

Review

# Singular modification effects of metal cations and metal complex ions on the catalytic properties of metal colloidal nanocatalysts

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## Abstract

A series of selective hydrogenation reactions, cinnamaldehyde to cinnamyl alcohol, crotonaldehyde to crotyl alcohol, citronellal to citronello, and *o*-chloronitrobenzene to *o*-chloroaniline, were studied over polymer-stabilized nanoscale noble metal colloid catalysts in solutions. Metal cations and metal complex ions significantly affected the catalytic performances of the noble metal colloidal nanocatalysts. Some metal cations increased both the activity and the selectivity of the nanosized catalysts, and metal complex ions exhibited more complicate effects.

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**Keywords:** Modification effect; Selective hydrogenation; Metal colloid; Metal cation; Metal complex; Nanoparticle; Nanocatalyst; Nanocatalysis

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## 1. Introduction

Colloid science is of ancient lineage. It was founded and developed by many pioneers including Selmi, Faraday, Graham, Tyndall, Rayleigh, Ostwald, Mie, Bredig and Rideal [1]. Then, Turkevich and Kim [2] and Nord et al. [3–5] carefully studied the formation mechanism of colloidal particles and the catalytic application of synthetic polymer-stabilized noble metal colloids, respectively. Due to the rapid development of nanoscience and nanotechnology, the ancient colloid science is given a new life.

Because of their great differences from single molecules and bulk materials, nanoscale materials, including colloids, have attracted much attention since the last decade, especially in the field of catalysis, particularly through the contributions of Bradley et al. [6,7], Torigoe and Esumi [8], Klabunde et al. [9–11], Lewis and Lewis [12,13], Moiseev et al. [14,15], Schmid et al. [16,17], Bönemann et al. [18–20], Reetz et al. [21–23], Gates et al. [24,25], Hirai et al. [26–32], Pileni et al. [33–35], Finke et al. [36–38], and many other researchers [39–53]. Owing to the intrinsic thermodynamic instability, studies on the catalytic application of colloidal nanoparticles (nanocatalysts) have mainly focused on the reactions conducted under mild conditions, such as hydrogenation of monoenes or dienes [29,39–41,54–56], hydration of acrylonitrile [28,31] and others [20,43,57–59] at ambient conditions. For the same reason, few papers reported the influence of additives to the catalytic systems of neat metal colloids [60]. It is well known in heterogeneous catalysis that additives, such as ions, can markedly affect the catalytic properties of the catalysts [61,62]. This has been studied by Adams et al. [63–65], Maxted [66,67], and recently reviewed in detail by Ponec [68] and Gallezot and Richard [69].

In the homogeneous liquid-phase selective hydrogenation of unsaturated aldehydes to unsaturated alcohols, e.g. cinnamaldehyde (3-phenyl-2-propenal, **1**) to cinnamyl alcohol (3-phenyl-2-propene-1-ol, **2**) [70–72], crotonaldehyde (2-butenal, **3**) to crotyl alcohol (2-butene-1-ol, **4**) [71,72], citronellal (3,7-dimethyl-6-octenal, **5**) to citronellol (3,7-dimethyl-6-octene-1-ol, **6**) [54,72,73], and the selective hydrogenation of *o*-chloronitrobenzene (**7**) to *o*-chloroaniline (**8**) [74–77], catalyzed by the poly(*N*-vinyl-2-pyrrolidone) (PVP)-stabilized nanoscale Pd, Pt, Ru colloids and Pd/Pt, Ru/Pt, Ru/Pd bimetallic colloids, we found that considerable increases in both the selectivity and the activity were observed when employing some metal cations ( $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , etc.) as modifiers. It has also been found that

some metal complex ions also showed substantial modification effect on the catalytic properties of metal colloid nanocatalysts [78,79].

This paper reviews our efforts on the singular modification effects of metal cations and metal complex ions on the above-mentioned selective catalytic hydrogenation reactions over noble metal colloidal nanocatalysts in liquid medium, and attempts to find some clues for the mechanism [80–83].

## 2. Materials and instruments

PVP (average molecular weight 40 000) was supplied by BASF. Sodium borohydride ( $\text{NaBH}_4$ ) was purchased from Sigma. **1**, **3** and **5** were purchased from Acros and were redistilled under reduced pressure before use. **7** was recrystallized in 95% ethanol. Other reagents were provided by Beijing Chemicals Corporation and had a level of analytical grade. Hydrogen ( $\text{H}_2$ ) 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 colloidal dispersion upon a copper grid covered with a perforated carbon film and then evaporating the solvent. The particle diameters were measured from the enlarged photographs and the particle size distribution histograms were obtained on the measurements of at least 400 randomly selected individual nanoparticles. The hydrogenation products were analyzed by a Bei-Fen SQ-204 gas chromatography (GC) using a 2-m PEG-20M column (for catalytic hydrogenation of **1**, **3**, **5**) or a DC-710 column (for **7**).

## 3. Preparation and characterization of PVP-stabilized metal colloids

Hirai et al. have carried out a comprehensive study on the preparation of nanoscale noble metal colloids by alcohol reduction [27,29]. The PVP-stabilized Pd, Pt colloids (PVP-Pd, PVP-Pt) and Pd/Pt bimetallic colloids (PVP-Pd/Pt) we used were synthesized by similar ways, but with some improvements [51]. The PVP-stabilized Ru and Ru/Pt, Ru/Pd colloids (PVP-Ru, PVP-Ru/Pt, PVP-Ru/Pd) were prepared by  $\text{NaBH}_4$  reduction [54,75]. For clarity, the detailed syntheses were described as follows.

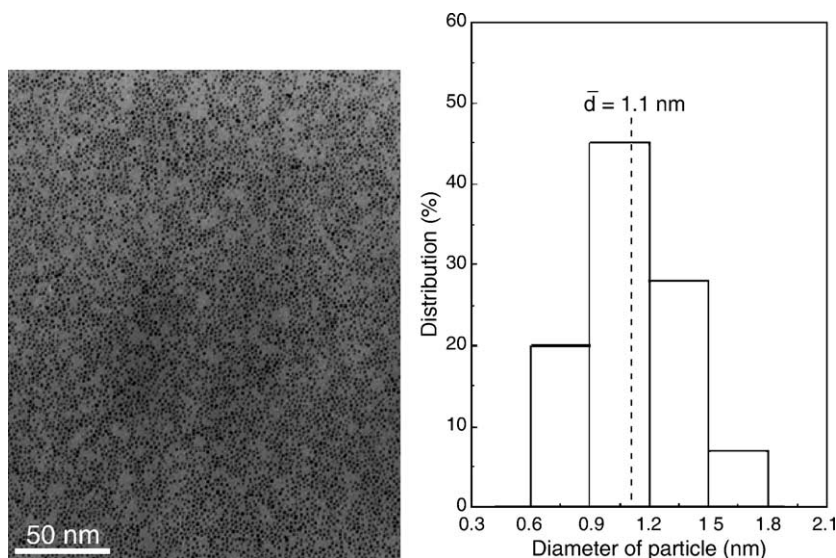


Fig. 1. TEM photograph (left) and the particle size distribution histogram (right) of PVP-Pt.

### 3.1. Preparation and characterization of PVP-Pt, PVP-Pd and PVP-Pd/Pt colloids

In a 500 mL flask equipped with a condenser, an oil bath and a magnetic stirrer, 1.11 g PVP ( $1.00 \times 10^{-2}$  mol as monomeric unit) and 0.130 g  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  ( $2.50 \times 10^{-4}$  mol) were dissolved in a mixed solvent of 130 mL methanol and 150 mL distilled water; then 20 mL 0.1 M methanol solution of NaOH was added dropwise with vigorous stirring. The reaction mixture was refluxed for 3 h to give a homogeneous black colloidal solution—PVP-Pt [51]. The TEM photograph showed that the average diameter of PVP-Pt colloid was 1.1 nm and the size distribution was narrow within a range of 0.6–1.8 nm with a standard deviation of 0.30 nm (Fig. 1).

PVP-Pd colloid was synthesized according to the literature [29]. 0.0443 g  $\text{PdCl}_2$  ( $2.50 \times 10^{-4}$  mol) was firstly stirred with 150 mL ethanol for 24 h at room temperature, then 150 mL distilled water and 1.11 g PVP ( $1.00 \times 10^{-2}$  mol) were added into the solution. After refluxing the reaction solution for 3 h, a homogeneous black colloidal dispersion, PVP-Pd, was obtained. The average particle diameter was 2.7 nm with a standard deviation of 0.59 nm.

PVP-Pd/Pt colloids were prepared similarly. Firstly 0.0443 g  $\text{PdCl}_2$  ( $2.50 \times 10^{-4}$  mol) was stirred with 150 mL ethanol for 24 h, then 0.130 g  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  ( $2.50 \times 10^{-4}$  mol), 2.22 g PVP ( $2.00 \times 10^{-2}$  mol) and 150 mL distilled water were added. The reaction mixture was refluxed for 3 h to produce a homogeneous black colloidal dispersion, PVP-Pd/Pt(1/1). Changing the relative amounts of  $\text{PdCl}_2$  and  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  by keeping the total amounts (in mole) of the metals constant, PVP-stabilized Pd/Pt bimetallic colloids with different molar ratios were obtained. Table 1 shows the TEM characterization results of a series of PVP-Pd/Pt colloids.

### 3.2. Preparation and characterization of PVP-Ru, PVP-Ru/Pt and PVP-Ru/Pd colloids

In a 500 mL flask, 1.04 g PVP ( $9.36 \times 10^{-3}$  mol) was dissolved in a mixed solvent of 200 mL methanol and 160 mL distilled water. Then, 0.115 g  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  ( $4.68 \times 10^{-4}$  mol) was added and dissolved. Forty milliliters of freshly made aqueous solution of  $\text{NaBH}_4$  (0.177 g,  $4.68 \times 10^{-3}$  mol) was poured into the vigorously stirred solution swiftly, and the color of the solution changed quickly from dark red-brown to gray blue to dark black in less than 1 s. This dark black solution was stirred for 6 h to give the PVP-stabilized ruthenium colloid (PVP-Ru) [54]. Its average size and the standard deviation were 1.4 and 0.51 nm, respectively.

PVP-Ru/Pt colloids were prepared as follows [75]. 0.0289 g  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  ( $1.17 \times 10^{-4}$  mol), 0.0606 g  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  ( $1.17 \times 10^{-4}$  mol) and 0.520 g PVP ( $4.68 \times 10^{-3}$  mol) were dissolved in a mixed solvent of 100 mL methanol and 80 mL distilled water to form a dark red-brown solution. Twenty milliliters of freshly made aqueous sodium borohydride (0.0885 g,  $2.34 \times 10^{-3}$  mol) was then added quickly to the solution with vigorous stirring. The color of the solution changed to black in about 1 s. This dark black solution was

Table 1  
Characterization of PVP-Pd/Pt colloids by TEM<sup>a</sup>

Colloid	Average diameter (nm)	Standard deviation (nm)
PVP-Pd/Pt(4/1)	2.6	0.39
PVP-Pd/Pt(3/1)	2.3	0.40
PVP-Pd/Pt(2/1)	2.3	0.38
PVP-Pd/Pt(1/1)	2.2	0.31
PVP-Pd/Pt(1/2)	2.2	0.33
PVP-Pd/Pt(1/3)	2.9	0.39
PVP-Pd/Pt(1/4)	1.7	0.30

<sup>a</sup> Preparation condition: molar ratio of PVP:(Pd + Pt) = 40:1.

Table 2  
Characterization of PVP-Ru/Pt colloids by TEM<sup>a</sup>

Colloid	Average diameter (nm)	Standard deviation (nm)
PVP-Ru/Pt(9/1)	1.3	0.35
PVP-Ru/Pt(4/1)	2.0	0.63
PVP-Ru/Pt(2/1)	2.1	0.55
PVP-Ru/Pt(1/1)	1.7	0.49
PVP-Ru/Pt(1/2)	2.7	0.62
PVP-Ru/Pt(1/4)	3.0	0.74

<sup>a</sup> Preparation conditions: molar ratios of PVP:(Pt + Ru) = 20:1 and NaBH<sub>4</sub>:(Pt + Ru) = 10:1.

stirred for 6 h to give PVP-stabilized Ru/Pt bimetallic colloid with the molar ratio of Ru/Pt = 1/1 (PVP-Ru/Pt(1/1)). Varying the amounts of RuCl<sub>3</sub>·*n*H<sub>2</sub>O and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O by maintaining the total amounts (in mole) of the metals constant, PVP-Ru/Pt bimetallic colloids with different molar ratios of Ru/Pt were obtained. The characterization data are listed in Table 2.

PVP-Ru/Pd colloids were prepared similar to those of PVP-Ru/Pt colloids except using H<sub>2</sub>PdCl<sub>4</sub>·*n*H<sub>2</sub>O (converted from PdCl<sub>2</sub> by concentrated hydrochloric acid) instead of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O [75]. Table 3 summarizes the TEM characterization results of PVP-Ru/Pd colloids.

All the nanoscale metal colloids used in the selective hydrogenation of **7** to **8** were re-dispersed in methanol after being dried by rotatory evaporation at 310 K under reduced pressure.

#### 4. Hydrogenation reactions

Hydrogenation of **1** was carried out in a 100 mL stainless steel autoclave [70–72]. The reaction solution contained 40 mL EtOH, 1.0 mg NaOH, 1.00 g **1** ( $7.58 \times 10^{-3}$  mol), 1.00 g *n*-tetradecanol (as an internal standard for GC analysis), 20 mL PVP-Pt colloidal dispersion (containing  $2.25 \times 10^{-5}$  mol Pt,  $1.13 \times 10^{-3}$  mol PVP, 10 mL H<sub>2</sub>O and 10 mL EtOH) and selected metal salt. The autoclave was charged several times with H<sub>2</sub> to replace air and the final pressure of H<sub>2</sub> was 4.0 MPa. The hydrogenation reaction was performed at 333 K for 1.5 h. The reaction products were periodically analyzed by GC.

Hydrogenation of **3** was similar to that of **1** [71,72]. The optimized reaction conditions were: 20 mL EtOH, 10 mL H<sub>2</sub>O, 3.0 mg NaOH, 1.00 g **3** ( $1.43 \times 10^{-2}$  mol), 0.200 g isobutanol (internal standard for GC analysis),  $2.25 \times 10^{-5}$  mol PVP-Pt or PVP-Ru (containing  $1.13 \times 10^{-3}$  mol PVP). The reaction time was 3 h at 333 K.

