Water dispersible acetate stabilized ruthenium(0) nanoclusters as catalyst for hydrogen generation from the hydrolysis of sodium borohyride

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Abstract

The development of new storage materials will facilitate the use of hydrogen as a major energy vector in near future. In the hydrogen economy, chemical hydrides such as $NaBH_4$, KBH_4, LiH, NaH have been tested as precursor materials for supplying hydrogen at ambient temperature. Among these chemical hydrides, sodium borohydride ($NaBH_4$) provides a safe and practical mean of producing hydrogen. Sodium borohydride is stable in basic solution; however, hydrolysis generates hydrogen gas in the presence of a suitable catalyst. All of the prior catalysts having been used for this hydrolysis reaction are heterogeneous and, therefore, have limited activity because of the surface area. Here, we report the employment of water dispersible metal(0) nanoclusters as catalyst for the hydrolysis of sodium borohydride. The water dispersible ruthenium(0) nanoclusters were prepared from the reduction of $RuCl_3 \cdot 3H_2O$ and stabilized by using acetate ion. They provide 5170 turnovers in the hydrolysis of sodium borohydride at $25.0 \pm 0.1\,^{\circ}C$ before deactivation. The acetate stabilized ruthenium(0) nanoclusters of $2.8 \pm 1.4\,nm$ particle size were characterized by TEM, XPS, and FTIR spectroscopy. Kinetic study shows that the ruthenium(0) nanocluster-catalyzed hydrolysis of sodium borohydride is first order in catalyst concentration and zero order in substrate concentration. The acetate stabilized ruthenium(0) nanoclusters provide a low activation energy for the hydrolysis of sodium borohydride. Even in basic solution, the activation energy was found to be smaller than that obtained by using the carbon-supported ruthenium as catalyst.
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Keywords: Ruthenium; Water dispersible; Nanoclusters; Catalyst; Hydrolysis; Sodium borohydride; Acetate; TEM; NIH image; X-ray photoelectron spectroscopy; FTIR

1. Introduction

Fossil fuels (i.e., petroleum, natural gas, and coal) will overwhelmingly be used to meet the increasing energy demand at least for the next few decades [1]. Because of increasing concern about the environmental problems, including global warming caused by the emission of gases from the combustion of fossil fuels, there has been a growing interest for the use of renewable energy sources such as solar and wind energy. However, besides their relatively high cost, energy production from renewable sources has the problem of discontinuity, for example, requirement of uninterrupted sunshine in the usage of solar energy can not be fulfilled. The obvious solution to this predicament is the storage of energy. In this context, hydrogen appears to be the best energy carrier as it is clean to use, renewable, and widely available from diverse sources [2]. Although hydrogen can be used in many ways for generating energy, the most efficient one is its conversion to electrical energy following combustion in a fuel cell [3]. Dramatic improvements, particularly in the existing technologies for production, storage, and usage of hydrogen, are still needed if hydrogen is to become a major energy carrier in the future. The hydrogen-based energy economy deals with the development of diversity of sources for hydrogen production using efficient technologies, finding viable methods for hydrogen storage, lowering the cost of fuel cells and improving their on-board usage. Advanced storage concepts include the use of metal hydrides and nanostructured materials, for example, encapsulation in the porous materials.

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Recently, sodium borohydride, $NaBH_4$, has been suggested as a new fuel source for supplying hydrogen under mild conditions [4]. $NaBH_4$ yields hydrogen gas and water-soluble sodium metaborate, $NaBO_2$, upon hydrolysis in the presence of certain catalysts.

$$NaBH_4 + 2H_2O \xrightarrow{\text{catalyst}} NaBO_2 + 4H_2,$$
$$\Delta H = -300 \, kJ \, mol^{-1} \tag{1}$$
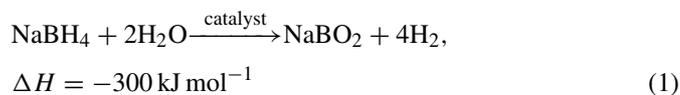
The catalysts tested for the hydrolysis of sodium borohydride, listed chronologically are: platinum or rhodium salts [5], cobalt salt [6], iron, ruthenium, palladium, osmium, iridium, and platinum salts [7], nickel, Raney nickel, and bulk cobalt [8], alloys such as $LaNi_{4.5}T_{0.5}$ (T = Mn, Cr, Co, Fe, Cu) [9], bulk ruthenium [10], mixed metal/metal oxides such as $Pt-LiCoO_2$ [11], nickel boride [12] and filamentary nickel–cobalt [13]. With the exception of metal salts of platinum, ruthenium [5] and cobalt [6] all the catalyst used for the hydrolysis of sodium borohydride are heterogeneous. The limited surface area of heterogeneous catalysts restricts their catalytic activity to a low value. As the activity of catalyst is directly related to its surface area, using water dispersible nanoclusters is a promising way to increase the catalytic activity.

At the present time there is a considerable interest in the study and use of metal nanoclusters because of their novel and attractive physical and chemical properties [14]. For example, transition metal nanoclusters have been studied as catalysts in various organic and inorganic reactions [15] and as electrocatalysts in fuel cells [16]. Metal nanoclusters are more active catalysts than the respective bulk metal counterparts, because a large percentage of metal atoms are on the surface of nanoclusters, and the surface atoms do not necessarily order themselves in the same way as those in the bulk do [17]. For the above reasons, we started an investigation of water-dispersible transition-metal nanoclusters as catalyst for the hydrolysis of sodium borohydride. We selected ruthenium, which is the most widely used catalyst in the hydrolysis of sodium borohydride, though in the bulk form, for the preparation of water dispersible metal nanoclusters and employ them herein as catalyst for the hydrolysis of sodium borohydride [18]. The results of our study show that acetate stabilized ruthenium(0) nanoclusters, prepared from the reduction of ruthenium(III) chloride with sodium borohydride in aqueous solution containing acetate anion, are highly active catalyst for the hydrolysis of sodium borohydride at room temperature.

