Silica embedded cobalt(0) nanoclusters: Efficient, stable and cost effective catalyst for hydrogen generation from the hydrolysis of ammonia borane

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Hydrogen Generation from the Hydrolysis of Ammonia-borane and Sodium Borohydride Using Water-soluble Polymer-stabilized Cobalt(0) Nanoclusters Catalyst

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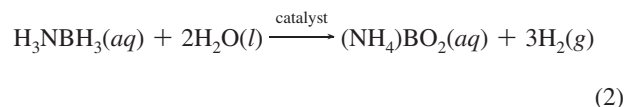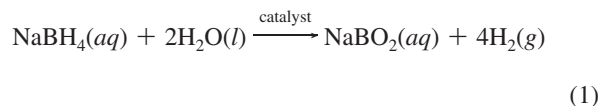
Polymer-stabilized cobalt(0) nanoclusters were prepared from the reduction of cobalt(II) chloride in the presence of poly(N-vinyl-2-pyrrolidone) (PVP) stabilizer in methanol solution. PVP-stabilized cobalt(0) nanoclusters were found to be stable in solution and could be isolated as solid material and characterized by TEM, XPS, FT-IR, and UV−visible electronic absorption spectroscopy. PVP-stabilized cobalt(0) nanoclusters were employed as catalyst in the hydrolysis of sodium borohydride and ammonia-borane, which have been considered as solid-state hydrogen storage materials for portable fuel cell applications. PVP-stabilized cobalt(0) nanoclusters were found to be highly active catalyst in both hydrolysis reactions, even at room temperature. Kinetic studies show that the catalytic hydrolyses of sodium borohydride and ammonia-borane are both first order with respect to catalyst and substrate concentration in aqueous medium. The effect of the NaOH concentration on the catalytic activity of the PVP-stabilized cobalt(0) nanoclusters in the hydrolysis of sodium borohydride was also studied. The activation parameters of these hydrolysis reactions were determined from the evaluation of the kinetic data. The PVP-stabilized cobalt(0) nanoclusters provide a lower activation energy for the hydrolysis of sodium borohydride both in aqueous medium ($E_a = 63 \pm 2$ kJ·mol^{-1}) and in basic solution ($E_a = 37 \pm 2$ kJ·mol^{-1}) compared to the value reported for bulk cobalt ($E_a = 75$ kJ·mol^{-1}).

1. Introduction

In the past few years, many efforts have been given for the exploration of high-capacity hydrogen storage materials[1] to solve one of the most important problems in the hydrogen economy toward sustainable energy future.[2−5] Among the chemical hydrides tested as solid hydrogen storage materials,[6] sodium borohydride, NaBH$_4$, appears to be a suitable hydrogen source, particularly for portable fuel cell applications,[7] due to a number of advantageous properties such as relatively high hydrogen content of 10.7 wt %, which meets the US Department of Energy criteria for hydrogen storage materials (6 wt %),[2] stability under ordinary conditions in solid state and solution, and liberating hydrogen in controllable way upon hydrolysis, yielding just environmentally benign products. Recent studies have shown[8] that ammonia-borane, H$_3$NBH$_3$, needs to be considered as hydrogen storage material as it has high hydrogen content 19.6 wt % and high stability under the ambient conditions.[9] Sodium borohydride and ammonia-borane both liberate hydrogen upon

hydrolysis as given in eqs 1 and 2, respectively, only in the presence of suitable catalysts.

$$\text{NaBH}_4(aq) + 2\text{H}_2\text{O}(l) \xrightarrow{\text{catalyst}} \text{NaBO}_2(aq) + 4\text{H}_2(g)$$

$$(1)$$

$$\text{H}_3\text{NBH}_3(aq) + 2\text{H}_2\text{O}(l) \xrightarrow{\text{catalyst}} (\text{NH}_4)\text{BO}_2(aq) + 3\text{H}_2(g)$$

$$(2)$$

Our recent studies[10] have shown that using water-dispersible transition metal(0) nanoclusters is a promising way to increase the catalytic activity in the hydrolysis of sodium borohydride, as the activity of heterogeneous catalyst is directly related to its surface area. Very recently we have also shown that zeolite-framework-stabilized rhodium(0) nanoclusters are highly active catalysts for hydrogen generation from the hydrolysis of ammonia-borane.[11] Here, we report for the first time the synthesis, characterization, and employment of PVP-stabilized cobalt(0) nanoclusters as highly active catalyst in hydrogen generation from the hydrolysis of sodium borohydride and ammonia-borane. PVP-stabilized cobalt(0) nanoclusters were prepared from the reduction of cobalt(II) chloride by sodium borohydride in the presence of PVP in methanol solution. PVP-stabilized cobalt(0) nanoclusters were found to be stable in solution and could be isolated as solid material and characterized by TEM, XPS, FT-IR, and UV−visible electronic absorption spectroscopy. The effect of the NaOH concentration on the catalytic activity of the PVP-stabilized cobalt(0) nanoclusters in the hydrolysis of sodium borohydride was also examined. The kinetics of the hydrolysis reactions were studied by

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measuring the volume of hydrogen generated by varying catalyst concentration, substrate concentration, and temperature. This is the first kinetic study on the hydrolysis of both sodium borohydride and ammonia-borane catalyzed by cobalt(0) nanoclusters. The PVP-stabilized cobalt(0) nanoclusters are found to be highly active and long-lived catalyst in two industrially important reactions: they provide 12 650 and 5100 turnovers in the hydrolyses of sodium borohydride and ammonia-borane, respectively. As highly active and long-lived catalyst they can find applications in hydrogen generation.

2. Experimental Section

Materials. Cobalt(II) chloride hexahydrate (>97%), sodium borohydride (98%), ammonia-borane (>97%), poly(N-vinyl-2-pyrrolidone) (PVP-40, average molecular weight 40 000), sodium hydroxide, and D_2O were purchased from Aldrich; methanol was purchased from Riedel-De Haen AG Hannover and used as received. 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 the PVP-stabilized Cobalt(0) Nanoclusters. PVP-stabilized cobalt(0) nanoclusters were prepared from the reduction of cobalt(II) chloride by sodium borohydride in the presence of PVP in methanol solution like the synthesis of PVP-stabilized nickel(0) nanoclusters in our previous study.[12] In a 250 mL three-necked round-bottom flask, 200 mg (0.9 mmol) of $CoCl_2 \cdot 6H_2O$ and 499 mg (4.5 mmol monomer unit) of PVP were dissolved in 100 mL of methanol (mol PVP/mol cobalt = 5). The mixture of metal precursor ($CoCl_2 \cdot 6H_2O$) and polymer (PVP-40) in methanol was refluxed at 80 °C for 1 h. Then, 10 mL of 150 mM solution of sodium borohydride (58 mg = 1.5 mmol $NaBH_4$) was added into the metal–polymer mixture immediately after the reflux at 80 °C. The addition of the sodium borohydride solution into the refluxed

solution should be dropwise because the bulk metal formation was observed in an experiment due to the fast addition of the sodium borohydride solution. The abrupt color change from pale green to dark brown indicates that the formation of PVP-stabilized cobalt(0) nanoclusters was completed. Methanol was removed from the solution by evaporation in a rotavap (Heidolph Laborata-4000). The cobalt nanoclusters in solid form were collected from the residue after evaporation in the round-bottom flask.