Table 3  
Characterization of PVP-Ru/Pd colloids by TEM<sup>a</sup>

Colloid	Average diameter (nm)	Standard deviation (nm)
PVP-Ru/Pd(4/1)	2.2	0.57
PVP-Ru/Pd(2/1)	3.5	0.74
PVP-Ru/Pd(1/1)	3.7	0.66
PVP-Ru/Pd(1/2)	3.4	0.82
PVP-Ru/Pd(1/4)	2.7	0.67

<sup>a</sup> Preparation conditions: molar ratios of PVP:(Pt + Ru) = 20:1 and NaBH<sub>4</sub>:(Pt + Ru) = 10:1.

The hydrogenation reaction solution of **5** contained 40 mL EtOH, 1.0 mg NaOH, 0.500 g **5** ( $3.24 \times 10^{-3}$  mol), 1.00 g ethylene glycol (internal standard for GC analysis), 20 mL PVP-Pt or PVP-Ru dispersion (containing  $2.34 \times 10^{-5}$  mol Pt or Ru,  $1.17 \times 10^{-3}$  mol PVP, 10 mL H<sub>2</sub>O and 10 mL EtOH) and certain metal salt; the pressure of H<sub>2</sub> was 6.0 MPa. The hydrogenation reaction was performed at 333 K for 2 h with 6.0 MPa H<sub>2</sub> [54,72,73].

The typical selective hydrogenation of **7** to **8** was carried out at 303 K and atmospheric pressure [74–77,79]. In a two-necked flask equipped with a magnetic stirrer and a thermostatic water bath, there were placed 2.0 mL noble metal colloidal nanocatalyst (PVP-Pt, PVP-Pd, PVP-Ru, PVP-Pd/Pt, PVP-Ru/Pt, or PVP-Ru/Pd, containing  $4.80 \times 10^{-6}$  mol noble metal,  $2.40 \times 10^{-4}$  mol PVP), 0.10 mL *n*-decanol (internal standard for GC) and 11.9 mL MeOH. H<sub>2</sub> was charged several times to replace air and the catalyst was activated at 303 K for 60 min. The reaction started right after 1.0 mL methanol solution of **7** (containing  $1.00 \times 10^{-3}$  mol **7**) was injected into the flask. The hydrogen consumption was monitored with a graduated gas burette. When the volume of the theoretical uptake of H<sub>2</sub> was reached, the reaction was stopped and the reaction solution was analyzed by GC.

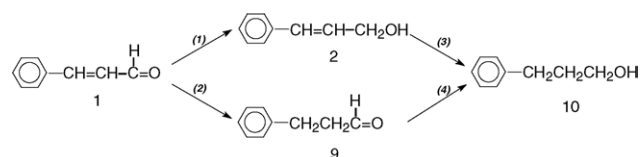
The selective hydrogenation of **7** to **8** was also carried out under high pressure of H<sub>2</sub> in a stainless steel autoclave [84]. The reaction solution contained  $1.87 \times 10^{-5}$  mol PVP-Ru colloid,  $1.87 \times 10^{-5}$  mol metal salts or metal complexes,  $1.00 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC) and MeOH (the whole volume was 15.0 mL). The reaction time was normally 120 min.

#### 5. Modification effect of metal cations to PVP-stabilized noble metal colloidal nanocatalysts

##### 5.1. Selective hydrogenation of **1** to **2** over PVP-Pt colloid [70–72]

The selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehyde to the corresponding  $\alpha,\beta$ -unsaturated alcohol is an important step for synthesis of fine chemicals. It is very easy for most ordinary heterogeneous and homogeneous catalysts to reduce the C=C double bond to yield hydrogenated cinnamaldehyde (3-phenylpropanal, **9**) as the main product (Scheme 1, reaction (2)); it is comparatively difficult for them to reduce the C=O double bond only to selectively produce **2** (Scheme 1, reaction (1)) [69,85,86].

When neat PVP-Pt colloid was employed alone as a catalyst, 12.0% selectivity to **2** with 37.5% conversion of **1** was obtained; when FeCl<sub>3</sub> or CoCl<sub>2</sub> was introduced into the catalytic system,



Scheme 1.

Table 4  
Hydrogenation of **1** to **2** over PVP-Pt-MCl<sub>x</sub> catalytic systems<sup>a</sup>

Catalytic system	Average rate (mol <b>1</b> /mol Pt h)	Conversion of <b>1</b> (%)	Selectivity <sup>b</sup> (%)		
			<b>2</b>	<b>9</b>	<b>10</b>
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 <sub>2</sub>	81.7	36.4	33.8	55.2	11.0
PVP-Pt-CaCl <sub>2</sub>	70.3	31.3	30.5	59.5	10.0
PVP-Pt-Ba(NO <sub>3</sub> ) <sub>2</sub>	88.7	39.5	28.1	57.4	14.5
PVP-Pt-MnCl <sub>2</sub>	75.7	33.7	57.6	31.7	10.7
PVP-Pt-AlCl <sub>3</sub>	68.5	30.5	34.3	58.2	17.5
PVP-Pt-CeCl <sub>3</sub>	69.2	30.8	30.7	54.3	15.0
PVP-Pt-Nd(NO <sub>3</sub> ) <sub>3</sub>	78.6	35.0	25.7	62.1	12.2
PVP-Pt-CuCl <sub>2</sub>	0	0	–	–	–
PVP-Pt-ZnCl <sub>2</sub>	29.2	13.0	99.8	0.2	0
PVP-Pt-Pb(NO <sub>3</sub> ) <sub>2</sub>	0	0	–	–	–
PVP-Pt-FeCl <sub>3</sub>	187.5	83.5	98.5	1.5	0
PVP-Pt-FeSO <sub>4</sub>	185.3	82.5	98.5	1.5	0
PVP-Pt-CoCl <sub>2</sub>	186.2	82.9	98.8	1.2	0
PVP-Pt-NiCl <sub>2</sub>	115.7	51.5	34.4	50.6	15.0

<sup>a</sup> Molar ratio of M:Pt = 1:1. Reaction conditions: 40 mL EtOH, 1.0 mg NaOH, 1.00 g **1** ( $7.58 \times 10^{-3}$  mol), 1.00 g *n*-tetradecanol (internal standard for GC), 20 mL PVP-Pt colloidal dispersion (containing  $2.25 \times 10^{-5}$  mol Pt,  $1.13 \times 10^{-3}$  mol PVP, 10 mL H<sub>2</sub>O and 10 mL EtOH) and  $2.25 \times 10^{-5}$  mol metal salt; 4.0 MPa H<sub>2</sub>, 333 K and 1.5 h.

<sup>b</sup> **9** = 3-phenylpropanal, **10** = 3-phenylpropan-1-ol.

the activity was enhanced 120% (conversion of **1** reached 83%) and the selectivity to **2** increased to 98.5% (Table 4).

It was found that CoCl<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub> led to the same activity and the same selectivity in a wide concentration range with the molar ratio of Co<sup>2+</sup>:Pt from 1:20 to 20:1 (Fig. 2). This indicates that weakly coordinating anions, such as Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, OAc<sup>-</sup>, etc. act merely as spectator ions. In another word, the modification effects are resulted from the metal cations. The modification effect of metal cations can be classified into four types (see Table 4): (a) the metal cations had no influence on the activity and the selectivity of PVP-Pt, such as Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>; (b) Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Mn<sup>2+</sup> and Al<sup>3+</sup>, Ce<sup>3+</sup>, Nd<sup>3+</sup> influenced lit-

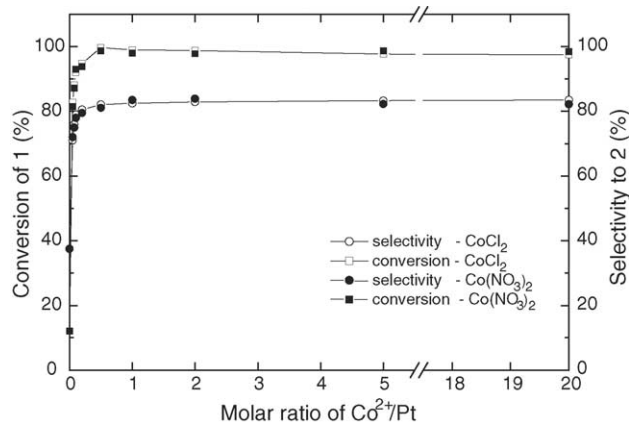


Fig. 2. Activity and selectivity at different molar ratios of Co<sup>2+</sup>/Pt in the selective hydrogenation of **1** to **2** over PVP-Pt with CoCl<sub>2</sub> or Co(NO<sub>3</sub>)<sub>2</sub>. Reaction conditions: 40 mL EtOH, 1.0 mg NaOH, 1.00 g **1** ( $7.58 \times 10^{-3}$  mol), 1.00 g *n*-tetradecanol (internal standard for GC), 20 mL PVP-Pt colloidal dispersion (containing  $2.25 \times 10^{-5}$  mol Pt,  $1.13 \times 10^{-3}$  mol PVP, 10 mL H<sub>2</sub>O and 10 mL EtOH) and metal salt; 4.0 MPa H<sub>2</sub>, 333 K and 1.5 h.

tle on the activity but increased the selectivity from 12.0 to ~30% (57.6% for Mn<sup>2+</sup>); (c) Cu<sup>2+</sup>, Pb<sup>2+</sup> or Zn<sup>2+</sup> usually acted as poisons to the catalyst, and here, they indeed poisoned the activity of PVP-Pt (conversions of **1** were 0, 0 and 13.0% with Cu<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup>, respectively, but the selectivity was 99.8% with Zn<sup>2+</sup>); (d) Fe<sup>3+</sup>, Fe<sup>2+</sup> and Co<sup>2+</sup> remarkably enhanced both the selectivity and the activity and Ni<sup>2+</sup> exerted a moderate effect.

The metal cations added in the reaction system can be completely recovered with their original oxide states under the reaction condition (hydrogen atmosphere) by super-filtration except for Cu<sup>2+</sup>, Pb<sup>2+</sup> and Fe<sup>3+</sup>. Cu<sup>2+</sup> and Pb<sup>2+</sup> converted into Cu<sup>0</sup> and Pb<sup>0</sup>; Fe<sup>3+</sup> converted into Fe<sup>2+</sup> (which was demonstrated by the formation of a blue precipitate with addition of K<sub>3</sub>Fe(CN)<sub>6</sub> to the solution). Thus, this modification effect was generated from metal cations with positive oxide states.

As shown in Fig. 2, the variation of molar percentage of Co<sup>2+</sup> in the PVP-Pt colloid does not affect the activity and selectivity in the way of conventional bimetallic catalysts, where the curves of activity and selectivity showed a typical volcanic shape [63–65,87–90]. Here, a little amount of Co<sup>2+</sup> (Co<sup>2+</sup>:Pt = 0.05:1) made the activity and the selectivity increase promptly to very high values and addition of more Co<sup>2+</sup> did not decrease them. When the molar ratio of Co<sup>2+</sup>:Pt was 0.1:1, the conversion and the selectivity increased to 79.6 and 92.8%, respectively. The maximum selectivity (99.7%) was achieved at Co<sup>2+</sup>:Pt = 1:3, where the conversion was 82.1% (Fig. 2). Fe<sup>3+</sup> or Fe<sup>2+</sup> also acted in a similar behavior as Co<sup>2+</sup> [71].

In the reaction, the conversion of **1** reached 89.5% in 3 h and changed little over another 3 h (conversion of **1** was 90.3% in 6 h) whereas the selectivity remained as 99.7% (Fig. 3). This phenomenon is similar to the reported results on the hydrogenation of **1** [63], furfuralcrolein [88] and citral [65] over platinum

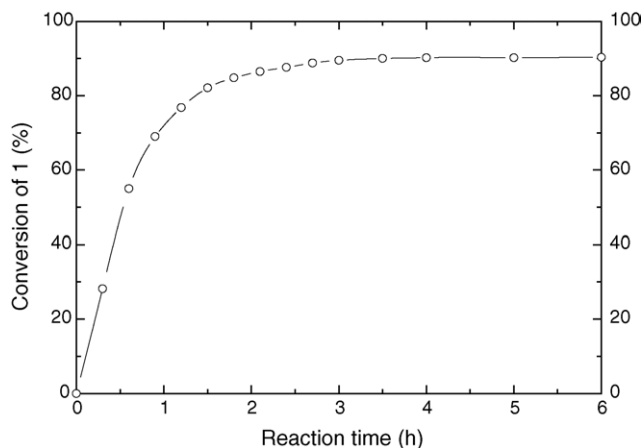


Fig. 3. Conversion curve in the selective hydrogenation of **1** to **2** over PVP-Pt-CoCl<sub>2</sub>. Reaction conditions: 40 mL EtOH, 1.0 mg NaOH, 1.00 g **1** ( $7.58 \times 10^{-3}$  mol), 1.00 g *n*-tetradecanol (internal standard for GC), 20 mL PVP-Pt colloidal dispersion (containing  $2.25 \times 10^{-5}$  mol Pt,  $1.13 \times 10^{-3}$  mol PVP, 10 mL H<sub>2</sub>O and 10 mL EtOH) and  $2.25 \times 10^{-5}$  mol CoCl<sub>2</sub>; 4.0 MPa H<sub>2</sub>, 333 K.

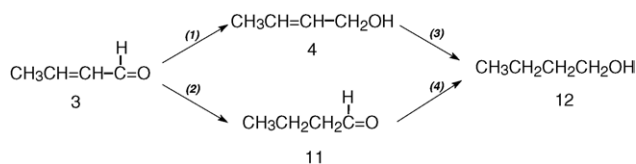
oxide-platinum black in the presence of both iron and zinc salts, where the hydrogenation reactions stopped automatically after one molecular equivalent of hydrogen had been absorbed. However, we currently could not find a satisfactory explanation for this.

## 5.2. Selective hydrogenation of **3** to **4** over PVP-Pt and PVP-Ru colloids

Similar to the hydrogenation of **1**, there are two competitive hydrogenation pathways starting from **3** (Scheme 2). To obtain **4** with high selectivity at high conversion of **3** is a challenging task (Scheme 2, reaction (1)) for the same reason as discussed above [85,91].