2. Experimental

Ruthenium(III) chloride trihydrate, sodium acetate trihydrate (99%), sodium borohydride (98%) were purchased from Aldrich. The water content of $RuCl_3 \cdot xH_2O$ was determined by TGA and found to be $x = 3$. Deionized water was distilled by water purification system (Şimşek SL-200, Turkey). 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 100 °C.

2.1. Preparation of acetate stabilized ruthenium(0) nanoclusters

Following the procedure given in the literature [19], acetate stabilized ruthenium(0) nanoclusters were prepared from the reduction of 1.33 mM solution of ruthenium(III) chloride by sodium borohydride (9.3 mM) in aqueous sodium acetate solution (80 mM) at room temperature. A molar ratio of $NaBH_4$ to $RuCl_3$ greater than 5 was used to ensure complete reduction of ruthenium(III) to its zerovalent state. Acetate stabilized-ruthenium(0) nanoclusters, dark brown in color, were found to be stable in aqueous media (no precipitation was observed after a few days of storage). Aliquots of the ruthenium(0) nanoclusters solution were used to catalyze the hydrolysis of sodium borohydride. The nanoclusters could be isolated by centrifugation followed by drying in vacuum. The isolated nanoclusters were characterized by XPS and TEM. The isolated ruthenium(0) nanoclusters are redispersed in water and were tested for their catalytic activity. When redipersed, the ruthenium(0) nanoclusters retain 70% of their initial catalytic activity in the hydrolysis of sodium borohydride.

2.2. Self-hydrolysis of sodium borohydride

In order to determine the rate of self hydrolysis of sodium borohydride in the absence of catalyst, 284 mg sodium borohydride was dissolved in 50 mL water and the solution was transferred with a 50 mL pipette into the reaction flask thermostated at 25.0 ± 0.1 °C. The experiment was started by closing the reaction flask and turning on the stirring at 1000 rpm simultaneously. The volume of hydrogen gas generated was measured every 30 s. The pH of the solution was recorded to be 9.6 at the beginning of reaction and to increase to its final value of 10.8 when all sodium borohydride was converted to sodium metaborate.

2.3. Catalytic activity test of ruthenium(0) nanoclusters in the hydrolysis of sodium borohydride

In a series of experiments, acetate stabilized-ruthenium(0) nanoclusters were tested for their catalytic activity in the hydrolysis of sodium borohydride. The catalytic activity of ruthenium(0) nanoclusters in the hydrolysis of sodium borohydride was determined by measuring the rate of hydrogen generation. Before starting the catalytic activity test, a jacketed reaction flask (75 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 (50 cm in height and 5.0 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, 284 mg (7.47 mmol) $NaBH_4$ was dissolved in 40 mL water (corresponding to 30 mmol = 672 mL H_2 at 25.0 ± 0.1 °C and 0.91 atm pressure). The solution was transferred with a 50 mL glass-pipette into the reaction flask thermostated at 25.0 ± 0.1 °C. Then, aliquots of acetate stabilized ruthenium(0) nanocluster solutions was transferred into the reaction flask using a 10 mL

gastight syringe. The initial pH of the solution was recorded to be same (pH 9.6) as in the self hydrolysis of sodium borohydride. 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 ceased when 70% conversion was achieved.

2.4. Kinetic study of Ru(0) nanocluster-catalyzed hydrolysis of sodium borohydride

In order to establish the rate law for catalytic hydrolysis of NaBH$_4$ using water dispersible Ru(0) nanoclusters, two different sets of experiments were performed in the same way as described in Section 2.3. In the first set of experiments, the concentration of NaBH$_4$ was kept constant at 150 mM and the Ru(0) nanoclusters concentration was varied in the range of 0.08, 0.16, 0.32, 0.48, 0.64, 0.8 and 1.12 mM. In the second set of experiments, Ru(0) nanoclusters concentration was held constant at 0.32 mM while the NaBH$_4$ concentration was varied to get various NaBH$_4$/Ru(0) ratio in the range of 100, 200, and 500. In all of these experiments, the initial pH of the solution was recorded to be same (pH 9.6) as in the self hydrolysis of sodium borohydride. Finally, we performed the catalytic hydrolysis of NaBH$_4$ in the presence of Ru(0) nanoclusters at constant NaBH$_4$ and Ru(0) concentrations at various temperatures in the range of 25–45 °C in order to obtain the activation energy (E_a), enthalpy ($\Delta H^\#$) and entropy ($\Delta S^\#$). The rate constants were found to be $k = 2.3, 3.8, 4.9, 6.1, 6.3$ [mol NaBH$_4$]·[mol Ru(0)]$^{-1}$ s^{-1} at 25, 30, 35, 40, 45 °C, respectively.

2.5. Effect of acetate concentration on the catalytic activity of Ru(0) nanoclusters

In order to study the effect of acetate concentration on the catalytic activity of Ru(0) nanoclusters in the hydrolysis of sodium borohydride (150 mM), catalytic activity tests were performed at 25.0 ± 0.1 °C starting with various concentrations of sodium acetate (0.5, 0.8, 1.0, 1.5, 2.0 and 10 M) in the preparation of Ru(0) nanoclusters. In all the experiments the total volume of solution was kept constant at 50 mL.

