PVP-Protected Pt-Ru Nanoparticles as Highly Efficient Catalysts for Hydrogen Generation from Hydrolysis of Sodium Borohydride

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Abstract The employment of poly(N-vinyl-2-pyrrolidone) (PVP)-protected platinum-ruthenium nanoparticles (3.2 ± 1.4 nm) as catalysts in the hydrolysis of sodium borohydride for hydrogen generation is reported. They have been prepared by co-reduction of two metal ions in ethanol/water mixture by an alcohol reduction method and characterized by UV-Vis spectroscopy, TEM-EDX analysis, and X-ray photoelectron spectroscopy. They are recyclable and highly efficient catalysts for hydrogen generation from the hydrolysis of sodium borohydride even at very low concentrations and temperature, providing record average turnover frequency (TOF) value (549 mol H2/mol-cat-min−1) and maximum hydrogen generation rate (16126 L H2·min−1 (mol-cat)−1). Poly(N-vinyl-2-pyrrolidone)-protected platinum-ruthenium nanoparticles also provide activation energy of 63.2 ± 2 kJ·mol−1 for the hydrolysis of sodium borohydride.

Keywords platinum, ruthenium, nanoparticles, sodium borohydride, hydrogen

Introduction

The safe and efficient hydrogen storage materials have attracted worldwide interest to implement fuel cell based portable devices over the last two decades.[19] Being a chemical hydride, sodium borohydride (NaBH₄, SBH) appears to be suitable candidate for this purpose due to a number of advantageous properties such as the high hydrogen storage capacity (10.8% wt) meeting the United States Department of Energy (US-DOE) criteria for hydrogen storage materials, the optimal control on hydrogen generation rate by supported catalysts, the acceptable hydrogen generation rate even at low temperature, high solubility in water, the availability and easy handling.[22,23] Sodium borohydride can liberate hydrogen upon hydrolysis at room temperature in the presence of suitable catalysts according to Eq. (1).

\[
\text{NaBH}_4(aq) + 2\text{H}_2\text{O}(l) \rightarrow \text{NaBO}_2(aq) + 4\text{H}_2(g)
\]

A number of catalysts including Ru(0) nanoclusters,[6] electrodeposited Co and Co-P,[7] Ni-C-B,[8] Co-Mn-B nanocomposite,[9] Co-B/Ni foam,[10] Co-W-B/Ni foam,[11] electrosily deposited Co-P,[12] PVP-stabilized Ni(0) nanoclusters,[13] Co-B/multi walled carbon nanotubes,[14] Ni-Ru nanocomposite,[15] Pt-Pd-carbon nanotubes,[16] intrazeolite Co(0) nanoclusters,[17] polymer-stabilized Co(0) NCs,[18] Co-Cr-B,[19] porous Fe-Co-B/Ni foam,[20] clay-supported Co-B,[21] Co-Ni-B,[22] attapulgite CoB,[23] Co-Cu-B,[24] NiX-B,[25] BMR07 (Ni based),[26] Ru-Pd-Pt,[27] PVP@Ru-Pd nanomaterials,[28] Ru-RuO₂/C,[29] SiO₂-supported Fe, Ni and Co,[30] Zr-Co/C,[31] Pt-Cu,[32] Pd-Ni-B nanoclusters,[33] mesoporous Co-B,[34] and Cu/Co/Ni foam[35] have been identified to be effective for accelerating the hydrolysis of sodium borohydride.

Among these catalysts, nanoparticle-types provided great catalytic activities as expected due to the small particle sizes. However, the addition of second element to the monometallic nanoparticles will definitely improve the catalytic properties. Therefore, the employment of highly active bimetallic-type nanoparticles as catalysts for hydrogen generation from the hydrolysis of sodium borohydride has recently been focused.

Hydrogen generation from the hydrolysis of sodium borohydride is reported. They have recently been prepared by an alcohol reduction method,[36] characterized by UV-Vis spectroscopy, TEM-EDX analysis, X-ray photoelectron spectroscopy, and employed as a highly efficient catalyst for hydrogen generation from the hydrolysis of sodium borohydride.[37] Which has prompted me to use them as catalysts in the hydrolysis of sodium borohydride. Although the cost of noble metal catalysts is assumed to be high, the high catalytic activity and recyclability of the Pt-Ru@PVP nanoparticles make them a very promising candidate to be used as a catalyst in developing efficient portable hydrogen generation systems using sodium borohydride as solid hydrogen storage material since it would compensate the cost concerns.