### 5.2.1. Selective hydrogenation of **3** to **4** over PVP-Pt colloid [71,72]

It can be seen from Table 5 that the addition of Fe<sup>3+</sup> and Co<sup>2+</sup> raised both the activity and the selectivity. When adding Zn<sup>2+</sup> in the PVP-Pt-FeCl<sub>3</sub> system, the activity decreased with a slight increase in the selectivity. The more Zn<sup>2+</sup>, the lower the activity and the higher the selectivity. This is similar to the known toxication effect. At the optimum conditions (Fe<sup>3+</sup>:Pt = 1:1, 3 mg NaOH, 20 mL EtOH, 10 mL H<sub>2</sub>O), we got 48.9% selectivity to **4** at 70.5% conversion of **3**. The yield of **4** was 34.5%, which is higher than most of the published results [91–94] through catalytic hydrogenation except for one [95]. The selectivity to **4** is not as high as to **2**, because the steric hindrance of the methyl group in **3** is not as significant as the phenyl group in **1**.



Scheme 2.

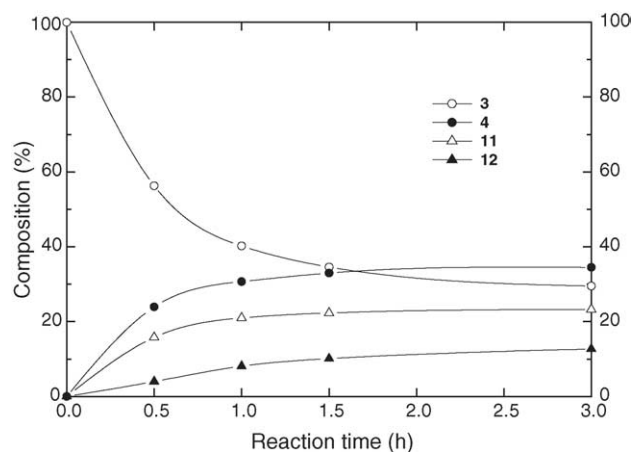


Fig. 4. Selective hydrogenation of **3** to **4** over PVP-Pt-FeCl<sub>3</sub>. Reaction conditions: 1.00 g **3** ( $1.43 \times 10^{-2}$  mol), 3.0 mg NaOH, 20 mL EtOH, 10 mL H<sub>2</sub>O, 0.20 g isobutanol (internal standard for GC),  $2.25 \times 10^{-5}$  mol PVP-Pt (containing  $1.13 \times 10^{-3}$  mol PVP) and  $2.25 \times 10^{-5}$  mol FeCl<sub>3</sub>; 4.0 MPa H<sub>2</sub>, 333 K.

The reaction time course has been recorded as Fig. 4. As the reaction progressed, the concentration of **3** declined, the main product (**4**) and byproducts (*n*-butanal, **11**, and *n*-butanol, **12**) increased, but **4** increased a little quicker than the other two components. However, there was still a tendency to stop automatically as that of **1** to **2**.

### 5.2.2. Selective hydrogenation of **3** to **4** over PVP-Ru colloid

Ruthenium is a member of the platinum-group metals. It is widely used for the selective hydrogenation of carbonyl groups (C=O) in the vicinity of C=C double bonds to hydroxyl groups (CH–OH). It is also applied in partial hydrogenation of aromatic compounds to the corresponding cycloalkenes [96]. However, when employing PVP-Ru as the catalyst in the selective hydrogenation of **3** to **4**, we got results far from the anticipated.

From Table 6, it can be seen that the addition of H<sub>2</sub>O and NaOH was not good for the selectivity to **4** (the selectivity was even 0 for no. 4), but good for the activity (the highest average rate of 244.0 mol **3**/mol Ru h was obtained with 1 mg NaOH and 5 mL H<sub>2</sub>O). A higher selectivity of 5.2% was obtained using absolute ethanol (H<sub>2</sub>O was controlled under 0.01%). This ascertained further that H<sub>2</sub>O was harmful to the selectivity. The incorporation of metal cations also played interesting roles in the catalytic process. Fe<sup>3+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup> raised the selectivity but lowered the activity (Table 6, nos. 1 and 6–8). The addition of H<sub>2</sub>O and NaOH to PVP-Ru-NiCl<sub>2</sub> exhibited similar results as neat PVP-Ru: the selectivity to **4** dropped to 0 (nos. 9 and 10)!

This is very different from the situations of the selective hydrogenation of **1** to **2**. It has been found that H<sub>2</sub>O and NaOH favored the activity and selectivity of the PVP-Pt-MCl<sub>x</sub> catalytic system in the selective hydrogenation of **1** to **2**. The effects of H<sub>2</sub>O and NaOH were presented in Table 7.

The activity of PVP-Pt rose with the addition of H<sub>2</sub>O, which could be attributed to its high polarity [62]. When more than the optimum amount of H<sub>2</sub>O was added, the solubility of **1** reduced and therefore the activity decreased. A suitable amount

Table 5  
Optimization of reaction condition in the selective hydrogenation of **3** to **4** over PVP-Pt colloid modified by metal cations<sup>a</sup>

Catalytic system <sup>b</sup>	NaOH (mg)	EtOH (mL)	H <sub>2</sub> O (mL)	Average rate (mol <b>3</b> /mol Pt h)	Conversion of <b>3</b> (%)	Selectivity <sup>c</sup> (%)			Yield of <b>4</b> (%)
						<b>4</b>	<b>11</b>	<b>12</b>	
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

<sup>a</sup> Other conditions: 1.00 g **3** ( $1.43 \times 10^{-2}$  mol), 0.20 g isobutanol (internal standard for GC),  $2.25 \times 10^{-5}$  mol PVP-Pt (containing  $1.13 \times 10^{-3}$  mol PVP); 4.0 MPa H<sub>2</sub>, 333 K and 3 h.

<sup>b</sup> The numbers in the brackets refer to the molar ratios of metal cations to Pt; Fe stands for FeCl<sub>3</sub>, Co stands for CoCl<sub>3</sub>, and Zn stands for ZnCl<sub>2</sub>.

<sup>c</sup> **11** = *n*-butanal, **12** = *n*-butanol.

Table 6  
Hydrogenation of **3** to **4** over PVP-Ru-MCl<sub>3</sub> catalytic systems<sup>a</sup>

No.	Catalytic system	NaOH (mg)	EtOH (mL)	H <sub>2</sub> O (mL)	Average rate (mol <b>3</b> /mol Ru h)	Conversion of <b>3</b> (%)	Selectivity <sup>b</sup> (%)		
							<b>4</b>	<b>11</b>	<b>12</b>
1	PVP-Ru	0	30	0	203.3	100	4.0	79.1	16.9
2	PVP-Ru	0	20	10	233.8	95.8	3.8	74.5	21.7
3	PVP-Ru	1	30	0	167.4	82.4	2.7	83.5	13.8
4	PVP-Ru	1	25	5	244.0	100	0	75.4	24.6
5	PVP-Ru <sup>c</sup>	0	30	0	150.4	74.0	5.2	84.0	10.8
6	PVP-Ru-FeCl <sub>3</sub>	0	30	0	85.0	41.8	13.6	86.4	0
7	PVP-Ru-CoCl <sub>2</sub>	0	30	0	96.7	95.0	5.8	74.3	19.9
8	PVP-Ru-NiCl <sub>2</sub>	0	30	0	170.4	97.8	4.9	80	15.1
9	PVP-Ru-NiCl <sub>2</sub>	0	25	5	197.5	97.2	0	83.0	17.0
10	PVP-Ru-NiCl <sub>2</sub>	1	25	5	198.4	97.6	0	75.9	24.1

<sup>a</sup> Molar ratio of M:Pt = 1:1. Other conditions: 1.00 g **3** ( $1.43 \times 10^{-2}$  mol), 0.20 g isobutanol (internal standard for GC),  $2.25 \times 10^{-5}$  mol PVP-Pt (containing  $1.13 \times 10^{-3}$  mol PVP); 4.0 MPa H<sub>2</sub>, 333 K and 3 h.

<sup>b</sup> **11** = *n*-butanal, **12** = *n*-butanol.

<sup>c</sup> The solvent was absolute ethanol.

of NaOH resulted in a higher activity and a considerable increase in selectivity, which was due to the suppression of the hydrogenation of C=C double bond [97]. This was also authenticated in the hydrogenation of cyclooctene over PVP-Pt (Table 8). The initial hydrogenation rates reduced from 0.081 to 0.076 and

0.025 mol H<sub>2</sub>/mol Pt s, with 0.2 and 1.0 mg NaOH, respectively. So did the average rates.

Furthermore, it was observed that in the selective hydrogenation of **3** to **4** over PVP-Pt H<sub>2</sub>O and NaOH were good for the selectivity and the activity, too (see Table 5). In view of the

Table 7  
Optimization of reaction condition in the selective hydrogenation of **1** to **2** over PVP-Pt-CoCl<sub>2</sub><sup>a</sup>

NaOH (mg)	H <sub>2</sub> O (mL)	EtOH (mL)	Selectivity to <b>2</b> (%)	Conversion of <b>1</b> (%)	Average rate (mol <b>1</b> /mol Pt 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

<sup>a</sup> Molar ratio of Co<sup>2+</sup>:Pt = 1:1. Other conditions: 1.00 g **1** ( $7.58 \times 10^{-3}$  mol), 1.00 g *n*-tetradecanol (internal standard for GC),  $2.25 \times 10^{-5}$  mol PVP-Pt colloid; 4.0 MPa H<sub>2</sub>, 333 K and 1.5 h.

Table 8  
Hydrogenation of cyclooctene over PVP-Pt colloid with NaOH<sup>a</sup>

Catalytic system	Initial rate (mol H <sub>2</sub> /mol Pt s)	Average rate (mol H <sub>2</sub> /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

<sup>a</sup> Reaction conditions: 2.0 mL PVP-Pt (containing  $4.68 \times 10^{-6}$  mol Pt), 2.0 mL cyclooctene ( $1.00 \times 10^{-3}$  mol); 0.1 MPa H<sub>2</sub> and 303 K (the whole volume was 15.0 mL, MeOH).

apparently contradicting observations between the two systems, more work needs to be done to look for a unified explanation [98].

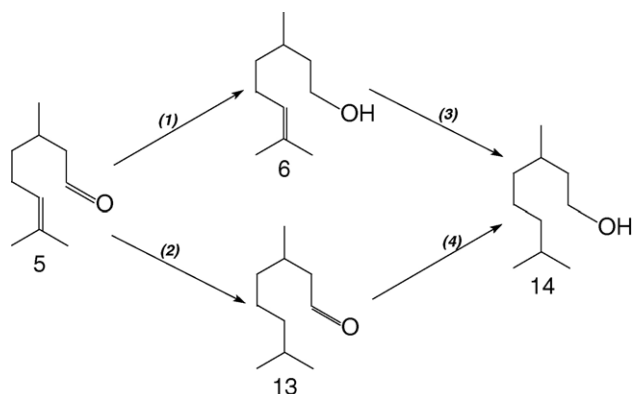
### 5.3. Selective hydrogenation of **5** to **6** over PVP-Pt and PVP-Ru colloids [54,72,73]

**5** is a non-conjugated unsaturated aldehyde, its corresponding unsaturated alcohol is **6** (Scheme 3). Both of them are essential components in many kinds of perfumes. Some papers have been published on the selective hydrogenation of citral (3,7-dimethyl-2,6-octadienal) to **6** over conventional supported catalysts, but rarely on the selective hydrogenation of **5** to **6** [88,99,100]. We found that by using metal cations modified PVP-Pt and PVP-Ru nanocatalysts, **5** could be hydrogenated to **6** with high selectivity.

#### 5.3.1. Selective hydrogenation of **5** to **6** over PVP-Pt colloid

From Figs. 5 and 6, it can be seen that the addition of Co<sup>2+</sup> to PVP-Pt increased both the activity (the conversion changed from 70.6 to 98.3%) and the selectivity (from 44.5 to 98.5%).

The modification effect of various metal cations on this reaction system has been systemically investigated. The effects can also be grouped into four types (see Table 9): (a) Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Al<sup>3+</sup>, Ce<sup>3+</sup>, Nd<sup>3+</sup> did not affect the catalytic properties of PVP-Pt; (b) Mg<sup>2+</sup>, Ca<sup>2+</sup> and Ba<sup>2+</sup> increased the selectivity slightly without influencing the activity; (c) Cu<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> acted as poisons to PVP-Pt with conversions of 0, 0 and 25.0%, respectively, the selectivity of Zn<sup>2+</sup> modified catalyst was 99.6%; (d)



Scheme 3.

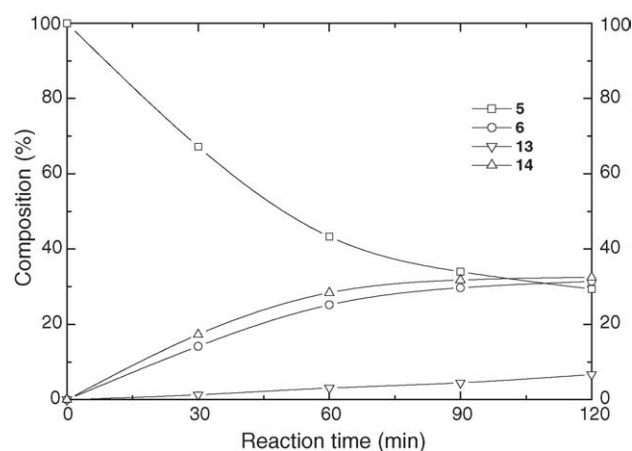


Fig. 5. Selective hydrogenation of **5** to **6** over PVP-Pt. Reaction conditions: 40 mL EtOH, 1.0 mg NaOH, 0.500 g **5** ( $3.24 \times 10^{-3}$  mol), 1.00 g ethylene glycol (internal standard for GC), 20 mL PVP-Pt colloidal dispersion (containing  $2.34 \times 10^{-5}$  mol Pt,  $1.17 \times 10^{-3}$  mol PVP, 10 mL H<sub>2</sub>O and 10 mL EtOH); 6.0 MPa H<sub>2</sub>, 333 K.

Fe<sup>3+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Mn<sup>2+</sup> boosted significantly both the selectivity and the activity. The overall results are similar to the selective hydrogenation of **1** to **2** catalyzed by PVP-Pt. Fe<sup>3+</sup> was reduced to Fe<sup>2+</sup> in the reaction, and showed the same effect as Fe<sup>2+</sup>; Cu<sup>2+</sup> and Pb<sup>2+</sup> were reduced to their metallic forms and therefore poisoned the catalysts.

The optimum amounts of NaOH, H<sub>2</sub>O and EtOH for this reaction were found to be 1 mg, 10 mL and 50 mL, respectively; which is similar to the selective hydrogenations of **1** to **2** and **3** to **4** over the PVP-Pt-MCl<sub>x</sub> catalytic systems (Table 10).

