



Synthesis and characterization of poly(*N*-vinyl-2-pyrrolidone)-stabilized water-soluble nickel(0) nanoclusters as catalyst for hydrogen generation from the hydrolysis of sodium borohydride

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ARTICLE INFO

Article history:

Received 27 March 2008
Received in revised form 12 August 2008
Accepted 16 August 2008
Available online 30 August 2008

Keywords:

Nickel
Nanoclusters
Catalyst
PVP
Polymer
Water soluble
Hydrolysis
Sodium borohydride

ABSTRACT

Water-soluble PVP-stabilized nickel(0) nanoclusters in particle size of 3.6 ± 1.6 nm were synthesized by using a modified version of alcohol reduction method and characterized by TEM, XPS and FT-IR. PVP polymer is coordinated to the nanoclusters surface through some of the carbonyl groups as concluded from a comparative FT-IR spectral study. The PVP-stabilized nickel(0) nanoclusters are very stable in solution and yet highly active catalyst providing 8700 turnovers of hydrogen gas generation from the hydrolysis of sodium borohydride over 27 h before deactivation. They can be isolated as stable solid material, which are redispersible in water and show still the same catalytic activity after redispersion. A kinetic study shows that the catalytic hydrolysis of sodium borohydride is first order with respect to nickel concentration and zero order with respect to substrate concentration. The activation energy of the hydrolysis of sodium borohydride catalyzed by PVP-stabilized nickel(0) nanoclusters was determined to be $E_a = 48 \pm 2$ kJ mol⁻¹.

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1. Introduction

Metal nanoclusters exhibit unique properties, which differ from their bulk materials, owing to the quantum size effects [1]. However, nanoclusters tend to be fairly unstable in solution and thus special precautions have to be taken to avoid their aggregation or precipitation during the preparation of such nanoclusters in solution [2]. In order to obtain stable nanoclusters dispersed in solution, a stabilizing agent is usually added into the reaction system. In the literature of colloidal stability [3] and in Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [4], colloidal stabilization is well established to involve both: (i) electrostatic stabilization by the surface adsorbed anions such as chloride or citrate ions [5] and (ii) steric stabilization by the presence of polymers such as the often used poly(vinylpyrrolidone) [6]. The use of polymeric matrix as stabilizer improves some properties of the nanoclusters such as the solubility, thermal stability and catalytic activity [7].

A variety of preparative methods is available for obtaining polymer-stabilized metal nanoclusters [8]. The most widely used

synthetic method involves reduction of the metal ion in solution to the colloidal metal in zerovalent state within the polymer medium, followed by coalescence of the polymer onto the nanoclusters formed [9].

Nickel is known as widely used catalyst for the variety of industrial catalytic processes such as hydrogenation of olefins. Our recent paper has shown that hydrogenphosphate-stabilized water-soluble nickel(0) nanoclusters are readily available and used as highly active catalyst in the hydrolysis of sodium borohydride [10]. However, the hydrogenphosphate-stabilized nickel(0) nanoclusters showed low catalytic lifetime as determined by measuring the total turnover number (TTO = 1450) for the hydrolysis of sodium borohydride which can be attributed to the weak electrostatic stabilization of nanoclusters. The electrostatic interactions become weaker at high pH, which is a requirement for the hydrolysis of sodium borohydride for application of safe hydrogen generation in fuel cells [11]. Therefore, a stronger stabilizer such as polymer is needed to prevent agglomeration of nickel(0) nanoclusters in aqueous solution at high pH medium, acting as catalyst in the hydrolysis of sodium borohydride.

Polymers possessing a hydrophobic backbone and hydrophilic side groups, such as vinyl addition homopolymers, are frequently employed as a stabilizer for the metal nanoclusters in polar solvents. Poly(*N*-vinyl-2-pyrrolidone) (PVP) is currently the most

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thoroughly investigated nonionic polymer, exhibiting a high protective function for the stabilization of metal colloids [12]. The formation of stable metal nanoclusters in the presence of PVP has been explained by the initial formation of complexes between the metal precursor ions and the polymer [13], and subsequent reduction of metal precursor to zerovalent state.

There are many studies on the synthesis of PVP-stabilized metal nanoclusters [9,14]. A very recent study shows the synthesis and the characterization of PVP-stabilized nickel(0) nanoparticles in organic medium by using a modified polyol process [15]. Here, we report for the first time, the synthesis, characterization and use of PVP-stabilized water-soluble nickel(0) nanoclusters as catalyst in the hydrolysis of sodium borohydride.

2. Experimental

Nickel(II) chloride hexahydrate (>98%), sodium borohydride (98%) and poly(*N*-vinyl-2-pyrrolidone) (PVP-40, average molecular weight 40,000) were purchased from Aldrich®, methanol (acetone free) were purchased from Riedel-De Haen AG Hannover, and pure carbon disulfide (CS₂) was purchased from Merck, and used as received. Deionized water was distilled by water purification system (Şimşek SL-200, Ankara, 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 150°C.

