP at room temperature. The nanoclusters were characterized by UV–vis spectroscopy, TEM, XRD, XPS and FT-IR techniques. PVP stabilized ruthenium(0) nanoclusters are highly active and stable catalyst in hydrogen generation from the methanolysis of AB with a turnover frequency (TOF) value of 4017 h^{-1} and 71,500 turnovers over 25 h. Mercury poisoning experiments showed that the PVP-stabilized ruthenium(0) nanoclusters are the true heterogeneous catalyst in the methanolysis of AB. The report also includes the results of a detailed kinetic study on the hydrogen generation from the methanolysis of AB catalyzed by PVP stabilized ruthenium(0) nanoclusters investigating the effect of the catalyst concentration, substrate concentration, and temperature as well as the activation parameters of catalytic methanolysis of AB calculated from the kinetic data.

1. Introduction

One of the most important challenges in the hydrogen economy is the storage of hydrogen because the low density of hydrogen makes it extremely difficult to store in compressed or liquefied form [1]. Recently, ammonia-borane (AB, H_3NBH_3) complex has been considered as an ideal hydrogen storage material because of its high hydrogen content (19.6 wt%), stability under operation conditions of fuel cell, and nontoxicity [2]. Hydrogen can be released from AB via either thermolysis or solvolysis route [3,4]. Solvolysis route seems to be more practical for mobile applications because of high temperature requirement of the thermolysis of AB [5]. Rapid hydrogen generation from AB can be achieved via catalytic hydrolysis or methanolysis at room temperature. Methanolysis of AB (Eq. (1)) appears to be advantageous over hydrolysis considering two important requirements for fuel cell applications: (i) no ammonia is liberated in methanolysis even at high AB concentrations and (ii) recycling of the methanolysis product, ammonium tetramethoxyborate, is easier than that in hydrolysis [3].

$$H_3NBH_3 + 4CH_3OH \xrightarrow{\text{catalyst}} NH_4B(OCH_3)_4 + 3H_2 \qquad (1)$$

The hydrogen generation from the methanolysis of AB takes place only in the presence of a suitable catalyst [6]. Hitherto, various transition metal salts including $RuCl_3$, $RhCl_3$, $PdCl_2$ [4], various copper nanoparticles [7] and non-noble transition metal–boron nanocomposites [8] have been tested in the methanolysis of AB. Our recent papers have reported the zeolite confined rhodium(0) nanoclusters [9] and in situ generated, PVP-stabilized palladium(0) nanoclusters [6] as catalysts in hydrogen generation from the methanolysis of AB. In situ generation of a catalyst in the medium of the catalytic reaction is significant because the separation processes generally result in a significant loss of catalyst. The in situ generated, PVP-stabilized Pd(0) nanoclusters were found to be highly active and stable catalysts in hydrogen generation from the methanolysis of AB providing 23,000 turnovers over 27 h before deactivation at room temperature. Obtaining such good results for in situ generated Pd catalyst, we extended the project to recover the in situ synthesis of polymer stabilized ruthenium(0) nanoclusters during the methanolysis of AB. Although a rapid hydrogen generation has been reported from the methanolysis of AB in the presence of $RuCl_3$ [4], the issue, whether the catalysis starting with the transition metal salt is homogeneous or heterogeneous has not been addressed and the report is lacking of information on the lifetime of the catalyst. In this regard, here we present a detailed study on in situ generation of poly(N-vinyl-2-pyrrolidone) stabilized ruthenium(0) nanoclusters having average particle size of 2.4 ± 1.2 nm as catalyst in the methanolysis of AB. In situ generated,

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PVP-stabilized ruthenium(0) nanoclusters could be isolated from the reaction solution and characterized by UV–vis spectroscopy, transmission electron microscope (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and FT-IR techniques. The heterogeneity of PVP-stabilized ruthenium(0) nanoclusters in the methanolysis of AB was assigned by performing mercury poisoning experiments. The detailed kinetics of the catalytic methanolysis of AB was also studied by measuring the volume of hydrogen generated during the reaction whilst varying the catalyst concentration, substrate concentration and temperature.

2. Experimental

2.1. Materials

Ruthenium(III) chloride ($RuCl_3$) (45–55%), borane-ammonia complex (>97%, AB), poly(N-vinyl-2-pyrrolidone) (PVP-40, average molecular weight 40,000) were purchased from Aldrich® and used as received. Methanol was purchased from Riedel-De Haen AG Hannover, and it was distilled over metallic magnesium. All methanolysis reactions were performed using the distilled methanol under inert gas atmosphere unless otherwise specified. Teflon coated magnetic stir bars and all glassware were cleaned with acetone and dried in oven at 150 °C.