Characterization of PVP-stabilized Cobalt(0) Nanoclusters. The TEM and X-ray photoelectron spectra were taken by following the procedure described elsewhere.[12] The FT-IR spectra of the PVP-stabilized cobalt(0) nanoclusters and neat PVP were taken from KBr pellet on a Nicolet 510 FTIR Spectrophotometer using Omnic software. The solid nanoclusters sample was washed twice with acetone to remove the residue before taking FT-IR spectrum. UV−vis electronic absorption spectra of cobalt(II) chloride and PVP-stabilized cobalt(0) nanoclusters were recorded in methanol solution on Varian-Carry100 double beam instrument. ^{11}B-NMR spectra were recorded on a Bruker Avance DPX 400 with an operating frequency of 128.15 MHz for ^{11}B-NMR. At the end of the hydrolysis reaction, the resulting solutions were filtered, and the filtrates were collected for ^{11}B-NMR analysis.

Method for Testing the Catalytic Activity of PVP-stabilized Cobalt(0) Nanoclusters in the Hydrolysis of Sodium Borohydride and Ammonia-borane. The catalytic activity of PVP-stabilized cobalt(0) nanoclusters in the hydrolysis of sodium borohydride and ammonia-borane in aqueous solution was determined by measuring the rate of hydrogen generation. To determine the rate of hydrogen generation, the catalytic hydrolysis of sodium borohydride and ammonia-borane were performed in a Parr-5101 low-pressure reactor equipped with a circulating water-bath for constant temperature control and a mechanical stirrer. The Parr-5101 low-pressure reactor was connected with a digital transmitter to a computer using a RS-232 module. The progress of an individual hydrolysis reaction was followed by monitoring the increase in the pressure of hydrogen gas with the program Calgrafix. The temperature was also controlled via a thermocouple placed inside the reactor. The pressure versus time data was processed using Microsoft Office Excel 2003 and 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 thermostatted at 25.0 ± 0.1 °C. In a typical experiment, 284 mg (7.47 mmol) of $NaBH_4$ or 63 mg (2 mmol) of H_3NBH_3 were dissolved in 40 and 20 mL of water, respectively. The solutions were transferred with a glass pipet into the reactor. Then, aliquots of aqueous solution of prepared cobalt(0) nanoclusters were transferred into the reactor using a 10 mL gastight syringe. The stirring rate of the mechanical mixer of the reactor was set to 600 rpm.

Self Hydrolysis of Sodium Borohydride and Ammonia-borane in Aqueous Medium. In a 100 mL beaker, 284 mg of sodium borohydride or 63 mg of ammonia-borane were dissolved in 50 mL of water, respectively. Then, the solution was transferred with a 50 mL pipet into the reactor thermostatted at 25.0 ± 0.1 °C. The experiment was started by closing the reactor and turning on the stirring at 600 rpm simultaneously, and the volume of hydrogen generated was measured exactly in the same way as described in the previous Section, "Method for Testing the Catalytic Activity of PVP-stabilized Cobalt(0) Nanoclusters in the Hydrolysis of Sodium Borohydride and Ammonia-Borane".

Kinetic Study of Catalytic Hydrolysis of Sodium Borohydride or Ammonia-Borane Catalyzed by PVP-stabilized Cobalt(0) Nanoclusters in Aqueous Medium. To establish the rate law for catalytic hydrolysis of $NaBH_4$ and H_3NBH_3 in aqueous solution using PVP-

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stabilized cobalt(0) nanoclusters as catalyst, three different sets of experiments were performed for each of these two substrates in the same ways described in the previous Section "Method for Testing the Catalytic Activity of PVP-stabilized Cobalt(0) Nanoclusters in the Hydrolysis of Sodium Borohydride and Ammonia-Borane".

Hydrolysis of Sodium Borohydride in Aqueous Medium. In the first set of experiments, the concentration of the $NaBH_4$ was kept constant at 150 mM, and the cobalt concentration was varied in the range of 0.50, 1.00, 1.50, 2.00, and 2.50 mM. In the second set of experiments, the cobalt concentration was held constant at 1.50 mM, and $NaBH_4$ concentration was varied in the range of 150, 300, 450, 600, and 750 mM. Finally, the catalytic hydrolysis of $NaBH_4$ was performed in the presence of the PVP-stabilized cobalt(0) nanoclusters at constant $NaBH_4$ (150 mM) and catalyst concentration (1.5 mM Co) at various temperatures in the range of 20−40 °C in order to obtain the activation energy (E_a), enthalpy ($\Delta H^\ddagger$), and entropy ($\Delta S^\ddagger$).

Hydrolysis of Ammonia-borane. In the first set of experiments, the hydrolysis reaction was performed starting with different initial concentration of the PVP-stabilized cobalt(0) nanoclusters in the range of 1.0, 1.5, 2.0, 2.5, and 3.0 mM by keeping the initial ammonia-borane concentration constant at 100 mM. The second set of experiments were performed by keeping the initial concentration of PVP-stabilized cobalt(0) nanoclusters constant at 2 mM and varying the AB concentration in the range of 50, 100, 150, 200, 250, and 300 mM. Finally, the catalytic hydrolysis of AB was performed in the presence of the cobalt(0) nanoclusters at constant substrate (100 mM) and catalyst concentration (2 mM Co) at various temperatures in the range of 20−40 °C in order to obtain the activation energy (E_a), enthalpy ($\Delta H^\ddagger$), and entropy ($\Delta S^\ddagger$). In addition to the volumetric measurement of the hydrogen evolution, in each experiment the conversion of ammonia-borane to ammonium metaborate was also checked by comparing the intensities of signals of ammonia-borane and metaborate anion at $\delta = -23.9$ and 9 ppm, respectively, in the ^{11}B-NMR spectra of the solution.

Determination of the Catalytic Lifetime of PVP-Stabilized Cobalt(0) Nanoclusters in the Hydrolysis of Sodium Borohydride or Ammonia-borane in Aqueous Medium. The catalytic lifetime of PVP-stabilized cobalt(0) nanoclusters in the hydrolysis of sodium borohydride and ammonia-borane was determined by measuring the total turnover number (TTO).

Hydrolysis of Sodium Borohydride in Aqueous Medium. Such a lifetime experiment was started with a 50 mL solution of PVP-stabilized cobalt(0) nanoclusters (1 mM) and 1 M $NaBH_4$ at 25.0 ± 0.1 °C. A new batch of 1.9 g $NaBH_4$ was added into the reaction solution after 80% conversion of sodium borohydride present in the solution. Hydrolysis of sodium borohydride reaction was continued until hydrogen gas evolution was slowed down to the level of self-hydrolysis. The volume of hydrogen versus time data were corrected by subtracting the self-hydrolysis data of sodium borohydride in order to obtain the volume of hydrogen generated only from the catalytic reaction.

Hydrolysis of Ammonia-borane. Lifetime experiment was started with a 20 mL solution containing 1 mM PVP-stabilized cobalt(0) nanoclusters and 1 M H_3NBH_3 at 25 ± 0.1 °C. A new batch of 310 mg H_3NBH_3 was added into the reaction solution after 80% conversion of ammonia-borane present in the solution.

Effect of Sodium Hydroxide Concentration on the Catalytic Activity of PVP-stabilized Cobalt(0) Nanoclusters in the Hydrolysis of Sodium Borohydride in Basic Medium. To examine the effect of the sodium hydroxide concentration on the catalytic activity of the PVP-stabilized cobalt(0) nanoclusters in the hydrolysis of sodium borohydride, six different experiments were performed starting with 40 mL aqueous solution of 150 mM of $NaBH_4$ and different amounts of NaOH (1, 2, 3, 4, 5, and 10 wt %). Then, aliquots of aqueous solution of prepared cobalt(0) nanoclusters (2 mM Co) were transferred into the reactor using a 10 mL gastight syringe. The catalytic activity of PVP-stabilized cobalt(0) nanoclusters was measured in the same way as described in the previous Section "Method for Testing the Catalytic Activity of PVP-stabilized

Cobalt(0) Nanoclusters in the Hydrolysis of Sodium Borohydride and Ammonia-Borane".