2.1. Synthesis of PVP-stabilized nickel(0) nanoclusters

PVP-stabilized nickel(0) nanoclusters were prepared by using a modified version of alcohol reduction method [16]. In 250 mL three-necked round bottom flask, 200 mg (0.9 mmol) of NiCl₂·6H₂O and 466 mg (4.5 mmol monomer unit) of PVP-40 were dissolved in 100 mL of methanol (mol PVP/mol nickel = 5). The mixture of metal precursor (NiCl₂·6H₂O) and polymer (PVP-40) in methanol was refluxed at 80°C for 1 h. Then, 10 mL of 300 mM solution of sodium borohydride (3.0 mmol = 116 mg NaBH₄) was added into metal-polymer mixture immediately after the reflux at 80°C. The abrupt color change from pale green to dark brown indicates that the formation of PVP-stabilized nickel(0) nanoclusters was completed. Methanol was removed from the solution by evaporation in a rotavap (Heidolph Laborata-4000). The nickel nanoclusters in solid form were collected from the residue after evaporation in the round bottom flask.

2.2. Characterization of PVP-stabilized nickel(0) nanoclusters

2.2.1. TEM analysis of PVP-stabilized nickel(0) nanoclusters

The samples used for the TEM experiments were harvested from the preparation of PVP-stabilized nickel(0) nanoclusters solution as described above: a 5-mL aliquot of PVP-stabilized nickel(0) nanoclusters solution in methanol was transferred into a clean screw-capped glass vial with a disposable polyethylene pipette. The colloidal solution was deposited on the silicon oxide coated copper TEM grid by immersing the grid into the solution for 5 s and then evaporating the volatiles from the grid under inert gas atmosphere. This sample on the grid was then sealed under N₂ and analyzed with a Hitachi H7600T TEM instrument operating at 120 kV and with a 2.0 Å point-to-point resolution. Samples were examined at magnification between 100 and 500k.

2.2.2. Particle size measurements

Particle size analysis was performed using the public domain NIH Image J 1.62 program, 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) as described elsewhere [17]. This table was then exported into Microsoft Excel 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.

2.2.3. XPS (X-ray photoelectron spectroscopy)

The dry solid samples of PVP-stabilized nickel(0) nanoclusters were sent to the METU Central Laboratory for XPS analysis using SPECS spectrometer equipped with a hemispherical analyzer, a monochromatic Mg K α radiation (1250.0 eV, the X-ray tube working at 15 kV and 350 W) and pass energy of 48 eV. To better access the Ni core in the sample by scraping off the polymer matrix from the surface, the sample surface was bombardment by argon ion by passing 2000 eV energy for 3 min. Peak fittings were done according to Gaussian function by using Origin 7.0 software.

2.2.4. FT-IR spectra

The FT-IR spectra of the PVP-stabilized nickel(0) nanoclusters having different PVP to nickel ratio (5, 0.5, 0.1) and neat PVP were taken from KBr pellet on a Nicolet 510 FT-IR Spectrophotometer using Omnic software.

2.3. Catalytic activity of PVP-stabilized nickel(0) nanoclusters in the hydrolysis of sodium borohydride

In a series of experiments PVP-stabilized nickel(0) nanoclusters were tested for their catalytic activity in the hydrolysis of sodium borohydride. The catalytic activity of PVP-stabilized nickel(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 (40 cm in height and 4.7 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) NaBH₄ was dissolved in 40 mL water (corresponding to generation of a maximum 30 mmol = 672 mL H₂ gas at 25.0 ± 0.1 °C and 0.91 atm pressure). The solution was transferred with a glass pipette into the reaction flask thermostated at 25.0 ± 0.1 °C. Then, aliquots of PVP-stabilized nickel(0) nanoclusters solutions were transferred into the reaction flask using a 10-mL gastight syringe. The volume of hydrogen gas evolved was measured by recording the displacement of water level every 5 min. The reaction was ceased when 80% conversion was achieved.

2.4. Self-hydrolysis of sodium borohydride

In order to avoid self-hydrolysis of borohydride, hydrogen generation from catalytic hydrolysis of borohydride has been carried out in highly concentrated alkaline solutions [18]. However nickel(0) nanoclusters were found to be unstable and converted to catalytically inactive form in highly concentrated alkaline solution. As

a consequence of this observation we had to avoid working in highly alkaline solution. Without added base, the self-hydrolysis of sodium borohydride solution may be significant and needs to be considered for quantifying the hydrogen generation from the sole catalytic reaction.

In a 100-mL beaker, 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 1200 rpm simultaneously, and the volume of hydrogen generated was measured exactly in the same way as described in Section 2.3.

2.5. Effect of PVP concentration on the catalytic activity of nickel(0) nanoclusters

In order to study the effect of PVP concentration on the catalytic activity of nickel(0) nanoclusters in the hydrolysis of sodium borohydride (150 mM), catalytic activity tests were performed at 25.0 ± 0.1 °C starting with nickel(0) nanoclusters synthesized having different PVP/Ni ratio (5, 10, 20, 30, 40). In all the experiments the total volume of solution was kept constant at 50 mL. All the experiments were performed in the same way as described in Section 2.3. The good stability and the highest activity of PVP-stabilized nickel(0) nanoclusters in the hydrolysis of sodium borohydride was obtained at PVP to nickel molar ratio of 5. Thus, the PVP concentration of 7 mM, corresponding to a PVP to nickel ratio of 5, was selected for the further experiments.

