

Selective hydrogenation of α,β -unsaturated aldehyde to α,β -unsaturated alcohol over polymer-stabilized platinum colloid and the promotion effect of metal cations

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Abstract

The modification of some metal cations to polymer-stabilized platinum colloid leads to remarkable increases in both the activity and the selectivity in liquid-phase selective hydrogenation of cinnamaldehyde to cinnamyl alcohol and of crotonaldehyde to crotyl alcohol. The promotion effect was due to the interaction of metal cations and the C=O groups in reactants. The adsorbed metal cations activated the C=O double bonds to accelerate the reaction rate and to increase the selectivity to α,β -unsaturated alcohols. The steric hindrance also played an important role in the reaction. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Selective hydrogenation; Cinnamaldehyde; Crotonaldehyde; Pt colloid; Metal cation

1. Introduction

The selective hydrogenation of α,β -unsaturated aldehyde to the corresponding α,β -unsaturated alcohol is an important step in the preparation of fine chemicals. It is a difficult work to hydrogenate the carbonyl group while reserve the conjugated olefinic function, since saturated aldehydes are the major primary products of reduction over most conventional catalysts [1].

Recently, researchers have paid much attention to materials with nanoscale dimensions for

their peculiar physical and chemical properties [2–6]. In the field of catalysis, metal colloids or nanoclusters, being looked as bridges between metal atoms and bulk metals, are expected to show novel catalytic performances [7]. Some researchers have reported the singular properties of nanoscale monometallic and bimetallic colloids in the hydrogenation of monoenes or dienes [8–12], the hydration of acrylonitrile [13], the light-induced evolution of hydrogen [14], and the hydroformylation of propylene [15] as well as the carbonylation of methanol [16,17]. So, using nanoscale metal colloids as catalysts to realize the above-mentioned research task may give some particular advantages.

Although the hydrogenation of α,β -unsaturated aldehyde on promoted platinum-based

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catalysts is a well documented field from the pioneering works of Carothers and Adams [18,19], Tuley and Adams [20], and Adams and Garvey [21], and recently reviewed in detail about the role of promoter by Ponc [22], very few papers have reported the influence of additives, especially the cations, to the homogeneous dispersion of metal colloidal catalysts for the reason of the instability of the system [23,24]. In a previous paper [23], we described that in the selective hydrogenation of cinnamaldehyde (3-phenyl-2-propenal, **1**) to cinnamyl alcohol (3-phenyl-2-propen-1-ol, **2**) catalyzed by the polymer-stabilized platinum colloid, considerable increases in both the selectivity and the activity were observed when employing some metal cations (Fe^{2+} , Co^{2+} , Ni^{2+} , etc.) as modifiers. Now, we report the further results on this modification effect as well as the modification of metal cations to platinum colloid in the selective hydrogenation of crotonaldehyde (2-butenal, **3**) to crotyl alcohol (2-buten-1-ol, **4**).

2. Experimental

2.1. Materials and instruments

Poly(*N*-vinyl-2-pyrrolidone) (PVP) (average molecular weight 40,000) was supplied by BASF. Other reagents were purchased from Beijing Chemicals and had a level of analytical grade. **1** and **3** were redistilled under reduced pressure before 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 histogram was obtained on the basis of the mea-

surements of about 300 particles. IR absorption spectra were recorded by placing the methanol solutions in two CaF_2 crystal sheets on a Bruker 130 FT-IR spectrometer and subtracting the background. UV-vis absorption spectra were made by a Shang-Fen 721 spectrometer. The hydrogenation products were analyzed by a Bei-Fen SQ-204 gas chromatograph using a 2 m PEG-20 M column.

2.2. Hydrogenation reaction

Polymer-stabilized platinum colloid (PVP-Pt) was prepared by a reported method [25] in the form of dark-brown homogeneous dispersions.

Hydrogenation of **1** was carried out in a 100 ml stainless steel autoclave. The reaction solution contained 40 ml EtOH, 1 mg NaOH and 1.00 g **1** (7.576×10^{-3} mol), 1.00 g tetradecanol (as an internal standard for gas chromatography), 20 ml PVP-Pt dispersion {containing Pt (2.249×10^{-5} mol), PVP [1.125×10^{-3} mol (monomeric unit)], 10 ml H_2O and 10 ml EtOH} and metal salt added. H_2 was charged several times to replace air and the final pressure of H_2 was 4.0 MPa. The hydrogenation reaction was performed at 333 K for 1.5 h. The reaction products were periodically analyzed by gas chromatography.

Hydrogenation of **3** was similar to that of **1**. The optimized reaction condition was: 20 ml EtOH, 10 ml H_2O , 3 mg NaOH and 1.00 g **3** (1.428×10^{-2} mol), 0.20 g isobutanol (as an internal standard for gas chromatography), 2.249×10^{-5} mol PVP-Pt (containing PVP 1.125×10^{-3} mol). The reaction time was 3 h and the others were the same as above.