Kinetic Study of the Hydrolysis of Sodium Borohydride Catalyzed by PVP-stabilized Cobalt(0) Nanoclusters in Basic Medium. To establish the rate law for catalytic hydrolysis of $NaBH_4$ in basic medium using PVP-stabilized cobalt(0) nanoclusters catalyst, three different sets of experiments were performed in the same way as described in the previous Section, "Effect of Sodium Hydroxide Concentration on the Catalytic Activity of PVP-stabilized Cobalt(0) Nanoclusters in the Hydrolysis of Sodium Borohydride in Basic Medium". First, the concentration of $NaBH_4$ was kept constant at 150 mM, and the cobalt concentration was varied in the range of 1.0, 1.5, 2.0, 2.5, and 3.0 mM at 25.0 ± 0.1 °C. In the second set of experiments, cobalt concentration was held constant at 2.0 mM while the $NaBH_4$ concentration was varied in the range of 150, 300, 450, 600, and 750 mM at 25.0 ± 0.1 °C. Finally, the PVP-stabilized cobalt(0) nanoclusters (2.0 mM Co) catalyzed hydrolysis of $NaBH_4$ (150 mM) in 2 wt % NaOH solution was performed at various temperatures in the range of 20−40 °C in order to obtain the activation energy (Ea), enthalpy ($\Delta H^\ddagger$), and entropy ($\Delta S^\ddagger$).

3. Results and Discussion

Preparation and Characterization of the PVP-stabilized Cobalt(0) Nanoclusters. PVP-stabilized cobalt(0) nanoclusters could be prepared following the procedure described elsewhere.[12] The PVP-stabilized cobalt(0) nanoclusters formed are stable in solution, and no bulk metal formation was observed in solution standing for one week at room temperature in inert gas atmosphere. The PVP-stabilized cobalt(0) nanoclusters can be isolated as dark-brown solid from the reaction mixture by removing the volatiles in vacuum. The isolated nanoclusters are stable in inert gas atmosphere for months. Furthermore, they are redispersible in water and yet catalytically active when redispersed in aqueous solution, for example, in the hydrolysis of sodium borohydride or ammonia-borane (see later).

The morphology and particle size of the PVP-stabilized cobalt(0) nanoclusters were studied by using TEM (Figure 1a). The cobalt nanoclusters of 7.2 ± 2.1 nm size were obtained as shown in the histogram (Figure 1b). Figure 2 shows the XPS spectrum of PVP-stabilized cobalt(0) nanoclusters obtained from the reduction of cobalt(II) chloride by sodium borohydride in the presence of PVP after refluxing for 1 h in methanol solution at 80 °C. The XPS spectrum exhibits two prominent bands at 778.6 and 794.2 eV, readily assigned to Co(0) $2p_{3/2}$ and Co(0) $2p_{1/2}$, respectively, by comparing with the values of bulk cobalt.[13] However, there are two additional bands observed at 783.8 and 799.2 eV, which can be attributed to a higher oxidation states of cobalt, presumably formed by oxidation during the XPS sample preparation, since the cobalt(0) nanoclusters are sensitive to aerobic atmosphere. Because the oxidation product may exist in different forms depending on the ligand (hydroxide, oxo group, or nitrogen donor), additional weak bands can be attributed to the different cobalt(II) species.[14] One particular aspect that came into the mind is the possibility of formation of cobalt boride species during the catalysis. However, Co_xB species are generally formed in the hydrolysis of sodium borohydride under the unaeorobic reaction conditions and low temperatures (5−10 °C).[15] Under aerobic reaction conditions, the Co_xB species are converted to metallic cobalt

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a)

b)
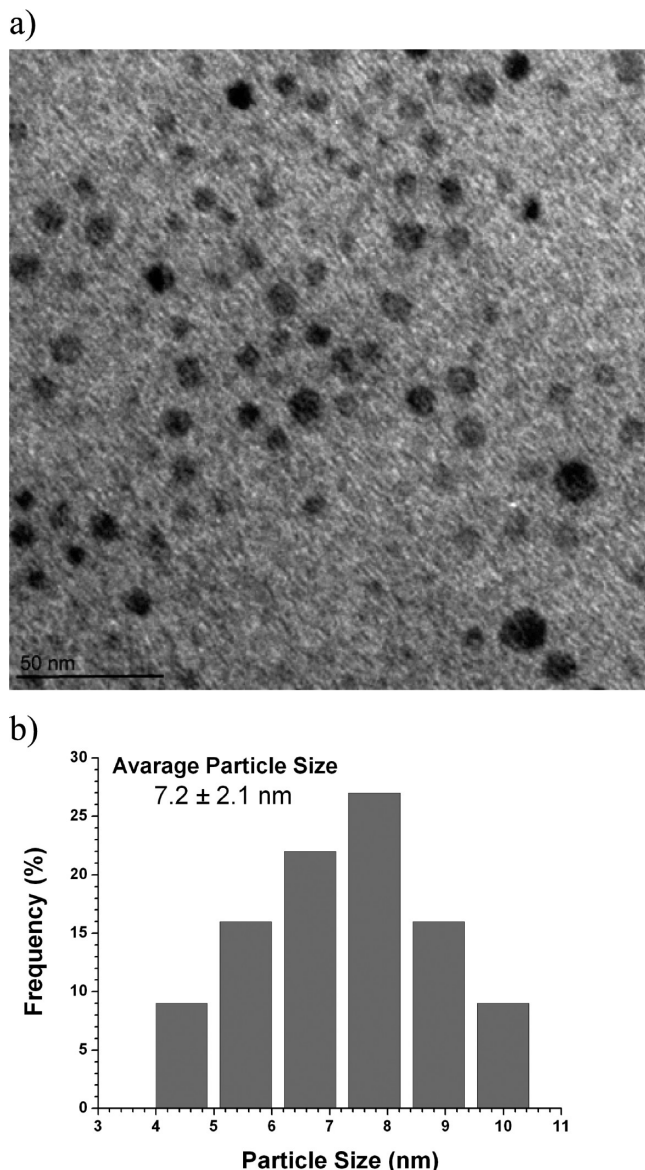
Figure 1. (a) TEM image and (b) associated histogram for PVP-stabilized cobalt(0) nanoclusters sample isolated from the reduction of cobalt(II) chloride (8.4 mM) in the presence of PVP (42 mM) by sodium borohydride (150 mM) after 1 h reflux in methanol at 80 °C.

and boron oxide. In our case, the catalyst isolated and used does not contain any boron as the XPS spectrum has no B-1s peak.

Comparison of the FT-IR spectra of PVP-stabilized cobalt(0) nanoclusters and neat PVP both taken from KBr pellet shows the existence of PVP in the nanoclusters sample, most probably adsorbed on the surface of nanoclusters, since the free PVP molecules should have been removed by washing three times with acetone.

Figure 3 shows the UV−visible electronic absorption spectra of a solution containing cobalt(II) chloride and PVP in methanol before and after addition of sodium borohydride. The broad absorption band at 510 nm observed for cobalt(II) chloride in methanol solution disappears after addition of sodium borohydride, whereas a broad absorption feature grows in at 295 nm, which is assigned to the characteristic surface plasmon resonance of the cobalt(0) nanoclusters.[16] This observation indicates the reduction of cobalt(II) to the metallic cobalt and formation of particles in nanosize upon addition of sodium borohydride.

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Catalytic Activity of the PVP-stabilized Cobalt(0) Nanoclusters in the Hydrolysis of Sodium Borohydride or Ammonia-borane in Aqueous Medium. PVP-stabilized cobalt(0) nanoclusters were found to be active catalyst for hydrogen generation from the hydrolysis of sodium borohydride and ammonia-borane, according to eqs 1 or 2, respectively, even at low catalyst concentrations and room temperature.

