Hydrogen generation from hydrolysis of sodium borohydride using Ru(0) nanoclusters as catalyst

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Abstract

Sodium borohydride is stable in aqueous alkaline solution, however, it hydrolyses in water to hydrogen gas in the presence of suitable catalyst. By this way hydrogen can be generated safely for the fuel cells. Generating H_2 catalytically from $NaBH_4$ solutions has many advantages: $NaBH_4$ solutions are nonflammable, reaction products are environmentally benign, rate of H_2 generation is easily controlled, the reaction product $NaBO_2$ can be recycled, H_2 can be generated even at low temperatures. All of the catalysts that has been used in hydrolysis of sodium borohydride are bulk metals and they act as heterogeneous catalysts. The limited surface area of the heterogeneous catalysts causes lower catalytic activity as the activity of catalyst is directly related to its surface area. Thus, the use of metal nanoparticles with large surface area provides potential route to increase the catalytic activity. Here, we report, for the first time, the use of ruthenium(0) nanoclusters as catalyst in the hydrolysis of sodium borohydride liberating hydrogen gas. The ruthenium nanoparticles are generated from the reduction of ruthenium(III) chloride by sodium borohydride in water and stabilized by specific ligand. The ruthenium(0) nanoclusters are found to be highly active catalyst for the hydrolysis of sodium borohydride.
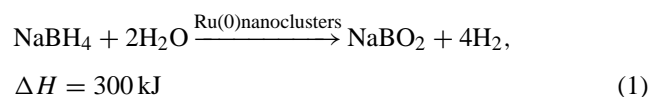
1. Introduction

In modern society, hydrogen is an important chemical material which is utilized in large amounts in synthetic chemical industries. In near future hydrogen is expected to become an energy vector. Hydrogen is produced from various energy sources, stored, transported and used in industries. Hence, fuel cells using hydrogen as fuel have been under development. Chemical energy released upon reaction of hydrogen and oxygen is directly converted into electric energy in fuel cell [1].

As new fueling concept, it can be suggested that the chemical hydrides ($NaBH_4$, KBH_4, LiH, NaH, etc.) act as new fuel source supplying hydrogen at normal temperature [2]. Chemical hydrides are very reactive toward hydrolysis in water, which results in releasing large amount of hydrogen gas. Among these chemical hydrides, sodium borohydride ($NaBH_4$) provides safe and practical mean of producing hydrogen. Hydrolysis of $NaBH_4$ produces hydrogen gas and water-soluble sodium metaborate, $NaBO_2$, in the presence of suitable catalyst [3]. By this way hydrogen can be generated safely for the fuel cells.

$$NaBH_4 + 2H_2O \xrightarrow{\text{Ru(0)nanoclusters}} NaBO_2 + 4H_2,$$
$$\Delta H = 300\,\text{kJ} \tag{1}$$

Generating H_2 catalytically from $NaBH_4$ solutions has many advantages: $NaBH_4$ solutions are nonflammable, reaction products are environmentally benign, rate of H_2 generation is easily controlled, the reaction product $NaBO_2$ can be recycled, H_2 can be generated even at low temperatures. Such hydrolysis of sodium borohydride can be accelerated by catalysts [4], by acid [5], or under elevated temperature [6].

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All of the catalysts used in hydrolysis of sodium borohydride so far are bulk metals and they act as heterogeneous catalysts [7]. The limited surface area of the heterogeneous catalysts causes to lower catalytic activity as the activity of catalyst is directly related to its surface area. Thus, the use of metal nanoparticles with large surface area provides potential route to increase the catalytic activity [8]. Here, we report for the first time the results of our study on the hydrogen generation from the catalytic hydrolysis of sodium borohydride using water-dispersible ruthenium(0) nanoclusters as catalyst.

2. Experimental

2.1. Preparation of Ru(0)—acetate stabilized nanoclusters

Ruthenium(III) chloride hydrate, sodium acetate (99%) and sodium borohydride (98%) from Aldrich were used as received. Deionized water was distilled by water purification system. All glass ware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven.

Ru(0) nanoclusters were prepared by following the general procedure given in the literature [9]: 1.0 mL of 1.0 M aqueous sodium acetate solution was added to 10 mL of 2.0 mM aqueous $RuCl_3$ solution and 1.0 mL of 0.112 M of aqueous $NaBH_4$ solution was added to this solution dropwise under vigorous stirring. Molar ratio of $NaBH_4$ to $RuCl_3$ greater than 5 was used to ensure complete reduction of Ru to its zero oxidation state. Ru(0) nanoclusters obtained was dark brown in color and very stable. No precipitation was observed even after few days of storage.