3. Results and discussion

3.1. Characterization of PVP-Pt colloid

TEM is a useful method to give the information about the size and size distribution of col-

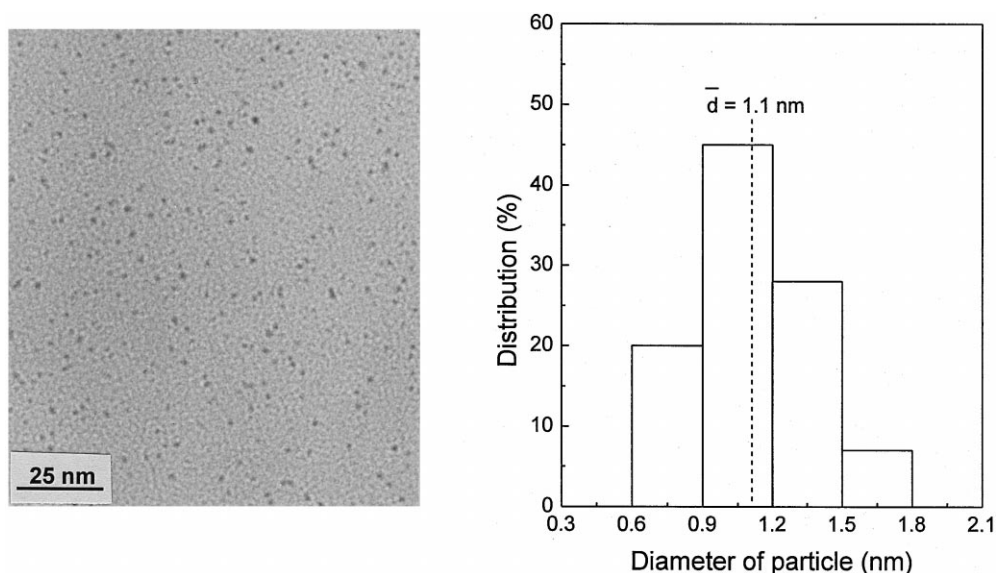


Fig. 1. Electromicroscopic photograph (left) and the corresponding particle size histogram (right) of PVP-Pt colloid.

loidal dispersions. The TEM photograph and the corresponding particle size distribution histogram of the platinum colloid are shown in Fig. 1. It can be seen from Fig. 1 that the average diameter of PVP-Pt colloid was 1.1 nm and the size distribution was narrow within the range of 0.6–1.8 nm with $\sigma = 0.30$ nm.

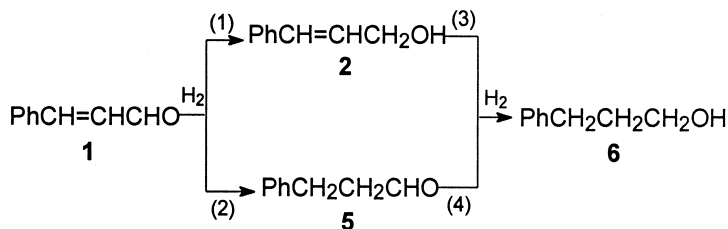
3.2. Selective hydrogenation of **1** to **2**

It is very easy for ordinary heterogeneous and homogeneous catalysts to reduce the C=C double bond to yield hydrogenated cinnamaldehyde (3-phenylpropanal, **5**) as the main product [Scheme 1, reaction (2)]; however, it is comparatively difficult for them to reduce the C=O

double bond only to get **2** with high selectivity at high conversion of **1** [Scheme 1, reaction (1)] [1].

Under the reaction conditions described above, 37.5% conversion of **1** with 12.0% selectivity for **2** was obtained when the neat PVP-Pt colloid was employed alone as a catalyst; nonetheless, the activity was enhanced to 120% (conversion of **1** reached 83%) and the selectivity for **2** increased to 98.5% when Fe^{3+} or Co^{2+} was introduced into the catalytic system (Table 1).

It has been verified that non-strongly coordinating anions, such as Cl^- , SO_4^{2-} , NO_3^- , OAc^- , etc. acted merely as spectator ions [23]. From Table 1, it can be seen that Li^+ , Na^+ and K^+



Scheme 1.

Table 1
Hydrogenation of **1** over PVP–Pt–MCl_x systems^a

Catalytic system	Average rate (mol 1 /mol Pt h)	Conversion of 1 (%)	Selectivity (%)		
			2	5	6
PVP–Pt	84.2	37.5	12.0	80.0	8.0
PVP–Pt–LiCl	57.9	25.8	15.7	75.0	9.3
PVP–Pt–NaCl	85.9	38.3	14.1	74.9	11.0
PVP–Pt–KCl	83.1	37.0	13.8	78.2	8.0
PVP–Pt–MgCl ₂	81.7	36.4	33.8	55.2	11.0
PVP–Pt–CaCl ₂	70.3	31.3	30.5	59.5	10.0
PVP–Pt–Ba(NO ₃) ₂	88.7	39.5	28.1	57.4	14.5
PVP–Pt–MnCl ₂	75.7	33.7	57.6	31.7	10.7
PVP–Pt–CuCl ₂	0	0	–	–	–
PVP–Pt–ZnCl ₂	29.2	13.0	99.8	0.2	0
PVP–Pt–Pb(NO ₃) ₂	0	0	–	–	–
PVP–Pt–FeCl ₃	187.5	83.5	98.5	1.5	0
PVP–Pt–FeSO ₄	185.3	82.5	98.5	1.5	0
PVP–Pt–CoCl ₂	186.2	82.9	98.8	1.2	0
PVP–Pt–NiCl ₂	115.7	51.5	34.4	50.6	15.0
PVP–Pt–CeCl ₃	69.2	30.8	30.7	54.3	15.0
PVP–Pt–Nd(NO ₃) ₃	78.6	35.0	25.7	62.1	12.2
PVP–Pt–AlCl ₃	68.5	30.5	34.3	58.2	17.5

^aMolar ratio of M:Pt = 1:1. Reaction condition: 40 ml EtOH, 1 mg NaOH, 1.00 g **1** (7.576×10^{-3} mol), 1.00 g tetradecanol (as an internal standard for gas chromatography), 20 ml PVP–Pt colloidal dispersion (containing Pt (2.249×10^{-5} mol), PVP [1.125×10^{-3} mol (monomeric unit)], 10 ml H₂O and 10 ml EtOH) and metal salt added. 4.0 MPa H₂, 333 K and 1.5 h.