Experimental

Materials

Ruthenium(III) chloride trihydrate (RuCl₃·3H₂O), hexachloroplatinic(IV) acid hexahydrate (H₂PtCl₆·6H₂O), poly(N-vinyl-2-pyrrolidone) (PVP-40) and sodium borohydride were purchased from Aldrich. Ethanol was purchased from Merck. 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 °C.

Preparation of Pt-Ru@PVP nanoparticles

Pt-Ru@PVP nanoparticles were prepared by an alcohol reduction method. Firstly, solutions of ruthenium(III) chloride trihydrate (0.25 mmol in 25 mL ethanol) and hexachloroplatinic(IV) acid hexahydrate (0.25 mmol in 25 mL water) were mixed and poly(N-vinyl-2-pyrrolidone) (PVP-40, 2.5 mmol of monomeric units) was added to this solution as a protecting polymer. Then, the mixed solution was refluxed at 90 °C for 2 h. The formed Pt-Ru nanoparticles have brownish black color and
are stable for months at room temperature. The total concentration of both metals was kept as 5.0 mM in 50 mL of the mixed solution.

**Characterization of Pt-Ru@PVP nanoparticles**

**UV-Vis analysis.** UV-Vis spectra were recorded on a Cary 5000 (Varian) UV-Vis spectrophotometer. A quartz cell with a path length of 1 cm was used and spectra were collected over the range of 200—900 nm.

**TEM-EDX analysis.** Transmission Electron Microscopy (TEM) analysis was carried out using a JEOL-2010 microscope operating at 200 kV, which is fitted with a LaB6 filament and has lattice and theoretical point resolutions of 0.14 and 0.23 nm, respectively. Samples were examined at magnification between 100 and 400 K. One drop of dilute suspension of sample was deposited on the TEM grids and the solvent was then evaporated. The diameter of each particle was determined from the enlarged photographs.

**X-Ray photoelectron spectroscopy.** X-ray photoelectron spectrum (XPS) of the isolated nanoparticles 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).

**11B NMR spectra.** 11B NMR spectra were recorded on a Bruker Avance DPX 400 with an operating frequency of 128.15 MHz for 11B. D2O and BF3·(C2H5)2O were used as a lock and external reference, respectively. At the end of the hydrolysis reaction, the resulting solutions were filtered and the filtrates were used for taking 11B NMR spectra.

**Method to test the catalytic activity of Pt-Ru@PVP nanoparticles in the hydrolysis of sodium borohydride**

The catalytic activity of Pt-Ru@PVP nanoparticles in the hydrolysis of sodium borohydride in aqueous solution was determined by measuring the rate of hydrogen generation. In all the experiments, a jacketed reaction flask (50 mL) containing a Teflon-coated stir bar was placed on a magnetic stirrer (Heidolph MR-301) and thermostated at 25.0 ± 0.1 °C by circulating water through its jacket from a constant temperature bath. Then, a graduated glass tube (40 cm in height and 2.5 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. In a typical experiment, 284 mg (7.47 mmol) of NaBH4 was dissolved in 20 mL of water. The solutions were transferred with a glass pipet into the reaction flask thermostatted at 25.0 ± 0.1 °C. Then, aliquots of Pt-Ru@PVP nanoparticles from the stock solution (5.0 mM) were added into the reaction flask. The experiment was started by closing the flask and the volume of hydrogen gas evolved was measured by recording the displacement of water level at the stirring speed of 100 rpm. In addition to the volumetric measurement of the hydrogen evolution, the conversion of sodium borohydride (δ ~42.1) to metabolite (δ 9) was also checked by 11B NMR spectroscopy.

**Determination of activation energy for Pt-Ru@PVP nanoparticles in the hydrolysis of sodium borohydride**

The hydrolysis of sodium borohydride (0.375 M) catalyzed by Pt-Ru@PVP nanoparticles (0.3 mM) was carried out by following the same way described in the previous section at various temperatures (in the range of 15, 20, 25, 30, and 35 °C) in order to obtain the activation energy (Ea) for the hydrolysis reaction.