Kinetics of the Hydrolysis of Sodium Borohydride in Aqueous Medium. Figure 4a shows the plots of the volume of hydrogen generated versus time during the catalytic hydrolysis of 150 mM NaBH$_4$ solution in the presence PVP-stabilized cobalt(0) nanoclusters catalyst in various metal concentration (0.5, 1, 1.5, 2, and 2.5 mM) at 25 ± 0.1 °C. The hydrogen generation rate was determined from the linear portion of the plot for each metal concentration. The inset shows the plot of hydrogen generation rate versus cobalt concentration, both in logarithmic scale, which indicates that the hydrolysis reaction is first order with respect to the concentration of catalyst.

The effect of NaBH$_4$ concentration on the hydrogen generation rate was also studied by performing a series of experiments starting with varying initial concentration of NaBH$_4$ while keeping the catalyst concentrations constant at 1.5 mM Co. Figure 5a shows the plots of the volume of hydrogen generated versus time during the catalytic hydrolysis of sodium borohydride at different sodium borohydride concentration. The hydrogen generation rate was determined from the linear portion of the plot for each sodium borohydride concentration and was used for the construction of the plot of hydrogen generation rate versus sodium borohydride concentration, both in logarithmic scale (the inset in Figure 5a). One obtains a straight line with a slope of 0.83 ≈ 1. This indicates that the hydrolysis reaction is also first order with respect to the sodium borohydride concentration. Consequently, the rate law for the catalytic hydrolysis of sodium borohydride catalyzed by PVP-stabilized cobalt(0) nanoclusters can be given as eq 3.

$$\frac{-4\,d[NaBH_4]}{dt} = \frac{d[H_2]}{dt} = k[Co][NaBH_4] \quad (3)$$

Both the self-hydrolysis and the PVP-stabilized cobalt(0) nanoclusters catalyzed hydrolysis of sodium borohydride were carried out at various temperature in the range of 20−40 °C, starting with the initial NaBH$_4$ concentration of 150 mM NaBH$_4$ and an initial catalyst concentration of 1.5 mM Co in the latter case. Figure 6a shows the plots of volume of hydrogen generated for the hydrolysis of sodium borohydride at five different temperatures. Note that the values used for the plots were obtained by subtracting the hydrogen volume for the self-hydrolysis from those of corresponding metal nanoclusters catalyzed hydrolysis of sodium borohydride at each temperature. The values of rate constant k (Table 1) for the sole catalytic hydrolysis were obtained from the slope of the linear part of each plot in Figure 6a and used to calculate the activation parameters (Arrhenius plot is shown in the Inset): Arrhenius activation energy $E_a = 63 \pm 2$ kJ·mol^{-1}, activation enthalpy $\Delta H^\ddagger = 61 \pm 2$ kJ·mol^{-1}, and activation entropy $\Delta S^\ddagger = -49 \pm 3$ J.(K·mol)$^{-1}$.

A catalyst lifetime experiment was performed starting with a 50 mL solution of PVP-stabilized cobalt nanoclusters containing 1.5 mM Co and 1 M NaBH$_4$ (1.9 g) at 25.0 ± 0.1 °C. PVP-stabilized cobalt(0) nanoclusters provide 5100 turnovers over 19 h in the hydrolysis of sodium borohydride. However, the hydrogen generation slows down as the reaction proceeds, maybe because of increasing viscosity of the solution as the continuously added sodium borohydride is converted to sodium
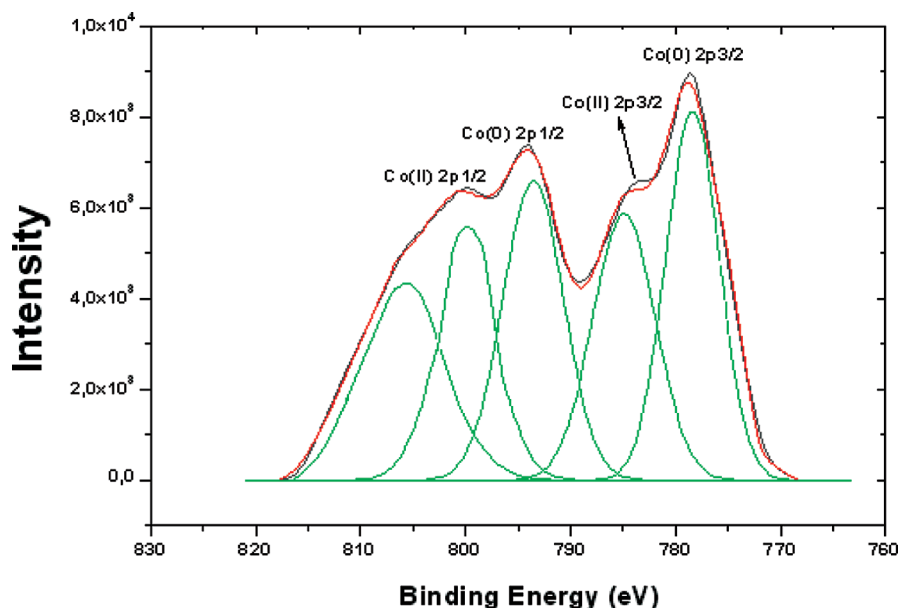
Figure 2. X-ray photoelectron spectrum of PVP-stabilized cobalt(0) nanoclusters sample isolated from the reduction of cobalt(II) chloride hexahydrate (8.4 mM) in the presence of PVP (42 mM) by sodium borohydride (150 mM) after one hour reflux in methanol at 80 °C.
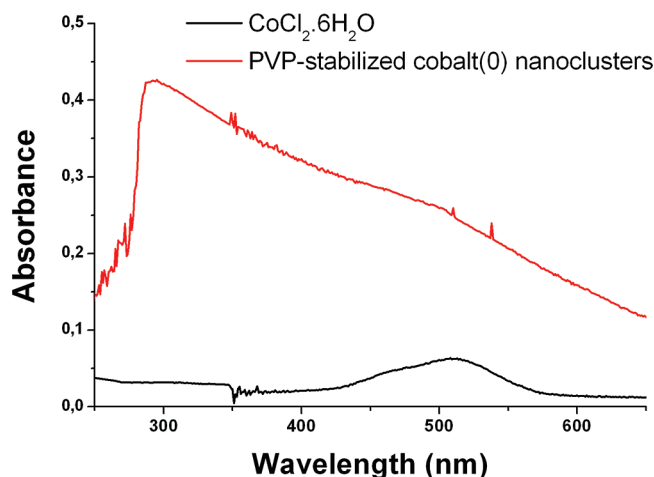
Figure 3. UV–visible spectra of cobalt(II) chloride and PVP-stabilized cobalt(0) nanoclusters taken from the methanol solutions.

metaborate. Therefore, this TTO value should be considered as a lower limit. A much higher TTO value might be obtained when the increase in viscosity could be avoided.

Kinetics of the Hydrolysis of Ammonia-borane. Figure 4b shows the plots of the volume of hydrogen generated versus time during the catalytic hydrolysis of 100 mM H_3NBH_3 solution in the presence of PVP-stabilized cobalt(0) nanoclusters catalyst in different metal concentration (1, 1.5, 2, 2.5, and 3 mM) at 25 ± 0.1 °C. The hydrogen generation rate was determined from the linear portion of the plot for each metal concentration. The plot of hydrogen generation rate versus metal concentration, both in logarithmic scale (the inset in Figure 4b) gives a straight line with a slope of $1.15 \approx 1$, indicating that the hydrolysis reaction is first order with respect to the catalyst concentration. The control tests using a trap containing copper(II) sulfate showed no ammonia evolution in detectable amount in the experiments.