#### 5.3.2. Selective hydrogenation of **5** to **6** over PVP-Ru colloid

It can be seen from Fig. 7 that without Co<sup>2+</sup>, conversion of **5** in 1 h was 88.4% and yield of **6** was 84.2% (selectivity 95.2%); the yield of **6** reached 86.4% in another hour but the selectivity

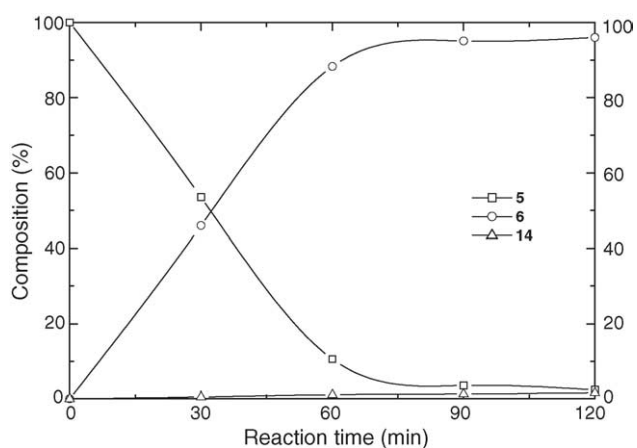


Fig. 6. Selective hydrogenation of **5** to **6** over PVP-Pt-CoCl<sub>2</sub>. Reaction conditions: 40 mL EtOH, 1.0 mg NaOH, 0.500 g **5** ( $3.24 \times 10^{-3}$  mol), 1.00 g ethylene glycol (internal standard for GC), 20 mL PVP-Pt colloidal dispersion (containing  $2.34 \times 10^{-5}$  mol Pt,  $1.17 \times 10^{-3}$  mol PVP, 10 mL H<sub>2</sub>O and 10 mL EtOH) and  $2.34 \times 10^{-5}$  mol CoCl<sub>2</sub>; 6.0 MPa H<sub>2</sub>, 333 K.



Table 9  
Hydrogenation of **5** to **6** over PVP-Pt-MCl<sub>x</sub> catalytic systems<sup>a</sup>

Catalytic system	Conversion of <b>5</b> (%)	Selectivity <sup>b</sup> (%)	
		<b>6</b>	<b>13</b>
PVP-Pt	70.6	44.5	46.0
PVP-Pt-LiCl	65.2	41.3	58.7
PVP-Pt-NaCl	72.3	46.2	53.8
PVP-Pt-KCl	68.8	45.8	54.2
PVP-Pt-AlCl <sub>3</sub>	73.3	42.2	57.8
PVP-Pt-CeCl <sub>3</sub>	68.5	47.4	52.6
PVP-Pt-Nd(NO <sub>3</sub> ) <sub>3</sub>	69.1	45.0	55.0
PVP-Pt-MgCl <sub>2</sub>	75.1	55.3	44.7
PVP-Pt-CaCl <sub>2</sub>	73.6	50.0	50.0
PVP-Pt-Ba(NO <sub>3</sub> ) <sub>2</sub>	73.8	57.5	42.5
PVP-Pt-CuCl <sub>2</sub>	0	–	–
PVP-Pt-ZnCl <sub>2</sub>	25.0	99.6	0.4
PVP-Pt-Pb(NO <sub>3</sub> ) <sub>2</sub>	0	–	–
PVP-Pt-FeCl <sub>3</sub>	97.6	97.6	2.4
PVP-Pt-FeSO <sub>4</sub>	97.5	97.6	2.4
PVP-Pt-CoCl <sub>2</sub>	98.3	98.5	1.5
PVP-Pt-NiCl <sub>2</sub>	97.2	88.9	11.1
PVP-Pt-MnCl <sub>2</sub>	97.8	74.7	25.3

<sup>a</sup> Molar ratio of M:Pt=1:1. Reaction conditions: 40 mL EtOH, 1.0 mg NaOH, 0.500 g **5** ( $3.24 \times 10^{-3}$  mol), 1.00 g ethylene glycol internal standard for GC, 20 mL PVP-Pt colloidal dispersion (containing  $2.34 \times 10^{-5}$  mol Pt,  $1.17 \times 10^{-3}$  mol PVP, 10 mL H<sub>2</sub>O and 10 mL EtOH) and  $2.34 \times 10^{-5}$  mol metal salt; 6.0 MPa H<sub>2</sub>, 333 K and 2 h.

<sup>b</sup> **13**=3,7-dimethyloctanal, the yield of 3,7-dimethyloctanol (**14**) was under the detectable level of GC except for neat PVP-Pt where the selectivity to **14** was 9.5%.

decreased to 90.2%. With the modification of Co<sup>2+</sup> (Fig. 8), the yield of **6** reached 97.8% in 1 h and changed little in another hour (selectivity was 98.8 and 97.5%, respectively), only 1.0% of **5** remained unreacted.

From Figs. 5 and 7, it can be concluded that the catalytic properties of PVP-Ru is much superior to PVP-Pt: in 1 h, the conversion of **5** and selectivity for **6** were, respectively, 88.4 and 95.2% catalyzed by PVP-Ru, 56.7 and 46.9% by PVP-Pt. This is in agreement with the traditional view that Ru is better than Pt in the selective hydrogenation of C=O double bonds.

Table 10  
Optimization of reaction condition in the selective hydrogenation of **5** to **6** over PVP-Pt-CoCl<sub>2</sub><sup>a</sup>

Co <sup>2+</sup> <sup>b</sup>	NaOH (mg)	H <sub>2</sub> O (mL)	EtOH (mL)	Conversion of <b>5</b> (%)	Selectivity to <b>6</b> (%)
0	0	10	20	62.3	37.5
0	1	10	20	70.6	44.5
5	0	10	20	98.3	91.7
1	1	10	20	98.4	98.5
1	3	10	20	98.4	90.1
1	5	10	20	98.5	89.5
1	1	0	30	67.2	99.1
1	1	5	25	82.2	98.8
1	1	15	15	98.3	85.4

<sup>a</sup> Other conditions: 0.500 g **5** ( $3.24 \times 10^{-3}$  mol), 1.00 g ethylene glycol (internal standard for GC),  $2.34 \times 10^{-5}$  mol PVP-Pt; 6.0 MPa H<sub>2</sub>, 333 K and 2 h.

<sup>b</sup> The numbers refer to the molar ratios of Co<sup>2+</sup>:Pt.

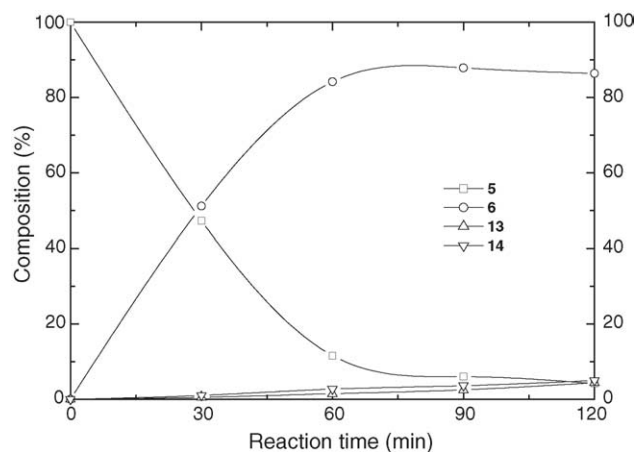


Fig. 7. Selective hydrogenation of **5** to **6** over PVP-Ru. Reaction conditions: 40 mL EtOH, 1.0 mg NaOH, 0.500 g **5** ( $3.24 \times 10^{-3}$  mol), 1.00 g ethylene glycol (internal standard for GC), 20 mL PVP-Ru colloidal dispersion (containing  $2.34 \times 10^{-5}$  mol Pt,  $1.17 \times 10^{-3}$  mol PVP, 10 mL H<sub>2</sub>O and 10 mL EtOH); 6.0 MPa H<sub>2</sub>, 333 K.

#### 5.4. Selective hydrogenation of **7** to **8** over PVP-Pt, PVP-Pd, PVP-Ru, PVP-Pd/Pt, PVP-Ru/Pt and PVP-Ru/Pd colloids [74–77]

Aromatic haloamines are important materials in the chemistry of dyes, pharmaceuticals, pesticides and herbicides. For the reason of environmental pollution of traditional production methods, many researchers try to make it with selective hydrogenation. However, the hydrogenation of halonitrobenzenes is very complicated. Taking **7** as an example, its N=O group may be hydrogenated (Scheme 4, reaction (2)) or it may be dehalogenated (Scheme 4, reactions (1) and (2')). Besides the desired product **8**, many byproducts such as aniline (**15**), nitrobenzene (**16**), *o*-chlorophenylhydroxylamine, *o*-chloronitrosobenzene, azo- and azoxy-dichlorobenzenes, chlorobenzene and so on may be formed at the same time. The reactions over conventional supported metal catalysts have been reviewed by Greenfield and

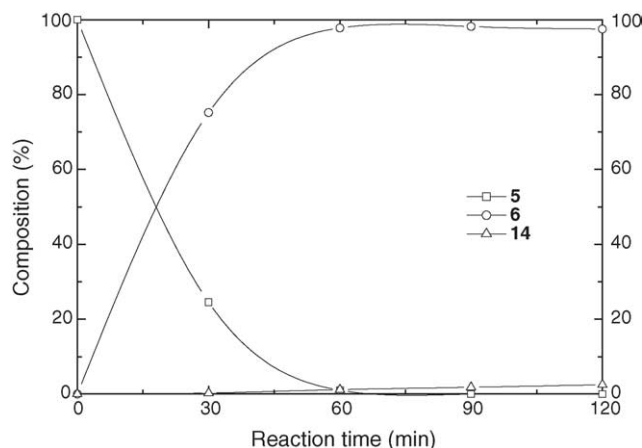
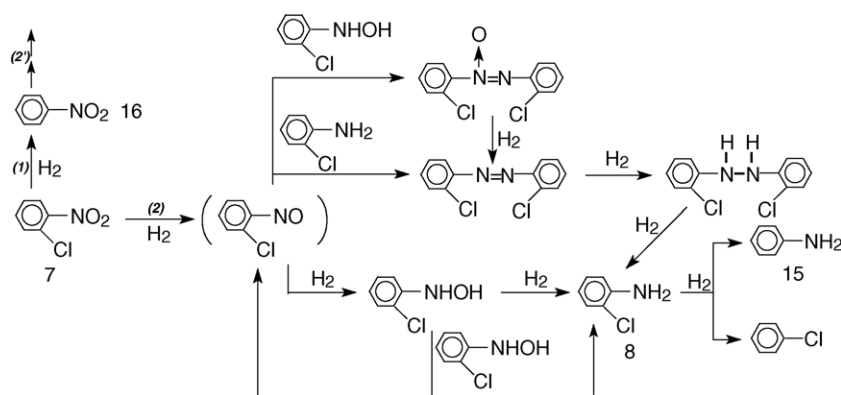


Fig. 8. Selective hydrogenation of **5** to **6** over PVP-Ru-CoCl<sub>2</sub>. Reaction conditions: 40 mL EtOH, 1.0 mg NaOH, 0.500 g **5** ( $3.24 \times 10^{-3}$  mol), 1.00 g ethylene glycol (internal standard for GC), 20 mL PVP-Ru colloidal dispersion (containing  $2.34 \times 10^{-5}$  mol Pt,  $1.17 \times 10^{-3}$  mol PVP, 10 mL H<sub>2</sub>O and 10 mL EtOH) and  $2.34 \times 10^{-5}$  mol CoCl<sub>2</sub>; 6.0 MPa H<sub>2</sub>, 333 K.



Scheme 4.

Dovell [101], Bond and Webster [102] and Kosak [103,104]. Coq et al. have studied carefully the selective hydrogenation of **7** to **8** over supported Pt catalysts with aspects to particle size, combination of two metals, precursors and supports [105–107]. In the following sections, we summarize our investigation on this reaction by noble metal colloidal nanocatalysts.

#### 5.4.1. Selective hydrogenation of **7** to **8** over PVP-Pt colloids

Pt is one of the most widely investigated metal catalysts for this reaction [105–107] and colloidal Pt is a well-discussed topic in literatures [44,51,108,109]. Due to their thermodynamic instability, colloidal particles will increase in size during storage in solution. We found that the PVP-Pt colloid stored in solution at ambient condition for 5 months had different catalytic properties from the freshly synthesized one (Fig. 9).

The initial rate, average rate and selectivity to **8** were, respectively, 2.20, 0.69 mol H<sub>2</sub>/mol Pt s and 63.0% for the fresh colloid; the corresponding values for the stored colloid were 1.50, 0.34 mol H<sub>2</sub>/mol Pt s and 46.0%. Furthermore, the modification effects of metal cations on them were also different. For example, the addition of Co<sup>2+</sup> increased very much the selectivity

of the fresh one and influenced little the activity; whereas, the same addition enhanced the selectivity just by 7.4% and lowered the initial rate of the outdated colloid sample. Anyhow, the selectivity was increased in the two colloids on modification by Fe<sup>3+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup>. The most pronounced improvements were observed by the addition of Co<sup>2+</sup> to the fresh colloid and the addition of Ni<sup>2+</sup> to the outdated colloids.

We initially suspected that this was due to the size effect. TEM observation showed that the size of the outdated colloid was 1.55 nm, but all the freshly synthesized PVP-Pt colloids with size of 1.1, 1.5, 1.7, 1.8 and 2.5 nm gave 60–70% selectivity, not 46%. This ruled out the effect of particle size. A more plausible explanation may be that the colloidal particles of the freshly prepared sample were in the nascent state, which has superior properties; these particles became more regular on aging and lost their reactivities [110].