2.6. Kinetic study of PVP-stabilized nickel(0) nanocluster in catalytic hydrolysis of sodium borohydride

In order to establish the rate law for catalytic hydrolysis of NaBH_4 using PVP-stabilized nickel(0) nanoclusters as catalyst, three different sets of experiments were performed in the same ways described in Section 2.3. In the first set of experiments, the hydrolysis reaction was performed starting with different initial concentration of PVP-stabilized nickel(0) nanoclusters (1, 1.2, 1.4, 1.6, 1.8, 2 mM Ni) and keeping the initial sodium borohydride concentration constant at 150 mM. The second set of experiments were performed by keeping the initial concentration of PVP-stabilized nickel nanoclusters constant at 1.4 mM and varying the NaBH_4 concentration of 150, 300, 450, 600 and 750 mM. Finally, the catalytic hydrolysis of NaBH_4 was performed in the presence of PVP-stabilized nickel(0) nanoclusters at constant substrate (150 mM) and catalyst (1.4 mM Ni) concentrations at various temperatures in the range of 25–45 °C in order to obtain the activation energy (E_a), enthalpy (ΔH^\ddagger), and entropy (ΔS^\ddagger).

2.7. Catalytic lifetime of PVP-stabilized nickel(0) nanoclusters

The catalytic lifetime of PVP-stabilized nickel(0) nanoclusters in the hydrolysis of sodium borohydride was determined by measuring the total turnover number (TON). Such a lifetime experiment was started with a 50 mL solution of PVP-stabilized nickel(0) nanoclusters containing 1.4 mM Ni and 1 M NaBH_4 (1.9 g) 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 was corrected by subtracting the self-hydrolysis data of sodium borohydride in order to obtain the volume of hydrogen generated only from the catalytic reaction.

2.8. Mercury poisoning as heterogeneity test for PVP-stabilized nickel(0) nanoclusters

To decide whether the PVP-stabilized water-soluble nickel(0) nanoclusters are acting as homogeneous or heterogeneous catalyst in the hydrolysis of sodium borohydride, 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. In a typical mercury poisoning experiment, 1.4 mM of PVP-stabilized nickel(0) nanoclusters in 50 mL of 150 mM sodium borohydride solution at 25.0 ± 0.1 °C was poisoned by using 70, 60, 50, 40, 30, 20, and 10 mg mercury corresponding to a Hg/Ni molar ratio of 7.0, 6.0, 5.0, 4.0, 3.0, 2.0 and 1.0, respectively. The catalytic activity was measured by monitoring the rate of hydrogen generation before and after the addition of mercury.

2.9. CS_2 poisoning of PVP-stabilized nickel(0) nanoclusters

The ability of CS_2 to poison metal-particle heterogeneous catalyst by adsorbing on the metal surface has been proposed in reducing reaction medium [19]. In a typical poisoning experiment, 1.4 mM of PVP-stabilized nickel(0) nanoclusters having a PVP/Ni molar ratio of 5 in 50 mL of 150 mM sodium borohydride solution at 25.0 ± 0.1 °C was poisoned by adding 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 mL of 0.7 mM CS_2 solution prepared in THF corresponding to a CS_2 /Ni molar ratio of 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, and 0.07, respectively. The catalytic activity was measured by monitoring the rate of hydrogen generation before and after the addition of CS_2 .

3. Results and discussions

3.1. Synthesis of PVP-stabilized nickel(0) nanoclusters

PVP-stabilized water-soluble nickel(0) nanoclusters were prepared by using a modified version of alcohol reduction method [16]. In a typical alcohol reduction method, an alcohol is used as a mild reducing agent. Thus, the metal precursor is reduced in the presence of water-soluble polymer under reflux in methanol for 2 h at 80 °C. However, in the case of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, no reduction was observed after 4 h reflux in methanol at 80 °C. Obviously, methanol is not a strong reducing agent for the nickel(II) precursor. Therefore, a stronger reducing agent, sodium borohydride, was added into the solution after reflux to reduce nickel(II) ions to zerovalent nickel. Upon addition of NaBH_4 , the color of the solution was immediately changed from pale green of the nickel(II) ion to dark brown of the nickel(0) nanoclusters. Prior to the reduction by sodium borohydride, a reflux of 1 h at 80 °C was found to be necessary to obtain the nickel(0) nanoclusters. Most probably, this preheating of the solution leads to the initial complex formation of nickel(II) ion with the PVP stabilizer [13], which can subsequently be reduced to zerovalent metal more easily.

The PVP-stabilized water-soluble nickel(0) nanoclusters formed in this way are stable in solution. For example, no bulk metal formation was observed in solution standing for two weeks at room temperature. The PVP-stabilized nickel(0) nanoclusters can be isolated as solid materials from solution 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 (see later).

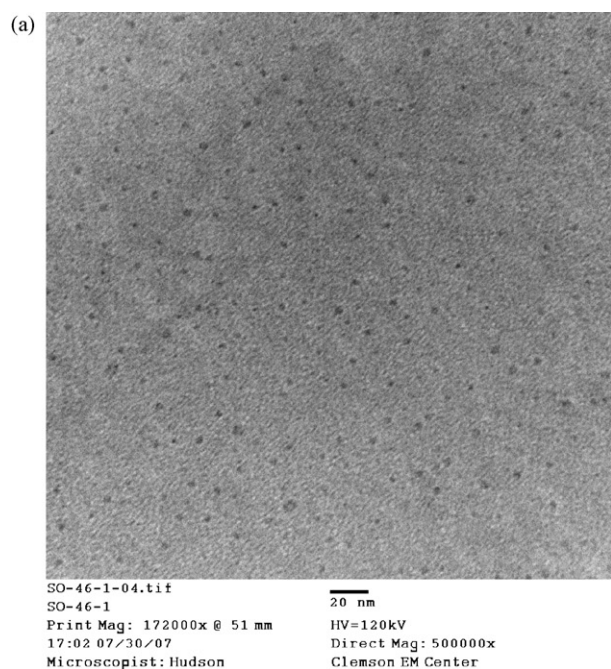


Fig. 1. (a) TEM image and (b) associated histogram for PVP-stabilized nickel(0) nanoclusters formed from the reduction of nickel(II) chloride hexahydrate (8.4 mM) in the presence of PVP (42 mM) by sodium borohydride (300 mM) after 1 h reflux in methanol at 80 °C. In the TEM image 200 non-touching particles were counted for the construction of histogram using the Microsoft Office Excel 2003, which gives a mean particle size of 3.6 nm and a standard deviation of 1.6 nm.