**Recyclability of Pt-Ru@PVP nanoparticles in the hydrolysis of sodium borohydride**

The recyclability of Pt-Ru@PVP nanoparticles in the hydrolysis of sodium borohydride was determined by a series of experiments started with a 20 mL solution containing 0.3 mM Pt-Ru@PVP nanoparticles and 0.375 M sodium borohydride at 25.0 ± 0.1 °C. When the complete conversion is achieved, another equivalent of sodium borohydride was added to reaction mixture immediately. The results were expressed as retained% initial catalytic activity of Pt-Ru@PVP nanoparticles versus the number of catalytic runs in the hydrolysis of sodium borohydride.

**Results and Discussion**

**Preparation and characterization of Pt-Ru@PVP nanoparticles**

Pt-Ru@PVP nanoparticles were prepared from the co-reduction of mixture of hexachloroplatinic(IV) acid hexahydrate and ruthenium(III) chloride trihydrate by an alcohol reduction method in the presence of PVP in ethanol-water mixture at refluxing temperature. PVP serves as a stabilizer and a reducing agent. After refluxing for 2 h, the color of the solution turned to brownish black, indicating the reductions of Pt4+ and Ru3+ ions to Pt0 and Ru2+ to form their nanoparticles. Monitoring the UV-Vis electronic absorption spectra of the solution provides the best way to follow this conversion. Figure 1 shows the UV-Vis spectrum of the Pt-Ru@PVP nanoparticles from the reduction corresponding platinum and ruthenium salts by PVP. The absorption bands due to d-d transitions in Pt4+ and Ru3+ ions completely disappear after refluxing the solution, indicating the complete reduction of the corresponding ions. (Figure 1 UV-Vis absorption spectrum of the Pt-Ru@PVP nanoparticles.)

The size, morphology and composition of Pt-Ru@PVP nanoparticles were investigated by TEM-EDX analysis. Figure 2 shows TEM image taken at 50 nm magnification (Figure 2a) and the EDX spectrum (Figure 2b) of Pt-Ru@PVP nanoparticles. The mean particle size was determined as 3.2 ± 1.4 nm from TEM image by counting non-touching particles.

Figure 3 shows the XPS spectrum of the Pt-Ru@PVP nanoparticles. The main peaks observed in the survey scan are C 1s, Pt 4d, Pt 4f, Ru 3d, Ru 3p, and O 1s located at 285, 320—350, 65—80, 280—285, 460—480, and 530 eV, respectively. The XPS spectra for Pt 4f are characterized by a doublet containing a binding energy of 70.3 eV for 4f7/2 and 73.8 eV for 4f5/2, confirming the presence Pt(0). (Figure 3 XPS spectrum of the Pt-Ru@PVP nanoparticles.)

Due to the overlap of the C 1s and Ru 3d peaks around 285 eV, it is very difficult to analyze this region for ruthenium properly. The peak located at 462 eV for Ru 3p2/3 is readily assigned to the Ru(0). (Figure 3 XPS spectrum of the Pt-Ru@PVP nanoparticles.)

There is no higher oxidation state peak for both metals of the catalyst in the
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Testing the catalytic activity of Pt-Ru@PVP nanoparticles in the hydrolysis of sodium borohydride

Pt-Ru@PVP nanoparticles were found to be highly efficient catalyst for the hydrolysis of sodium borohydride. Figure 4 shows the plot of the volume of generated hydrogen gas versus time during the catalytic hydrolysis of 0.375 M NaBH₄ solution in the presence of Pt-Ru@PVP nanoparticles in different catalyst concentrations at 25.0 ± 0.1 °C. The linear hydrogen generation starts immediately without an induction period and continues until the complete hydrolysis of sodium borohydride although the results in this figure show only 80% conversion of sodium borohydride to make the kinetic calculations.

![Figure 4](image_url)

Figure 4 Plot of the volume of generated hydrogen gas versus time for the hydrolysis of 0.375 M sodium borohydride solution in the presence of Pt-Ru@PVP nanoparticles in different catalyst concentrations at 25.0 ± 0.1 °C.