2.2. Catalytic activity of Ru(0) nanoclusters in the hydrolysis of sodium borohydride

The catalytic activity of Ru(0) nanoclusters was determined by measuring the amount of hydrogen generated from the hydrolysis of sodium borohydride. In all experiments total volume of solution was held constant at 50 mL, $NaBH_4$ solution was thermostated to a preset temperature in the sealed flask and given amount of catalyst, prepared in aqueous solution in separate flask, was added to the reaction flask and the reaction was started while the solution was stirred vigorously. Graduated glass column filled with water was connected to the top outlet of the flask as gas burette. The volume of hydrogen gas evolved was measured by the displacement of water level in the column.

3. Kinetic study

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 first set of experiments the concentration of $NaBH_4$ was kept constant at 150 mM, and the Ru(0) nanoclsuters concentration was varied in the range of 0.2, 0.4, 0.6, 0.8, 1.0 and 1.4 mM. In the second set of experiments, Ru(0) nanoclusters concentration was held constant at 0.4 mM while the $NaBH_4$ concentration was varied to get various $NaBH_4$/Ru(0) ratio in the range of 100, 200, and 500.

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 different temperatures 30, 35, 40, and 45 °C.

4. Results and discussion

Water-dispersible ruthenium(0) nanoclusters were prepared from the reduction of ruthenium(III) chloride by sodium borohydride in water and stabilized by acetate. These Ru(0) nanoclusters were used, for the first time, as catalyst in the hydrolysis of sodium borohydride liberating hydrogen gas. The ruthenium(0) nanoclusters are 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) nanoparticles in different concentrations at 25 °C. It is seen that Ru(0) nanoclusters have high catalytic activity in the hydrolysis of $NaBH_4$ even at low concentrations and room temperature. The hydrogen evolution starts immediately without any induction period as we used preformed catalyst. The hydrogen evolution rate remains constant until all the sodium borohydride react. The hydrogen generation rate was determined from the linear portion of the plot for each experiment with different Ru(0) concentration. Fig. 3 shows the plot of hydrogen generation rate versus Ru(0) concentration, both in logarithmic scale. One obtainsstraight line, the slope of which is found to be 1.073. This indicates that the hydrolysis is first order with respect to the concentration of Ru(0) nanoclusters catalyst.

Fig. 2 shows the change in concentration of $NaBH_4$ with time during the catalytic hydrolysis starting with three different initial concentrations of sodium borohydride but constant
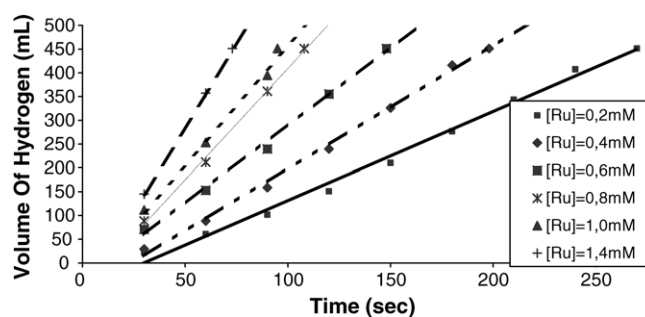

Fig. 1. The graph of volume of hydrogen (mL) vs. time (s) in different Ru(0) concentrations in all sets [$NaBH_4$] = 150 mM at 25 °C.
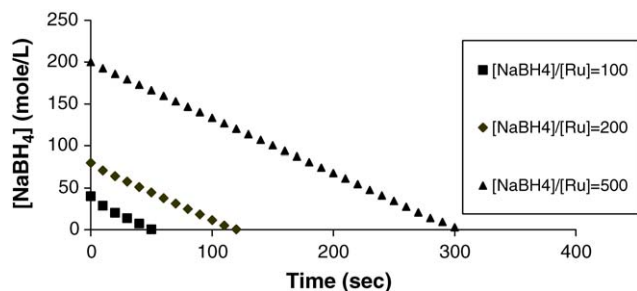
Fig. 2. The graph of $NaBH_4$ concentration vs. time in three different $NaBH_4/Ru(0)$ ratios at 25 °C ([Ru] = 0,4 mM in all three sets).
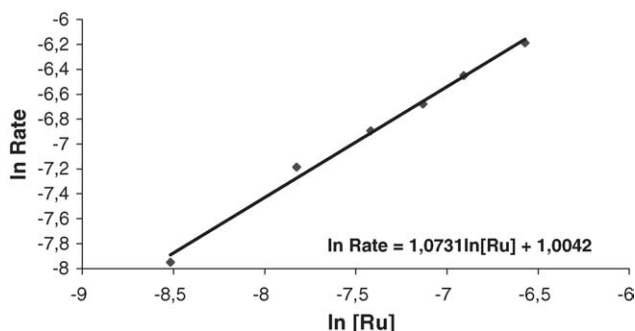

