Preparation and characterization of polymer-protected Pt/Co bimetallic colloids and their catalytic properties in the selective hydrogenation of cinnamaldehyde

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Abstract

Polymer-protected Pt/Co bimetallic colloids with Pt/Co molar ratios of 3:1 and 1:1 have been prepared by the polyol process and characterized by TEM and XRD. Over the above Pt/Co bimetallic colloid catalyst (Pt/Co = 3:1), cinnamaldehyde can be selectively hydrogenated to cinnamyl alcohol with 99.8% selectivity at 96.2% conversion. The activity and selectivity can be affected by H_2O and NaOH added to the reaction system; the former leads to a highly polar solution and the latter retards the olefinic hydrogenation. The Pt/Co bimetallic colloid is stable enough to withstand the hydrogenation reaction at 333 K and 4.0 MPa.

Keywords: Pt/Co bimetallic colloid; Selective hydrogenation; Cinnamaldehyde

1. Introduction

Compared to bulk metal or single metal atoms, nanoscopic clusters or colloids of metal display singular properties, especially in the field of catalysis [1,2]. The applications of bimetallic catalysts in industry have promoted the research on bimetallic colloids. Some papers have reported the synthesis and the catalytic action of the bimetallic colloids composed of two noble metals [3–5]. It can be expected that bimetallic colloids composed of a light transition metal and a noble metal may provide a greater potential for tailoring the catalytic properties since

there is great difference between their electronic structures and redox potentials. Several such bimetallic colloids have been prepared by different methods [6–8].

The selective hydrogenation of α,β-unsaturated aldehydes to α,β-unsaturated alcohols is an important step in the preparation of various fine chemicals. It is a difficult task to reduce only the C=O group when it is conjugated to a C=C double bond, since almost all metal catalysts readily reduce the C=C double bond to yield a saturated aldehyde as the main product [9]. As a model reaction, many researchers have attempted to develop a suitable catalytic system for selective hydrogenation of cinnamaldehyde (**1**) to cinnamyl alcohol (**2**) [10–16]. A supported Pt/Co bimetallic catalyst

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has been prepared by H_2 reduction at high-temperature and effected high conversion, 90%, and good selectivity, 80% [10]. In a recent study, Arai et al. have improved the activity and selectivity to **2** by the ambient temperature preparation of alumina-supported platinum catalyst [16]. In view of these results it would be valuable to catalyze this reaction by Pt/Co bimetallic colloids prepared at a relatively lower temperature. The surfactant-protected Pt/Co bimetallic colloid prepared by Bönnemann's group [6] via hydrotriorganoborate reduction was characterized only by an elemental analysis. Furthermore, the neat colloids they prepared, seemed to be unstable in hydrogenation and showed the tendency to aggregate easily thus causing a drastic loss of activity. Here, we will report the preparation of polymer-protected Pt/Co bimetallic colloids and their catalytic properties in selective hydrogenation of **1** to **2**.

2. Experimental

2.1. Materials and instruments

Poly(N-vinyl-2-pyrrolidone) (PVP) (average molecular weight 40000) was purchased from BASF. Other reagents were supplied by Beijing Chemicals and had a level of analytical grade. **1** was redistilled under reduced pressure before use. All reagents were degassed and stored under nitrogen prior to use. Hydrogen (H_2) with a purity of 99.999% was supplied by Beijing Gases Factory.