The effect of ammonia-borane concentration on the hydrogen generation rate was also studied by performing a series of experiments starting with various initial concentration of H_3NBH_3 while keeping the catalyst concentration constant at 2.0 mM Co. Figure 5b shows the plots of the volume of hydrogen generated versus time during the catalytic hydrolysis

of ammonia-borane at various substrate concentration. The hydrogen generation rate was determined from the linear portion of the plot for each ammonia-borane concentration and used for constructing the plot of hydrogen generation rate versus ammonia-borane concentration, both in logarithmic scale (the inset in Figure 5b). The slope of the line given in the inset of Figure 5b, $0.91 \approx 1$, indicates that the hydrolysis reaction is first order with respect to the ammonia-borane concentration. Consequently, the rate law for the catalytic hydrolysis of ammonia-borane catalyzed by PVP-stabilized cobalt(0) nanoclusters can be given as,

$$\frac{-3 \, d[H_3NBH_3]}{dt} = \frac{d[H_2]}{dt} = k[Co][H_3NBH_3] \quad (4)$$

PVP-stabilized cobalt(0) nanoclusters catalyzed hydrolysis of ammonia-borane was carried out at various temperature in the range of 20–40 °C, starting with the initial substrate concentration of 100 mM H_3NBH_3 and an initial catalyst concentration of 2 mM Co. The values of rate constant k (Table 1) for PVP-stabilized cobalt(0) nanoclusters catalyzed hydrolysis of ammonia-borane were calculated from the slope of the linear part of each plot in Figure 6b and used to calculate the activation parameters (Arrhenius plot is shown in the inset): Arrhenius activation energy $E_a = 46 \pm 2$ kJ·mol^{-1}, activation enthalpy $\Delta H^\ddagger = 43 \pm 3$ kJ·mol^{-1} and activation entropy $\Delta S^\ddagger = -126 \pm 3$ J·(K·mol)$^{-1}$. The value of activation energy is lower than the value reported for the hydrolysis of ammonia-borane using Co/γ–Al$_2$O$_3$ (62 kJ/mol),[9b] and Ru/C (76 kJ/mol).[9g]

A catalyst lifetime experiment was performed starting with a 20 mL solution of PVP-stabilized cobalt(0) nanoclusters containing 1.5 mM Co and 1 M H_3NBH_3 at 25.0 ± 0.1 °C. PVP-stabilized cobalt(0) nanoclusters provide 12 640 turnovers over 15 h. The ^{11}B-NMR spectral shift at $\delta = 11.8$ ppm of the crystalline product at the bottom of the reactor indicates the formation of $[NH_4][BO_2]$ during the TTO experiment. The deactivation of the catalyst in 15 h can be explained by the increasing viscosity and pH due the formation of $[NH_4][BO_2]$.

For the first time, kinetic data are available for the hydrolyses of two important chemical hydrogen storage materials by using the same catalyst and reactor under the same
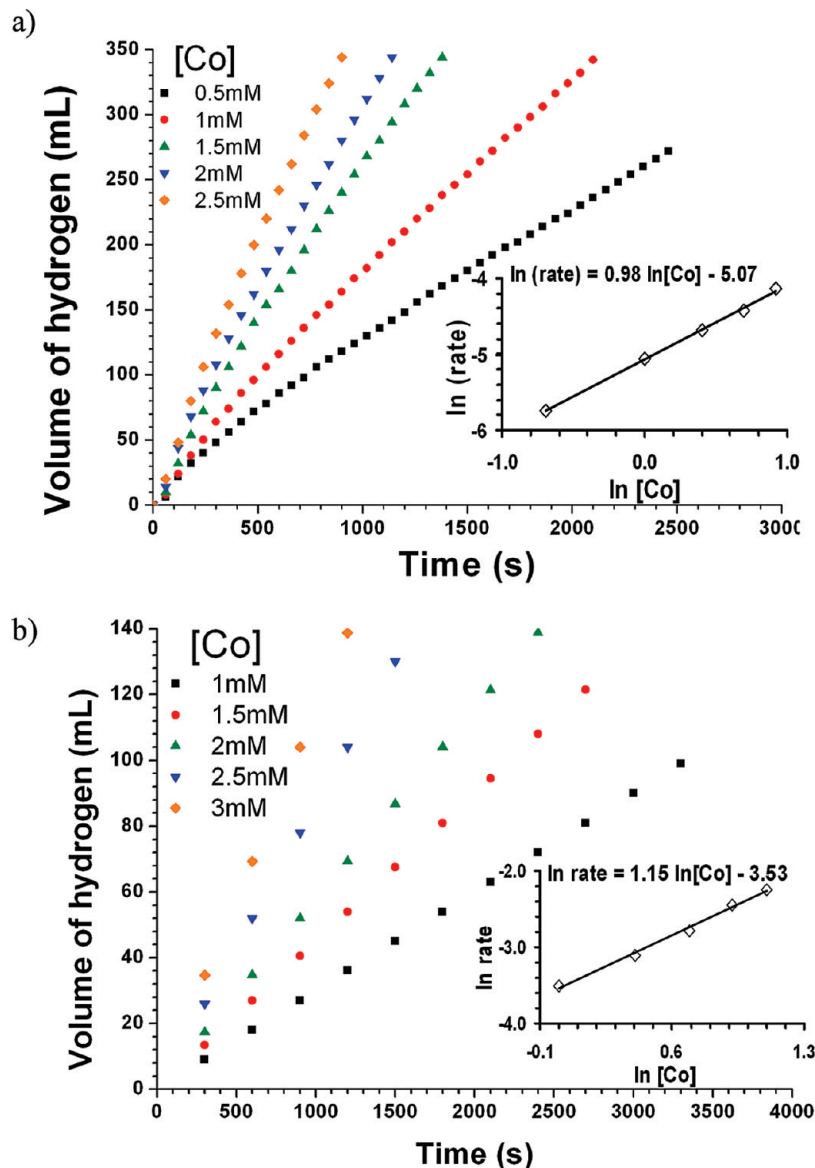
Figure 4. The volume of hydrogen versus time plots depending on the cobalt concentrations for (a) the hydrolysis of sodium borohydride (150 mM) at 25 ± 0.1 °C and (b) the hydrolysis of ammonia-borane (100 mM) at 25 ± 0.1 °C. The inset of each figure shows the plot of hydrogen generation rate vs the concentration of cobalt (both in logarithmic scale).

experimental conditions. It is worthwhile to compare these two catalytic hydrolyses credibly in terms of hydrogen generation rates and activation energies. First of all, the rate constant k has similar values for both reactions under the same conditions in the absence of added base (See Table 1). However, the hydrolysis of sodium borohydride has a larger activation energy ($E_a = 63 \pm 2$ kJ·mol^{-1}) and larger Arrhenius constant ($A = 4.15 \times 10^9$) than that of ammonia-borane ($E_a = 46 \pm 2$ kJ·mol^{-1}, $A = 4.16 \times 10^6$). Since the mechanisms of these two catalytic reactions have not been established completely, the difference in their activation energies is difficult to explain. However, hydrogen generation from the ammonia-borane has a big advantage over the hydrolysis of sodium borohydride, as the latter requires stabilization by sodium hydroxide to prevent the acid-catalyzed self-hydrolysis. It is noteworthy that PVP-stabilized cobalt(0) nanoclusters provide 12 650 turnovers in the hydrolysis of ammonia-borane but only 5100 turnovers in the hydrolysis of sodium borohydride. The faster deactivation of cobalt(0) nanoclusters catalyst in the hydrolysis of sodium borohydride than that in the hydrolysis of ammonia-borane

might be attributed to the pH effect. The initial pH of the solution is 9.8 in the hydrolysis of sodium borohydride[7v] and 9.1 in the hydrolysis of ammonia-borane solution.[17] In both cases the pH increases as the hydrolysis proceeds.