2.2. In situ generation of PVP-stabilized ruthenium(0) nanoclusters and concomitant catalytic methanolysis of AB

Both the in situ generation of PVP stabilized ruthenium(0) nanoclusters and the catalytic methanolysis of AB were performed in the same medium. The catalytic activity of PVP-stabilized ruthenium(0) nanoclusters in the methanolysis of AB was determined by measuring the rate of hydrogen generation. To determine the rate of hydrogen generation, the catalytic methanolysis of AB were performed in a Parr-5101 low-pressure reactor equipped with a circulating water-bath and mechanical stirrer. The Parr-5101 low-pressure reactor was connected with a digital transmitter to a computer using RS-232 module. The progress of an individual catalytic methanolysis reaction was followed by monitoring the increase in the pressure of hydrogen gas with the program Calgrafix. The temperature was also controlled via thermocouple within the reactor. The pressure (psi) versus time (min) data was processed using Origin 7.0, and then converted into the values in the proper unit, volume of hydrogen (mL). Before starting the catalytic activity test experiments, the reactor (300 mL) was thermostated at 25.0 ± 0.5 °C. In order to eliminate the analytical errors in the preparation of very low concentration of Ru solutions for different catalytic reactions, a stock solution of $RuCl_3$ (5.0 mM) was prepared in 20 mL methanol. Next, to prepare a desired concentration of Ru solution, certain aliquots were taken from the stock solution and diluted. For example, in order to prepare the 1.5 mM Ru catalyst and measure the hydrogen generation from the concomitant methanolysis of AB, 3 mL of the stock solution was transferred with a glass pipette into the reactor. Then 33 mg PVP (polymer to metal ratio of 20) was added to the reactor and mixed well for 5 min. Next, 63 mg (200 mM) AB were dissolved in 7.0 mL methanol and added into the polymer–metal mixture solution. The stirring rate of the reactor was set to 700 rpm. In a control experiment, the stirring rate was varied in the range 0–1000 rpm. It was found that after 700 rpm, the stirring rate has no significant effect on the catalytic activity. This indicates that the system is in a non-MTL (mass transfer limitation) regime at stirring rates higher than 700 rpm. In other words, there is no diffusion problem due to the presence of the polymer. In addition to the volumetric measurement of the hydrogen evolution, the conversion of ammonia borane to ammonium tetramethoxyborate was also checked by ^{11}B NMR spectroscopy.

2.3. Characterization of PVP-stabilized ruthenium(0) nanoclusters

The transmission electron microscope (TEM) image was obtained using a JEM-2010 (JEOL) TEM instrument operating at 200 kV. The samples used for the TEM experiments were harvested from the in situ-generated PVP-stabilized ruthenium(0) nanoclusters solution described in the previous section. The nanocluster solution was centrifuged at 8000 rpm for 8 min. The separated nanoclusters were washed with ethanol to remove the excess PVP and other residuals. Then, the nanoclusters were redispersed in 5 mL methanol. One drop of the colloidal solution was deposited on the silicon oxide coated copper grid and evaporated under inert atmosphere. Samples were examined at magnifications between 150 and 600 K. X-ray photoelectron spectrum (XPS) was taken by using SPECS spectrometer equipped with a hemispherical analyzer and using monochromatic Mg-Kα radiation (1250 eV, the X-ray tube working at 15 kV and 350 W) and pass energy of 48 eV. To better access the metal core in the sample by scraping off the polymer matrix from the surface, the sample surface was bombarded by argon ion by passing 3000 eV energy for 5 min. UV–vis electronic absorption spectra of ruthenium(III) chloride and PVP-stabilized ruthenium(0) nanoclusters were recorded in methanol solution on Varian-Carry100 double beam instrument. X-ray diffraction (XRD) pattern of PVP-stabilized ruthenium(0) nanoclusters was recorded on a Rigaku Miniflex diffractometer with CuKα (30 kV, 15 mA, $\lambda = 1.54051$ Å), over a 2θ range from 5 to 90° at room temperature. The sample prepared for the XPS analysis was also used for FT-IR analysis. FT-IR spectra of neat PVP and PVP-stabilized ruthenium(0) nanoclusters were taken from KBr pellet on a Bruker-Advance FTIR Spectrophotometer using Opus software. To examine the reaction product by ^{11}B NMR, a certain amount of sample was taken directly from the Schlenk tube into quartz NMR tube after the stoichiometric hydrogen generation from the catalytic methanolysis of AB completed. Then a few drops of $CDCl_3$ solution were added to the solution in the quartz NMR tube. NMR spectra were recorded on a Bruker Avance DPX 400 with an operating frequency of 128.15 MHz for ^{11}B.