3.2. Characterization of PVP-stabilized nickel(0) nanoclusters

Fig. 1 shows the TEM image and the corresponding histogram of nickel(0) nanoclusters prepared from the reduction of nickel(II) chloride hexahydrate (8.4 mM) by sodium borohydride in the presence of PVP-40 (42 mM) after refluxing for 1 h in methanol at 80 °C. In the TEM image 200 non-touching particles were counted for the construction of histogram. The particle size of the PVP-stabilized nickel(0) nanoclusters ranges from 2.0 to 6.0 nm with a mean value of 3.6 nm and a standard deviation of 1.6 nm, compared well with the ones (3.8 nm) prepared very recently in ethylene glycol [15].

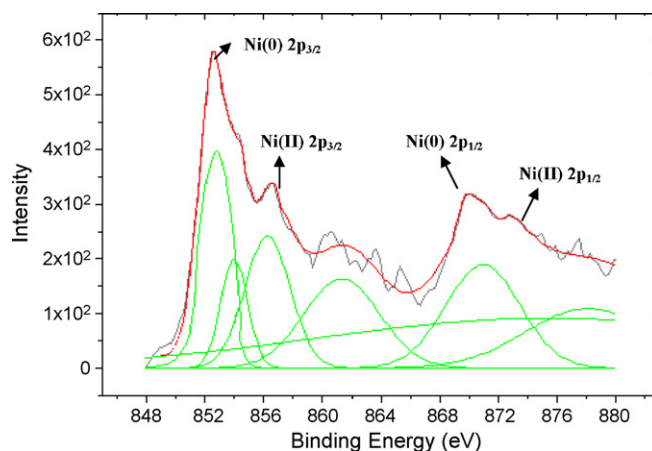


Fig. 2. X-ray photoelectron spectrum of PVP-stabilized nickel(0) nanoclusters formed from the reduction of nickel(II) chloride hexahydrate (8.4 mM) in the presence of PVP (42 mM) by sodium borohydride (300 mM) after 1 h reflux in methanol at 80 °C.

Fig. 2 shows the XPS spectrum of PVP-stabilized nickel(0) nanoclusters obtained from the reduction of nickel(II) chloride by sodium borohydride in the presence of PVP after refluxing for 1 h in methanol solution at 80 °C. The XPS spectrum in **Fig. 2** exhibits essentially two bands at 852.5 and 869.9 eV which can be assigned to Ni(0) 2p_{3/2} and Ni(0) 2p_{1/2}, respectively, by comparing with the values of bulk nickel (852.3 and 869.7 eV, respectively) [20]. The XPS spectrum shows two additional, slightly higher energy bands at 853.8 and 872.8 eV, though in relatively weak intensities, attributable to Ni(II) 2p_{3/2} and Ni(II) 2p_{1/2}, respectively. By comparing to the spectral data for NiO, these bands indicate the presence of a small amount of NiO, presumably in the form of a thin oxide film on the surface of nickel(0) nanoclusters. Upon argon ion bombardment, the former two bands of Ni(0) gain intensity while the latter two bands of Ni(II) lose intensity relatively. This observation supports the assumption that NiO is formed on the surface of nanoclusters. Ni(II) species might have been formed by oxidation during the XPS sampling, whereby the nanoclusters are exposed to air for a few seconds. Since the oxidation product may exist in different form depending on the ligand (hydroxide, oxo group or nitrogen donor), additional weak bands can be attributed to the different Ni(II) species. Taking the results together, the main conclusion is that assays of the PVP-stabilized nickel nanoclusters consist primarily of nickel in metallic state. Another important finding obtained from the XPS is that there exist no boron in the PVP-stabilized nickel(0) nanoclusters samples as XPS does not show any band around 190 eV for B 1s, in contrast to the NiB nanoclusters [21].

Comparative FT-IR spectra of both the PVP-stabilized nickel(0) nanoclusters having different PVP to nickel ratio and the neat PVP polymer give insight to the bonding mode of PVP on the nanoclusters surface. The FT-IR spectra of neat PVP and PVP-stabilized nickel(0) nanoclusters samples show no essential difference with the exception of carbonyl band. **Fig. 3** demonstrates the spectral change in the CO stretching range of 2000–1500 cm⁻¹ with the PVP/Ni ratio. In low PVP/Ni ratio, one observes an additional band for the CO stretching at lower wavenumber (1600 cm⁻¹) than the main band at 1663 cm⁻¹ of the neat PVP polymer. This additional lower frequency band is assigned to the carbonyl group coordinated to the nickel atoms on the nanoclusters surface [22]. The appearance of a relatively weak band with large coordination shift ($\Delta\nu_{C=O} = 63 \text{ cm}^{-1}$) indicates that a small portion of the carbonyl groups on the PVP chain are bound to the nanoclusters surface. As the PVP/Ni ratio increases the fraction of the bound carbonyl