Catalytic Activity of PVP-stabilized Cobalt(0) Nanoclusters in the Hydrolysis of Sodium Borohydride in Basic Medium. According to the established mechanism,[18] in acidic medium the hydrolysis of sodium borohydride is initiated by the attack of hydronium ion on the borohydride anion. In alkaline solution, the reduction of proton concentration causes a decrease in the rate of hydrolysis. Since most of the prior studies on the catalytic hydrolysis of sodium borohydride have been carried out in alkaline medium, for comparison we also performed the hydrolysis of sodium borohydride in the basic

(17) Chandra, M.; Xu, Q. *J. Power Sources* **2006**, *159*, 855–860.
(18) Mesmer, R. E.; Jolly, W. L. *Inorg. Chem.* **1962**, *1*, 608–612, In these studies on the acid-catalyzed hydrolysis of sodium borohydride, a mechanism has been suggested involving the formation of BH$_5$ in the transition state: Two activated complexes have been found to be reasonable, one having an attack on hydrogen, the other on boron of the borohydride ion.
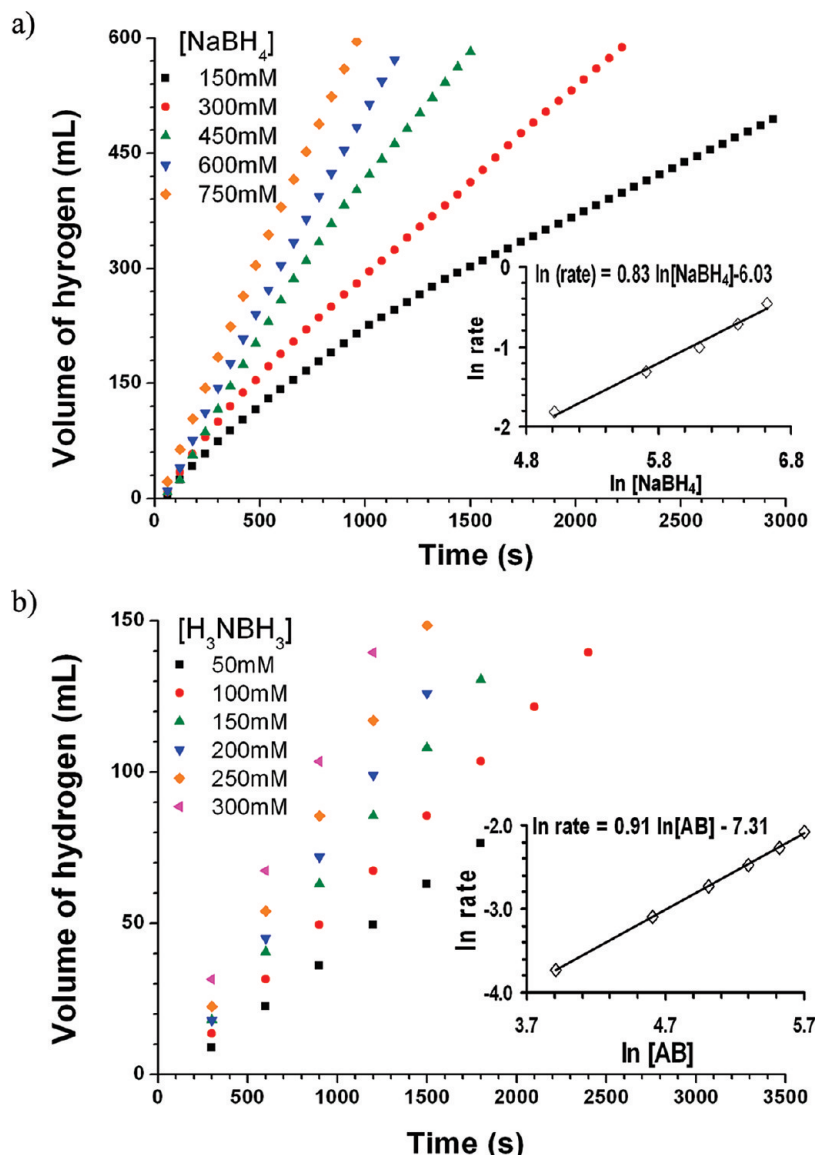
Figure 5. The volume of hydrogen vs time plots depending on the substrate concentrations at constant catalyst concentration for (a) the hydolysis of sodium borohydride and (b) the hydrolysis of ammonia-borane. The inset of each figure shows the plot of hydrogen generation rate vs the concentration of the substrate (both in logarithmic scale).
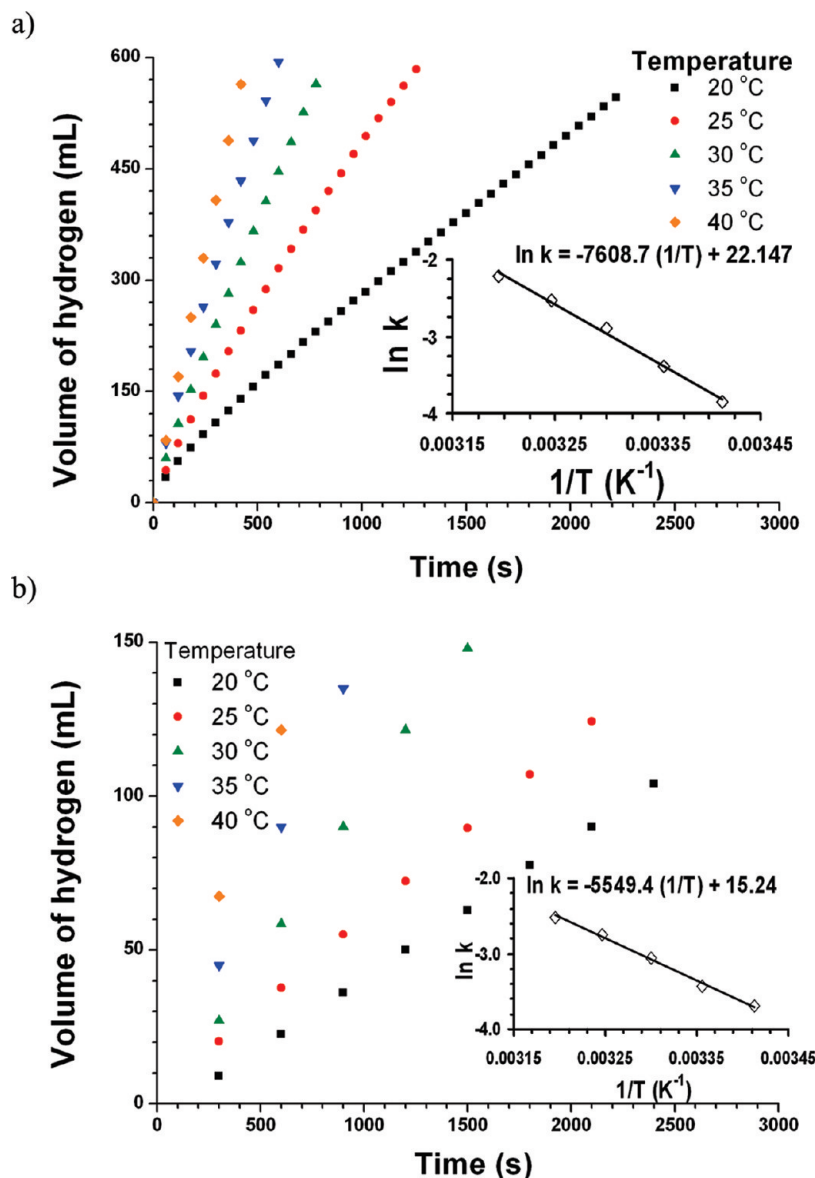
medium by using PVP-stabilized cobalt(0) nanoclusters as catalyst. To understand the effect of NaOH concentration on the catalytic activity of PVP-stabilized cobalt(0) nanoclusters, the catalytic hydrolysis of sodium borohydride was performed in six different NaOH solutions (1.0, 2.0, 3.0, 4.0, 5.0, and 10 wt % NaOH). Figure 7 shows the volume of hydrogen generated versus time during the hydrolysis of 150 mM sodium borohydride in various NaOH solutions at 25.0 ± 0.1 °C catalyzed by PVP-stabilized cobalt(0) nanoclusters (2.0 mM Co). As cleary seen from the inset of Figure 7, the rate of hydrogen generation first increases until the 2 wt % NaOH, surprisingly, and then decreases with the increasing concentration of NaOH, expectedly. This observation dictates the use of 2 wt % NaOH for the kinetic studies of catalytic hydrolysis of sodium borohydride using PVP-stabilized cobalt(0) nanoclusters catalyst.