2.6. Effect of sodium hydroxide on the Ru(0) nanocluster-catalyzed hydrolysis of sodium borohydride

In order to study the hydrolysis of sodium borohydride in strongly basic solution, the same catalytic hydrolysis of sodium borohydride was performed in a solution containing 10% (w/w) NaOH solution having an initial pH of 12.4. Here again, a control experiment was also performed to determine the rate of the self hydrolysis of sodium borohydride in the absence of ruthenium(0) nanoclusters; it was observed that there is no significant amount of hydrogen production, 0.013 mL H$_2$/s, i.e., 0.02% of the rate in a normal catalytic run using 0.08 mM Ru(0) nanoclusters. A critical reexamination of the literature shows that the catalytic activity of some heterogeneous catalysts in the hydrolysis of sodium borohydride has been investigated in basic solutions (<10% NaOH). Hence, for the purpose of comparison,

we performed a catalytic activity test of Ru(0) nanoclusters for the hydrolysis of sodium borohydride in aqueous solution containing 10% NaOH (w/w), exactly in the same way as described above. Hydrolysis of sodium borohydride (150 mM) in the presence of Ru(0) nanoclusters (0.32 mM) in 10% NaOH (w/w) solution was performed at four different temperatures, 25, 35, 45, and 55 °C.

2.7. Catalytic lifetime of acetate stabilized-ruthenium(0) nanoclusters

The catalytic lifetime of acetate stabilized-ruthenium(0) nanoclusters in the hydrolysis of sodium borohydride was determined by measuring the total turnover number (TTO). Such a lifetime experiment was started with a 50 mL solution containing 0.32 mM Ru(0) nanoclusters and 450 mM NaBH$_4$ (corresponding to maximum possible total turnover number of 5400) at 25.0 ± 0.1 °C. The reaction was continued until no hydrogen gas evolution was observed. Acetate stabilized ruthenium(0) nanoclusters could provide 5170 turnovers for the hydrolysis of sodium borohydride over 1.4 h before deactivation.

2.8. Mercury poisoning of acetate stabilized-ruthenium(0) nanoclusters

In a poisoning experiment 0.80 mM ruthenium(0) nanoclusters used in the hydrolysis of 150 mM sodium borohydride (54.8 mg) in 10 mL solution was poisoned by using 4.1, 3.3, 2.5, 1.65, 0.83, 0.41 and 0.20 mg mercury corresponding to a Hg/Ru molar ratio of 0.125, 0.100, 0.075, 0.05, 0.025, 0.013, and 0.063, respectively, and the rate of hydrogen generation measured at 25.0 ± 0.1 °C.

2.9. Isolation of acetate stabilized-ruthenium(0) nanoclusters

The acetate stabilized ruthenium(0) nanoclusters were isolated by centrifugation at 5000 rpm for 6 h and then drying under vacuum. Then the catalytic activity of these isolated ruthenium(0) nanoclusters was tested for the hydrolysis of sodium borohydride.

2.10. TEM sample preparation and TEM analyses

The samples used for the TEM experiments were harvested from the preparation of acetate stabilized-ruthenium(0) nanoclusters solution as described above: 5 mL aliquot of acetate stabilized-ruthenium(0) nanoclusters solution was transferred into a clean screw-capped glass vial with a disposable polyethylene pipette. This sample was sent to the University of Oregon for TEM investigation. There, one drop of the colloidal solution was deposited on the chloroform cleaned, carbon coated Cu TEM grid and the solvent was then evaporated. TEM analyses were performed at the University of Oregon with expert assistance of Dr. Eric Schabtach, using the sample preparation procedure and Philips CM-12 TEM with a 70 μm lens operating at 100 kV and with a 2.0 Å point-to-point resolution. Samples were

examined at magnification between 100 and 400k. One drop of desired colloidal solution was deposited on the amorphous carbon membrane of the transmission electron microscope grid and the solvent was then evaporated.

2.11. Particle size measurements

Particle size analysis was performed using the public domain NIH Image J 1.62 program [20], developed at the U.S. National Institutes of Health and available on the Internet at http://www.rsb.info.nih.gov/nih-image/. The image was obtained as a TIF file directly from the TEM measurement. Using Adobe Photoshop the contrast and brightness and channel curves were adjusted so that particles stand out clearly from the background. In NIH Image J 1.62, after having set the scale and the threshold, the "analyze particles" feature was used to generate a table of particle areas and diameters (major and minor axes). This table was then exported into Microsoft Excel XP where histograms, statistical analysis and histogram plotting were performed. For each particle, the diameter was calculated from the area by assuming that the nanoclusters are circular. Size distributions are quoted as the mean diameter ± the standard deviation.

2.12. XPS sample preparation and XPS analysis

Briefly, 10 mL of aliquots of acetate stabilized-ruthenium(0) nanoclusters solutions were transferred via disposable pipette into eight new 15 mm × 100 mm glass tubes separately and each samples was simultaneously centrifuged for 3 h. The centrifuged material was rinsed three times with a 30% (v/v) water/ethanol mixture to remove water-soluble impurities. Next, the precipitates were dried under vacuum for 2 h. All the nanoclusters samples dried were collected in a screw-capped glass-vial and sent to the Colorado State University for XPS analysis. X-ray photoelectron spectroscopy (XPS) was performed at the Colorado State University using a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al Kα radiation (1486.6 eV, the X-ray tube working at 15 kV and 350 W) and pass energy of 23.5 eV.

2.13. FTIR analyses

The sample prepared for the XPS analysis was also used for the FTIR analysis. FTIR spectrum of the acetate stabilized-ruthenium(0) nanoclusters was taken from KBr pellet on a Nicolet 510 FTIR spectrophotometer using Omnic software.