did not affect the catalytic properties of PVP–Pt. Mg²⁺, Ca²⁺, Ba²⁺ and Mn²⁺ influenced little on the selectivity and activity. Ce³⁺, Nd³⁺ and Al³⁺ also acted as spectators. To the other metal cations, Fe³⁺, Fe²⁺ and Co²⁺ remarkably enhanced both the selectivity and the activity, whereas Ni²⁺ exerted a moderate effect. It is well known that Cu²⁺, Pb²⁺ or Zn²⁺ usually acted as poisons to catalysts. Here, they indeed toxicated the activity of PVP–Pt catalyst (conversions of **1** were 0, 0 and 13.0% to Cu²⁺, Pb²⁺ and Zn²⁺, respectively, but the selectivity was 99.8% when Zn²⁺ was added).

Maxted [26,27] have summarized a systematic survey of the toxicity of metal ions towards a platinum catalyst in the hydrogenation of cinnamic acid which indicated that the toxic metal ions were those in which all five orbitals of a *d* shell, immediately preceding *s* or *p* valency orbitals are occupied by electron pairs or at least by single *d* electrons, because they may form the adsorption complex which in some respect may be regarded as an intermetallic compound.

Thus, Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Ba²⁺, Ce³⁺, Nd³⁺, Al³⁺ are nontoxic and Mn²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Fe³⁺, Fe²⁺, Co²⁺, Ni²⁺ are toxic. This is obviously not a satisfactory explanation to the results listed in Table 1.

In 1920s, Carothers and Adams [18,19], Tuley and Adams [20], and Adams and Garvey [21] have extensively studied the effects of various substrates, especially metal ions of Fe²⁺, Co²⁺ and Zn²⁺, on the platinum oxide–platinum black catalyst of the reduction of aldehydes. But in their experiments, oxygen was absolutely necessary for the activity of the catalyst—the pure platinum oxide–platinum black catalysts needed several times of reactivation to finish the reaction by shaking with air. So they concluded that aldehydes, being readily oxidizable substances, robbed the catalyst of its oxygen and made it inactive when added to the mixture of aldehydes and active platinum catalysts, FeCl₂ acted as a powerful anti-oxidizer toward the oxidation of the aldehydes. The oxygen in the platinum catalyst thus only very slowly re-

moved and the catalyst, therefore, remains active toward the reduction of the aldehydes [18]. They [19] have also put forward another possible reason for the promotion effect of metal ions: the function of the promoter was in some way to cause a desorption of the aldehyde and so permitted a renewal of the platinum surface. This may perhaps be performed through the formation of a salt or complex between promoter and adsorbed aldehyde which subsequently dissociate in solution.

Richard et al. [28] and Goupil et al. [29] investigated the promotion effect of $\text{Fe}(\text{NO}_3)_3$ and FeCl_2 in the selective of **1** to **2** over the active charcoal-supported platinum catalysts, respectively. It should be noted that the method to prepare the catalyst by Richard et al. was the same as preparation a conventional bimetallic catalyst: soaking the active charcoal in a solution of $\text{Fe}(\text{NO}_3)_3$ and H_2PtCl_6 , then reduction at 673 K by H_2 . The second component (metallic or ionic state) diffused in the main metal lattice and therefore usually induced changes in the size, shape and structure of the catalyst particles. So the complicity of the comparison of modified and unmodified metal catalyst raised.

The addition of metal cations in this paper is after the formation of the colloidal platinum catalyst, so the possibility of change in the size, shape and structure of the platinum colloidal particles is scarce. Although the procedure used by Goupil et al. is the same as ours—adding FeCl_2 after the preparation of catalyst, Pt/C, the iron in both of these two works [Refs. [28,29]] were zero oxide state determined by energy dispersive X-ray emission by pretreatment (H_2 reduction) in the preparation of catalyst or before the addition of the reactant. So it is easily understandable that there should be a most suitable amount of iron salt in the catalyst system, where, the selectivity and the activity will reach their maxima. Surely, in these two works, when the molar percent of $\text{Fe}/(\text{Fe} + \text{Pt})$ was about 0.2, the activity reached its maximum as well as the selectivity. More or less of the existence of iron salt (in atom state) will de-

crease the selectivity and the activity. The curves of the activity and selectivity vs. molar percentage of atomic iron in the catalyst system displayed volcanic shapes (the works of Carothers and Adams [18,19], Tuley and Adams [20], and Adams and Garvey [21] also showed that there should be a optimum content of salts).

However, as stated in the previous paper [23], the change of molar percentage of Co^{2+} in the PVP–Pt colloid does not influence the activity and selectivity in a similar way as literature reported [18–21,28,29]. The addition of a very small amount of Co^{2+} ($\text{Co}^{2+}:\text{Pt} = 0.05:1$) made the activity and the selectivity increased promptly to the very high values and more amount of Co^{2+} does not decrease them. Surely, Cu^{2+} and Pb^{2+} are reduced to atom state under the reaction conditions, which covered the surface of platinum nanoparticles therefore completely suppressed the activity of PVP–Pt. But what about Co^{2+} , Fe^{3+} , Fe^{2+} and Ni^{2+} , etc.?