Transmission electron microscopy (TEM) photographs were taken by using a Hitachi-9000NAR instrument. Specimens were prepared by placing a drop of the colloid solution upon a copper grid covered with a perforated carbon film and then evaporating the solvent. The particle diameters were measured from the enlarged photographs. The particle size distribution histograms were obtained on the basis of the measurements of about 300 particles. X-Ray diffraction (XRD) patterns were recorded by a Rigaku

D/Max-2400 diffractometer at 40 kV and 100 mA employing a Cu $K\alpha$ radiation. Specimens were prepared by evaporating the solvent of the colloid. All the specimens were prepared in a glove-box and stored under nitrogen before to be examined, for Co^0 in the colloid state was oxidized easily by oxygen in the air. The hydrogenation products were analyzed by a Shang-Fen Model 103 gas chromatograph (GC) using a 2 m PEG-20 M column.
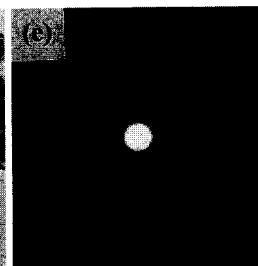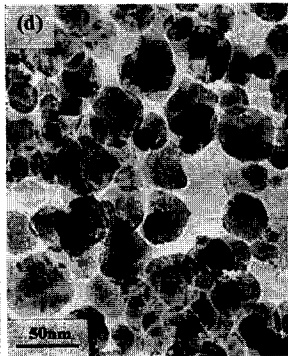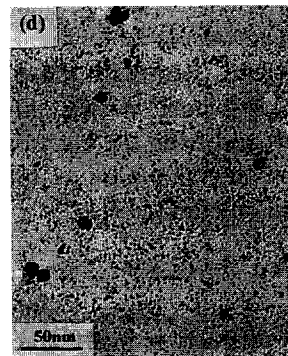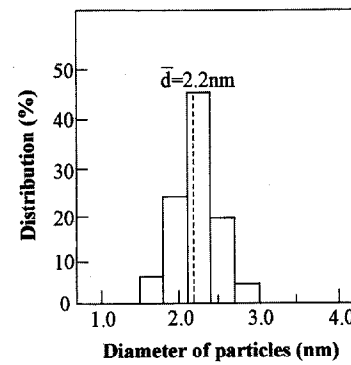
2.2. Preparation of polymer-protected Pt/Co bimetallic colloids

Preparation of polymer-protected Pt/Co bimetallic colloids were carried out similar to the literature [7,17,18]. For example, in a four-necked flask, PVP (1.76 g, 15.84 mmol as monomeric residue), cobalt(II)chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 31.26 mg, 0.1314 mmol) and chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, 204.2 mg, 0.3942 mmol) were dissolved in a mixture of ethylene glycol (240 ml) and diethylene glycol (60 ml), the pH of the solution was adjusted to 11 by dropwise addition of an aqueous solution of sodium hydroxide (NaOH, 0.1 M) with vigorous stirring. The reaction mixture was refluxed at 475 K for 2 h with a nitrogen current sweeping over the liquid layer removing the water vapor produced to give the PVP-protected Pt/Co bimetallic colloid (with Pt/Co molar ratio of 3:1) as a dark-brown homogeneous dispersi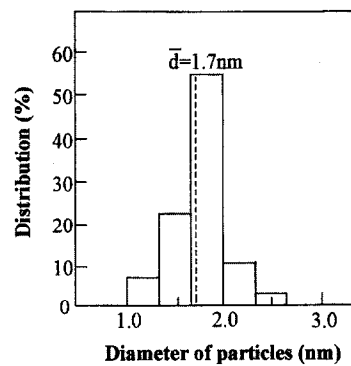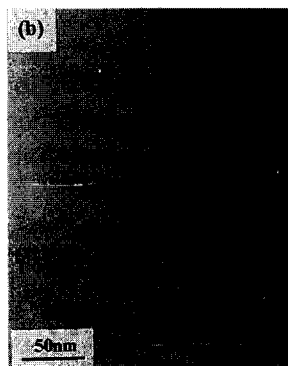on. The colloid was redispersed in absolute ethanol after precipitation by adding acetone and stored under nitrogen for use as a catalyst (designated as PVP–Pt/Co (3:1)). The PVP–Pt/Co (1:1) was obtained via the same way by changing the molar ratio of $H_2PtCl_6 \cdot 6H_2O$ to $CoCl_2 \cdot 6H_2O$.