3. Results and discussion

3.1. Use of water dispersible acetate stabilized ruthenium(0) nanoclusters as catalyst for the hydrolysis of sodium borohydride

Water dispersible acetate stabilized-ruthenium(0) nanoclusters were used as catalyst in the hydrolysis of sodium borohy-

dride liberating hydrogen gas, Eq. (2).

$$NaBH_4 + 2H_2O \xrightarrow{\text{Ru(0) nanoclusters}} NaBO_2 + 4H_2 \qquad (2)$$
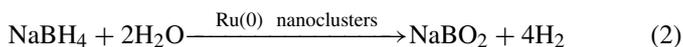
First of all, the rate of hydrogen generation from the self hydrolysis of sodium borohydride was measured in a control experiment starting with 150 mM sodium borohydride solution, that is, under the exactly same conditions. The observed rate is less than 0.8 mL H_2/min (the total amount of hydrogen gas produced over 120 min is 94 mL).

The acetate stabilized-ruthenium(0) nanoclusters were found to be highly active catalyst for the hydrolysis of sodium borohydride as shown in Fig. 1, which plots the volume of H_2 generated versus time during the catalytic hydrolysis of 150 mM $NaBH_4$ solution in the presence of Ru(0) nanoclusters in different concentrations at $25.0 \pm 0.1\,°C$ and an initial pH of 9.6. It is seen that acetate stabilized-ruthenium(0) nanoclusters have high catalytic activity, in the range of 20–370 mL H_2/min even at low catalyst concentrations (0.08–1.12 mM Ru(0), respectively) and room temperature. The hydrogen evolution starts immediately without any induction period since preformed nanocluster catalyst was used. The hydrogen generation rate was determined from the linear portion of the plot for each experiment with different Ru(0) concentration. Fig. 2 shows the plot of hydrogen generation rate versus Ru(0) concentration, both on logarithmic scales. One obtains a straight line, the slope of which is found to be 1.07–1.0 within experimental error. This result indicates that the hydrolysis is first order with respect to the concentration of acetate stabilized ruthenium(0) nanoclusters catalyst.

The effect of $NaBH_4$ substrate concentration on the hydrogenation rate was also studied by performing a series of experiments starting with varying initial concentration of $NaBH_4$ while keeping the catalyst concentration constant at 0.32 mM Ru(0). Fig. 3 shows the plot of hydrogen generation rate versus $NaBH_4$ concentration, both on logarithmic scales and indicates that the catalytic hydrolysis is zero order with respect to substrate concentration. Taking both results together, the rate law for the
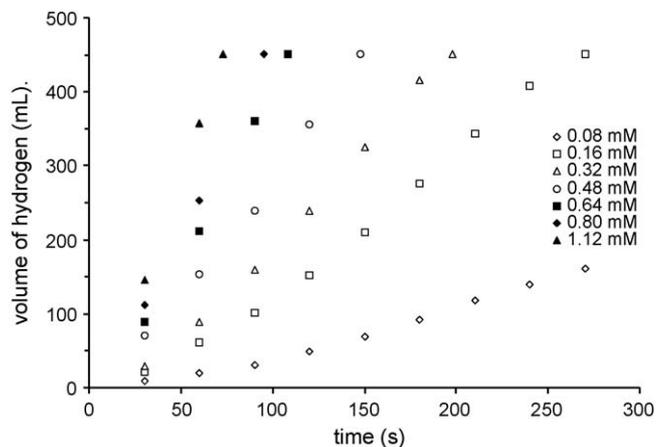
Fig. 1. Plot of the volume of hydrogen (mL) vs. time (s) for the hydrolysis of sodium borohydride catalyzed by ruthenium(0) nanoclusters with different catalyst concentrations at $25.0 \pm 0.1\,°C$. $[NaBH_4]_0 = 150$ mM.
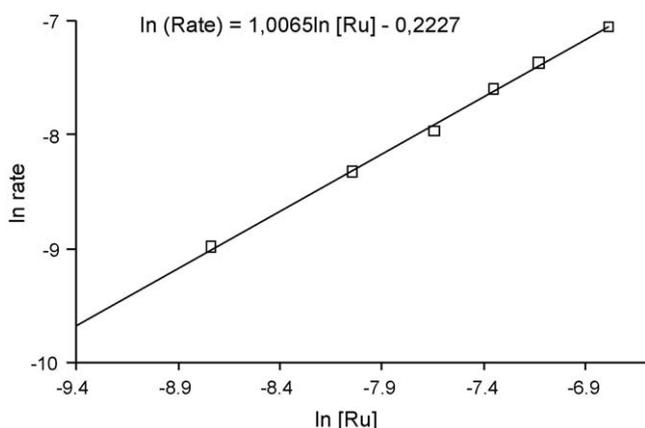
Fig. 2. Plot of the hydrogen generation rate vs. the catalyst concentration (both in ln scale) in the hydrolysis of 150 mM NaBH$_4$ catalyzed by ruthenium(0) nanoclusters at 25.0 ± 0.1 °C.