We calculated the redox potential of H_2 and Co^{2+} under the reaction conditions ($P_{\text{H}_2} = 4.0$ MPa, $T = 333$ K). It presents that when adding Co^{2+} up to 20 times of Pt, the reduced Co is just 0.575:1 to Pt. The reason why no more Co^{2+} was reduced is that there would be a large amount of H^+ released which prevented from the further reduction of Co^{2+} to Co^0 . From this calculation, a conclusion might be drawn that no more Co^{2+} was reduced to cobalt atom therefore more Co^{2+} did not affect the activity and the selectivity of PVP–Pt. However, it can be seen from the literature [23] that when the molar ratio of $\text{Co}^{2+}:\text{Pt}$ reached 0.1:1, the conversion and selectivity were as high as 79.6% and 92.8%, respectively. Moreover, under the reaction condition (hydrogen atmosphere), the Co^{2+} in the used colloidal dispersion can be quantitatively separated out by super-filtration, and the amount of the reduced Co^{2+} was under the detectable level. So the experiment verified that cobalt existed in +2 oxide state.

The redox potential of Fe^{3+} and Fe^{2+} was also calculated [30]. The results indicated that all the Fe^{3+} can be reduced to Fe^{2+} but can not

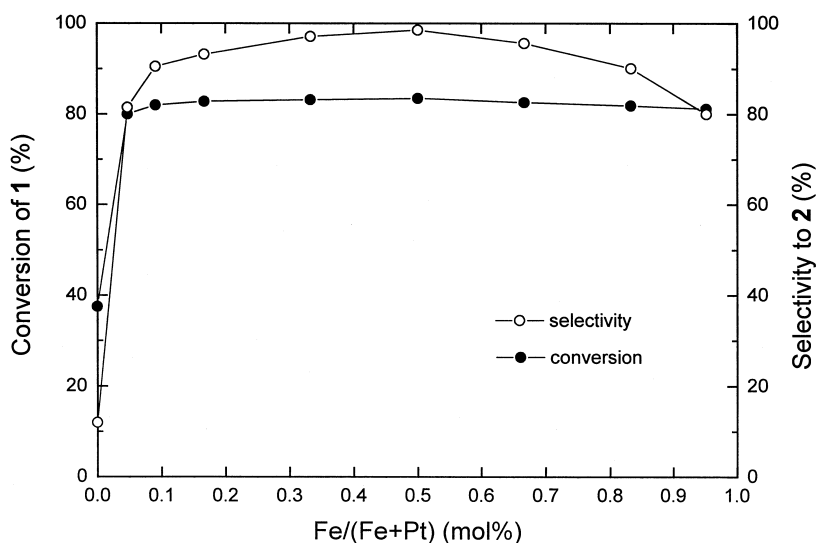


Fig. 2. Conversion of **1** and selectivity to **2** vs. molar percentage of FeCl_3 in the PVP–Pt catalytic system (reaction condition: 40 ml EtOH, 1 mg NaOH, 1.00 g **1** (7.576×10^{-3} mol), 1.00 g tetradecanol (as an internal standard for gas chromatography), 20 ml PVP–Pt colloidal dispersion [containing Pt (2.249×10^{-5} mol), PVP [1.125×10^{-3} mol (monomeric unit)], 10 ml H_2O and 10 ml EtOH] and Fe^{3+} ; 4.0 MPa H_2 , 333 K and 1.5 h).

be reduced further to Fe atom, because the released H^+ inhibited the reduction of Fe^{2+} to Fe^0 . The result of adding FeCl_3 is the same as FeSO_4 is consistent with this calculation. It was found that when adding $\text{K}_3\text{Fe}(\text{CN})_6$ to the PVP–Pt– FeCl_3 system after reaction, a blue deposit was observed which indicated the quantity existence of Fe^{2+} . Fig. 2 shows a similar curve as Co^{2+} reported in the literature [23]. The small decrease of selectivity to **2** at the molar ratio of FeCl_3 :Pt > 1:1 was due to the released H^+ (this will be discussed more detailed in the following text). Both of these two figures indicated that this modification of metal cations to nanoscale platinum colloid is much different from the previous results [18–21,28,29] and this modification can not be explained by the results of conventional redox potential calculation.

It has been found that in the hydrogenation of cyclooctene, the addition of metal cations could stop the reaction (Table 2). In another word, the hydrogenation of olefinic group was completely suppressed by Co^{2+} and Ni^{2+} . This indicated that Co^{2+} , etc. can suppress the hydrogenation

of olefinic group but accelerate the hydrogenation of carbonyl group at the same time.

Ponec [22] has reviewed in detail about the role of the promoter, especially the metal ions. Many types of promotion mechanism were summarized, but most of them can not give a reasonable interpretation about our experiment facts. (1) The cations in the reaction system remained as ionic state (except for Cu^{2+} , Pb^{2+}). (2) There was no support for this catalyst. PVP may be regarded as a kind of support for platinum colloidal particles, but the interaction of cations to it is very weak (see below). (3) The possibility of change in the size and the mor-

Table 2
Hydrogenation of cyclooctene over PVP–Pt catalyst^a

Catalytic system	Initial rate (mol H_2 / mol Pt s)	Average rate (mol H_2 / mol Pt s)
PVP–Pt	0.081	0.046
PVP–Pt– CoCl_2	0	0
PVP–Pt– NiCl_2	0	0

^aReaction condition: PVP–Pt 2.0 ml (containing Pt 4.68×10^{-6} mol, MeOH), cyclooctene 2.0 ml (0.5 M, MeOH), CoCl_2 or NiCl_2 (4.68×10^{-6} mol, MeOH), 1 atm H_2 and 303 K (the whole volume was 15.0 ml, MeOH).