2.3. Hydrogenation of cinnamaldehyde

Into a 150 ml stainless steel autoclave, were placed 40 ml EtOH, 10 ml H_2O, 1 mg NaOH and 2.00 g **1** (15.2 mmol), 2.00 g tetradecanol (as an internal standard for GC), 10 ml PVP–

Pt/Co (3:1) dispersion (containing 2.57×10^{-2} mmol metal). Care must be taken that the whole system was protected under nitrogen before H_2 was charged. H_2 was introduced several times to replace nitrogen and the final pressure of H_2 was 4.0 MPa and the hydrogenation reaction underwent at 333 K. Liquid samples were analyzed periodically by GC.

3. Results and discussion

3.1. Preparation and characterization of Pt / Co bimetallic colloids

There is great difference between Co^{II}/Co^0 and Pt^{IV}/Pt^0 in their redox potentials. Therefore, it is difficult to form an alloy of Co–Pt by simple liquid phase reduction. To overcome this problem, Toshima and Wang [7] have reported a method by reducing the corresponding hydroxide precursors with a modified polyol process. The PVP-protected Pt/Co bimetallic colloids with Pt/Co molar ratio of 3:1 and 1:1 can be prepared by the same process as follows:

$PVP + Co^{II} + Pt^{IV}$

$$\xrightarrow[\text{pH 11 in the mixed solvent}]{\text{1. NaOH}} \text{PVP-protected Pt}$$

/Co bimetallic hydroxide colloid

$$\xrightarrow{\text{2. 475 K, N}_2 \text{ flow}} \text{PVP-protected Pt}$$

/Co bimetallic colloid   (1)

It was also simple to prepare a PVP-protected Pt colloid by this method, but the attempts to

Table 1
Formation of PVP-protected bimetallic and monometallic colloids by a modified process

Dispersion	Formation of colloid	Average diameter, d (nm)	Standard deviation, σ (nm)
Pt	Yes	1.1	0.21
Pt/Co (3:1)	Yes	1.7	0.33
Pt/Co (1:1)	Yes	2.2	0.42
Co	No	–	–

Table 2
Interplanar spacings obtained by the electron diffractogram of the Co particles

Radius of diffraction circle (mm)	Calculated value of d (Å)	d of Co (4F) phase [19] (Å)
10.2	2.05	2.05
16.7	1.25	1.25
19.6	1.07	1.07

prepare a colloidal dispersion of PVP-protected Co were unsuccessful. Instead, a turbid dispersion of Co particles with large amount of precipitates was obtained, which indicated that the protective ability of PVP to Co colloid was not strong enough. This is similar to the condition of Cu [7]. Results of preparation of some PVP-protected bimetallic and monometallic colloids by this method are listed in Table 1.

3.1.1. TEM observation

Transmission electron microscopy is a conventional method to give detailed information about the shapes, mean size and size distribution of colloidal dispersions. The TEM photographs and corresponding particle size distribution histograms of some bimetallic and monometallic colloids protected by PVP are shown in Fig. 1.

From Fig. 1, it can be seen that there are increases in the particle size and the width of the size distribution when incorporating Co from 0 to 100 atom%. The Co particles in the turbid dispersion have a very wide size distribution from 1 to 10^5 nm. An electron diffraction pattern of the Co particles was obtained by TEM (Fig. 1e). Table 2 shows that the interplanar spacings (d) calculated by the formula $L\lambda = Rd$ were well consistent with those of the phase of Co (4F) [19], none of the other Co^{II} phases could be found from the electron diffractogram. Thus, it is sure that Co^{II} is totally reduced to Co^0 by this method [17].