catalytic hydrolysis of sodium borohydride can be given as

$$\text{Rate} = \frac{d[H_2]}{dt} = k[\text{Ru}] \tag{3}$$

The hydrolysis of sodium borohydride was carried out at various temperature in the range of 25–45 °C starting with the initial substrate concentration of 150 mM NaBH$_4$ and an initial catalyst concentration of 0.32 mM Ru(0). The values of the rate constant k determined at five different temperatures are used to create the Arrhenius and Eyring plots shown in Fig. 4. The Arrhenius activation energy was found to be $E_a = 41 \pm 2$ kJ/mol for the acetate stabilized ruthenium(0) nanoclusters catalyzed hydrolysis of sodium borohydride. This value compares favorably with the activation energy of 47 kJ/mol found at 5.6 M NaBH$_4$ concentration [21] and 56 kJ/mol found at 2 M NaBH$_4$ concentration for the hydrolysis catalyzed by bulk ruthenium [4a]. It is less than the activation energies found for the same hydrolysis using various bulk metal catalyst: 75 kJ/mol for cobalt, 71 kJ/mol for nickel, and 63 kJ/mol for Raney nickel [8]. The Eyring plot in Fig. 4b provides the activation enthalpy and activation entropy values:
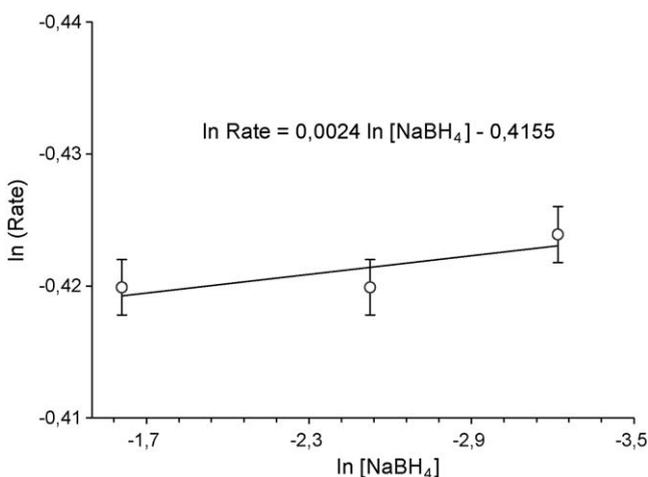
Fig. 3. Plot of the hydrogen generation rate vs. the NaBH$_4$ concentration (both in ln scale) in the hydrolysis of NaBH$_4$ catalyzed by ruthenium(0) nanoclusters ([Ru] = 0.32 mM) at 25.0 ± 0.1 °C.
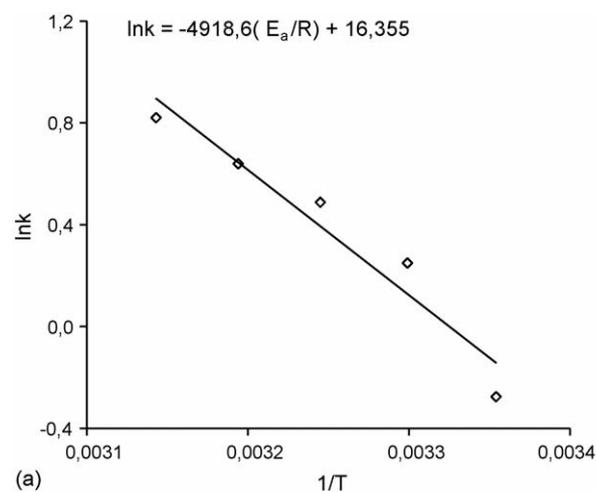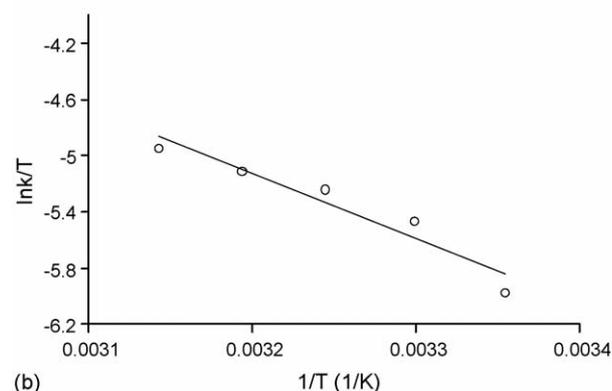
Fig. 4. (a) Arrhenius and (b) Eyring plots for the ruthenium(0) nanoclusters-catalyzed hydrolysis of 150 mM NaBH$_4$. [Ru] = 0.32 mM.

$\Delta H^{\#} = 38 \pm 1$ kJ/mol and $\Delta S^{\#} = -117 \pm 6$ J/K mol for the ruthenium(0) nanoclusters catalyzed hydrolysis of 150 mM sodium borohydride solution. The small value of activation enthalpy and the large negative value of activation entropy are indicative of an associative mechanism for the ruthenium(0) nanocluster-catalyzed hydrolysis of sodium borohydride, in line with the mechanism suggested for the hydrolysis of sodium borohydride given in the literature [22] consisting of [BH$_5$]* formed as transient.

Since most of the prior studies on the catalytic hydrolysis of sodium borohydride have been carried out in basic medium, mostly in the presence of 10% (bw) NaOH, for comparison we also performed the hydrolysis of sodium borohydride in the same medium by using the acetate stabilized ruthenium(0) nanoclusters as catalyst. The values of the rate constant k of the catalytic hydrolysis of sodium borohydride solution containing 10% sodium hydroxide at varying temperatures were used to obtain the Arrhenius plot shown in Fig. 5. The Arrhenius activation energy was found to be 43 ± 2 kJ/mol. This is slightly greater than the activation energy in the absence of sodium hydroxide (41 ± 2 kJ/mol), but still smaller than the literature value of 47 kJ/mol found for bulk ruthenium at 5.6 M NaBH$_4$ concentration [21]. The small increase in the activation energy upon addition of sodium hydroxide indicates that the hydrolysis reaction can be inhibited by the hydroxide ion in agreement with