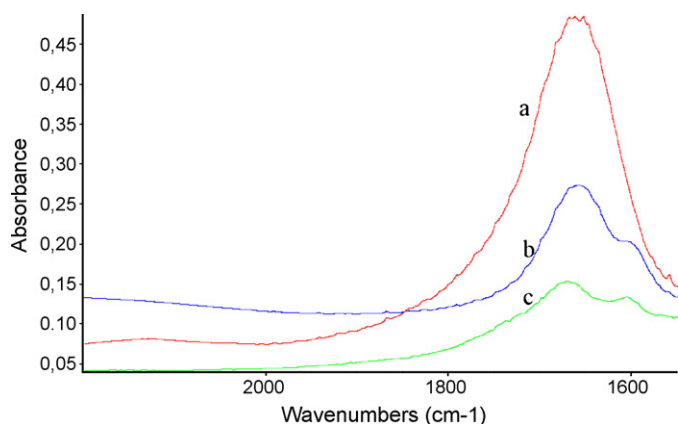


Fig. 3. FT-IR spectra of PVP-stabilized nickel(0) nanoclusters taken from KBr pellets in the CO stretching range: (a) neat PVP, (b) PVP/Ni=0.5, and (c) PVP/Ni=0.1.

decreases, so that the additional band at lower frequency due to the bound carbonyl groups is losing intensity. In the spectrum of sample with PVP/Ni ratio of 5, the band is not discernible as the fraction of the bound carbonyl groups is negligibly small compared to that of free PVP.

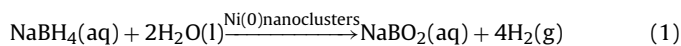
3.3. Effect of PVP concentration on the catalytic activity of nickel(0) nanoclusters

In order to study the effect of PVP concentration on the catalytic activity of nickel(0) nanoclusters in the hydrolysis of sodium borohydride (150 mM), catalytic activity tests were performed at $25.0 \pm 0.1^\circ\text{C}$ starting with five sets of nickel(0) nanoclusters having different PVP/Ni ratio (5, 10, 20, 30, and 40). Fig. 4a shows the plots for the hydrogen generation from the hydrolysis of sodium borohydride catalyzed by nickel(0) nanoclusters with different PVP/Ni ratio. The rate of hydrogen generation measured from the slope of the linear portion of curves decreases with the increasing PVP/Ni ratio as shown in Fig. 4b.

The PVP polymer adsorbed on the nanoclusters surface via carbonyl groups provides steric stabilization against coagulation of the particles. The PVP polymer in high concentration will cover the whole nanoclusters surface; thus, block the active sites on the surface leading to the deactivation of catalyst. In low concentration of PVP, the nanoclusters are not stable enough to be employed as catalyst. Hence, one has to make a compromise between stability and catalytic activity. In this case, the optimum PVP/Ni ratio was found to be 5 (the PVP concentration of 7 mM monomer), for obtaining nickel(0) nanoclusters which are stable and show the highest catalytic activity in the hydrolysis of sodium borohydride. Thus, the PVP to nickel ratio of 5 was selected for the further experiments.

3.4. Catalytic activity of PVP-stabilized nickel(0) nanoclusters in the hydrolysis of sodium borohydride

PVP-stabilized nickel(0) nanoclusters were used as a catalyst in the hydrolysis of sodium borohydride liberating hydrogen gas, Eq. (1)



The PVP-stabilized nickel(0) nanoclusters are found to be active catalyst for the hydrolysis of sodium borohydride even at low concentrations and room temperature. Fig. 5a shows the plots of the volume of hydrogen generated versus time during the catalytic hydrolysis of 150 mM NaBH₄ solution in the presence of nickel(0) nanoclusters in different nickel concentrations at $25 \pm 0.1^\circ\text{C}$. The

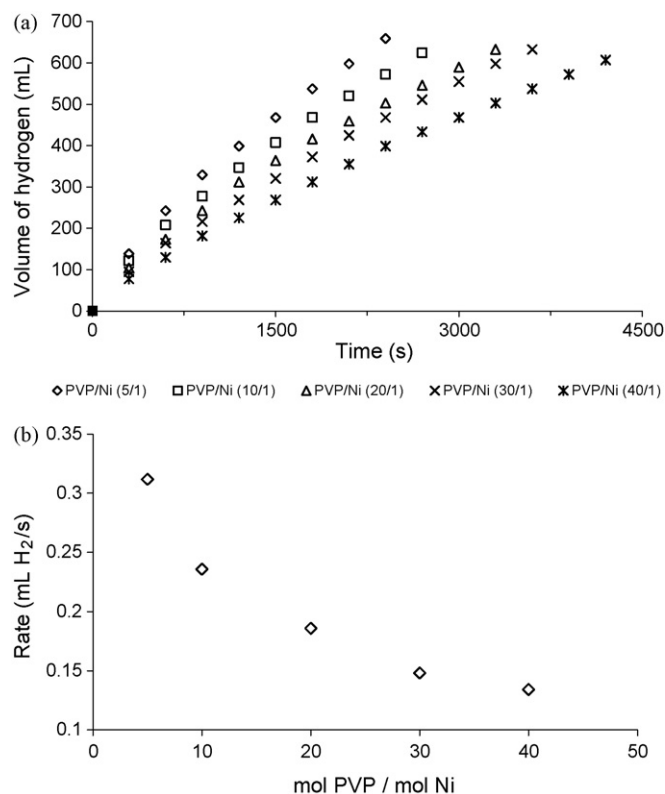


Fig. 4. (a) The volume of hydrogen versus time plot for the hydrolysis of sodium borohydride catalyzed by nickel(0) nanoclusters having different PVP to nickel ratio at $25 \pm 0.1^\circ\text{C}$. (b) The rate of hydrogen generation versus the molar ratio of PVP to nickel.

hydrogen generation rate was determined from the linear portion of the plot for each nickel concentration. Fig. 5b shows the plot of hydrogen generation rate versus nickel concentration, both in logarithmic scale. The slope of the line in Fig. 5b is $1.1 \approx 1.0$ indicating that the hydrolysis reaction is first order with respect to the concentration of nickel(0) nanoclusters catalyst in line with the previous observations [10,23,24].