2.4. Mercury-poisoning heterogeneity test for PVP-stabilized ruthenium(0) nanoclusters in the methanolysis of AB

A typical in situ generation of PVP-stabilized ruthenium(0) nanoclusters and concomitant methanolysis of AB experiment described in Section 2.2 was started with 400 mM AB, 1.5 mM ruthenium(III) chloride and 30 mM PVP in 10 mL methanol at 25 ± 0.5 °C. After about 40% conversion of AB completed, elemental Hg ([Hg]/[Ru] = 350) was added to the solution under vigorous stirring and the reaction was monitored depending on hydrogen generation for further 3 h.

2.5. Kinetics of methanolysis of AB catalyzed by PVP-stabilized ruthenium(0) nanoclusters

In order to determine the rate law of the methanolysis of AB catalyzed by PVP-stabilized ruthenium(0) nanoclusters, three different sets of experiment were performed as described in Section 2.2. Firstly, AB concentration was kept constant at 200 mM varying the Ru concentration at 0.5, 1.0, 1.5, 2.0 and 2.5 mM. In the second set, Ru concentration was kept constant at 1.5 mM varying the AB concentration in the range of 0.1–5.0 M. Finally, the methanolysis reaction was performed at constant catalyst (1.5 mM Ru) and AB (200 mM) concentrations varying the temperature in the range

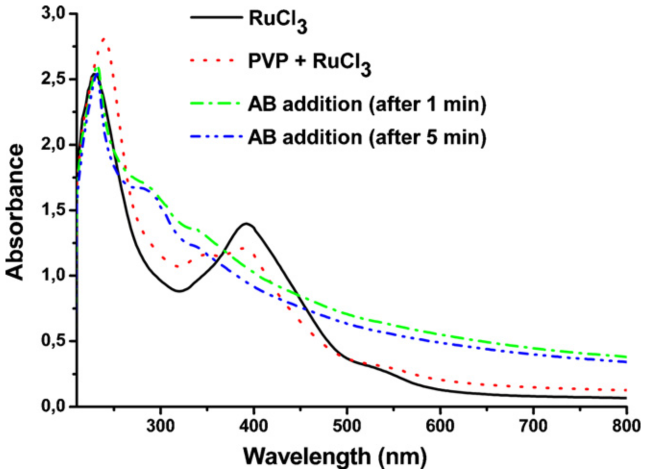

Fig. 1. UV–vis spectra of ruthenium(III) chloride, ruthenium(III) chloride plus PVP and PVP-stabilized Ru(0) nanoclusters taken from the methanol solution.

of 15–35 °C to obtain the activation parameters; activation energy (E_a), enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$).

2.6. *Catalytic lifetime of PVP-stabilized ruthenium(0) nanoclusters in the methanolysis of AB*

The catalytic lifetime of PVP-stabilized ruthenium(0) nanoclusters in the methanolysis of AB was determined by measuring the total turnover number (TTON). Such a lifetime experiment was started with a 20 mL of solution containing 0.125 mM ruthenium(III) chloride and 200 mM AB (128 mg) at 25 ± 0.5 °C. After conversion of added AB completed by checking stoichiometric H_2 gas evolution (3.0 mol H_2/mol H_3NBH_3), a new batch of 128 mg AB was added and the reaction was kept on in this way until no hydrogen gas evolution was observed. To detect whether ammonia was generated during the TTO experiments, the gas generated from the catalytic reaction was passed through 25 mL standardized solution of 0.001 M HCl at room temperature. After gas generation was ceased, the resulted solution was titrated with standard solution of 0.01 M NaOH by using phenolphthalein acid–base indicator. The amount of ammonia released from the reaction can be calculated by titrating two HCl solutions before and after the hydrolysis reaction [4].

3. Results and discussion

3.1. *In situ generation and characterization of PVP-stabilized ruthenium(0) nanoclusters*