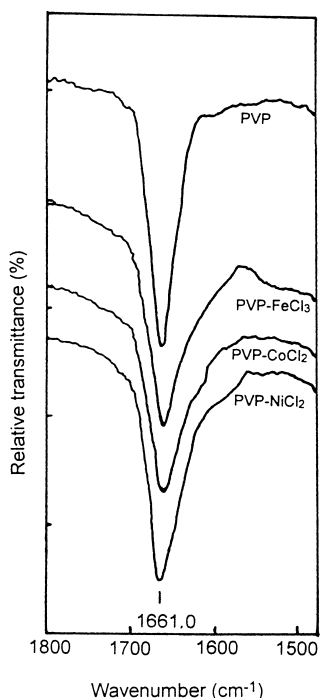


Fig. 3. IR spectra of PVP and PVP-MCl_x in MeOH (298 K, 0.25 M).

phology of the colloidal catalyst particles is scarce, however, there may still be some changes but could not be observed accurately by conventional means.

According to our experiment results, the authors inclined to the ‘chemical’ promotion mechanism: the chemical bonding between the reactant and the metal cation.

In our system, besides the solvents of EtOH and H₂O, there are four components: stabilizer, PVP; reactant, **1**; catalyst, platinum nanocluster and metal salts. For the purpose of investigating the mechanism of the modification, we studied the interactions of metal cations with PVP and **1**, respectively.

IR is a convenient method to detect the interaction of two species. The IR spectra of PVP-metal cations showed very weak interaction of them: the peak of C=O double bond in PVP was a little asymmetric when adding Fe³⁺, Co²⁺ and Ni²⁺ (Fig. 3). This is consistent with the study of the UV-vis spectra of them. According to the method of Miller and Dorough [31], we tried to obtain the coordination constants of PVP-Fe³⁺, PVP-Co²⁺ and PVP-Ni²⁺. The absorbance curve of PVP, Co²⁺ and PVP-Co²⁺ in EtOH and H₂O are shown in Figs. 4 and 5, respectively.

Figs. 4 and 5 indicated that (1) there are interaction (coordination) of PVP and metal cations; (2) the coordination is very weak; (3)

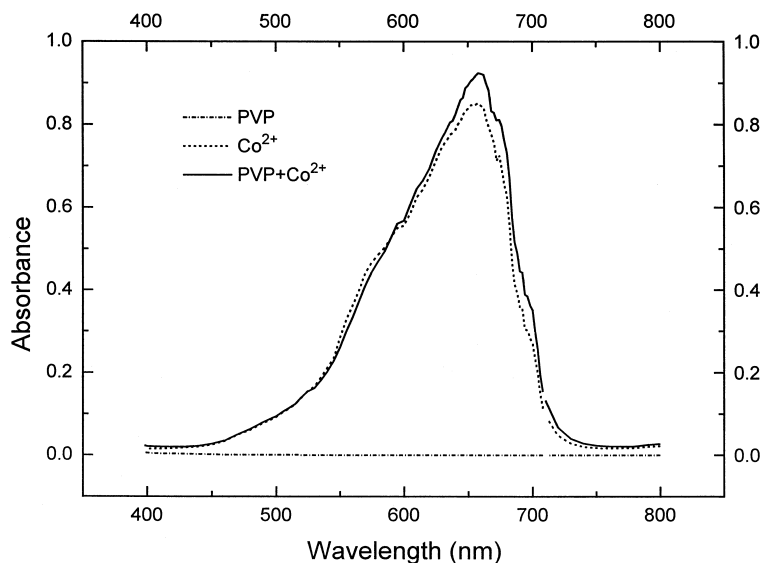


Fig. 4. UV-vis absorption of PVP, Co²⁺ and PVP-Co²⁺ in absolute EtOH (287 K, 4 × 10⁻³ M).

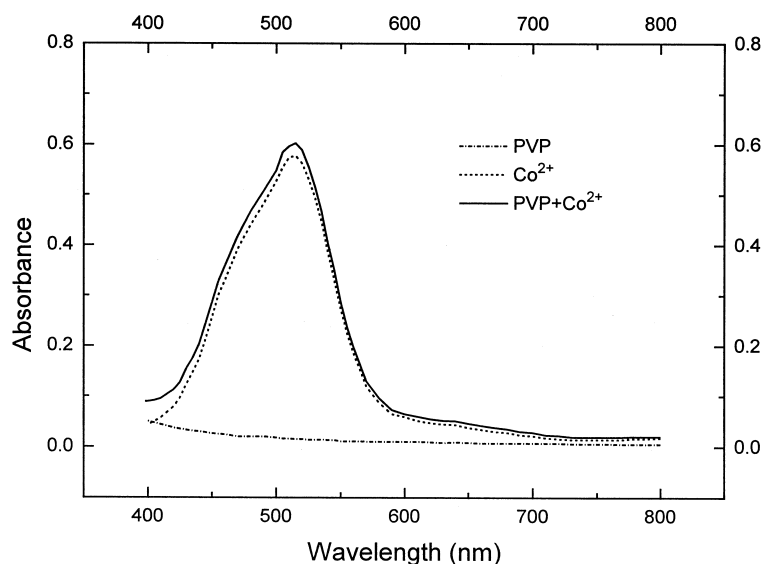


Fig. 5. UV-vis absorption of PVP, Co^{2+} and PVP- Co^{2+} in H_2O (287 K, 4×10^{-3} M).

the existence of water further reduces the coordination of PVP to metal cations for the formation of hydrate metal cations. The molar absorption coefficients (ϵ_{max}) of metal cations and PVP-metal cations were calculated as Table 3. However, it is difficult to accurately determine the coordination constants of PVP-metal cations for so weak a coordination. According to the method of Miller and Dorough, we calculated the coordination constants roughly: the coordination constant of PVP- Fe^{3+} is estimated as 0.2–10. Those of PVP- Co^{2+} and PVP- Ni^{2+} are lower than 10^{-2} and 10^{-3} , respectively.