For the outdated PVP-Pt colloid (average diameter was 1.55 nm), we have studied the modification by metal cations in detail [77]. From Table 11, it can be seen that the influence of metal cations can be grouped into three categories: (a) Li<sup>+</sup>, Cr<sup>3+</sup>, Ba<sup>2+</sup>, Al<sup>3+</sup> and Mn<sup>2+</sup> did not affect the catalytic properties of PVP-Pt; (b) Sn<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> toxicated the PVP-Pt catalyst

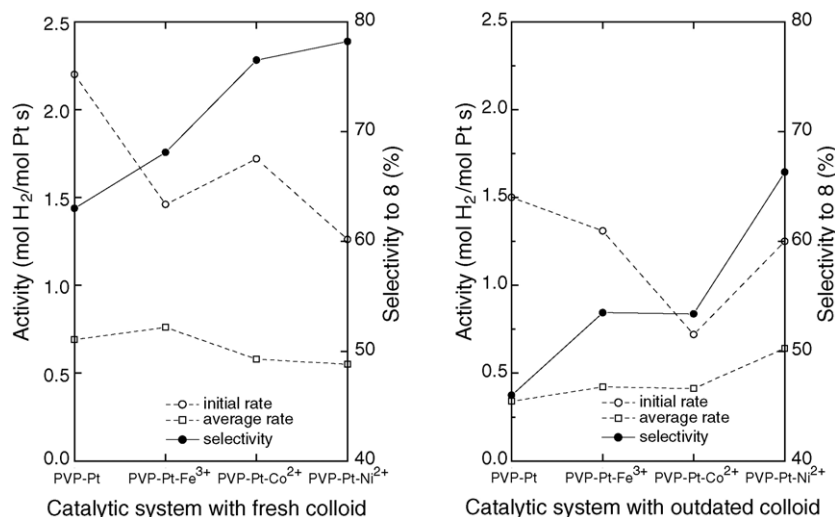


Fig. 9. Selective hydrogenation of **7** to **8** over fresh and outdated PVP-Pt with metal cations. Reaction conditions:  $4.49 \times 10^{-6}$  mol PVP-Pt colloid,  $1.70 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (as an internal standard for GC) and  $4.49 \times 10^{-6}$  mol metal salt; 0.1 MPa H<sub>2</sub>, 303 K (the whole volume was 15.0 mL, MeOH).

Table 11  
Hydrogenation of **7** to **8** over PVP-Pt-MCl<sub>x</sub> catalytic systems<sup>a</sup>

Catalytic system	Average rate (mol H <sub>2</sub> /mol Pt s)	Conversion of <b>7</b> (%)	Selectivity <sup>b</sup> (%)			
			<b>8</b>	<b>15</b>	<b>16</b>	Others
PVP-Pt	0.34	97.2	46.0	0.9	1.2	51.9
PVP-Pt-LiCl	0.39	100	51.7	Trace	1.0	47.3
PVP-Pt-CrCl <sub>3</sub>	0.34	100	40.2	2.1	2.4	55.3
PVP-Pt-BaCl <sub>2</sub>	0.30	100	46.0	Trace	3.0	51.0
PVP-Pt-AlCl <sub>3</sub>	0.32	95.8	48.0	2.4	10.5	39.1
PVP-Pt-MnCl <sub>2</sub>	0.34	100	43.0	4.4	5.2	47.4
PVP-Pt-SnCl <sub>2</sub>	0.06	66.9	55.5	20.9	0	23.6
PVP-Pt-CuCl <sub>2</sub>	0	0	–	–	–	–
PVP-Pt-ZnCl <sub>2</sub>	0.02	11.1	50.3	25.1	0	24.6
PVP-Pt-FeCl <sub>3</sub>	0.42	95.1	53.5	Trace	0	46.5
PVP-Pt-CoCl <sub>2</sub>	0.41	95.0	53.4	1.4	1.1	44.1
PVP-Pt-NiCl <sub>2</sub>	0.64	100	66.3	0	0	33.7

<sup>a</sup> Molar ratio of M:Pt=1:1. Reaction conditions:  $4.49 \times 10^{-6}$  mol PVP-Pt colloid,  $1.70 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC) and  $4.49 \times 10^{-6}$  mol metal salt; 0.1 MPa H<sub>2</sub> and 303 K (the whole volume was 15.0 mL, MeOH).

<sup>b</sup> **15** = aniline; **16** = nitrobenzene; others = mixture of *o*-chlorophenylhydroxylamine, *o*-chloronitrosobenzene, chlorobenzene, azo- and azoxy-dichlorobenzenes.

with a slight increase in selectivity (5–10%); (c) Fe<sup>3+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup> increased both the activity and the selectivity of PVP-Pt.

It has been known that in the selective hydrogenation of C=O double bonds (**1** → **2**, **3** → **4** and **5** → **6**), the best metal cations were Fe<sup>3+</sup> (Fe<sup>2+</sup>) and Co<sup>2+</sup>, followed by Ni<sup>2+</sup>. However, for the hydrogenation of N=O double bonds over the outdated Pt colloid, Ni<sup>2+</sup> was the best, followed by Fe<sup>3+</sup> (Fe<sup>2+</sup>) and Co<sup>2+</sup>.

Further study on the hydrogenation of **7** over poly(vinylpyrrolidone-co-acrylic acid)-stabilized Pt colloid (PVPAA-Pt) showed better overall results than PVP-Pt with or without metal cation modification (Table 12) [111]. Both the average rate and selectivity to **8** were increased by at least 50%, possibly due to the stronger interaction of metal cations to the C=O group in carboxylic acid [111,112], which draws more metal cations around the nanoparticles and therefore benefits the activity and selectivity of the nanocatalysts (see Section 6 for more discussion on the mechanism).

#### 5.4.2. Selective hydrogenation of **7** to **8** over PVP-Pd colloid

Pd catalyst is very efficient for the hydrogenation of C=C double bond, and it has higher activity for dehalogenation

Table 12  
Hydrogenation of **7** to **8** over PVPAA-Pt colloidal nanocatalyst<sup>a</sup>

No.	Catalytic system <sup>b</sup>	Average rate (mol H <sub>2</sub> /mol Pt s)	Selectivity to <b>8</b> <sup>c</sup> (%)
1	PVP-Pt	0.72	69.2
2	PVP-Pt-FeCl <sub>3</sub>	0.61	72.1
3	PVP-Pt-CoCl <sub>2</sub>	0.78	78.1
4	PVP-Pt-NiCl <sub>2</sub>	0.63	97.1

<sup>a</sup> Reaction conditions:  $4.80 \times 10^{-6}$  mol PVP-Pt colloid,  $1.00 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC); 0.1 MPa H<sub>2</sub> and 303 K (the whole volume was 15.0 mL, MeOH).

<sup>b</sup> The molar ratio of metal salt:Pt = 6:1.

<sup>c</sup> The conversion of **7** was 100%; the other products included aniline, nitrobenzene, *o*-chlorophenylhydroxylamine, *o*-chloronitrosobenzene, chlorobenzene, azo- and azoxy-dichlorobenzenes.

than hydrogenation of the N=O double bond [60,103]. Thus, one may expect PVP-Pd colloid to exhibit higher activity and lower selectivity to **8** than PVP-Pt colloid. However, our results indicated that PVP-Pd exhibited not only lower selectivity but also lower activity than PVP-Pt; its activity and selectivity were even lower than the outdated PVP-Pt colloid (Table 13).

It can be seen from Table 13 that the addition of metal cations influenced little on the selectivity. The activity was increased by 45% by Ni<sup>2+</sup>, which is not surprising. However, Zn<sup>2+</sup>, which was a poison for PVP-Pt (vide ante), acted as a promoter to PVP-Pd: the activity was nearly doubled.

#### 5.4.3. Selective hydrogenation of **7** to **8** over PVP-Pd/Pt bimetallic colloids

Bimetallic catalysts have been employed more widely than monometallic catalysts, which promote the study on bimetallic colloids [8,30,32,40,41]. It is expected that the bimetallic colloids may provide a greater potential for tailoring the catalytic properties since the difference between the electronic structures of the two metals can be varied over a wide range. We hope that the Pd/Pt bimetallic colloids will combine the higher selectivity of PVP-Pt and higher activity of PVP-Pd.

A series of PVP-Pd/Pt colloids with different molar ratios of Pd/Pt (4/1, 3/1, 2/1, 1/1, 1/2, 1/3 and 1/4) were synthesized by ethanol reduction. The selective hydrogenation of **7** to **8** over PVP-Pd/Pt colloids with the modification by metal cations were explored as shown in Fig. 10.

Most PVP-Pd/Pt colloids displayed higher activity than PVP-Pd and PVP-Pt, except for PVP-Pd/Pt(4/1) which was less active than PVP-Pt. PVP-Pd/Pt(3/1) gave the highest activity at 3.20 mol H<sub>2</sub>/mol Me s. The selectivity increased with the increase in Pt content, with a maximum value of 77.5% obtained in Pd/Pt = 1/3.

Six metal cations (Li<sup>+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup>) were tested as modifiers for the PVP-Pd/Pt bimetallic colloids with different Pd/Pt molar ratios. Generally speaking, metal cations increased the selectivity to **8** over PVP-Pd/Pt series, with

Table 13  
Hydrogenation of **7** to **8** over PVP-Pd-MCl<sub>x</sub> catalytic systems<sup>a</sup>

Catalytic system	Initial rate (mol H <sub>2</sub> /mol Pd s)	Average rate (mol H <sub>2</sub> /mol Pd s)	Conversion of <b>7</b> (%)	Selectivity <sup>b</sup> (%)			
				<b>8</b>	<b>15</b>	<b>16</b>	Others
PVP-Pd	0.40	0.39	89.1	38.4	51.0	2.2	8.4
PVP-Pd-LiCl	0.34	0.33	85.9	29.2	38.2	4.5	28.1
PVP-Pd-MnCl <sub>2</sub>	0.38	0.36	87.0	29.0	38.8	3.4	28.5
PVP-Pd-NiCl <sub>2</sub>	0.58	0.61	94.0	33.1	40.6	3.7	22.9
PVP-Pd-FeCl <sub>3</sub>	0.46	0.42	86.4	32.2	32.6	5.3	29.9
PVP-Pd-CoCl <sub>2</sub>	0.35	0.36	100	35.8	53.2	6.1	4.9
PVP-Pd-ZnCl <sub>2</sub>	0.79	0.72	87.2	42.9	41.8	2.5	41.7
PVP-Pd-AlCl <sub>3</sub>	0.27	0.33	81.1	30.7	25.5	2.1	12.8
PVP-Pd-MgCl <sub>2</sub>	0.38	0.44	83.5	32.6	37.0	6.8	23.6

<sup>a</sup> Molar ratio of M:Pd = 1:1. Reaction conditions:  $4.80 \times 10^{-6}$  mol PVP-Pd colloid,  $1.00 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (as an internal standard for GC) and  $4.80 \times 10^{-6}$  mol metal salt; 0.1 MPa H<sub>2</sub> and 303 K (the whole volume was 15.0 mL, MeOH).

<sup>b</sup> **15** = aniline; **16** = nitrobenzene; others = mixture of *o*-chlorophenylhydroxylamine, *o*-chloronitrosobenzene, chlorobenzene, azo- and azoxy-dichlorobenzenes.

Zn<sup>2+</sup> as the most efficient modifier. But they displayed complicated effects on the activity with regular patterns. Typically, Mn<sup>2+</sup> and Ni<sup>2+</sup> increased the activity of PVP-Pd/Pt(1/2) by 65 and 37%, respectively.

#### 5.4.4. Selective hydrogenation of **7** to **8** over PVP-Ru colloid

Coq et al. have reported that supported Ru catalyst displayed high selectivity and very low activity in the selective hydrogenation of **7** to **8** [113]. The PVP-Ru prepared by NaBH<sub>4</sub> reduction also exhibited very low activity. We carried out this reaction under a pressure of 4.0 MPa H<sub>2</sub> at 320 K in a 100 mL stainless steel autoclave for 4 h; GC analysis showed that all the **7** was quantitatively hydrogenated to **8** with a selectivity of >99.9% to **8**.

The metal cations effect was also studied on ruthenium colloid. The results are summarized in Table 14. The metal cations surveyed improved the activity to different extent while maintaining the high selectivity (>99.9%). The maximum activity was obtained by the modification with Fe<sup>3+</sup>. It is interesting to note that Sn<sup>2+</sup> promoted the activity by 7% and Zn<sup>2+</sup> influenced little the activity of PVP-Ru. This is different from the hydrogenation of **7** over PVP-Pt catalyst where Ni<sup>2+</sup> gave the best result and Sn<sup>2+</sup> and Zn<sup>2+</sup> acted as poisons. A similar positive effect upon alloying Sn to Ru was reported in the hydrogenation of *p*-chloronitrobenzene to *p*-chloroaniline over

Table 14  
Hydrogenation of **7** to **8** over PVP-Ru-MCl<sub>x</sub> catalytic systems<sup>a</sup>

Catalytic system	Conversion of <b>7</b> (%)	Selectivity to <b>8</b> (%)
PVP-Ru	39.0	>99.9
PVP-Ru-ZnCl <sub>2</sub>	36.2	>99.9
PVP-Ru-SnCl <sub>2</sub>	46.2	>99.9
PVP-Ru-FeCl <sub>3</sub>	62.0	>99.9
PVP-Ru-CoCl <sub>2</sub>	42.1	>99.9
PVP-Ru-NiCl <sub>2</sub>	53.4	>99.9

<sup>a</sup> Molar ratio of M:Pt = 1:1. Reaction conditions:  $1.87 \times 10^{-5}$  mol PVP-Ru colloid,  $1.00 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC) and  $1.87 \times 10^{-5}$  mol metal salt; 4.0 MPa H<sub>2</sub>, 320 K and 1.5 h (the whole volume was 15.0 mL, MeOH).

Ru-Sn/Al<sub>2</sub>O<sub>3</sub>, in which Sn was believed in zero oxidation state [113]. However, it is not easy to make Sn in zero oxidation state [114].

It should be noted that the reaction was strictly zero-order with respect to the reactant, **7** [74]. This is different from the other catalytic systems, such as PVP-Pt, PVP-Pd, PVP-Pd/Pt, and PVP-Ru/Pt and PVP-Ru/Pd described in the next section, and other supported metal catalysts [101–107].

#### 5.4.5. Selective hydrogenation of **7** to **8** over PVP-Ru/Pt and PVP-Ru/Pd bimetallic colloids

PVP-Ru exhibited very good catalytic performance—100% selectivity at 100% conversion; however, the reaction rate was very low, just 0.00028 mol H<sub>2</sub>/mol Ru s. This was much lower than those with PVP-Pt, PVP-Pd or PVP-Pd/Pt colloids. We synthesized PVP-Ru/Pt and PVP-Ru/Pd bimetallic colloids, expecting they will display the high selectivity of PVP-Ru and the high activity of PVP-Pt or PVP-Pd.

The results of the selective hydrogenation of **7** to **8** over PVP-Ru/Pt and PVP-Ru/Pd colloidal catalysts are shown in Figs. 11 and 12, respectively.

Although the activity of PVP-Ru/Pt(9/1) was not very high (just 0.030 mol H<sub>2</sub>/mol Me s (Fig. 11)), it was already 100-fold higher than that of PVP-Ru (0.00028 mol H<sub>2</sub>/mol Ru s). However, the selectivity decreased from 100 to 70.0%. In another word, alloying of only 10% Pt to Ru colloid, much higher activity and a little lower selectivity (comparing with PVP-Ru) were obtained. The PVP-Ru/Pd colloids also exhibited similar behaviors, but both the activity and the selectivity were lower than the corresponding PVP-Ru/Pt colloids (Fig. 12).