Water soluble polymer stabilized ruthenium(0) nanoclusters were generated for the first time in situ from the reduction of ruthenium(III) chloride in the presence of PVP during the methanolysis of AB. In our established protocol [10], PVP was used as a stabilizer and AB as both reducing agent and substrate. The observation of abrupt color change from dark yellow to dark brown and concomitant hydrogen generation after addition of AB into the metal–polymer mixture indicate the formation of PVP stabilized ruthenium(0) nanoclusters. The reduction of Ru(III) to Ru(0) nanoclusters in the presence of PVP upon addition of AB was followed by UV–vis spectroscopy. Fig. 1 shows the UV–vis electronic absorption spectra of the methanol solution of ruthenium(III) chloride before and after addition of AB. The d–d absorption band at 390 nm of the ruthenium(III) disappeared within 1 min leaving an absorption feature characteristic for the ruthenium(0) nanoclusters [11]. The growing weak absorption around 280 nm was attributed to the methanolysis product, tetramethoxyborate anion, by comparing the spectrum with one of the ammonium tetramethoxyborate solution. The disappearance of the absorption band and increasing scattering absorption between 600 and 200 nm indicate the complete reduction of Ru(III) to Ru(0) and formation of the PVP-stabilized ruthenium(0) nanoclusters [12]. Survey experiments performed at different polymer to metal ratio reveal that the highest stability and catalytic activity of the PVP-stabilized ruthenium(0) nanoclusters were obtained at PVP/Ru ratio of 20 in the methanolysis of AB. This optimum ratio was used for further kinetic studies. The PVP-stabilized ruthenium(0) nanoclusters are highly stable in solution, even for months, and they can be isolated from the solution as solid materials by removing the volatiles in vacuum. The isolated PVP stabilized ruthenium(0) nanoclusters are also stable for months under inert atmosphere and they are readily redispersible in methanol by preserving their catalytic activity in the methanolysis of AB.

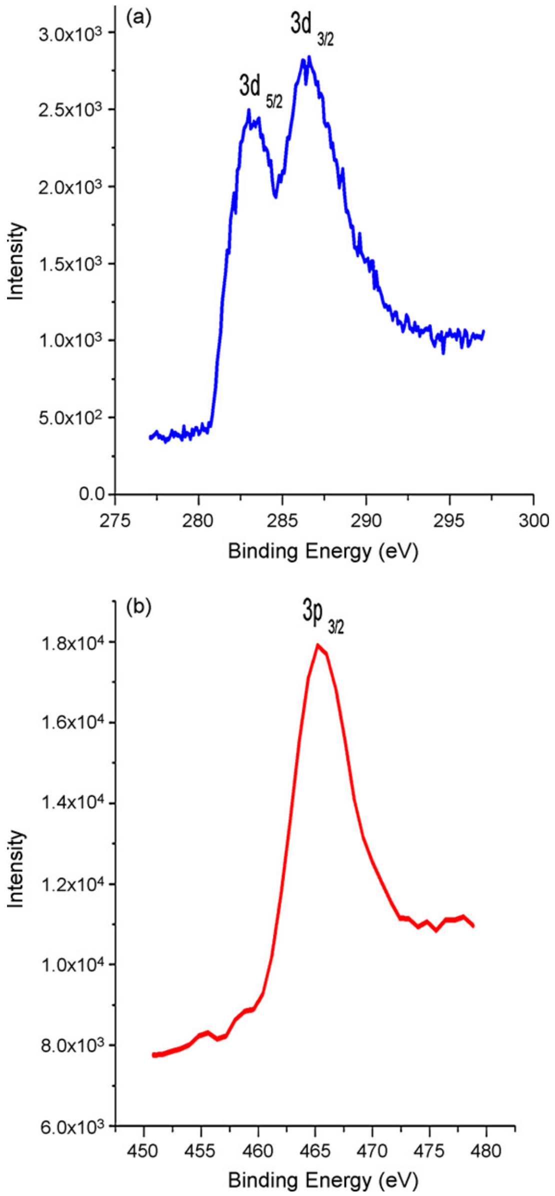

Fig. 2. X-ray photoelectron spectrum of PVP-stabilized ruthenium(0) nanoclusters: (a) 3d region; (b) 3p region.

Fig. 2 shows the XPS spectra of PVP-stabilized ruthenium(0) nanoclusters corresponding two 3d and 3p region of Ru. Two well