Bright et al. [32] have prepared a $[\text{Ni}(\text{NMV})_6](\text{ClO}_4)_2$ compound (NMP = *N*-methylpyrrolidone). It was a ‘poorly defined’ light-yellow crystal and could only be stored in a desiccator.

The ϵ_{max} of it in NMP was 6.81, which is at the same quantity level as that of PVP- Ni^{2+} . Wuepper and Popov [33] have found that there was a little shift of C=O double bond in NMP when adding basic metal cations to NMP. Both

Table 3

Molar absorption coefficients of metal cations and PVP-metal cations in absolute EtOH at 287 K

System	Wavelength (nm)	ϵ_{max} (l/cm mol)
Fe^{3+}	386.5	3023.3
PVP- Fe^{3+}	386.5	2336.7
Co^{2+}	659.0	112.5
PVP- Co^{2+}	659.0	141.7
Ni^{2+}	406.0	7.2
PVP- Ni^{2+}	406.0	8.4

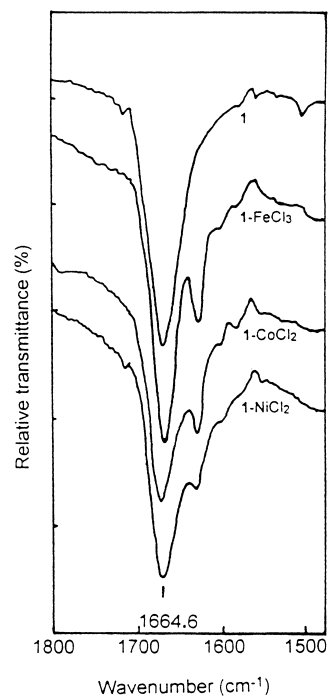


Fig. 6. IR spectra of **1** and **1**- MCl_x in MeOH (298 K, 0.25 M).

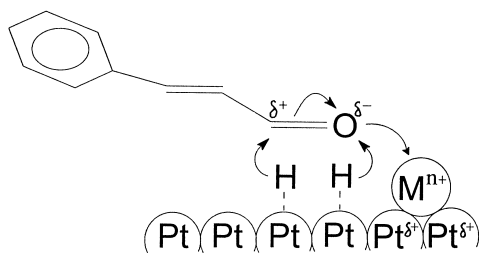


Fig. 7. Mechanism of the modification of metal cations to Pt colloid (M = Fe, Co, Ni, etc.).

of the above research results verified the interaction of PVP and metal cations. However, the interaction is so weak that it can not play an important role in the reaction process.

On the other hand, IR spectra of **1** and metal cations gave positive results. From Fig. 6, It can be seen that a small peak appeared when adding Fe^{3+} , Co^{2+} or Ni^{2+} to the solution of **1**. This strongly demonstrated the interaction of C=O double bond in **1** with metal cations. The activation of the C=O double bond with metal cations over ‘polarization’ effect has been proposed by some researchers [22,34–38], but they did not give a conclusive evidence. Based on the previous works and our experiment result (IR spectra), we put forward a similar model to explain the modification mechanism (Fig. 7).

The adsorbed metal cations activated the polar C=O group, then the nearby dissociated H atoms attacked the C and O atom of C=O group to give a hydroxyl group. This model also

Table 5
Hydrogenation of cyclooctene over PVP–Pt catalyst^a

Catalytic system	Initial rate (mol H ₂ /mol Pt s)	Average rate (mol H ₂ /mol Pt s)
PVP–Pt	0.081	0.046
PVP–Pt–NaOH (0.2 mg)	0.076	0.034
PVP–Pt–NaOH (1.0 mg)	0.025	0.010

^aReaction condition: PVP–Pt 2.0 ml (containing Pt 4.68×10^{-6} mol, MeOH), cyclooctene 2.0 ml (0.5 M, MeOH), 1 atm H₂ and 303 K (the whole volume was 15.0 ml, MeOH).

emphasizes the steric effect to the high selectivity. Traditionally, the beneficial effect of metal ions (especially in the metallic state) has been attributed to an electron transfer from them to platinum [39]. Here, another possibility could be suspected that the electron transferred from platinum to the adsorbed metal cation, which enhanced the adsorbing ability of C=O double bond onto the platinum surface and therefore increased the reactivity and the selectivity.

The above-mentioned reaction condition was optimized. It has been found that H₂O and NaOH can affect the activity and selectivity of the PVP–Pt–MCl_x catalytic system. The effects of the amounts of H₂O and NaOH were studied. The results are listed in Table 4.

The activity increased with the addition of H₂O to the reaction system. Chen et al. [40] have noticed that the activity of the hydrogenation of **1** can be greatly affected by solvents, so

Table 4
Optimization of reaction condition in the selective hydrogenation of **1** to **2** over the PVP–Pt–CoCl₂^a

NaOH (mg)	H ₂ O (ml)	EtOH (ml)	Selectivity to 2 (%)	Conversion of 1 (%)	Average rate (mol 1 /mol metal h)
0	0	60	84.2	60.7	136.3
1	0	60	93.3	73.9	166.0
1	5	55	98.0	78.4	176.1
1	10	50	98.8	82.9	186.2
1	15	45	98.8	80.1	179.9
0	10	50	85.2	71.5	160.6
2	10	50	98.5	80.2	180.1
5	10	50	98.1	76.7	172.3

^aMolar ratio of Co^{2+} :Pt = 1:1. Reaction condition: 40 ml EtOH, 1 mg NaOH, 1.00 g **1** (7.576×10^{-3} mol), 1.00 g tetradecanol (as an internal standard for gas chromatography), 20 ml PVP–Pt colloidal dispersion {containing Pt (2.249×10^{-5} mol), PVP [1.125×10^{-3} mol (monomeric unit)], 10 ml H₂O and 10 ml EtOH} and metal salt added. 4.0 MPa H₂, 333 K and 1.5 h.