From the above results, it is clear that the activity of the bimetallic colloids was much higher than that of PVP-Ru, but the selectivity dropped. It has been observed that some metal cations can increase the activity and/or the selectivity of PVP-Pt, PVP-Pd, PVP-Pd/Pt and PVP-Ru in this reaction system (**7** → **8**). We thus investigated the effects of metal cations on catalytic properties of PVP-Ru/Pt and PVP-Ru/Pd bimetallic colloids. Table 15 lists some of the results.

Zn<sup>2+</sup> poisoned the PVP-Ru/Pt colloid catalysts; Fe<sup>3+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup> enhanced the selectivity to >99%, but dimin-

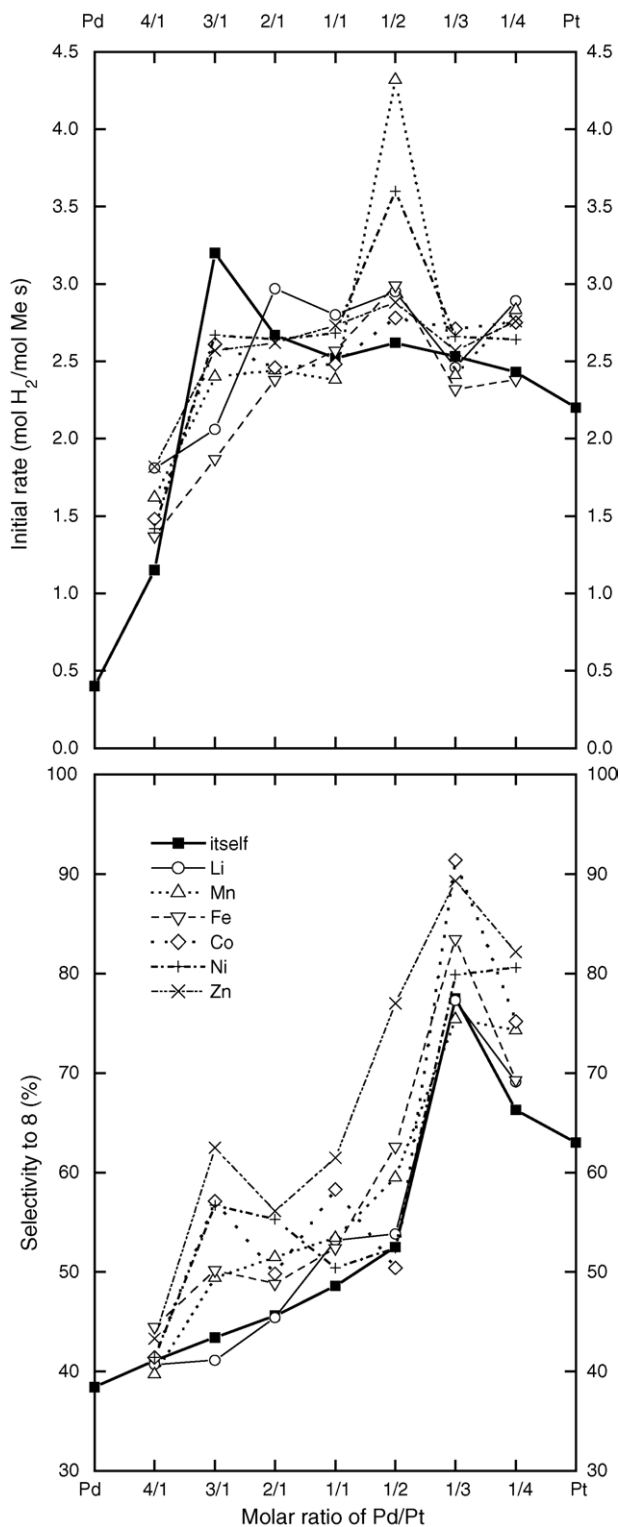


Fig. 10. Modification of metal cations to PVP-Pd/Pt in the selective hydrogenation of **7** to **8**. Reaction conditions:  $4.80 \times 10^{-6}$  mol PVP-Pd/Pt colloid,  $1.00 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC) and  $4.80 \times 10^{-6}$  mol metal salt; 0.1 MPa  $H_2$  and 303 K (the whole volume was 15.0 mL, MeOH).

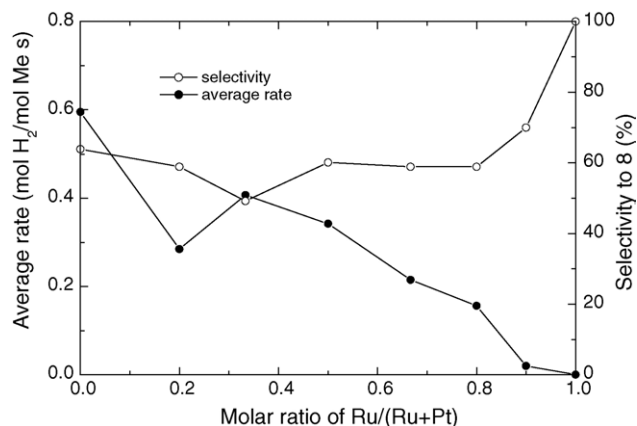


Fig. 11. Selective hydrogenation of **7** to **8** over PVP-Ru/Pt. Reaction conditions:  $1.87 \times 10^{-5}$  mol PVP-Ru/Pt colloid,  $1.00 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC); 0.1 MPa  $H_2$ , 303 K (the whole volume was 15.0 mL, MeOH).

ished the activity by 50–90% except for PVP-Ru/Pt(9/1). In PVP-Ru/Pt(9/1)- $CoCl_2$  catalytic system, the activity was 0.018 mol  $H_2$ /mol Me s (which was 63-fold higher than that of PVP-Ru) and the selectivity was also high at 99%. To PVP-Ru/Pd,  $Fe^{3+}$  was the best modifier: both the activity and the selectivity were increased by nearly one-fold. Unlike in other catalytic systems,  $Ni^{2+}$  acted as a poison on PVP-Ru/Pd(1/1).

## 6. Modification mechanism of metal cations on the catalytic properties of PVP-stabilized metal colloids

The modification by metal cations on polymer-stabilized noble metal colloid catalysts is very complicated. Table 16 summarizes some typical results on the four reaction systems over different colloid catalysts.

From the above discussion and Table 16 it can be deduced that:

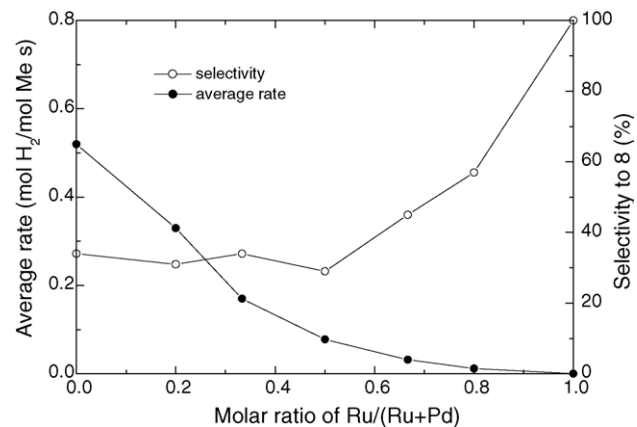


Fig. 12. Selective hydrogenation of **7** to **8** over PVP-Ru/Pd. Reaction conditions:  $1.87 \times 10^{-5}$  mol PVP-Ru/Pd colloid,  $1.00 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC); 0.1 MPa  $H_2$ , 303 K (the whole volume was 15.0 mL, MeOH).

Table 15  
Hydrogenation of **7** to **8** over PVP-Ru/Pt(Pd)-MCl<sub>x</sub> catalytic systems<sup>a</sup>

No.	Catalytic system	Initial rate <sup>b</sup> (mol H <sub>2</sub> /mol Me s)	Average rate <sup>b</sup> (mol H <sub>2</sub> /mol Me s)	Conversion of <b>7</b> (%)	Selectivity <sup>c</sup> (%)			
					<b>8</b>	<b>15</b>	<b>16</b>	Others
1	PVP-Ru <sup>d</sup>	0.00028	0.00028	100	>99.9	0	0	Trace
2	PVP-Pt <sup>e</sup>	1.98	0.60	100	63.9	8.3	0	27.8
3	PVP-Ru/Pt(4/1)	0.24	0.16	100	58.9	14.1	4.3	22.7
4	PVP-Ru/Pt(4/1)-LiCl	0.14	0.092	99.0	52.7	10.3	0.8	36.2
5	PVP-Ru/Pt(4/1)-ZnCl <sub>2</sub> <sup>f</sup>	0.012	–	–	–	–	–	–
6	PVP-Ru/Pt(4/1)-FeCl <sub>3</sub>	0.030	0.052	100	97.7	Trace	0.8	1.5
7	PVP-Ru/Pt(4/1)-NiCl <sub>2</sub>	0.036	0.071	100	94.6	1.1	1.0	3.3
8	PVP-Ru/Pt(4/1)-CoCl <sub>2</sub>	0.13	0.11	100	99.5	0.4	Trace	0
9	PVP-Ru/Pt(9/1)	0.030	0.020	93.0	70.0	8.0	0	22.0
10	PVP-Ru/Pt(9/1)-CoCl <sub>2</sub>	0.033	0.018	99.0	99.0	0.9	0	Trace
11	PVP-Ru/Pt(1/4)	0.48	0.29	100	58.9	14.1	3.3	23.7
12	PVP-Ru/Pt(1/4)-CoCl <sub>2</sub>	0.15	0.071	100	>99.9	0	0	Trace
13	PVP-Pd <sup>e</sup>	0.60	0.52	90.5	34.2	53.4	2.2	10.2
14	PVP-Ru/Pd(1/1)	0.10	0.078	88.2	29.1	41.6	0.6	28.7
15	PVP-Ru/Pd(1/1)-FeCl <sub>3</sub>	0.18	0.12	98.2	55.5	34.9	1.7	7.9
16	PVP-Ru/Pd(1/1)-CoCl <sub>2</sub>	0.052	0.071	88.3	45.0	30.6	4.0	20.4
17	PVP-Ru/Pd(1/1)-NiCl <sub>2</sub> <sup>f</sup>	0.015	–	–	–	–	–	–

<sup>a</sup> Molar ratio of M:Pt = 1:1. Reaction conditions:  $1.87 \times 10^{-5}$  mol metal colloid,  $1.00 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC) and  $1.87 \times 10^{-5}$  mol metal salt; 0.1 MPa H<sub>2</sub> and 303 K (the whole volume was 15.0 mL, MeOH).

<sup>b</sup> Me = Ru, Pt, Pd, or Ru + Pt, Ru + Pd.

<sup>c</sup> **15** = aniline; **16** = nitrobenzene; others = mixture of *o*-chlorophenylhydroxylamine, *o*-chloronitrosobenzene, chlorobenzene, azo- and azoxy-dichlorobenzenes.

<sup>d</sup> Reaction conditions:  $1.87 \times 10^{-5}$  mol PVP-Ru colloid,  $1.00 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (as an internal standard for GC); 4.0 MPa H<sub>2</sub>, 320 K and 4 h (the whole volume was 15.0 mL, MeOH).

<sup>e</sup> PVP-Pt and PVP-Pd in this table were prepared by NaBH<sub>4</sub> reduction as PVP-Ru with average diameters and standard deviations of 3.5 and 0.53 nm, 3.1 and 0.71 nm, respectively; the precursor of PVP-Pd was H<sub>2</sub>PdCl<sub>4</sub>·*n*H<sub>2</sub>O converted from PdCl<sub>2</sub> by concentrated hydrochloric acid.

<sup>f</sup> These two reactions could not be preceded completely, only 2–5% conversion of **7** was obtained.

- (1) For the hydrogenation of the C=O double bonds, the metal cation effects can be sorted into four styles: (a) no effect; (b) toxication; (c) increasing the selectivity only; (d) increasing both the activity and the selectivity.
- (2) For the hydrogenation of the N=O double bonds, the effects of metal cations are more complicate.
  - (i) For PVP-Pt and PVP-Ru colloid catalysts, metal cations display three kinds of effects: (a) no effect; (b) toxication; (c) increasing both the activity and the selectivity.
  - (ii) For PVP-Pd: (a) no effect; (b) increasing the activity only.
  - (iii) For PVP-Ru/Pt colloids, metal cations increase the selectivity but decrease the activity except PVP-Ru/Pt(9/1) in which the activity was not affected.
  - (iv) For PVP-Ru/Pd and PVP-Pd/Pt colloids, the selectivity increased, the activity may be raised or lowered.
- (3) For different reaction systems and different colloids, the most favorable metal cations are different. For example, Fe<sup>3+</sup> (Fe<sup>2+</sup>) and Co<sup>2+</sup> are the best modifiers for the hydrogenation of the C=O double bonds over PVP-Pt or PVP-Ru colloids, whereas Ni<sup>2+</sup> and Zn<sup>2+</sup> are the best for N=O double bonds over PVP-Pd colloid.
- (4) The same metal cation displays different effects to different reaction systems and different colloids. For instance, Zn<sup>2+</sup> acted as a poison for the hydrogenation of the C=O and N=O double bonds over PVP-Pt, but was the best one for N=O double bonds over PVP-Pd.

The study of metal ion effect can be traced back to 1920s, when Adams and coworkers have studied extensively the effects of various substrates, especially metal ions of Fe<sup>2+</sup>, Co<sup>2+</sup> and Zn<sup>2+</sup>, on the platinum oxide-platinum black catalyst in the reduction of aldehydes [63–65,87,88]. But they thought FeCl<sub>2</sub> acted as a powerful anti-oxidizer toward the oxidation of the aldehydes, and 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.

Maxted summarized the results of a systematic study on the toxicity of metal ions to a platinum catalyst in the hydrogenation of cinnamic acid [66,67]. They concluded that the toxic metal ions were those in which all five orbitals of a d shell, immediately preceding the s or the 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<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Ce<sup>3+</sup>, Nd<sup>3+</sup>, Al<sup>3+</sup> are non-toxic and Mn<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> are toxic. This is obviously not a satisfactory explanation to the results listed in Tables 4, 6, 9 and 11–16, and Figs. 6 and 8–10.