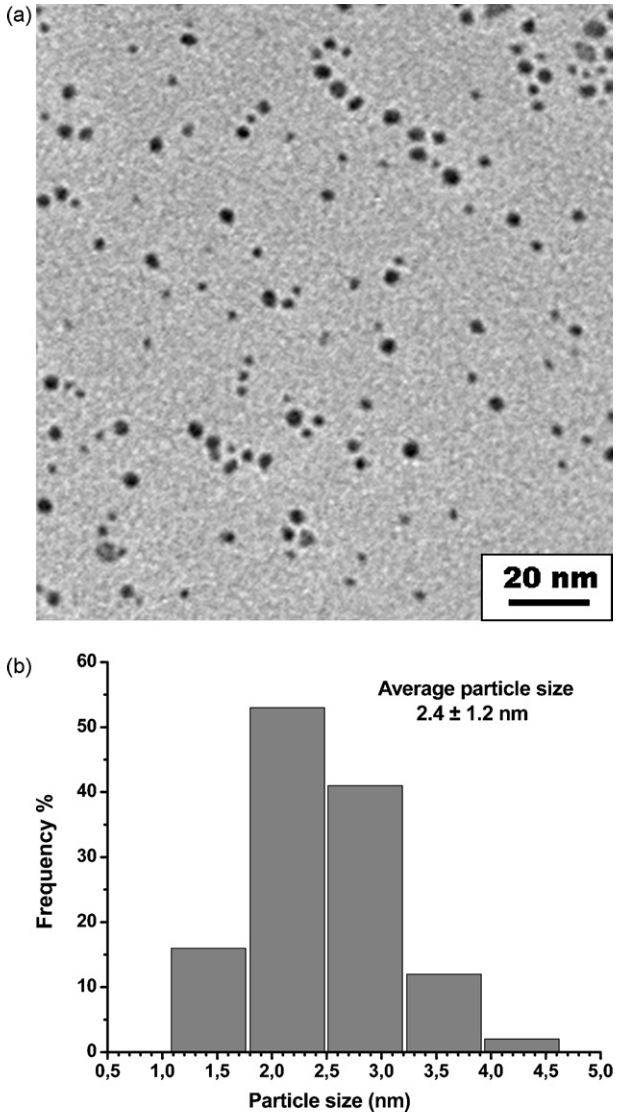

Fig. 3. (a) TEM image and (b) corresponding particle size histogram of PVP-stabilized ruthenium(0) nanoclusters.

resolved peaks were observed at 283.8 and 288.1 eV in Fig. 2a for Ru(0) $3d_{5/2}$ and Ru(0) $3d_{3/2}$ and one prominent signal was observed at 462 eV for Ru $3p_{3/2}$ which are readily assigned to the Ru(0) by comparing to the values of metallic Ru [13]. There was no peak observed for the higher oxidation state of Ru in the XPS spectra indicating the protection of Ru(0) by the attachment of PVP during the sample preparation. The FT-IR spectra of the PVP-stabilized ruthenium(0) nanoclusters show the presence of PVP in the nanoclusters samples (absorption band at 1683 cm^{-1} for CO stretching).

Fig. 3 shows the TEM image and corresponding particle size histogram of PVP-stabilized ruthenium(0) nanoclusters. The nearly spherical ruthenium(0) nanoclusters with an average particle size of 2.4 ± 1.2 nm (Fig. 3b) were obtained from the in situ reduction of ruthenium(III) chloride in the presence of PVP during the methanolysis of AB. It is also noteworthy that in situ generated PVP-stabilized ruthenium(0) nanoclusters are very stable and dispersible in methanol solution while the nanoparticles previously used as catalysts in the methanolysis of AB [8] have been shown to undergo rapid agglomeration.

Fig. 4 shows the XRD pattern of the in situ generated PVP stabilized ruthenium(0) nanoclusters. The XRD pattern of the ruthenium(0) nanoclusters shows a single diffuse peak observed at $2\theta = 42.8°$ with the d value of 2.11 Å which could be attributed to 1 0 1 plane of fcc-Ru [14]. A broadening observed at Ru(1 0 1) diffraction is characteristic of materials having a nanometer particle size [15]. The particle size of the nanoclusters (2.5 nm) calculated by the Scherrer formula is close to the average diameter (2.4 nm) determined by TEM image.

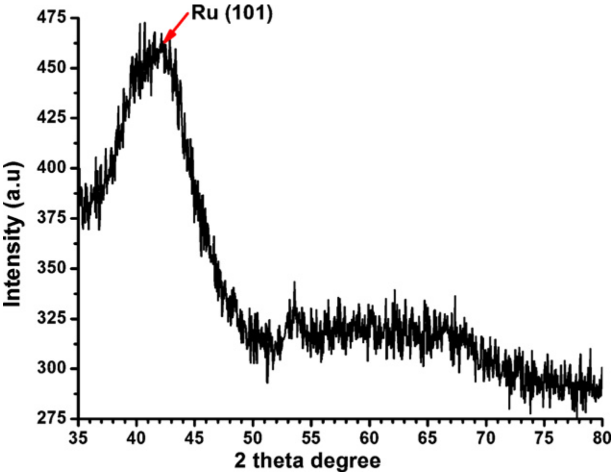

Fig. 4. Powder X-ray diffraction pattern of PVP stabilized ruthenium(0) nanoclusters.

The ^{11}B NMR spectra taken from reaction solution after the complete methanolysis of AB catalyzed by PVP stabilized ruthenium(0) nanoclusters show a single intense peak at $\delta = 8.6$ ppm which is readily assigned to the tetramethoxyborate $[B(OCH_3)_4]^-$ anion [4].