Figure 8 shows the volume of hydrogen generated versus time in the catalytic hydrolysis of sodium borohydride (150 mM) in the presence of PVP-stabilized cobalt(0) nanoclusters with different cobalt concentration (1.0−3.0 mM Co) in 2 wt % NaOH solution at 25.0 ± 0.1 °C. Although the hydrolysis reactions were performed in alkaline solution, the hydrogen generation starts immediately after addition of

the catalyst. The presence of sodium hydroxide does not cause an induction period in the formation of the nanoclusters catalyst. Plotting the hydrogen generation rate versus cobalt concentration, both on logarithmic scales, gives a straight line (the inset in Figure 8), the slope of which is found to be 0.94. This result indicates that the hydrolysis of sodium borohydride using PVP-stabilized cobalt(0) nanoclusters as catalyst in 2 wt % NaOH solution is first-order with respect to the catalyst concentration. The effect of substrate concentration on the hydrogen generation rate was also studied by performing a series of experiments starting with various initial concentration of $NaBH_4$ while the catalyst concentration is kept constant at 2.0 mM Co in 2 wt % NaOH solution at 25.0 ± 0.1 °C (Figure 9). The slope of plot (the inset of Figure 9) shows that the catalytic hydrolysis is zero-order with respect to sodium borohydride concentration. Consequently, the rate law for the catalytic hydrolysis of sodium borohydride catalyzed by PVP-stabilized cobalt(0) nanoclusters in 2 wt % NaOH solution can be given as eq 5.

$$\frac{-4 \, d[NaBH_4]}{dt} = \frac{d[H_2]}{dt} = k[Co] \qquad (5)$$

Figure 6. The volume of hydrogen vs time plots at different temperatures for (a) the hydrolysis of sodium borohydride (150 mM) catalyzed by PVP-stabilized cobalt(0) nanoclusters (1.5 mM Co) in the temperature range 20−40 °C and (b) the hydrolysis of ammonia-borane (100 mM) catalyzed by PVP-stabilized cobalt(0) nanoclusters (1.5 mM Co) in the temperature range 20−40 °C. The inset of each figure shows Arrhenius plot (ln k vs the reciprocal absolute temperature $1/T$ (K^{-1})).

Table 1. The Values of Rate Constants k for the Sole Hydrolysis of Sodium Borohydride (1.5 mM Co, 150 mM NaBH$_4$), Hydrolysis of Sodium Borohydride in Basic Medium (1.5 mM Co, 150 mM NaBH$_4$, and 2 wt % NaOH) and Hydrolysis of Ammonia-borane (2 mM Co, 100 mM H$_3$NBH$_3$) Catalyzed by PVP-stabilized Cobalt(0) Nanoclusters at Different Temperatures

temperature (K)	rate constant, k, for hydrolysis of NaBH$_4$ in aqueous medium mol H$_2$·(mol Co)$^{-1}$·(mol NaBH$_4$)$^{-1}$·s^{-1}	rate constant, k, for hydrolysis of NaBH$_4$ in basic medium mol H$_2$·(mol Co)$^{-1}$·s^{-1}	rate constant, k, for hydrolysis of H$_3$NBH$_3$ mol H$_2$·(mol Co)$^{-1}$·(mol H$_3$NBH$_3$)$^{-1}$·s^{-1}
293	0.021	0.277	0.025
298	0.034	0.376	0.033
303	0.055	0.496	0.047
308	0.080	0.626	0.064
313	0.108	0.763	0.081

The hydrolysis of sodium borohydride was carried out at various temperatures in the range of 20−40 °C, starting with the initial substrate concentration of 150 mM NaBH$_4$ and an initial catalyst concentration of 2.0 mM Co in 2 wt % NaOH solution (Figure 10). The values of rate constant k (Table 1) determined from the linear portions of the volume of hydrogen versus time plots at six different temperatures are used to draw Arrhenius plot (the inset of Figure 10) and to calculate the activation parameters Arrhenius activation energy, $E_a = 37 \pm$ 2 kJ/mol; activation enthalpy, $\Delta H^{\ddagger} = 36 \pm 2$ kJ/mol; and activation entropy, $\Delta S^{\ddagger} = -134 \pm 3$ J/K·mol for the PVP-stabilized cobalt(0) nanoclusters catalyzed hydrolysis of 150 mM sodium borohydride in 2 wt % NaOH solution. The value of activation energy is lower than the value reported for the hydrolysis of sodium borohydride in basic solution using bulk cobalt (75 kJ/mol), nickel (71 kJ/mol), and Raney nickel (63 kJ/mol),[7b] bulk ruthenium (47 kJ/mol),[7c] and Co−B catalyst (45 kJ/mol).[7m,p,r] It is noteworthy that the activation energy and
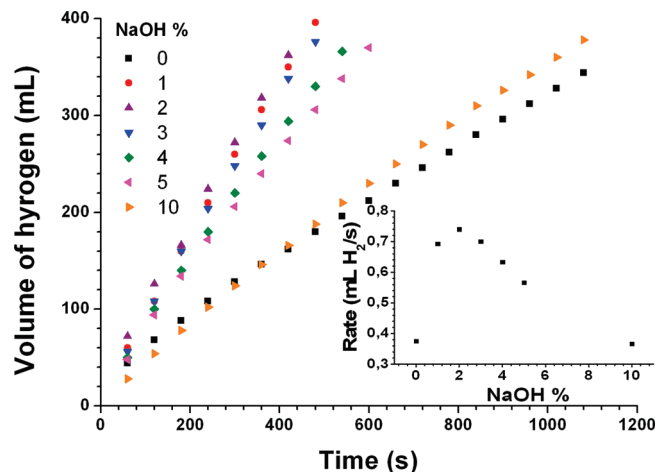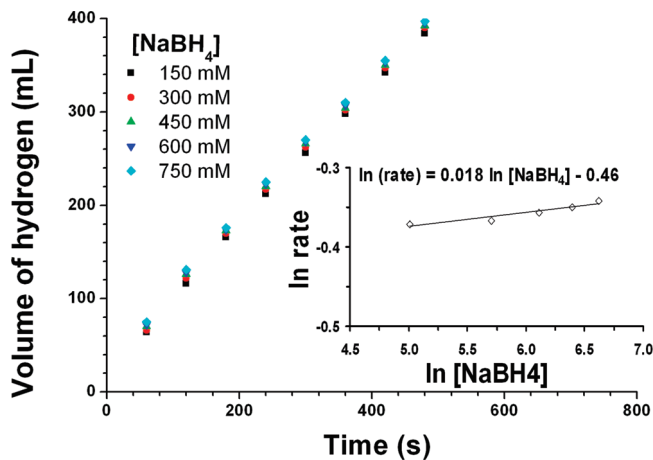
Figure 7. Plot of the volume of hydrogen (mL) vs time (s) for the hydrolysis of 50 mL of 150 mM sodium borohydride catalyzed by PVP-stabilized cobalt(0) nanoclusters (2 mM Co) in 1.0, 2.0, 3.0, 4.0, 5.0, and 10.0 wt % NaOH solutions at 25.0 ± 0.1 °C. The inset shows the plot of hydrogen generation rate change depending on the wt % of NaOH.
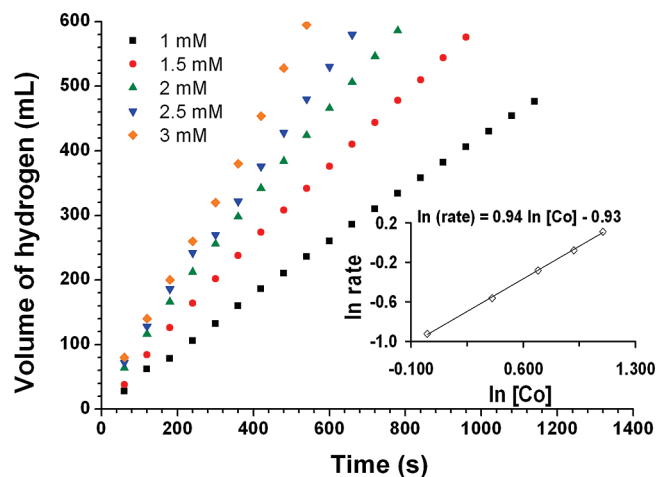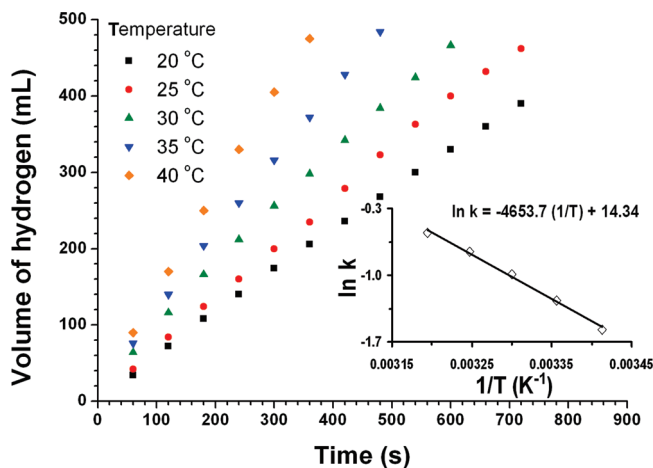