$\ln k = -5205.1(E_a/R) + 17.328$
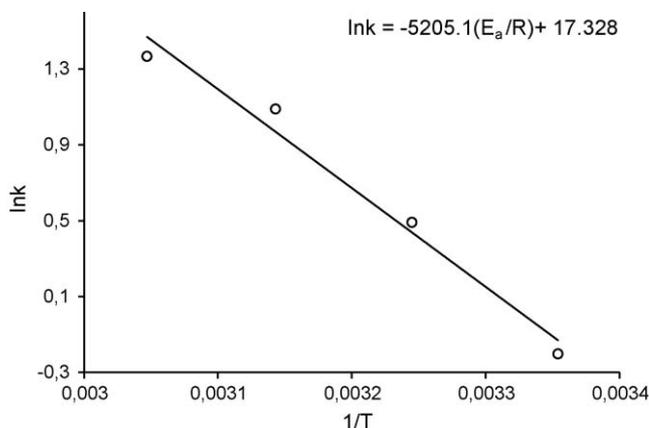
Fig. 5. Arrhenius plot for ruthenium(0) nanoclusters catalyzed hydrolysis of sodium borohydride in the alkaline solution containing 10% NaOH (w/w), [Ru] = 0.32 mM, [NaBH$_4$] = 150 mM, at different temperatures 25, 35, 45, and 55 °C.

the previous finding [4a]. According to the established mechanism [22], the hydrolysis of sodium borohydride is initiated by the attack of borohydride anion on the hydronium ion. In basic solution the reduction of proton concentration causes a decrease in the rate of hydrolysis. However, the activation energy obtained for the ruthenium(0) nanoclusters catalyzed hydrolysis of sodium borohydride in basic medium is still lower than the ones reported for the use of heterogeneous bulk ruthenium [4a]. As a result, Ru(0) nanoclusters are more active catalyst than bulk ruthenium metal in the hydrolysis of sodium borohydride in the absence or presence of sodium hydroxide.

The effect of the stabilizer concentration on the catalytic activity of the ruthenium(0) nanoclusters was investigated by performing the catalytic hydrolysis of sodium borohydride starting with 0.16 mM ruthenium(III) ion and different acetate ion concentration. Fig. 6 shows how crucial the effect of concentration of the stabilizer is on the catalytic activity of ruthenium(0) nanoclusters. The highest catalytic activity was achieved for ruthenium(0) nanoclusters stabilized by 1.0 M sodium acetate. It is worth to note that the high activity of ruthenium(0) nanoclusters is obtained only in a narrow range around 1.0 M acetate ion concentration. The acetate ion is adsorbed on the nanoclusters surface generating a double layer, which provides electrostatic
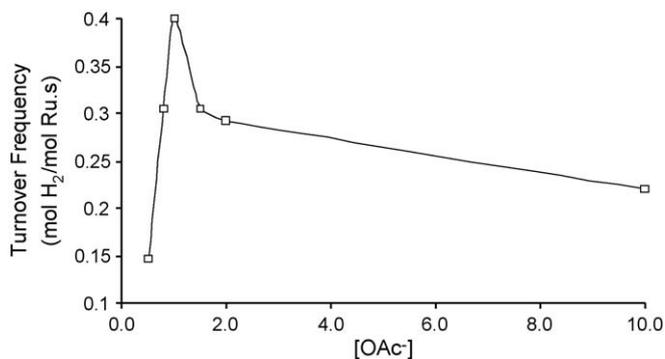
stabilization against coagulation of the particles. The acetate ion adsorbed on the nanoclusters surface is in dynamic equilibrium with the acetate ion in the solution, so that some of the surface metal atoms are still available providing active sites for the catalysis. However, at higher stabilizer concentration, the surface active sites are blocked by the acetate ions adsorbed on the surface and the catalytic activity decreases with the increasing concentration of the acetate ion. The acetate ion concentration around 1.0 appears to be the optimum one.

Ruthenium(0) nanoclusters were isolated by centrifugation followed by drying in vacuum. These isolated ruthenium(0) nanoclusters were redispersed in water and tested for their catalytic activity for sodium borohydride hydrolysis after 2 days of storage. The isolated ruthenium(0) nanoclusters could be easily dispersed in water and giving rise to a transparent dark brown colloidal solution of ruthenium. After 2 days of storage, the sample prepared by redispersing the isolated ruthenium(0) nanoclusters was found to be highly active catalyst in the hydrolysis of sodium borohydride. The reaction rates indicate that ruthenium(0) nanoclusters retain 70% of their catalytic activity in the hydrolysis of sodium borohydride, when isolated and redispersed in water. The deactivation of ruthenium(0) nanoclusters catalyst may be due to agglomeration or partial oxidation of ruthenium. In fact, an XPS study shows the presence of ruthenium oxide.

(a)

Fig. 6. Turnover frequency for the hydrolysis of sodium borohydride (150 mM) catalyzed by acetate stabilized Ru(0) nanoclusters with different acetate concentrations at 25 °C. [Ru] = 0.16 mM.
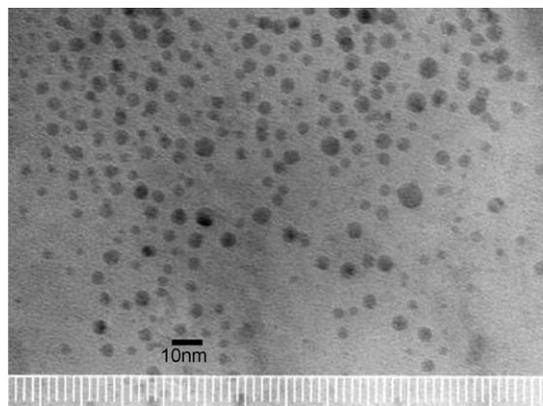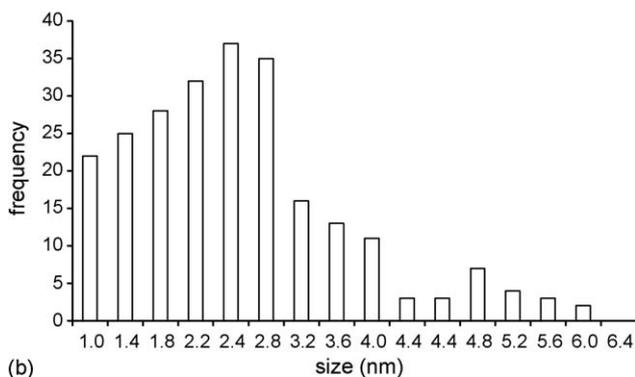
(b)

Fig. 7. (a) TEM image and (b) associated histogram for acetate-stabilized ruthenium(0) nanoclusters prepared from the reduction of 1.33 mM ruthenium(III) chloride trihydrate by 9.3 mM sodium borohydride in the presence of 1.0 M acetate ion in aqueous solution.