3.2. *Kinetics of methanolysis of AB catalyzed by PVP-stabilized ruthenium(0) nanoclusters*

In our previous studies [6,9], we tested the methanolysis of AB in the absence of a catalyst at various temperatures in the range of 15–35 °C. In these control experiments, no detectable hydrogen gas generation was observed over a period of 24 h. In situ generated PVP-stabilized ruthenium(0) nanoclusters are found to be highly active catalysts for the methanolysis of AB even at low concentrations and room temperature. Fig. 5 shows the plots of the volume of hydrogen generated versus time during the catalytic methanolysis of 200 mM AB solution at different Ru concentrations (0.50, 1.00,

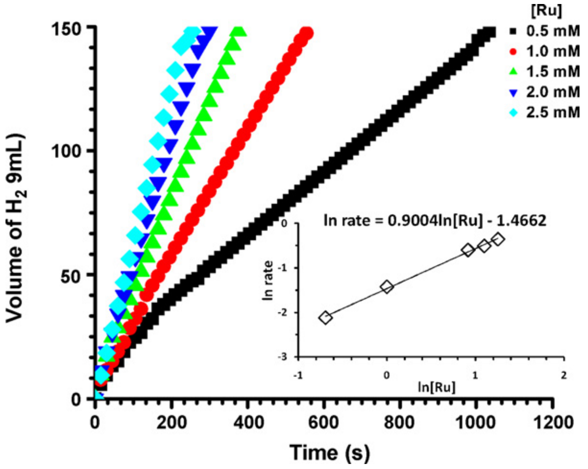

Fig. 5. The volume of hydrogen versus time plots for the methanolysis of AB catalyzed by PVP-stabilized ruthenium(0) nanoclusters at different Ru concentrations at 25 ± 0.5 °C. The inset shows the plot of hydrogen generation rate versus Ru concentration (both in logarithmic scale).

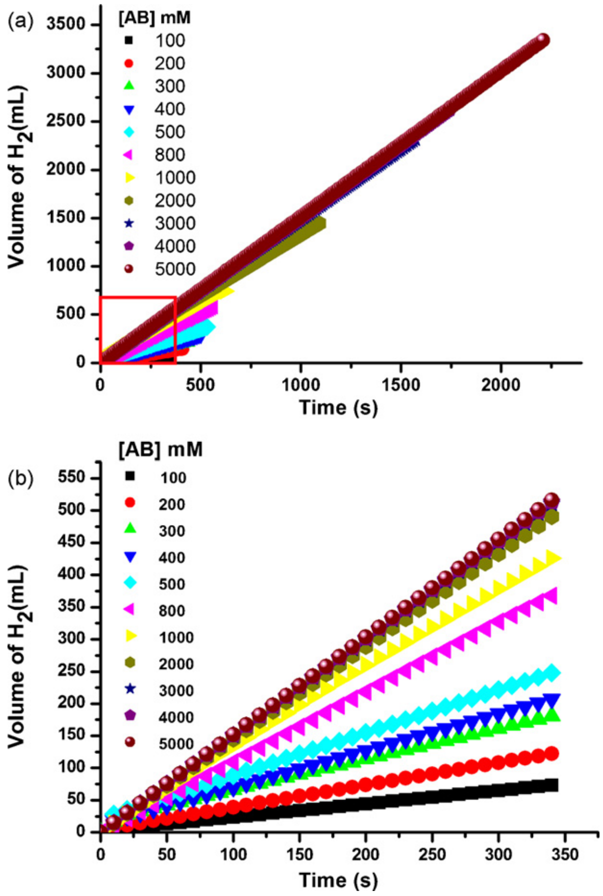

Fig. 6. (a) The volume of hydrogen versus time plot and (b) the higher magnified red rectangular area. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

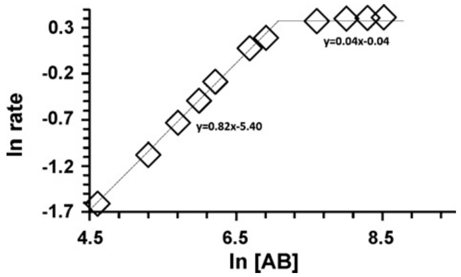

Fig. 7. The plot of hydrogen generation rate versus AB concentration (both in logarithmic scale) for the methanolysis of AB catalyzed by PVP-stabilized ruthenium(0) nanoclusters at different AB concentrations at 25 ± 0.5 °C.