3.1.2. X-Ray diffraction analysis

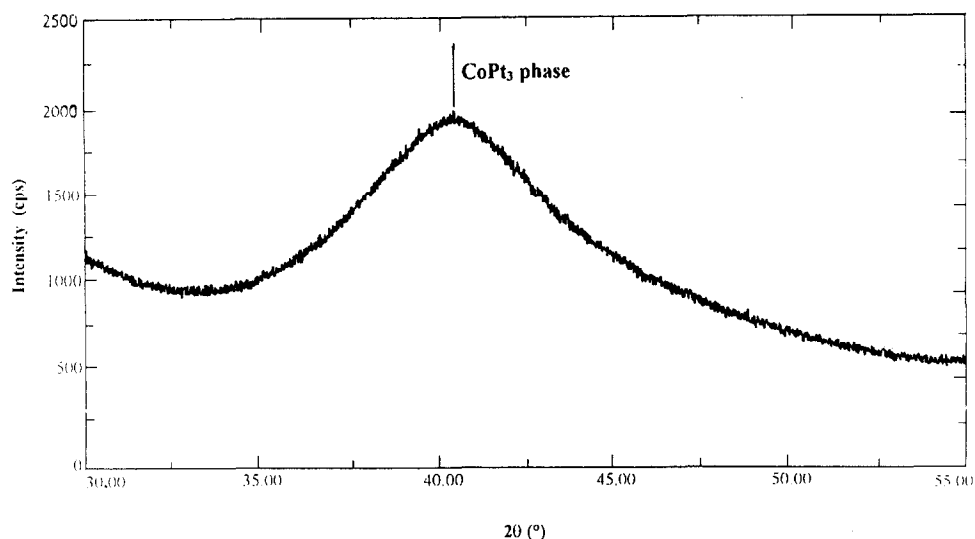Metal colloids generally are polycrystalline, so X-ray diffraction analysis can offer useful

Fig. 2. X-ray diffraction pattern of the PVP–Pt/Co (3:1).

information about the formation of the alloy phases. Metal Pt and Co can form a series of solid solutions consisted of Co from 0 to 100 atom% [20], and there are two crystal alloy phases: CoPt and $CoPt_3$ [19,20]. Fig. 2 shows the XRD pattern of PVP–Pt/Co (3:1).

It can be seen from Fig. 2 that there is not any diffraction lines of metal Co or its oxides, but a dispersed peak, the position is in accord with the crystal datum of the alloy phase of $CoPt_3$ [19]. A dispersed peak is the particularity of metal colloids [3,4,6], because the sizes of colloidal particles are very small (such as the average diameter of the PVP–Pt/Co (3:1) de-termined by TEM is 1.7 nm). Furthermore, the peak width of the X-ray diffraction line showed that the crystal size of the Pt/Co (3:1) was 1.4–1.5 nm predicted from the Scherrer formula [21]. This is well consistent with the TEM observation.

Nevertheless, it is noteworthy that the strongest X-ray diffraction peaks of metal Pt, alloys of $CoPt_3$ and CoPt are so close that they cannot be told apart, the same is true with the

Table 3
Positions of X-ray diffraction peaks of Pt, $CoPt_3$ and CoPt [19]

Phase	The strongest peak		The strongest peak but one	
	d (Å)	2θ (°)	d (Å)	2θ (°)
Pt	2.27	39.7	1.96	46.3
$CoPt_3$	2.22	40.6	1.93	47.1
CoPt	2.17	41.6	1.90	47.8

strongest peaks but one (see Table 3). So, it cannot be determined whether it is a real alloy of $CoPt_3$ or a mixture of metal Pt and a solid solution of Co–Pt.

It is well known that a sharp peak is obtained by heat-treatment of the XRD specimen. But there still remains a dispersed peak after treating the PVP–Pt/Co (3:1) at 573 K for 4 h under ultra-pure nitrogen (PVP began to decompose at 623 K under nitrogen according to our thermal analysis measurement). This may be ascribed to the limitation of the heat-treatment under the lower temperature and shorter time. On the other hand, considering that the diffraction peaks

Fig. 1. Electron micrographs (left) and the corresponding particle size distribution histograms (right) of the PVP-protected bimetallic and monometallic dispersions (a) Pt; (b) Pt/Co (3:1); (c) Pt/Co (1:1); (d) Co; (e) electron diffractogram of the Co particles.