The effect of NaBH₄ substrate concentration on the hydrogen generation rate was also studied by performing a series of experiments starting with varying initial concentration of NaBH₄ while keeping the catalyst concentration constant at 1.4 mM Ni. The hydrogen generation rate was found to be practically independent of the NaBH₄ concentration. Hence, the hydrolysis reaction is zero order with respect to the concentration of NaBH₄. This might be due to the much higher concentration of the substrate during the reaction compared to the catalyst concentration (substrate concentration is at least two hundred times greater than the catalyst concentration). Consequently, the rate law for the catalytic hydrolysis of sodium borohydride can be given as, Eq. (2)

$$\frac{-4d[\text{NaBH}_4]}{dt} = \frac{d[\text{H}_2]}{dt} = k[\text{Ni}] \quad (2)$$

Both PVP-stabilized nickel(0) nanoclusters catalyzed and self-hydrolysis of sodium borohydride were carried out at various temperature in the range of $25\text{--}45^\circ\text{C}$ starting with the initial substrate concentration of 150 mM NaBH₄ and an initial catalyst concentration of 1.4 mM Ni. The values of rate constant *k* for the sole catalyzed hydrolysis (Table 1) were calculated from the hydrogen volume versus time data obtained by subtracting the self-hydrolysis hydrogen generation values from those of nickel(0) nanoclusters catalyzed hydrolysis of sodium boro-

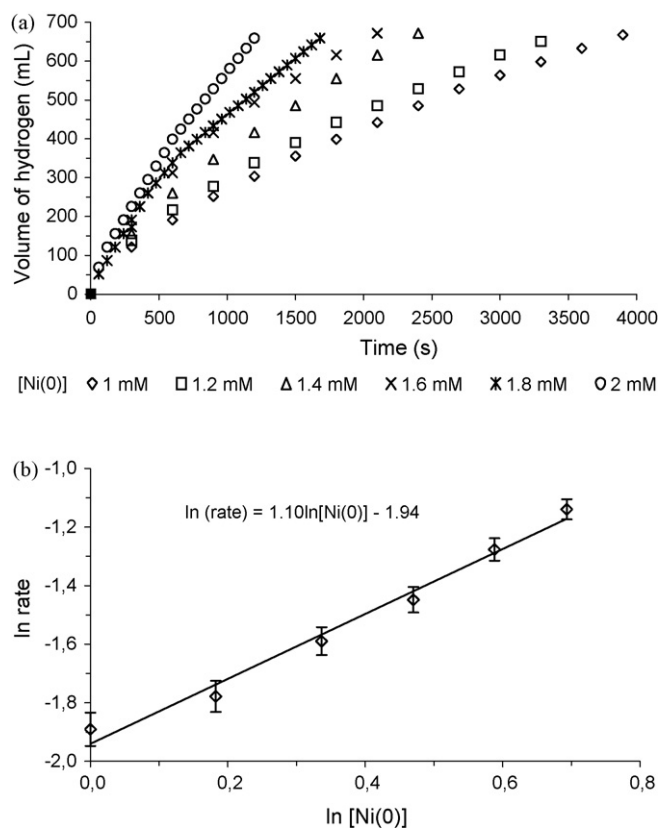


Fig. 5. (a) The volume of hydrogen versus time plot depending on the nickel concentration for the catalytic hydrolysis of sodium borohydride (150 mM) at 25 ± 0.1 °C and (b) the plot of hydrogen generation rate versus the concentration of nickel (both in logarithmic scale) for the hydrolysis of sodium borohydride (150 mM) at 25 ± 0.1 °C.

hydride and evaluated in Arrhenius and Eyring plots (Fig. 6) to obtain the activation energy ($E_a = 48 \pm 2 \text{ kJ mol}^{-1}$) and activation enthalpy ($\Delta H^\ddagger = 45 \pm 2 \text{ kJ mol}^{-1}$) plus activation entropy ($\Delta S^\ddagger = -94 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$), respectively.

Activation energies for the hydrolysis of sodium borohydride catalyzed by PVP-stabilized nickel(0) nanoclusters and other catalysts are listed in Table 2 for comparison. PVP-stabilized nickel(0) nanoclusters provide a lower activation energy for the hydrolysis of sodium borohydride compared to the value of $E_a = 54 \text{ kJ mol}^{-1}$ for the hydrogenphosphate-stabilized nickel(0) nanoclusters [10], and the value of $E_a = 71 \text{ kJ mol}^{-1}$ for the bulk nickel [25].