Recently, Ponc reviewed in detail the role of promoters, especially the metal ions [68]. Many mechanisms were discussed, but none of them can give a reasonable interpretation to all of our experiment facts: (a) the cations in the reaction system remained in the ionic state (except for Cu<sup>2+</sup>, Pb<sup>2+</sup>); (b) there was no support for this catalyst (PVP may be regarded as a kind of support for the platinum colloidal particles, but the interac-

Table 16  
Modification effect of metal cations to noble metal colloidal nanocatalysts

Reaction system	Catalytic system	Relative rate	Selectivity (%)
1 → 2	PVP-Pt	1.00	12.0
	PVP-Pt-FeCl <sub>3</sub>	2.23	98.5
	PVP-Pt-CoCl <sub>2</sub>	2.21	98.8
3 → 4	PVP-Pt	1.00	10.2
	PVP-Pt-FeCl <sub>3</sub>	1.10	48.9
	PVP-Ru	1.00	4.0
	PVP-Ru-FeCl <sub>3</sub>	0.42	13.6
5 → 6	PVP-Pt	1.00	44.5
	PVP-Pt-FeCl <sub>3</sub>	1.38	97.6
	PVP-Pt-CoCl <sub>2</sub>	1.39	98.5
	PVP-Ru	1.00	95.2
	PVP-Ru-CoCl <sub>2</sub>	1.13	99.8
7 → 8	PVP-Pt	1.00	46.0
	PVP-Pt-NiCl <sub>2</sub>	1.88	66.3
	PVP-Pd	1.00	38.1
	PVP-Pd-NiCl <sub>2</sub>	1.45	33.1
	PVP-Pd-ZnCl <sub>2</sub>	1.98	42.9
	PVP-Ru	1.00	100
	PVP-Ru-FeCl <sub>3</sub>	1.59	100
	PVP-Ru-NiCl <sub>2</sub>	1.37	100
	PVP-Pd/Pt(1/2)	1.00	52.5
	PVP-Pd/Pt(1/2)-FeCl <sub>3</sub>	1.45	62.6
	PVP-Pd/Pt(1/3)	1.00	77.5
	PVP-Pd/Pt(1/3)-ZnCl <sub>2</sub>	0.20	89.3
	PVP-Ru/Pt(4/1)	1.00	58.9
	PVP-Ru/Pt(4/1)-CoCl <sub>2</sub>	0.54	99.5
	PVP-Ru/Pt(1/4)	1.00	58.9
	PVP-Ru/Pt(1/4)-CoCl <sub>2</sub>	0.31	>99.9
	PVP-Ru/Pd(1/1)	1.00	29.1
	PVP-Ru/Pd(1/1)-FeCl <sub>3</sub>	1.80	55.5
	PVP-Ru/Pd(1/1)-CoCl <sub>2</sub>	0.52	45.0

tion with the cations is very weak [71,112]); (c) the addition of metal cations in this study is done after the formation of the colloidal noble metal catalyst, so that the possibility of change in the size, shape and structure of the platinum colloidal particles is minima.

Although the procedure used by Goupil et al. [89] is the same as ours—adding FeCl<sub>2</sub> after the preparation of catalyst, Pt/C, the iron in their work (and the work from Richard et al. [90]) was in the zero oxidation state as determined by energy dispersive X-ray emission, because they pretreated the catalytic system by H<sub>2</sub> reduction in the preparation of catalysts or before the addition of the reactants.

As mentioned in the previous discussion, the change of molar percentage of Co<sup>2+</sup> in the PVP-Pt colloid does not influence the activity and selectivity in the way as reported for supported catalysts (see Fig. 2) [63–65,87–90]. The addition of a very small amount of Co<sup>2+</sup> (Co<sup>2+</sup>:Pt = 0.05:1) increased the activity and the selectivity promptly to high values and further addition of Co<sup>2+</sup> did not lower them.

We also found that the addition of metal cations depressed the hydrogenation of olefin (see Table 17). This indicates that Co<sup>2+</sup>, etc. can suppress the hydrogenation of olefinic group but accelerate the hydrogenation of carbonyl group at the same time.

Table 17  
Hydrogenation of cyclooctene over PVP-Pt colloid with metal salts<sup>a</sup>

Catalytic system	Initial rate (mol H <sub>2</sub> /mol Pt s)	Average rate (mol H <sub>2</sub> /mol Pt s)
PVP-Pt	0.081	0.046
PVP-Pt-CoCl <sub>2</sub>	0	0
PVP-Pt-NiCl <sub>2</sub>	0	0

<sup>a</sup> Reaction conditions: 2.0 mL PVP-Pt (containing  $4.68 \times 10^{-6}$  mol Pt), 2.0 mL cyclooctene ( $1.00 \times 10^{-3}$  mol), CoCl<sub>2</sub> or NiCl<sub>2</sub> ( $4.68 \times 10^{-6}$  mol); 0.1 MPa H<sub>2</sub> and 303 K (the whole volume was 15.0 mL, MeOH).

Further IR characterization showed that there was a weak interaction between the C=O group and metal cations (Fig. 13). This is demonstrated by the appearance of a small peak adding Fe<sup>3+</sup>, Co<sup>2+</sup> or Ni<sup>2+</sup> to the solution of **1**. This clearly demonstrated the interaction of C=O double bond in **1** with metal cations.

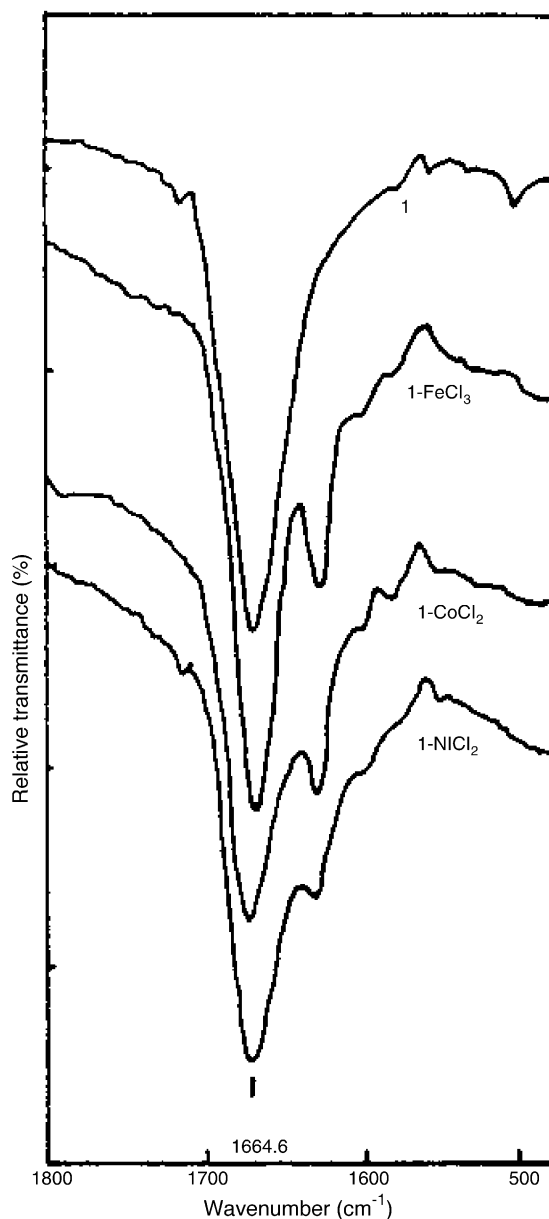


Fig. 13. IR spectra of **1** and **1**-MCl<sub>x</sub> in MeOH (298 K, 0.25 M) (M = Fe, Co, Ni).

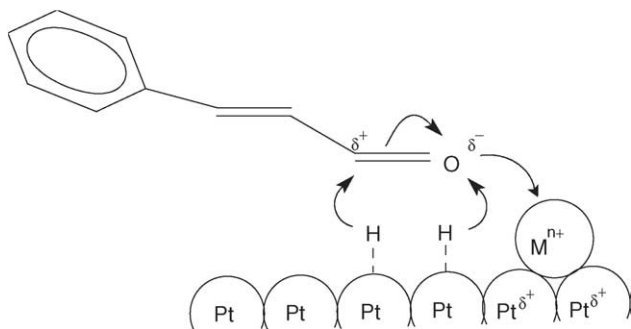


Fig. 14. Mechanism of the modification effect of metal cations to platinum colloidal nanocatalyst ( $M = \text{Fe}, \text{Co}, \text{Ni}, \text{etc.}$ ).

Activating the  $\text{C}=\text{O}$  double bonds with metal cations via “polarization” effect has been proposed by some researchers, but they did not give a conclusive evidence [68,115,116]. Based on the other published works and our experiment results, we propose a modified model to explain the modification mechanism tentatively (Fig. 14).

The adsorbed metal cations motivates the polar  $\text{C}=\text{O}$  group, then the nearby dissociated H atoms attack the C and O atoms of  $\text{C}=\text{O}$  group to generate a hydroxyl group. This model also highlights the steric hindrance effect to the high selectivity. Traditionally, the favorable effect of metal ions (especially in the metallic state) has been attributed to an electron transfer from them to platinum [117]. Here, we speculate another possibility that the electron transfers from platinum to the adsorbed metal cation and boosts the adsorbing ability of  $\text{C}=\text{O}$  double bond onto the platinum surface, therefore increases the activity and the selectivity.

To  $\text{N}=\text{O}$  double bonds, the influence of  $\text{Ni}^{2+}/\text{Pt}$  molar ratio to PVP-Pt gave another condition which is not like  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  in the reaction systems of  $1 \rightarrow 2$  and  $3 \rightarrow 4$ . It can be seen from Fig. 15 that the activity and the selectivity grew gradually with the increase of the addition of  $\text{Ni}^{2+}$ . When the molar ratio of  $\text{Ni}^{2+}/\text{Pt}$  reached 6:1, the activity and the selectivity reached their maxims, and changed little with more  $\text{Ni}^{2+}$ .

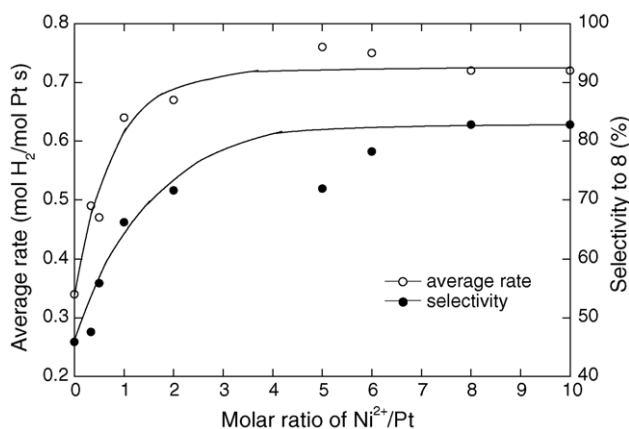


Fig. 15. Influence of the molar ratio of  $\text{Ni}^{2+}/\text{Pt}$  in the selective hydrogenation of **7** to **8** over PVP-Pt- $\text{NiCl}_2$ . Reaction conditions:  $4.49 \times 10^{-6}$  mol PVP-Pt colloid,  $1.70 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC) and  $\text{NiCl}_2$ ; 0.1 MPa  $\text{H}_2$  and 303 K (the whole volume was 15.0 mL, MeOH).

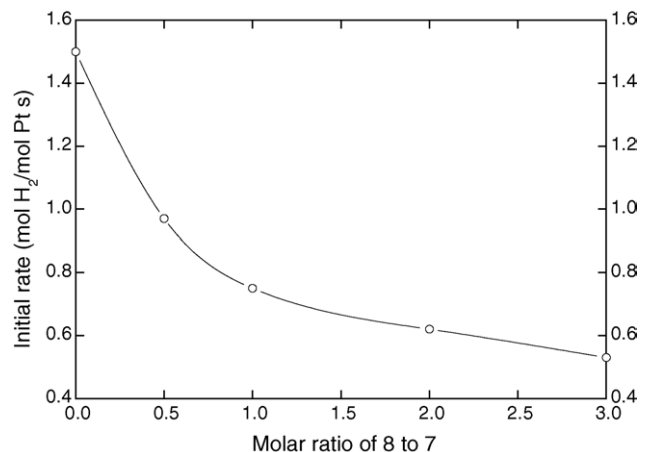


Fig. 16. Depressing effect of **8** in the selective hydrogenation of **7** to **8** over PVP-Pt. Reaction conditions:  $4.49 \times 10^{-6}$  mol PVP-Pt colloid,  $1.70 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC); 0.1 MPa  $\text{H}_2$  and 303 K (the whole volume was 15.0 mL, MeOH).

Coq et al. found that there was an adsorption competition between **7** and **8** [105–107]. Our work also indicated that the initial rate declined when adding **8** into the reaction system in advance (Fig. 16). So, it can be assumed that  $\text{Ni}^{2+}$  coordinates with the amino group in **8**, which blocks the adsorption of amino group on Pt colloidal particles, and also shields the effective concentration of  $\text{Ni}^{2+}$ . In another word, it needs more  $\text{Ni}^{2+}$  to take effect.

In summary, metal cations adsorbed on colloidal particles modify the particle’s surface electronic structures, as a result alter their catalytic performances. The differences of the inherent properties and of the interaction with metal cations to the nanostructured metal particles lead to the different modification effects of metal cations.

On the other hand, metal cations can be regarded as aqua metal complex ions. It can be expected that there are more different effects considering the large variations in the charge of the central metal ions, the type, volume, charge and number of the ligands, the space geometry configuration of the metal complex ions, the solvation, etc., which will tailor the catalysts’ performances in a greater extent. In fact, we did find some examples, and three of them are discussed here.

## 7. Modification of metal complex ions to PVP-stabilized metal colloids

In this study, metal complexes were formed in situ by mixing a metal salt (mostly from their chlorides) with a corresponding ligand at a given molar ratio. For the sake of simplicity, metal complex ions with stepwise stability constants  $k_1$  above ca.  $10^5$  were selected for the test [118,119]; the reaction temperature was reduced to 303 K and no NaOH was added in order to lower the possible dissociation of the complex ions.