Figure 8. Plot of the volume of hydrogen (mL) vs time (s) for the hydrolysis of sodium borohydride (150 mM) in 2 wt % NaOH solution catalyzed by PVP-stabilized cobalt(0) nanoclusters with different cobalt(0) concentrations ([Co] = 1.0, 1.5, 2.0, 2.5, and 3.0 mM) at 25.0 ± 0.1 °C. The inset shows the plot of hydrogen generation rate versus catalyst concentration (both in logarithmic scale) for the PVP-stabilized cobalt(0) nanoclusters catalyzed hydrolysis of $NaBH_4$ in 2 wt % NaOH solution at 25.0 ± 0.1 °C.

enthalphy for the hydrolysis of sodium borohydride in basic solution are both lower than the values found for the same reaction catalyzed by PVP-stabilized cobalt(0) nanoclusters in the absence of sodium hydroxide.

Note that the hydrolysis of sodium borohydride catalyzed by PVP-stabilized cobalt(0) nanoclusters is first order with respect to the substrate concentration in the absence of NaOH and zero order in the presence of NaOH. Although the effect of substrate concentration on the rate of catalytic hydrolysis of sodium borohydride has been an issue that remains unresolved,[7b−d,j,v] the mechanism proposed by Holbrook and Twist[19] can give some insights in understanding the effect of sodium hydroxide on the reaction order with respect to the substrate concentration. In this mechanism, reaction begins with the attachment of the BH_4^- ion to a catalytic site yielding M-H plus BH_3, electron and M ultimately, the reaction of which with water or hydroxide are the rate-determining steps. Increasing hydroxide concentra-

(19) Holbrook, K. A.; Twist, P. J. *J. Chem. Soc. A.* **1971**, 890–894.

Figure 9. Plot of the volume of hydrogen (mL) vs time (s) for the hydrolysis of sodium borohydride in 2 wt % NaOH solution catalyzed by PVP-stabilized cobalt(0) nanoclusters with different $NaBH_4$ concentrations ([$NaBH_4$] = 150, 300, 450, 600, and 750 mM) at 25.0 ± 0.1 °C. The inset shows the plot of hydrogen generation rate vs $NaBH_4$ concentration (both in logarithmic scale) for the PVP-stabilized cobalt(0) nanoclusters catalyzed hydrolysis of $NaBH_4$ in 2 wt % NaOH solution at 25.0 ± 0.1 °C.

Figure 10. Plot of the volume of hydrogen (mL) generated vs time (s) for the hydrolysis of 50 mL of 150 mM sodium borohydride in 2 wt % NaOH solution at different temperatures (15, 20, 25, 30, and 35 °C) catalyzed by PVP-stabilized cobalt(0) nanoclusters ([Co] = 2.0 mM). The inset shows the Arrhenius plot for the PVP-stabilized cobalt(0) nanoclusters catalyzed hydrolysis of sodium borohydride in 2 wt % NaOH solution.

tion makes the rate-determining step faster and, thus, independent of borohydride concentration.

4. Conclusions

In summary, our study of the synthesis and characterization of PVP-stabilized cobalt(0) nanoclusters as catalyst for the hydrolysis of sodium borohydride and ammonia-borane have led to the following conclusions and insights.

• Water-soluble PVP-stabilized cobalt(0) nanoclusters can easily be prepared from the reduction of a commercially available precursor, $CoCl_2 \cdot 6H_2O$ in the presence of PVP stabilizer in methanol solution.

• PVP-stabilized cobalt(0) nanoclusters are stable in aqueous solution under inert atmosphere. They can be isolated as solid materials by removing the volatiles in vacuum. In solid state, PVP-stabilized cobalt(0) nanoclusters are stable for months.

• Water-soluble PVP-stabilized cobalt(0) nanoclusters are highly active catalyst in the hydrogen generation from the hydrolysis of sodium borohydride or ammonia-borane.

• A kinetic study shows that the catalytic hydrolyses of sodium borohydride and ammonia-borane are both first order with respect to catalyst and substrate concentration in aqueous solution.

• PVP-stabilized cobalt(0) nanoclusters are long-lived catalyst providing 5100 and 12 640 turnovers in the hydrolysis of sodium borohydride and ammonia-borane, respectively.

• Activation energies for the sole catalytic hydrolysis of sodium borohydride and ammonia-borane in the presence of PVP-stabilized cobalt(0) nanoclusters were determined as E_a = 63 ± 2 kJ·mol^{-1} and E_a= 46 ± 2 kJ·mol^{-1} in aqueous solution, respectively.

• PVP-stabilized cobalt(0) nanoclusters are also found to be highly active catalyst in hydrogen generation from the hydrolysis of sodium borohydride in basic medium (2 wt % NaOH).

• A kinetic study shows that the catalytic hydrolysis of sodium borohydride in 2 wt % NaOH solution is first order with respect to the catalyst concentration and zero-order with respect to the NaBH$_4$ concentration.

• Activation energy for catalytic hydrolysis of sodium borohydride in the presence of PVP-stabilized cobalt(0) nanoclusters as catalyst in 2 wt % alkaline solution is E_a = 37 ± 2 kJ·mol^{-1}. This is the lowest activation energy ever reported for the catalytic hydrolysis of sodium borohydride in basic medium.

Water-soluble PVP-stabilized cobalt(0) nanoclusters appear to be a promising catalyst with high activity and long-lived catalyst for practical applications to supply hydrogen from the hydrolysis of sodium borohydride or ammonia-borane for proton exchange membrane fuel cells (PEMFC) when considering their easy preparation using commercially available precursor, non-toxicity, water solubility, and overall low cost.