3.5. Catalytic lifetime

A catalyst lifetime experiment was performed starting with a 50-mL solution of PVP-stabilized nickel(0) nanoclusters containing 1.4 mM Ni and 1 M NaBH₄ (1.9 g) at 25.0 ± 0.1 °C. It was found that

Table 1

The values of rate constant k for the sole catalytic hydrolysis starting with a solution of 150 mM NaBH₄ and 1.4 mM PVP-stabilized nickel(0) nanoclusters at different temperatures, calculated from the hydrogen volume versus time data corrected by subtracting the volume of hydrogen generated from the self-hydrolysis of sodium borohydride

Temperature (°C)	Rate constant ($\text{K mol H}_2 (\text{mol Ni})^{-1} \text{ s}^{-1}$)
25	0.170
30	0.240
35	0.326
40	0.436
45	0.579

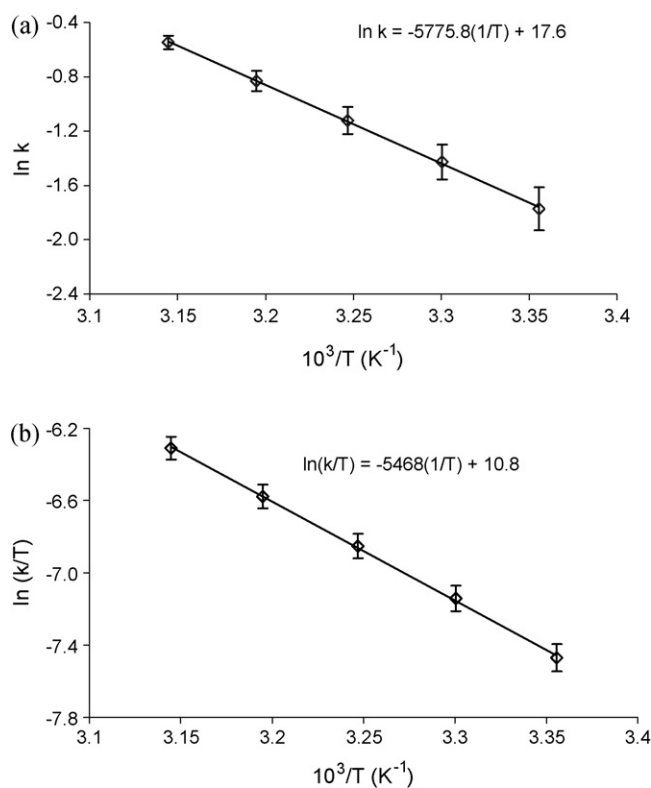


Fig. 6. (a) Arrhenius plot ($\ln k$ versus the reciprocal absolute temperature $10^3/T (\text{K}^{-1})$), (b) Eyring plot ($\ln(k/T)$ versus the reciprocal absolute temperature $10^3/T (\text{K}^{-1})$) for the hydrolysis of sodium borohydride (150 mM) catalyzed by PVP-stabilized nickel(0) nanoclusters (1.4 mM Ni) in the temperature range 25–45 °C.

the PVP-stabilized nickel(0) nanoclusters provide 8700 turnovers of hydrogen gas generation from the hydrolysis of sodium borohydride over 27 h before deactivation (Fig. 7). However, that the hydrogen generation slows down as the reaction proceeds may be because of increasing viscosity of the solution as the continuously added sodium borohydride is converted to sodium metaborate. Therefore, this value should be considered as a lower limit. A much higher TTO value might be obtained when the increase in viscosity could be avoided. Note that the turnover frequency starts with an initial value of $\text{TOF} = 0.17 \text{ mol H}_2 (\text{mol Ni})^{-1} \text{ s}^{-1}$ or $2.9 \text{ mmol H}_2 (\text{g Ni})^{-1} \text{ s}^{-1}$. Both TTO and TOF values refer to the sole catalytic hydrogen generation after subtraction of self-hydrolysis.

3.6. Catalyst poisoning

The ability of Hg(0) to poison metal-particle heterogeneous catalysts, by amalgamating the metal or adsorbing on the metal surface, has been known for more than 80 years and is a widely used test [26]. This experiment is performed by adding Hg(0) to the reaction solution. The suppression of catalysis by Hg(0) is con-

Table 2

Arrhenius activation energy for various catalyst systems used for the hydrolysis of sodium borohydride

Catalyst	Activation energy (kJ mol^{-1})	Reference
PVP-stabilized nickel(0) nanoclusters	48	This work
HPO ₄ ²⁻ -stabilized nickel(0) nanoclusters	54	[10]
Ru(0) nanoclusters	42	[24]
Bulk nickel	71	[25]
Bulk cobalt	75	[25]

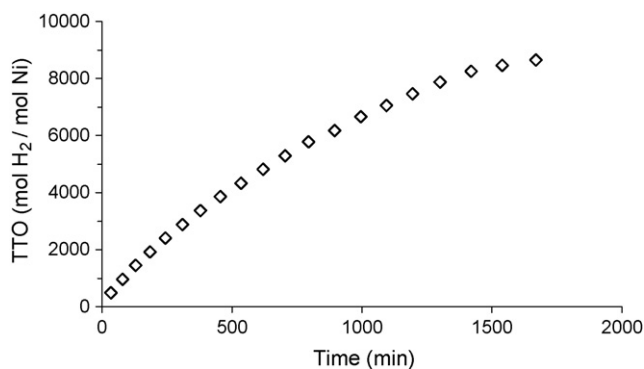


Fig. 7. Total turnover number (TTO) versus time (min) plot for the sole catalytic hydrolysis of sodium borohydride starting with a 50-mL solution of PVP-stabilized nickel(0) nanoclusters containing 1.4 mM Ni and 1 M NaBH₄ (1.9 g) at 25.0 ± 0.1 °C. A new batch of 1.9 g NaBH₄ was added into the reaction solution when ever 80% conversion of sodium borohydride present in the solution. Note that 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.