Fig. 3. The graph of ln rate vs. ln [Ru] at 25 °C and 150 mM $NaBH_4$.

Table 1
Rate constants for the hydrolysis of sodium borohydride catalyzed by Ru(0) nanoclusters starting with solution of 150 mM $NaBH_4$ and 0.4 mM Ru(0) nanoclusters at different temperatures

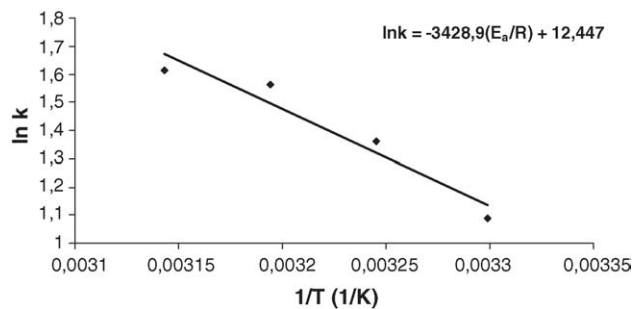| Temperature (°C)	Rate constant (turnover frequency) (mol $NaBH_4$ [mol Ru(0)]$^{-1}$ s^{-1})
30	2.9
35	3.9
40	4.8
45	5.1

Fig. 4. The Arrhenius plot, ln k vs. the reciprocal absolute temperature $1/T$, in the temperature range is 30–45 °C.

Table 2
Turnover frequencies for the hydrolysis of sodium borohydride catalyzed by Ru(0) nanoclusters starting with solution of 0.4 mM Ru(0) nanoclusters and various concentration of $NaBH_4$ (different $NaBH_4$ /Ru(0) ratio) at 35 °C

$NaBH_4/Ru(0)$	Turnover frequency (s^{-1})
100	7.9
200	6.8
500	6.6

Ru(0) concentration at 25 °C. It is seen that the concentration of sodium borohydride decreases linearly as the reaction proceeds. Furthermore, the lines for all the three experiments have the same slope, indicating that the catalytic hydrolysis is zero order in substrate concentration. Thus, the rate law for the catalytic hydrolysis of sodium borohydride can be given as

$$\frac{-4d[NaBH_4]}{dt} = \frac{d[H_2]}{dt} = k[Ru] \tag{2}$$

The values of the rate constant k were determined at various temperatures and listed in Table 1. Fig. 4 shows the Arrhenius plot, ln k versus the reciprocal absolute temperature $(1/T)$. The slope of the straight line gives an activation energy of 28.51 kJ/mol for the Ru(0) nanoclusters catalyzed hydrolysis of sodium borohydride. This value compares favorably with the activation energy found by Amendola [2a] at higher $NaBH_4$ and NaOH concentrations, and activation energies found by Kaufman and Sen [10] for the same hydrolysis but with different bulk metal catalysts; 75 kJ/mole for cobalt, 71 kJ/mol for nickel, and 63 kJ/mol for Raney nickel.

The catalytic efficiency of Ru(0) nanoclusters for the hydrolysis of sodium borohydride is expressed by the turnover frequency (N). The turnover frequencies were given in Table 1 for different temperatures and Table 2 for different $NaBH_4/Ru[0]$ ratios.

5. Conclusion

We have shown that water-dispersible ruthenium(0) nanoparticles can be obtained by using acetate anion stabilizer. These water-dispersible ruthenium(0) nanoclusters are highly active catalyst in the hydrolysis of sodium borohydride which has been used as an effective source for producing H_2. Using ruthenium(0) nanoclusters catalyst provides the lowest activation energy ever found for the hydrolysis of sodium borohydride. Thus, the catalytic hydrolysis of sodium borohydride can be performed at ambient temperature and hydrogen gas can be generated at an appreciable rate.

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