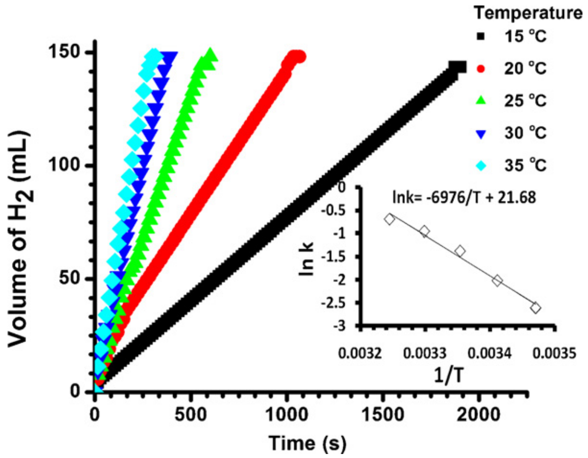

Fig. 8. Volume of hydrogen versus time plot at different temperatures for the methanolysis of AB (200 mM) catalyzed by PVP-stabilized ruthenium(0) nanoclusters (1.5 mM) in the range of 15–35 °C. The inset shows Arrhenius plot (ln *k* versus 1/*T* (K^{-1})).

1.50, 2.00, and 2.50 mM) at 25 ± 0.5 °C. The hydrogen generation rate was determined from the linear portion of the plot for each Ru concentration. The plot of hydrogen generation rate versus Ru concentration, both in logarithmic scale (the inset in Fig. 5), gives a straight line with a slope of 0.90–1 indicating that the methanolysis reaction is first order with respect to the catalyst concentration. The effect of AB concentration on the hydrogen generation rate was also studied by performing a series of experiments starting with various initial concentrations of AB while keeping the catalyst concentration constant at 1.5 mM Ru. Fig. 6 shows the plots of volume of hydrogen generated versus time during the catalytic methanolysis of AB at various substrate concentrations. The hydrogen generation rate was determined from the linear portion of the plot for each AB concentration and used for constructing the plot of hydrogen generation rate versus AB concentration both in logarithmic scale (Fig. 7). The slope of the line in the first part of the plot ([AB] = 0.1–1.0 M) is 0.82–1, but the slope of the line in the second part ([AB] is greater than 1.0) is 0.04–0. PVP stabilized Ru(0) nanoclusters with an average particle size of 2.4 nm have very large surface area, so that a lower concentration of AB is not enough to saturate the catalytically active sites on the nanoclusters surface. However, the reaction becomes independent of the substrate concentration in higher AB concentrations as all catalytically active sites will be saturated. These results indicate that when the pseudo first order conditions are established, [AB] ≫ [Ru], the reaction becomes zero order with respect to AB concentration.

In order to determine activation parameters of the reaction, methanolysis of AB catalyzed by PVP-stabilized ruthenium(0) nanoclusters was carried out at different temperatures in the range of 15–35 °C (Fig. 8), starting with an initial substrate concentration of 200 mM AB and a catalyst concentration of 1.5 mM Ru. The values of rate constant *k* (Table 1) were calculated from the slope of the linear part of each plot in Fig. 8 and used in the calculation of activation parameters: Arrhenius activation energy, $E_a = 58 \pm 2\,\mathrm{kJ\,mol^{-1}}$; activation enthalpy, $\Delta H^{\neq} = 56 \pm 2\,\mathrm{kJ\,mol^{-1}}$; activation entropy, $\Delta S^{\neq} = -75 \pm 5\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

3.3. *Catalytic life time of PVP-stabilized ruthenium(0) nanoclusters in the methanolysis of AB*

A catalyst lifetime experiment was performed starting with a 20 mL solution of PVP-stabilized ruthenium(0) nanoclusters containing 0.125 mM Ru and 200 mM H_3NBH_3 at 25.0 ± 0.5 °C. The in situ-generated PVP-stabilized ruthenium(0) nanoclusters are long-lived catalysts providing 71,500 turnovers in the methanolysis of AB over 25 h before deactivation (Fig. 9). The average TOF value

Table 1
The values of rate constant *k* for the catalytic methanolysis of AB starting with a solution of 200 mM H_3NBH_3 and in situ generated PVP-stabilized ruthenium(0) nanoclusters (1.5 mM Ru) at different temperatures calculated from hydrogen volume versus time.