Table 4
Catalytic properties of different catalysts [a]

Catalyst	Selectivity (%)	Conversion (%)	Average rate (mol 1/mol metal h)
PVP–Pt	70.5	30.5	36.1
Co	80.0	24.8	29.4
PVP–Pt+Co [b]	73.0	28.6	33.9
PVP–Pt/Co (1:1)	99.0	40.8	48.3
PVP–Pt/Co (1:1)+ PVP–Pt [b]	80.2	34.2	40.5
PVP–Pt/Co (3:1)	99.8	92.8	114.0

[a] Reaction conditions: EtOH 50 ml, H_2O 10 ml, NaOH 1 mg, 1 2.00 g, tetradecanol 2.00 g, metal (Pt or Co or Pt + Co) 2.57×10^{-2} mmol, H_2 4.0 MPa, temperature 333 K, time 5 h.
[b] + meant a simple mixture of the two dispersions, and the molar ratio of Pt/Co was maintained 3:1.

are very near, it can be estimated that they could not be separated well enough even after treating the specimen at higher temperature for a longer time.

However, the results of TEM gave different average diameters and size distributions of PVP–Pt/Co (3:1) and PVP–Pt/Co (1:1): 1.7 nm ($\sigma = 0.33$ nm) and 2.2 nm ($\sigma = 0.42$ nm), respectively. This may be reflected by the different compositions and structures of PVP–Pt/Co (3:1) and PVP–Pt/Co (1:1) [3,4,6].

From the above, it is impossible to verify if the PVP–Pt/Co (3:1) obtained is a real $CoPt_3$ phase or a mixture of Pt with a solid solution of Co–Pt by the XRD measurement. Thus, we turned to the chemical study of the colloids.

3.1.3. Catalytic properties

Table 4 lists the activities and selectivities of different colloidal catalysts. It can be observed from Table 4 that different catalysts exhibited different catalytic properties in selective hydrogenation of 1 to 2. First, the PVP–Pt, the Co particles and their mechanical mixtures exhibited inferior selectivities and activities. This meant that the PVP-protected Pt/Co colloids (3:1 and 1:1) formed alloy structures not the physical mixtures of metal Pt with Co (the single metal Co phase was not found by XRD). Second, although high selectivity was obtained,

the PVP–Pt/Co (1:1) only displayed about 40% activity compared to the PVP–Pt/Co (3:1). Moreover, when a physical mixture of PVP–Pt/Co (1:1) and PVP–Pt was used as a catalyst, it showed quite a lower selectivity or activity. So, it is sure that the PVP–Pt/Co (3:1) is not a mixture of metal Pt and a solid solution of Co–Pt.

From the above results (XRD determination, TEM measurement and the study of catalytic behavior), a conclusion can be drawn that an alloy phase of $CoPt_3$ was definitely formed in the preparation of the PVP–Pt/Co (3:1).

3.2. Selective hydrogenation of 1 to 2

Hydrogenation of 1 can be schematically shown as follows:
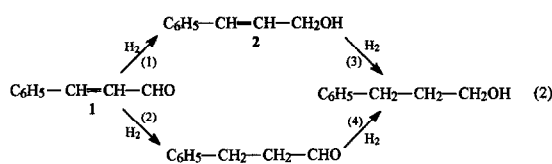
It has been found that H_2O and NaOH can affect the activity and selectivity of the PVP–Pt/Co (3:1) catalyst. The effects of the amounts of NaOH and H_2O were studied. The results are listed in Table 5.