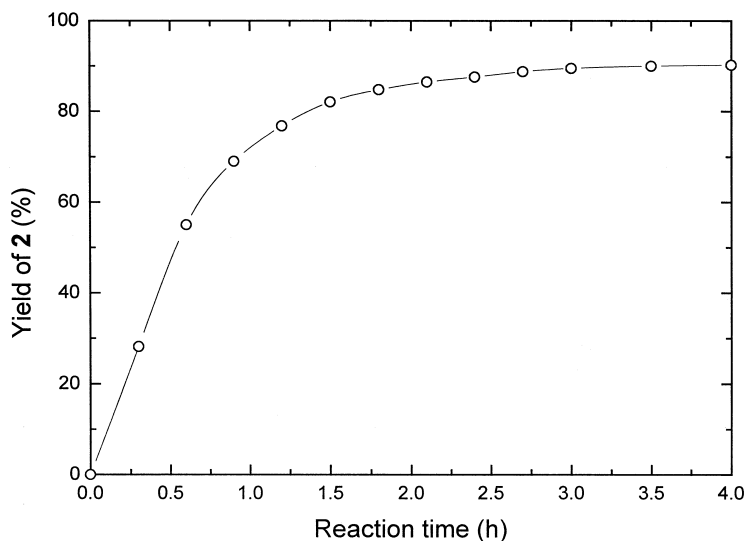
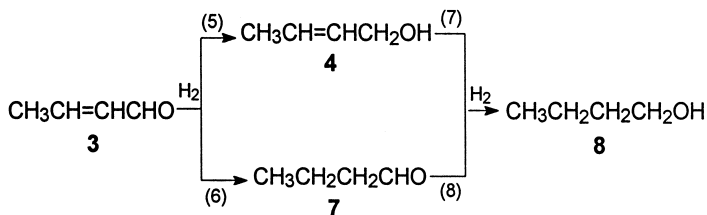


Fig. 8. Yield of **2** vs. reaction time (reaction condition: 40 ml EtOH, 1 mg NaOH, 1.00 g **1** (7.576×10^{-3} mol), 1.00 g tetradecanol (as an internal standard for gas chromatography), 20 ml PVP–Pt colloidal dispersion {containing Pt (2.249×10^{-5} mol), PVP [1.125×10^{-3} mol (monomeric unit)], 10 ml H₂O and 10 ml EtOH} and 2.249×10^{-5} mol Co²⁺; 4.0 MPa H₂, 333 K).

the influence of H₂O would be ascribed to its high polarity. When adding more H₂O than the optimum amount, the solubility of **1** decreased and therefore the activity reduced. A higher activity and a considerable increase in selectivity were achieved by incorporating a suitable amount of NaOH. It has been found that the rate of the hydrogenation of **2** (reaction (3)) was markedly reduced and a very low conversion of **2** was obtained with the addition of KOH in the reaction [41]. Thus, a conclusion can be drawn that the high selectivity to **2** in the presence of NaOH was due to the suppression of the hydrogenation of C = C double bond. This was also evidenced in the hydrogenation of cyclooctene. When adding 0.2 mg and 1.0 mg NaOH into the

PVP–Pt catalytic system, the initial rate of the hydrogenation of cyclooctene decreased from 0.081 to 0.076 and 0.025 mol H₂/mol Pt s and so did the average rate (Table 5). From Table 4, it is obvious that the optimum amounts of H₂O and NaOH are 10 ml and 1 mg, respectively.

In the reaction, the yield of **2** could reach 84% in 2 h and changed little over another 2 h where the selectivity remained 99.7% (Fig. 8). This phenomenon was similar to that of the hydrogenation of **1** [20], furfural [21] and citral [42] over platinum oxide–platinum black in the presence of both iron and zinc salts, where the hydrogenation reactions stopped automatically after one molecular equivalent of hydrogen had been absorbed.



Scheme 2.

Table 6
Optimization of reaction condition in the selective hydrogenation of **3** to **4** over the PVP–Pt catalyst modified by metal cations^a

Catalytic system ^b	NaOH (mg)	EtOH (ml)	H ₂ O (ml)	Average rate (mol 3 /mol Pt h)	Conversion of 3 (%)	Selectivity (%)			Yield of 4 (%)
						4	7	8	
PVP–Pt	1	30	0	127.4	60.2	10.2	85.3	4.5	6.14
PVP–Pt	1	25	5	135.2	63.9	13.1	80.7	6.2	8.37
PVP–Pt–Fe(1)	1	30	0	148.6	70.2	17.4	78.6	4.0	12.2
PVP–Pt–Fe(1)	1	25	5	150.9	71.3	31.1	54.2	14.7	22.3
PVP–Pt–Co(1)	1	30	0	147.1	69.5	18.6	73.4	8.0	12.9
PVP–Pt–Co(1)	1	25	5	149.6	70.7	16.8	74.3	8.9	11.9
PVP–Pt–Fe(1)–Zn(0.2)	1	25	5	129.7	61.3	37.4	54.6	8.0	22.9
PVP–Pt–Fe(1)–Zn(0.4)	1	25	5	88.7	41.9	39.4	51.6	9.0	16.5
PVP–Pt–Fe(1)–Zn(0.8)	1	25	5	0	0	–	–	–	0
PVP–Pt–Fe(1)	3	25	5	155.8	73.6	44.6	38.9	16.5	32.8
PVP–Pt–Fe(1)	3	20	10	149.2	70.5	48.9	33.1	18.0	34.5

^aReaction condition: 1.00 g **3** (1.428×10^{-2} mol), 0.20 g isobutanol (as an internal standard for gas chromatography), 2.249×10^{-5} mol PVP–Pt (containing PVP 1.125×10^{-3} mol) and metal salt added. 4.0 MPa H₂, 333 K and 3 h.