Temperature (°C)	Rate constant, *k* (mol H_2 (mol Ru)$^{-1}$ (mol AB)$^{-1}$ s^{-1})
15	0.074
20	0.133
25	0.185
30	0.276
35	0.361

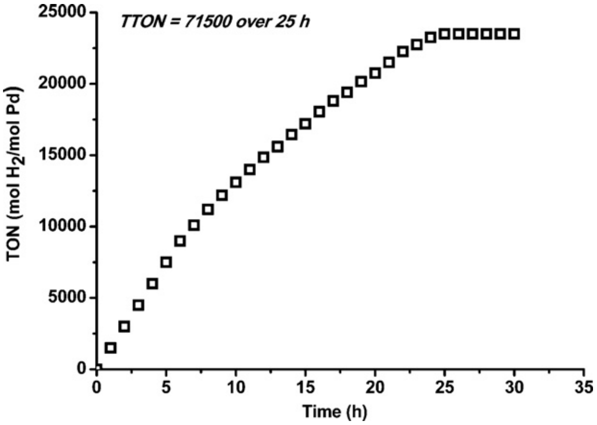

Fig. 9. The turnover number (TON) versus time plot for the methanolysis of AB catalyzed by PVP-stabilized ruthenium(0) nanoclusters at 25.0 ± 0.5 °C.

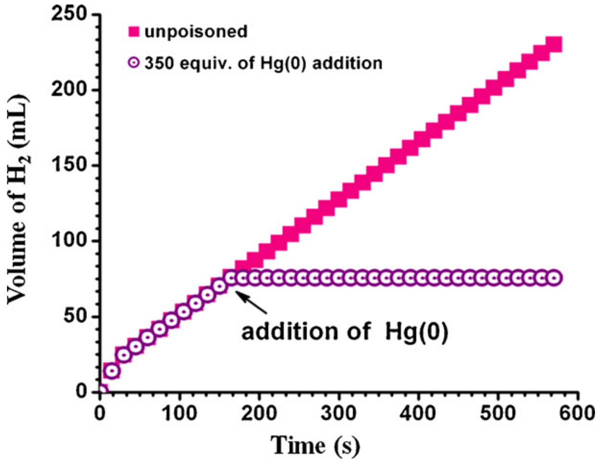

Fig. 10. The volume of hydrogen versus time plot for catalytic methanolysis of AB (400 mM) with and without addition of 350 equiv. Hg(0) at 25 ± 0.5 °C.

was found as 2860 h^{-1}. The hydrogen generation slows down as the reaction proceeds and ultimately stops, may be, because of increasing viscosity of the solution or deactivation effect of increasing metaborate concentration. Therefore, this TTO value should be considered as a lower limit. Much higher TTO values might be obtained when the increase in viscosity could be avoided. Additionally, a reusability test performed by washing and drying the catalysts after a catalytic experiment shows that the PVP stabilized ruthenium(0) nanoclusters maintain their initial activity. It is noteworthy that this is the first total turnover number and turnover frequency reported for ruthenium catalyst in the methanolysis of AB.

3.4. Mercury poisoning heterogeneity test for PVP-stabilized ruthenium(0) nanoclusters in the methanolysis of AB

Hg(0) has been used for a long time to poison heterogeneous metal(0) catalysts [16] by amalgamating the metal catalyst or being adsorbed on its surface. The suppression of catalysis by Hg(0) is considered as an evidence for heterogeneous catalysis [17]. After about 40% of conversion in a typical methanolysis experiment described in Section 2.2, 350 equivalents of mercury per ruthenium were added into the reaction solution and the progress of reaction was followed by monitoring the H_2 volume, as shown in Fig. 10. The complete cessation of the catalytic methanolysis of AB upon mercury addition is additional evidence that ruthenium(0) nanoclusters are heterogeneous catalyst in the methanolysis of AB.

4. Conclusions

PVP-stabilized ruthenium(0) nanoclusters having average particle size of 2.4 nm were easily generated in situ during the methanolysis of AB via the reduction of ruthenium(III) chloride by AB in the presence of PVP. The PVP stabilized ruthenium(0) nanoclusters are stable in solution for months under inert atmosphere and yet highly active catalysts for hydrogen generation from the methanolysis of AB even at room temperature with a TOF value of 2860 h^{-1}. In situ generated PVP stabilized ruthenium(0) nanoclusters could be isolated as stable solid materials and they are readily redispersible in methanol and preserving their activity in the methanolysis of AB. Furthermore, PVP-stabilized ruthenium(0) nanoclusters are long-lived catalysts in the methanolysis of AB providing 71,500 turnovers over 25 h before deactivation at room temperature. The superb catalytic activity and long lifetime of the nanoclusters stem from their small size and well-dispersion in the reaction medium. Easy preparation, outstanding stability, and the high catalytic activity of in situ-generated PVP-stabilized ruthenium(0) nanoclusters make them leading candidate to be employed in developing highly efficient portable hydrogen generation systems using AB as a solid hydrogen storage material.

Acknowledgements

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