Table 5
Optimization of reaction condition in the selective hydrogenation of 1 to 2 over the PVP–Pt/Co (3:1) [a]

NaOH (mg)	H_2O (ml)	EtOH (ml)	Selectivity (%)	Conversion (%)	Average rate (mol 1/mol metal h)
0	0	60	87.6	69.2	81.6
1	0	60	99.5	78.2	92.2
1	5	55	99.1	86.0	104.9
1	10	50	99.8	92.8	114.0
1	15	45	99.6	90.5	111.2
0	10	50	89.0	84.1	103.3
3	10	50	99.6	89.0	109.3
6	10	50	99.4	86.7	106.5

[a] Reaction conditions: 1 2.00 g, tetradecanol 2.00 g, metal (Pt + Co) 2.57×10^{-2} mmol, H_2 4.0 MPa, temperature 333 K, time 5 h.

The activity increased with the addition of a suitable amount of H_2O to the reaction system. Considered the results that the activity of the hydrogenation of 1 can be greatly affected by solvents [11], the influence of H_2O would be attributed to its high polarity. When adding more H_2O than the optimum amount, the solubility of 1 decreased and therefore reduced the activity. In addition to a higher activity, a considerable increase in the selectivity was obtained by adding a suitable amount of NaOH. Satagopan and Chandalia [12] have observed that with the incorporation of KOH in the reaction, the rate of the hydrogenation of 2 (reaction (3)) was markedly reduced and a very low conversion of 2 was found. Thus, the conclusion can be drawn that the high selectivity for 2 in the presence of KOH was due to the retardation of the olefinic hydrogenation of 2 to hydrocinnamyl alcohol. From Table 4, it is obvious that the optimum amounts of H_2O and NaOH are 10 ml and 1 mg, respectively. Under this condition, the PVP–Pt/Co (3:1) bimetallic colloid exhibited good activity and selectivity. The average activity was 114 mol/mol metal h and the selectivity was 99.8% at 96.2% conversion, which showed that the hydrogenation almost proceeded under reaction (1).

In the reaction, the yield of 2 reached its maximum (96%) in 5 h and did not change any more over another 5 h where the selectivity remained 99.8% (Fig. 3). This phenomenon was similar to that of the hydrogenation of 1 [13], furfuracrolein [22] and cital [23] over platinum oxide–platinum black in the presence of iron and zinc salts, where the hydrogenation reactions stopped automatically after one molecular equivalent of hydrogen had been absorbed.

Galvagno and coworkers [14] have reported that a larger size of particles favored the selectivity toward 2. The highest selectivity (61%) was obtained when the average diameter of supported Ru particles was 16.8 nm. But in this study, a much higher selectivity (99.8%) was obtained where the average diameter of the PVP–Pt/Co (3:1) bimetallic colloid particles
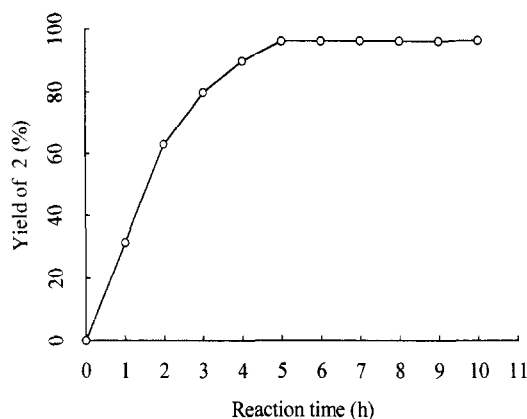

Fig. 3. Yield of 2 vs. reaction time (reaction condition: EtOH 50 ml, H_2O 10 ml, NaOH 1 mg, 1 4.00 g, tetradecanol 4.00 g, metal (Pt + Co) 2.57×10^{-2} mmol, H_2 4.0 MPa, temperature 333 K).

was only 1.7 nm. It means that considerably smaller metal colloid particles may exhibited very different catalytic properties from big metal particles in a supported catalyst.

Experiments indicated that the reaction was first-order to the pressure of H_2, the concentrations of 1 and the catalyst, respectively (see Fig. 4).

We found that the rate of hydrogenation changed little when varying the reaction temperature from 313 to 353 K. The reason is that the concentration of H_2 dissolved in solvent decreased when the temperature increased. This partly countervailed the effect of increasing temperature as described in the literature [24].