Figure 5 shows the plot of the volume of generated hydrogen gas versus time in the hydrolysis of NaBH₄ (0.375 M) solution catalyzed by Pt-Ru@PVP nanoparticles (0.3 mM) at various temperatures in the range of 15—35 °C. It is worth to note that using Pt-Ru@PVP nanoparticles (0.3 mM) leads to 80% conversion for the hydrolysis of NaBH₄ within 420 s, providing record average turnover frequency (TOF) value of 549 mol-H₂/mol-cat min⁻¹ and maximum hydrogen generation rate of 16126 L·H₂·min⁻¹ (mol-cat)⁻¹ at 25.0 ± 0.1 °C. For comparison, maximum hydrogen generation rate values of some other catalyst are as follows: 460 mL·H₂·min⁻¹ (g catalyst)⁻¹ for Co-Ni-P/Pd-TiO₂⁴³ 5000 mL·H₂·min⁻¹ (g cobalt)⁻¹ for Co(0)-

![Figure 5](image_url)

Figure 5 Plots of the volume of generated hydrogen gas versus time in the catalytic hydrolysis of 0.375 M NaBH₄ solution in the presence of Pt-Ru@PVP nanoparticles (0.3 mM) at various temperatures (in the range of 15—35 °C).

XPS spectra, indicating the protection of Pt(0) and Ru(0) species by the attachment of PVP during catalyst preparation procedure.

Additionally, the formation of PVP-protected Pt-Ru nanoparticles rather than the physical mixtures of individual monometallic nanoparticles was confirmed by comparing (not shown) the catalytic activities of all the types (monometallic Pt and Ru nanoparticles, their 1:1 physical mixture, and 1:1 Pt-Ru bimetallic nanoparticles) in the hydrolysis of sodium borohydride. Pt-Ru@PVP nanoparticles provided a much higher catalytic activity than the physical mixture of Pt and Ru monometallic nanoparticles, clearly indicating that the prepared catalyst is composed of Pt-Ru@PVP bimetallic nanoparticles rather than a mixture of the individual monometallic nanoparticles. This much higher catalytic activity of bimetallic nanoparticles stems from the synergistic effects of platinum and ruthenium⁴⁴ and the reduced particles size compared to the individual platinum (4.6 nm) and ruthenium (4.2 nm) nanoparticles.

![Figure 2](image_url)

Figure 2 TEM image (a, 50 nm) and the EDX spectrum (b) of Pt-Ru@PVP nanoparticles.

![Figure 3](image_url)

Figure 3 X-Ray photoelectron spectrum of Pt-Ru@PVP nanoparticles.
HAP nanoparticles,\textsuperscript{[44]} 8701 mL·H₂·min\textsuperscript{−1} (g cobalt)\textsuperscript{−1} for Co/SiO\textsubscript{2},\textsuperscript{[30]} 307 mL·H₂·min\textsuperscript{−1} (g nickel)\textsuperscript{−1} for Ni/SiO\textsubscript{2},\textsuperscript{[30]} 130 mL·H₂·min\textsuperscript{−1} (g iron)\textsuperscript{−1} for Fe/SiO\textsubscript{2},\textsuperscript{[30]} 1708 mL·H₂·min\textsuperscript{−1} (g catalyst)\textsuperscript{−1} for Zr-Co/C,\textsuperscript{[31]} 5965 mL·H₂·min\textsuperscript{−1} (g catalyst)\textsuperscript{−1} for Co-P@Cu,\textsuperscript{[32]} 3350 mL·H₂·min\textsuperscript{−1} (g catalyst)\textsuperscript{−1} for mesoporous Co-B,\textsuperscript{[24]} 2650 mL·H₂·min\textsuperscript{−1} (g catalyst)\textsuperscript{−1} for CoNi foam,\textsuperscript{[39]} 400 mL·H₂·min\textsuperscript{−1} (g catalyst)\textsuperscript{−1} for Ni-Ru,\textsuperscript{[19]} 920 L·H₂·min\textsuperscript{−1} (g metal)\textsuperscript{−1} for Pt-Pd-Ru,\textsuperscript{[27]} 300 L·H₂·min\textsuperscript{−1} (g metal)\textsuperscript{−1} for Pd-Pt/CNT,\textsuperscript{[19]} and 3100 mL·H₂·min\textsuperscript{−1} (g catalyst)\textsuperscript{−1} for Pt-LiCoO\textsubscript{2}.\textsuperscript{[5]}