sidered as a compelling evidence for the heterogeneous catalyst; if Hg(0) does not suppress catalysis, that is (negative) evidence for a homogeneous catalyst [19]. Fig. 8a 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 Ni. Experimental points can be fitted to a line, the intersection of which with the concentration axis provides the critical molar ratio of mercury to nickel. Thus, the minimum amount of

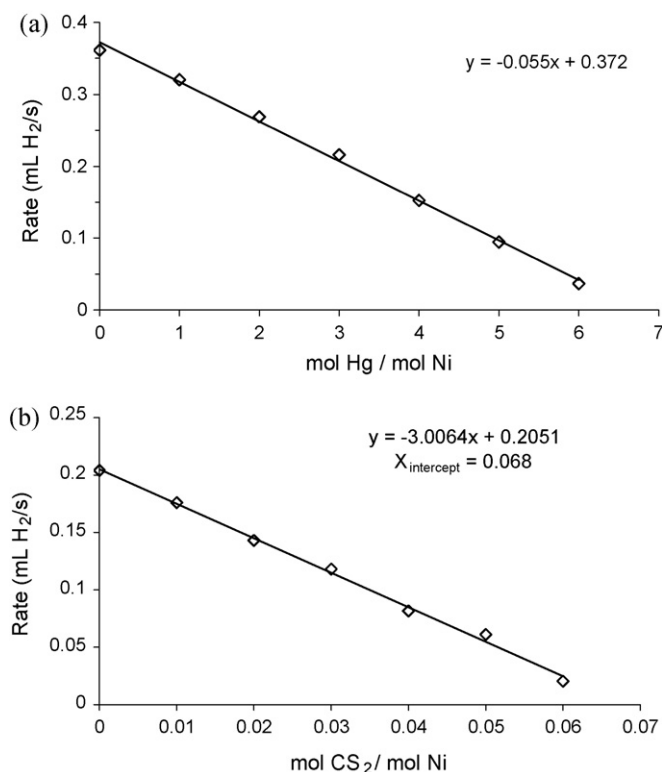


Fig. 8. (a) Plot of the relative rate of hydrogen generation versus the relative Hg concentration as mol Hg/mol Ni ratio for the hydrolysis of sodium borohydride (150 mM) catalyzed by PVP-stabilized nickel(0) nanoclusters ([Ni(0)] = 1.4 mM). (b) Plot of the relative rate of hydrogen generation versus the relative CS₂ concentration as mol CS₂/mol Ni ratio for the hydrolysis of sodium borohydride (150 mM) catalyzed by PVP-stabilized nickel(0) nanoclusters ([Ni(0)] = 1.4 mM).

mercury required for the complete poisoning of the nickel(0) nanoclusters catalyst was found to be 6.75 ± 0.10 mol of Hg/mol of total nickel. This result indicates that PVP-stabilized nickel(0) nanoclusters are indeed heterogeneous catalysts in the hydrolysis of sodium borohydride.

A series of poisoning experiments were also carried out by adding CS₂ in varying amount during the catalytic hydrolysis of sodium borohydride and measuring the catalytic activity before and after addition. Fig. 8b shows the results of eight independent experiments as a plot of the relative rate of hydrogen generation versus the relative CS₂ concentration as mol CS₂/mol Ni. Experimental points can be fitted to a line, the intersection of which with the concentration axis provides the critical molar ratio of CS₂ to nickel. Thus, the minimum amount of CS₂ required for the complete poisoning of the nickel(0) nanoclusters catalyst was found to be 0.068 ± 0.0032 mol of CS₂/mol of total nickel. By assuming a 1/1 CS₂/Ni(0) stoichiometry [27] for the poisoning, one obtains 6.8% of the total nickel atoms to be active in catalysis. The most important conclusion drawn from these results is that the PVP-stabilized nickel(0) nanoclusters are indeed heterogeneous catalyst.

4. Conclusions

In summary, our study of the synthesis and characterization of PVP-stabilized water-dispersible nickel(0) nanoclusters as catalyst for the hydrolysis of sodium borohydride has led to the following conclusions and insights.

- Water-dispersible PVP-stabilized nickel(0) nanoclusters can be formed from the reduction of a commercially available precursor NiCl₂·6H₂O by sodium borohydride in the presence of a water-soluble polymer, PVP.
- Compared to the hydrogenphosphate-stabilized nickel(0) nanoclusters [10], PVP-stabilized nickel(0) nanoclusters are much more stable, and catalytically more active providing 8700 total turnovers in the hydrolysis of sodium borohydride over 27 h at ambient temperatures.
- PVP polymer is coordinated to the nanoclusters surface through some of the carbonyl groups as concluded from a comparative FT-IR spectral study.
- A kinetic study shows that the catalytic hydrolysis of sodium borohydride is first order with respect to nickel concentration and zero order with respect to substrate concentration.
- Activation parameters for the sole catalytic hydrolysis of sodium borohydride in the presence of PVP-stabilized nickel(0) nanoclusters were determined as $E_a = 48 \pm 2 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 45 \pm 2 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -94 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$. The activation energy is much smaller than that found for the same hydrolysis catalyzed by bulk nickel.

Acknowledgment

Partial support of this work by Turkish Academy of Sciences, METU-DPT-OYP Program is gratefully acknowledgment.

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