Further research showed that there was not any change in the PVP–Pt/Co (3:1) colloid after the reaction. X-Ray diffraction pattern of the used PVP–Pt/Co (3:1) colloid was the same as Fig. 2, which inferred that its size remained as before and the colloid was not oxidized. Moreover, under nitrogen, when adding a known amount of Co^{II} ions into the used colloidal dispersion, more than 98% of the added Co^{II} ions can be separated out by super-filtrating, but no Co^{II} ions can be found in the filter liquor if there is only the PVP–Pt/Co (3:1) colloid. However, when the PVP–Pt/Co (3:1) colloid was exposed in the air, the component Co^0 was oxidized quickly into Co^{II} no matter if it was
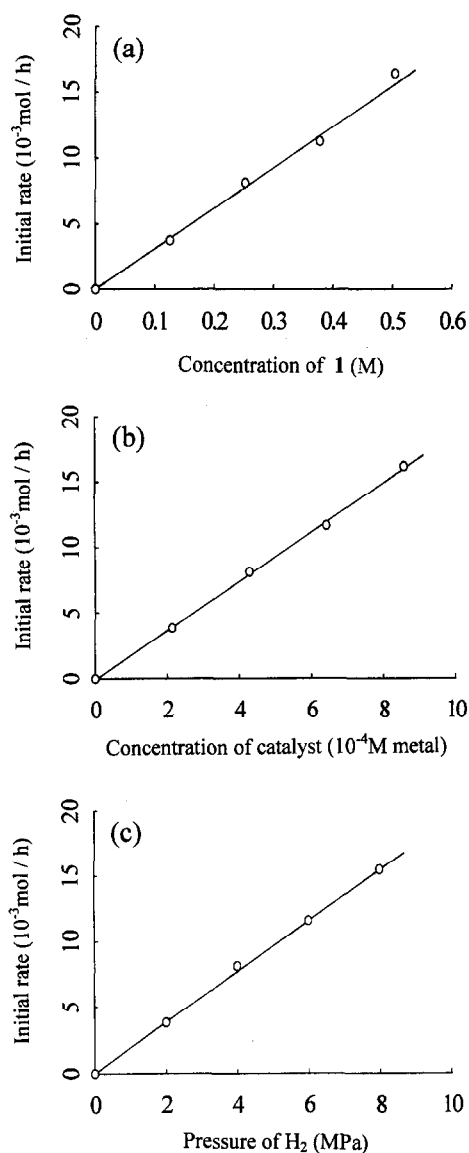
Fig. 4. First-order rate plots (reaction condition: EtOH 50 ml, H_2O 10 ml, NaOH 1 mg) (a) concentration of **1**; (b) concentration of catalyst; (c) pressure of H_2.

used or not, at that time all of the Co^{II} in the dispersion can be separated by super-filtrating (> 99%). This illustrated that cobalt remained Co^0 in the alloy Pt/Co (3:1) after the reaction.

4. Conclusion

This paper described the preparation of PVP-protected Pt/Co bimetallic colloids with Pt/Co having a molar ratio of 3:1 and 1:1, and the catalytic properties of PVP–Pt/Co (3:1).

(1) The bimetallic colloids composed the light transition metal Co and the noble metal Pt, can be prepared by the polyol reduction process.

(2) The Pt/Co bimetallic colloid exhibited good activity and selectivity for the selective hydrogenation of **1** to **2**. By using the PVP–Pt/Co (3:1) bimetallic catalyst, a 99.8% selectivity toward **2** was obtained in the hydrogenation of **1** at 96.2% conversion.

(3) The Pt/Co bimetallic alloy colloid was stable enough to sustain the hydrogenation reaction at 333 K and 4.0 MPa. This differs from the view that colloids are unstable in catalytic reactions especially at elevated temperature and pressure [1,6,25].

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