The apparent rate constants (\(k_{app}\)) of hydrogen generation from the hydrolysis of sodium borohydride were measured from the linear portions of each plot in Figure 5 at five different temperatures for the calculation of activation energy from the Arrhenius plot (Figure 6). The apparent Arrhenius activation energy (\(E_{a\,app}\)) was found to be 63.2 ± 2 kJ·mol\textsuperscript{−1} for the hydrolysis of sodium borohydride. Keeping in mind that the activation energy is not a direct measure of catalytic activity, this activation energy value for the hydrolysis of sodium borohydride is lower than the activation energies reported in the literature for the same reaction using different catalysts: 76 kJ·mol\textsuperscript{−1} for Ru-promoted sulphated zirconia,\textsuperscript{[45]} 70 kJ·mol\textsuperscript{−1} for PtHCoO\textsubscript{2},\textsuperscript{[46]} 68 kJ·mol\textsuperscript{−1} for RuHCoO\textsubscript{2},\textsuperscript{[46]} 57 kJ·mol\textsuperscript{−1} for Ru/C.\textsuperscript{[47]} However, it is still higher than 55 kJ·mol\textsuperscript{−1} for Co-Mn-B nanoclusters,\textsuperscript{[17]} 33 kJ·mol\textsuperscript{−1} for Co-B/Ni foam,\textsuperscript{[10]} 38 kJ·mol\textsuperscript{−1} for NiB,\textsuperscript{[25]} 28 kJ·mol\textsuperscript{−1} for Pd-C powder,\textsuperscript{[49]} 50 kJ·mol\textsuperscript{−1} for Ru/IR-120,\textsuperscript{[50]} 42 kJ·mol\textsuperscript{−1} for cobalt powder,\textsuperscript{[51]} 45 kJ·mol\textsuperscript{−1} for Co-B,\textsuperscript{[52]} 19 kJ·mol\textsuperscript{−1} for PtPd-carbon nanotubes,\textsuperscript{[10]} and 29 kJ·mol\textsuperscript{−1} for Co-W-B/Ni.\textsuperscript{[11]}

Recyclability of Pt-Ru@PVP nanoparticles in the hydrolysis of sodium borohydride

The recyclability of Pt-Ru@PVP nanoparticles in the hydrolysis of sodium borohydride was investigated by successive additions of sodium borohydride after the first cycle of the hydrolysis reaction. Figure 7 shows the results of the recyclability tests for the hydrolysis of sodium borohydride catalyzed by Pt-Ru@PVP nanoparticles. The Pt-Ru@PVP nanoparticles catalyst retains 72% of its initial catalytic activity in the hydrolysis of sodium borohydride, even at the fifth run. The decrease in the catalytic activity of Pt-Ru@PVP nanoparticles in the hydrolysis of sodium borohydride most probably due to the passivation of nanoparticles’ surface by increasing amount of metabolite, which decreases accessibility of active sites\textsuperscript{[33]} and the aggregation of nanoparticles.

Figure 6 Arrhenius plot for the hydrolysis of sodium borohydride (0.375 M) solution catalyzed by 0.3 mM Pt-Ru@PVP nanoparticles.

Figure 7 Retained% catalytic activity of 0.3 mM Pt-Ru@PVP nanoparticles in the successive catalytic runs for the hydrolysis of 0.375 M sodium borohydride solution at 25.0 ± 0.1 °C.

Conclusions and Perspectives

In summary, the employment of Pt-Ru@PVP nanoparticles as a catalyst for the hydrolysis of sodium borohydride has led to the following conclusions and insights:

1. Pt-Ru@PVP nanoparticles can be easily prepared from the co-reduction of corresponding platinum and ruthenium salts by an alcohol reduction method.

2. Pt-Ru@PVP nanoparticles are highly efficient catalysts for hydrogen generation from the hydrolysis of sodium borohydride.

3. They provide a record average TOF value (549 mol·H₂·mol·cat·min\textsuperscript{−1}) and maximum hydrogen generation rate (16126 L·H₂·min\textsuperscript{−1}·(mol·cat)\textsuperscript{−1}) for the hydrolysis of sodium borohydride.

4. Activation energy for the catalytic hydrolysis of sodium borohydride in the presence of Pt-Ru@PVP nanoparticles was calculated as 63.2 ± 2 kJ·mol\textsuperscript{−1}.

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Conflict of Interest

The author declare no conflict of interest.

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