3.2. Characterization of water-dispersible acetate stabilized ruthenium(0) nanoclusters catalyst

Fig. 7 gives the TEM image and histogram of ruthenium(0) nanoclusters prepared from the reduction of ruthenium(III) chloride trihydrate by sodium borohydride in the presence of sodium acetate. The histogram was constructed from the TEM image by using NIH image program, whereby 235 non-touching particles were counted. The particle size ranges from 1.0 to 6.0 nm with a mean value of 2.8 nm and a standard deviation of 1.4 nm.

Fig. 8 shows the XPS spectrum of acetate stabilized ruthenium(0) nanoclusters exhibits two signals at 280 and 462 eV for Ru $3d_{5/2}$ and Ru $3p_{3/2}$, respectively. These signals are readily assigned to the Ru(0). Additional peaks are observable at 284 and 466 eV, which can be assigned to higher oxidation states of ruthenium such as Ru(IV) in RuO_2. The formation of Ru oxides in the XPS sampling procedure is a known phenomenon [23]. The signals beyond C 1s peak at 285 eV are attributable to the Ru $3d_{3/2}$ of higher oxidation species [24,19].

Fig. 9 shows the FTIR spectrum of the isolated ruthenium(0) nanoclusters taken from KBr pellet shows the absorption bands due to the acetate ion at 1580 and 1425 cm^{-1} indicating the existence of acetate ion in the nanocluster sample, most probably on the surface of ruthenium(0) nanoclusters.

3.3. Catalyst poisoning

Catalyst poisoning experiments are vital to show that the acetate stabilized ruthenium(0) nanoclusters are the true (heterogeneous; metal particle) catalyst [25]. A series of mercury poisoning experiments were carried out by adding mercury in varying amount during the catalytic hydrolysis of sodium borohydride and measuring the catalytic activity before and after addition. Fig. 10 shows the results of eight independent experiments as a plot of the relative rate of hydrogen generation versus the relative mercury concentration as mol Hg/mol Ru. Experimental points can be fitted to a line, the intersection of which with the concentration axis provides the critical molar ratio of mer-
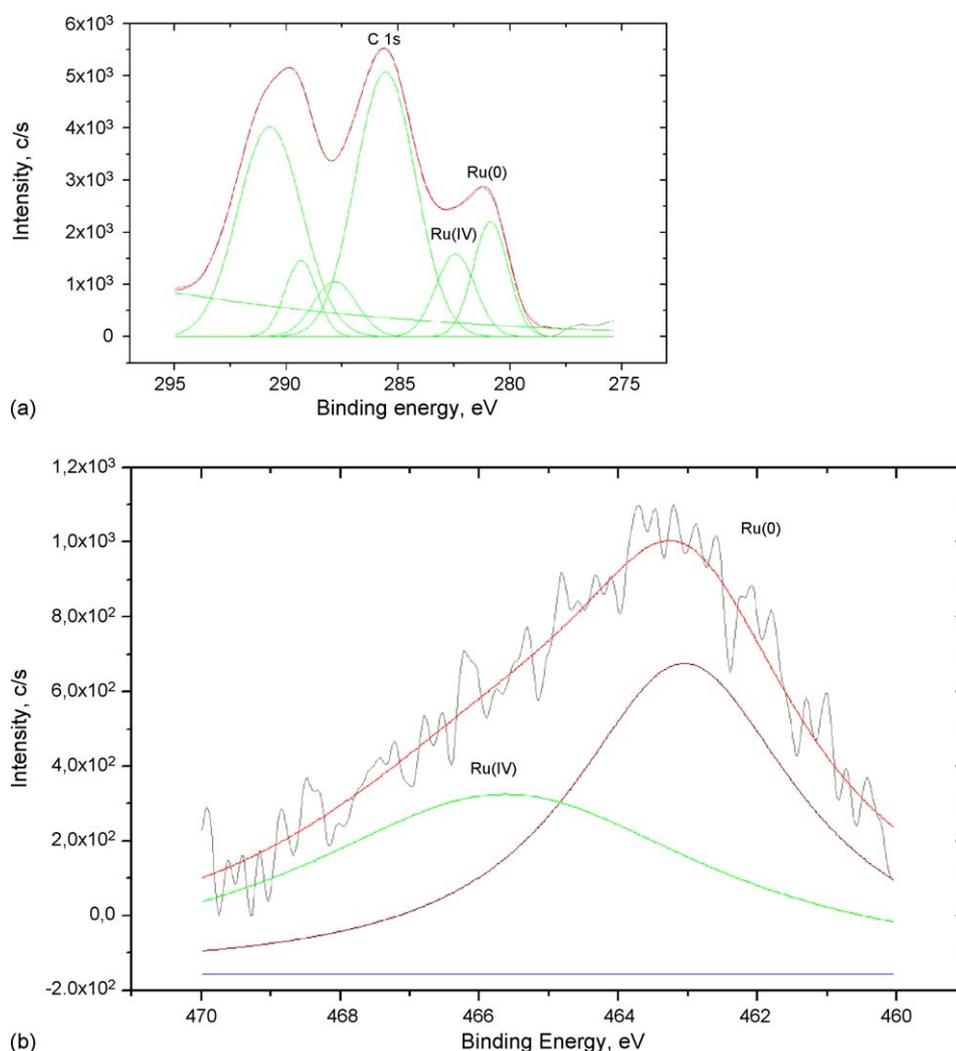
Fig. 8. X-ray photoelectron spectrum of acetate stabilized ruthenium(0) nanoclusters: (a) in the region of 275–295 eV and (b) in the region of 458–478 eV, exhibiting two prominent signals at 280 and 462 eV for Ru(0) $3d_{5/2}$ and Ru(0) $3p_{3/2}$, respectively. The peaks at 284 and 466 eV are due to a Ru(IV) species. The peaks higher beyond the C 1s peak at 285 eV are attributable to the Ru $3d_{3/2}$ in higher oxidation states.
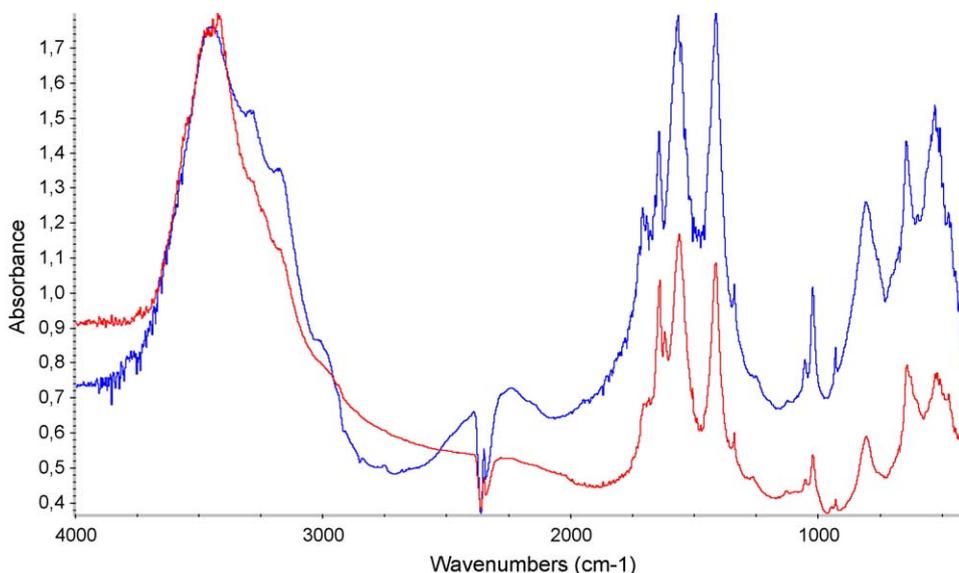
Fig. 9. FTIR spectra of free acetate anion (top curve) and acetate stabilized Ru(0) nanoclusters (bottom curve).