^bThe numbers in the brackets refer to the molar ratio of metal cations to Pt; Fe stands for FeCl₃ and Zn stands for ZnCl₂.

Experiments indicated that the reaction was first-order to the pressure of H_2 , the concentrations of **1** and the amount of the platinum colloid, respectively.

Our previous paper [23] has shown that the maximum selectivity (99.7%) was achieved using Co^{2+} as a modifier to the PVP–Pt system at a Co^{2+} :Pt molar ratio of 1:3 (conversion was 82.1%). It was found that our data can be arranged in the front rank among the references' results [20,37,38,40,41,43–56].

3.3. Selective hydrogenation of **3** to **4**

Similar to that of **1**, there are two competitive hydrogenation reaction starting from **3** (Scheme 2). To obtain **4** is a challenging task [Scheme 2, reaction (5)] for the same reason stated above.

By using metal cations to modify the PVP–Pt catalyzed reaction, 48.9% selectivity for **4** at 70.5% conversion of **3** can be obtained (Table 6).

It can be seen from Table 6 that the addition of Fe^{3+} and Co^{2+} can increase both the activity and selectivity. When adding Zn^{2+} in the PVP–Pt– $FeCl_3$ system, the activity decreased with a

slight increase in the selectivity. The more the amount of Zn^{2+} , the lower the activity and the higher the selectivity. This is similar to the known toxication effect. The amount of EtOH, H_2O and NaOH also affected the reaction (the reason is similar to those discussed in the hydrogenation of **1** to **2**). At the optimum condition (1:1 molar ratio of $FeCl_3$:Pt, 3 mg NaOH, 20 ml EtOH, 10 ml H_2O), we got 48.9% selectivity to **4** at 70.5% conversion of **3** (yield of **4** was 34.5%, which is above almost all the published results by catalytic hydrogenation [57–63] except an early Ref. [55] which claimed 90% yield of **4** in a letter, but no further explanation was offered). The selectivity to **4** is not as high as to **2**, because there is not a steric hindrance as a phenyl group in **1**.

The reaction course has been recorded as Fig. 9. With time went, the concentration of **3** decreased, the main product (**4**) and by-products (**7** and **8**) increased, but **4** increased a little quicker than the other two components.

As the same as the hydrogenation of **1** to **2**, the reaction was first-order to the pressure of H_2 , the concentrations of **3** and the amount of the platinum colloid, respectively.

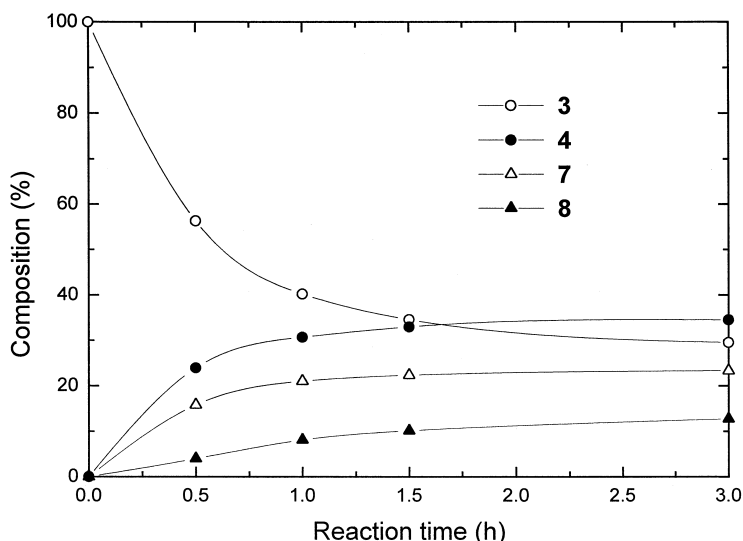


Fig. 9. Compositions of the four substances in the reaction process (reaction condition: 20 ml EtOH, 10 ml H_2O , 3 mg NaOH, 1.00 g **3** (1.428×10^{-2} mol), 0.20 g isobutanol (as an internal standard for gas chromatography), 2.249×10^{-5} mol PVP–Pt (containing PVP 1.125×10^{-3} mol) and 2.249×10^{-5} mol Fe^{3+} ; 4.0 MPa H_2 , 333 K and 3 h).

Combining the hydrogenation results of **1** to **2** and **3** to **4**, the steric hindrance also affects the reaction progress. This is consistent with the previous works [64].

4. Conclusions

(1) Some metal cations (Fe^{3+} , Co^{2+} and Ni^{2+}) can markedly increase both the activity and selectivity of PVP-stabilized platinum colloid in homogeneous liquid-phase selective hydrogenation of **1** to **2** and **3** to **4**.

(2) By the modification of CoCl_2 , the selectivity to **2** was 99.7% at 82.1% conversion of **1**; using FeCl_3 as a modifier, the selectivity to **4** was 48.9% at 70.5% conversion of **3**.

(3) The modification was due to the interaction of metal cations with the C=O groups in the reactants. The adsorbed metal cations activated the C=O double bonds and accelerated the reaction rate thus increased the selectivity to α,β -unsaturated alcohols. The steric hindrance also played an important role in the reaction. The metal cations can promote the hydrogenation of C=O double bonds and suppress the hydrogenation of C=C double bonds in the same time.

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