cury to ruthenium [26]. Thus, the minimum amount of mercury required for the complete poisoning of the ruthenium(0) nanoclusters catalyst was found to be 0.13 ± 0.05 mol of Hg/mol of total ruthenium. This indicates that the acetate stabilized ruthenium(0) nanoclusters are the true, heterogeneous catalyst. By assuming a 1/1 Hg/Ru stoichiometry for the poisoning [25], one estimates 13% of the total ruthenium atoms to be active in catalysis. Note that about 42% ruthenium atoms are on the nanoclusters surface as estimated from the magic number nanoclusters size [14a].

3.4. Catalyst lifetime

A catalyst lifetime experiment was performed starting with 0.32 mM Ru(0) nanoclusters and 450 mM sodium borohydride in 50 mL aqueous solution at $25.0 \pm 0.1\,^{\circ}\mathrm{C}$, corresponding to a maximum total turnover number of 5625. It was found that the acetate stabilized ruthenium(0) nanoclusters provide 5170 turnovers of hydrogen gas generation from the hydrolysis of

Fig. 10. Plot of relative rate of hydrolysis of sodium borohydride vs. moles of Hg/mol of total Ru(0) for the hydrolysis of sodium borohydride by 2.8 ± 1.4 nm ruthenium(0) nanoclusters.

sodium borohydride over 84 min before deactivation. This corresponds to a turnover frequency of $1.0\,\mathrm{s^{-1}}$.

4. Conclusion

In summary, our study of the synthesis and characterization of water soluble ruthenium(0) nanoclusters as catalyst for the hydrolysis of sodium borohydride have led to the following conclusions and insights.

Water dispersible acetate stabilized ruthenium(0) nanoclusters can be formed from the reduction of a commercially available precursor $RuCl_3 \cdot 3H_2O$ by sodium borohydride in the presence of acetate anion [19], which are stable enough to be isolated, but which retain high catalytic activity for the hydrolysis of sodium borohydride in aqueous solution, Eq. (2).

A kinetic study shows that the catalytic hydrolysis of sodium borohydride is first order in ruthenium concentration and zero order in substrate concentration. The apparent saturation kinetics in $NaBH_4$ implies that the nanocluster surface is saturated by borohydride anions.

Using ruthenium(0) nanoclusters as catalyst provides ≈10% lower activation energy for the hydrolysis of sodium borohydride compared to the bulk counterpart, so that the reaction occurs even at room temperature. The acetate stabilized ruthenium(0) nanoclusters are highly active catalyst with long lifetime providing 5170 total turnovers in the hydrolysis of sodium borohydride at $25.0 \pm 0.1\,^{\circ}\mathrm{C}$ over 1.4 h before they are deactivated.

Overall, acetate-stabilized ruthenium(0) nanoclusters can easily be formed by using a commercially available precursor material and serve as highly active catalysts even at ambient temperatures for the hydrolysis of sodium borohydride to generate hydrogen gas.

Acknowledgments

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