Table 18

The effect of metal complex ions on the hydrogenation of **1** to **2** over PVP-Pt colloidal nanocatalyst<sup>a</sup>

No.	Catalytic system <sup>b</sup>	Average rate (mol l/mol Pt h)	Conversion of <b>1</b> (%)	Selectivity <sup>c</sup> (%)	
				<b>2</b>	<b>9</b>
1	PVP-Pt	220.6	65.5	17.7	82.3
2	PVP-Pt-FeCl <sub>3</sub>	267.8	79.5	62.0	38.0
3	PVP-Pt-NaF	143.1	42.5	15.3	84.7
4	PVP-Pt-Na <sub>3</sub> AlF <sub>6</sub>	221.3	65.7	21.0	79.0
5	PVP-Pt-Na <sub>3</sub> FeF <sub>6</sub>	262.7	78.0	75.0	25.0
6	PVP-Pt-Al(acac) <sub>3</sub>	188.6	56.0	25.0	75.0
7	PVP-Pt-Cr(acac) <sub>2</sub> Cl	276.8	82.2	19.7	80.3
8	PVP-Pt-Fe(acac) <sub>3</sub>	233.1	69.2	58.8	41.2
9	PVP-Pt-Co(acac) <sub>2</sub>	268.1	79.6	30.4	69.6
10	PVP-Pt-Ni(acac) <sub>2</sub>	230.7	68.5	25.5	74.5
11	PVP-Pt-Cu(acac) <sub>2</sub>	236.4	70.2	16.4	83.6
12	PVP-Pt-Ce(acac) <sub>3</sub>	253.0	75.1	18.6	81.4
13	PVP-Pt-Co(bpy) <sub>3</sub> Cl <sub>2</sub>	241.8	71.8	25.1	74.9
14	PVP-Pt-Ni(bpy) <sub>3</sub> Cl <sub>2</sub>	276.6	82.1	3.6	96.4
15	PVP-Pt-Fe(gly) <sub>3</sub>	253.9	75.4	34.9	65.1
16	PVP-Pt-Ni(gly) <sub>2</sub>	266.1	79.0	22.2	77.8
17	PVP-Pt-Zn(gly) <sub>2</sub>	214.6	63.7	26.7	73.3
18	PVP-Pt-Fe(sal) <sub>3</sub>	207.1	61.5	44.4	55.6

<sup>a</sup> Reaction conditions: 20 mL EtOH, 1.00 g **1** ( $7.58 \times 10^{-3}$  mol), 1.00 g tetradecanol (internal standard for GC), 20 mL PVP-Pt colloidal dispersion (containing  $1.13 \times 10^{-5}$  mol Pt,  $5.63 \times 10^{-4}$  mol PVP, 5 mL H<sub>2</sub>O and 5 mL EtOH) and metal complex; 4.0 MPa H<sub>2</sub>, 303 K and 2 h.

<sup>b</sup> Metal complexes were prepared in situ by mixing a metal salt with a corresponding ligand at a proper molar ratio; the molar ratio of metal complex:Pt = 1:20; acac = acetylacetonate, bpy = bipyridyl, gly = glycinate, sal = salicylate.

<sup>c</sup> **9** = 3-phenylpropanal, no 3-phenylpropan-1-ol (**10**) was detected by GC.

### 7.1. Selective hydrogenation of **1** to **2** over PVP-Pt [78]

The complex ions composed of the same central metal ion with different ligands (Table 18, nos. 2, 5, 8, 15, 18; 4, 6, 9, 13; 14, 16) or of different central metal ions with the same ligand (nos. 4, 5; 6–12; 13, 14, 15–17) displayed distinct influences on the catalytic properties. The iron complex ions, FeF<sub>6</sub><sup>3-</sup> (no. 5) and Fe(gly)<sub>3</sub> (no. 15) raised both the activity and the selectivity, while Fe(acac)<sub>3</sub> (no. 8) and Fe(sal)<sub>3</sub> (no. 18) increased the selectivity only. The acetylacetonate complex ions, Cr(acac)<sub>2</sub><sup>+</sup> (no. 7) or Ce(acac)<sub>3</sub> (no. 12), boosted the activity remarkably; but Ni(acac)<sub>2</sub> (no. 10) increased the selectivity moderately. The bipyridyl complex ions, Co(bpy)<sub>3</sub><sup>2+</sup> (no. 13) exerted a moderate effect; Ni(bpy)<sub>3</sub><sup>2+</sup> (no. 14) increased the conversion considerably to 82.1%, and the main product was not **2** but **9** with the selectivity to **9** as high as 97.3%. Cu<sup>2+</sup> and Zn<sup>2+</sup> were known poisons, but the activity and the selectivity were slightly fluctuated compared with the neat PVP-Pt while forming Cu(acac)<sub>2</sub> (no. 11) and Zn(gly)<sub>2</sub> (no. 17) complex ions. It thus provides an effective way to diminish the toxicity of some metal cations by adding proper ligands.

Fig. 17 shows the concentration dependence of FeF<sub>6</sub><sup>3-</sup> on PVP-Pt's performance. Both the activity and the selectivity reached near their maximum by a very small amount of complex ion as FeF<sub>6</sub><sup>3-</sup>:Pt = 0.1:1. This is similar to Co<sup>2+</sup> (Fig. 2).

### 7.2. Selective hydrogenation of **7** to **8** over PVP-Pt [79]

Table 19 lists the modification effects of some metal complex ions on the selective hydrogenation of **7** over the outdated PVP-Pt colloid. Although the results were diversified with the

complexes composed of the same central metal ion with different ligands (Table 19, nos. 2, 11, 18; 3, 12, 17; 4, 13; 5, 8, 14, 19; 6, 9, 15, 20) or of different central ions with the same ligand (nos. 8, 9; 11–15; 18–22), it is unquestionable that the modification effect of complex ions is not a simple sum of the central metal ions and the ligands. Generally speaking, the metal bipyridine complex ions lowered the hydrogenation reaction rate, the metal acetylacetonate complex ions displayed a more favorable effect comparing with the metal cations, the metal ethylenediamine complex ions lower the hydrogenation activity with an increase of the selectivity to **8**. This can be deduced clearly from Fig. 18.

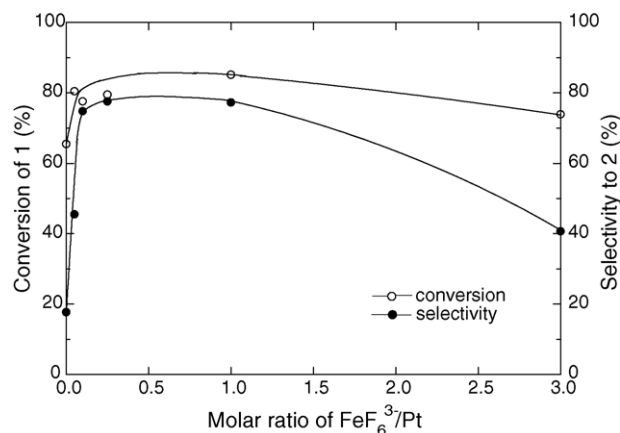


Fig. 17. Influence of the molar ratio of FeF<sub>6</sub><sup>3-</sup>/Pt in the selective hydrogenation of **1** to **2** over PVP-Pt-Na<sub>3</sub>FeF<sub>6</sub>. Reaction conditions: 20 mL EtOH, 1.00 g **1** ( $7.58 \times 10^{-3}$  mol), 1.00 g tetradecanol (internal standard for GC), 20 mL PVP-Pt colloidal dispersion (containing  $1.13 \times 10^{-5}$  mol Pt,  $5.63 \times 10^{-4}$  mol PVP, 5 mL H<sub>2</sub>O and 5 mL EtOH) and Na<sub>3</sub>FeF<sub>6</sub>; 4.0 MPa H<sub>2</sub>, 303 K and 2 h.

Table 19

The effect of metal complex ions on the hydrogenation of **7** to **8** over PVP-Pt colloidal nanocatalyst<sup>a</sup>

No.	Catalytic system <sup>b</sup>	Average rate (mol H <sub>2</sub> /mol Pt s)	Conversion of <b>7</b> (%)	Selectivity <sup>c</sup> (%)			
				<b>8</b>	<b>15</b>	<b>16</b>	Others
1	PVP-Pt	0.41	100	42.6	1.3	0	56.1
2	PVP-Pt-CrCl <sub>3</sub>	0.34	100	40.2	2.1	2.4	55.3
3	PVP-Pt-MnCl <sub>2</sub>	0.34	100	43.0	4.4	5.2	47.4
4	PVP-Pt-FeCl <sub>3</sub>	0.42	95.5	53.5	Trace	10.8	35.7
5	PVP-Pt-CoCl <sub>2</sub>	0.41	83.9	53.4	1.1	1.4	45.1
6	PVP-Pt-NiCl <sub>2</sub>	0.64	100	66.2	0	0	33.8
7	PVP-Pt-bpy	0.15	80.0	35.2	4.6	0	60.2
8	PVP-Pt-Co(bpy) <sub>3</sub> Cl <sub>2</sub>	0.11	64.2	31.8	0	0	68.2
9	PVP-Pt-Ni(bpy) <sub>3</sub> Cl <sub>2</sub>	0.18	83.9	31.3	2.2	0	66.5
10	PVP-Pt-Hacac	0.52	100	48.3	7.9	0	43.8
11	PVP-Pt-Cr(acac) <sub>3</sub>	0.36	86.9	34.9	4.0	0	61.1
12	PVP-Pt-Mn(acac) <sub>2</sub>	0.54	100	41.5	2.9	0	55.6
13	PVP-Pt-Fe(acac) <sub>3</sub>	0.44	100	62.9	6.9	0	30.2
14	PVP-Pt-Co(acac) <sub>2</sub>	0.83	100	76.5	1.5	0	22.0
15	PVP-Pt-Ni(acac) <sub>2</sub>	0.72	100	76.2	0	0	23.8
16	PVP-Pt-en	0.14	100	43.0	24.1	0	32.9
18	PVP-Pt-Cr(en) <sub>3</sub> Cl <sub>3</sub>	0.14	92.1	52.9	9.7	0	37.4
17	PVP-Pt-Mn(en)Cl <sub>2</sub>	0.088	100	39.1	22.8	0	38.1
19	PVP-Pt-Co(en)Cl <sub>2</sub>	0.27	100	70.0	1.7	0	28.3
20	PVP-Pt-Ni(en) <sub>3</sub> Cl <sub>2</sub>	0.16	100	94.0	0	0	6.0
21	PVP-Pt-Cu(en) <sub>2</sub> Cl <sub>2</sub>	0	0	–	–	–	–
22	PVP-Pt-Zn(en) <sub>2</sub> Cl <sub>2</sub>	0	0	–	–	–	–

<sup>a</sup> Reaction conditions:  $4.80 \times 10^{-6}$  mol PVP-Pt colloid,  $1.00 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC); 0.1 MPa H<sub>2</sub> and 303 K (the whole volume was 15.0 mL, MeOH).

<sup>b</sup> Metal complexes were prepared in situ by mixing a metal salt with a corresponding ligand at a proper molar ratio; the molar ratio of metal complex:Pt = 1:1; bpy = bipyridyl, acac = acetylacetonate, en = ethylenediamine.

<sup>c</sup> **15** = aniline; **16** = nitrobenzene; others = mixture of *o*-chlorophenylhydroxylamine, *o*-chloronitrosobenzene, chlorobenzene, azo- and azoxy-dichlorobenzenes.

With respect to the nickel(II) ethylenediamine complex ions, different complex ions existed as Ni(en)<sup>2+</sup>, Ni(en)<sub>2</sub><sup>2+</sup> and Ni(en)<sub>3</sub><sup>2+</sup>, exerted distinct influence on the performances of the catalyst. The activity decreased with the increase in molar ratio of en:Ni<sup>2+</sup> from 0 to 3, whereas the selectivity to **8** increased significantly (Fig. 19). The best yield to **8** (94.0%) was achieved when using Ni(en)<sub>3</sub><sup>2+</sup> as a modifier. These results show that the behavior of the metal complexes is also closely connected to the number of coordinating ligands. The much lower activity of Ni(en)<sub>3</sub> in Fig. 19 may be ascribed to the increased ethylenediamine concentration dissociated from the complex ion, which suppresses the reaction (Table 19, no. 16).

### 7.3. Selective hydrogenation of **7** to **8** over PVP-Ru [84]

It can be seen from Table 20 that the activity decreased upon adding metal cations to the PVP-Ru nanocatalyst (prepared according to Ref. [120]) but increased by using some organic ligands and metal complexes as modifiers. In the case of Zn(en)<sub>2</sub>Cl<sub>2</sub>, the activity increased 14.9 times without any loss in the selectivity (Table 20, no. 13).

Detailed results on the modification effect of multi-amine ligands and their Zn(II) complexes on this system are listed in Table 21. The highest average rate was obtained when using Zn(trien)<sub>2</sub>Cl<sub>2</sub> as modifier: the activity increased 35.4 times while the selectivity remained as high as >99.9%. It is clearly shown from Tables 20 and 21 that the modification effect of metal com-

Table 20

The effect of metal complex ions on the hydrogenation of **7** to **8** over PVP-Ru colloidal nanocatalyst<sup>a</sup>

No.	Catalytic system <sup>b</sup>	Relative rate	Selectivity to <b>8</b> <sup>c</sup> (%)
1	PVP-Ru	1.00	>99.9
2	PVP-Ru-FeCl <sub>3</sub>	0.902	>99.9
3	PVP-Ru-CoCl <sub>2</sub>	0.732	>99.9
4	PVP-Ru-NiCl <sub>2</sub>	0.661	>99.9
5	PVP-Ru-ZnCl <sub>2</sub>	0.768	>99.9
6	PVP-Ru-bpy	1.29	>99.9
7	PVP-Ru-Co(bpy) <sub>3</sub> Cl <sub>2</sub>	1.63	>99.9
8	PVP-Ru-Hacac	1.10	>99.9
9	PVP-Ru-Fe(acac) <sub>3</sub>	1.62	>99.9
10	PVP-Ru-en	9.11	>99.9
11	PVP-Ru-Co(en)Cl <sub>2</sub>	2.92	>99.9
12	PVP-Ru-Ni(en) <sub>3</sub> Cl <sub>2</sub>	3.71	>99.9
13	PVP-Ru-Zn(en) <sub>2</sub> Cl <sub>2</sub>	15.9	>99.9
14	PVP-Ru-HQ	1.49	>99.9
15	PVP-Ru-Co(HQ) <sub>2</sub>	1.07	>99.9

<sup>a</sup> Reaction conditions:  $1.87 \times 10^{-5}$  mol PVP-Ru colloid,  $1.00 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC); 4.0 MPa H<sub>2</sub> and 320 K (the whole volume was 15.0 mL, MeOH). The reaction time was normally 120 min except the experiments no. 10 (30 min) and no. 13 (35 min).

<sup>b</sup> Metal complexes were prepared in situ by mixing a metal salt with a corresponding ligand at a proper molar ratio; the molar ratio of metal complex:Pt = 1:1; bpy = bipyridyl, acac = acetylacetonate, en = ethylenediamine, HQ = 8-hydroxyquinoline.

<sup>c</sup> The other products were less than 0.1%, including aniline, nitrobenzene, *o*-chlorophenylhydroxylamine, *o*-chloronitrosobenzene, chlorobenzene, azo- and azoxy-dichlorobenzenes.

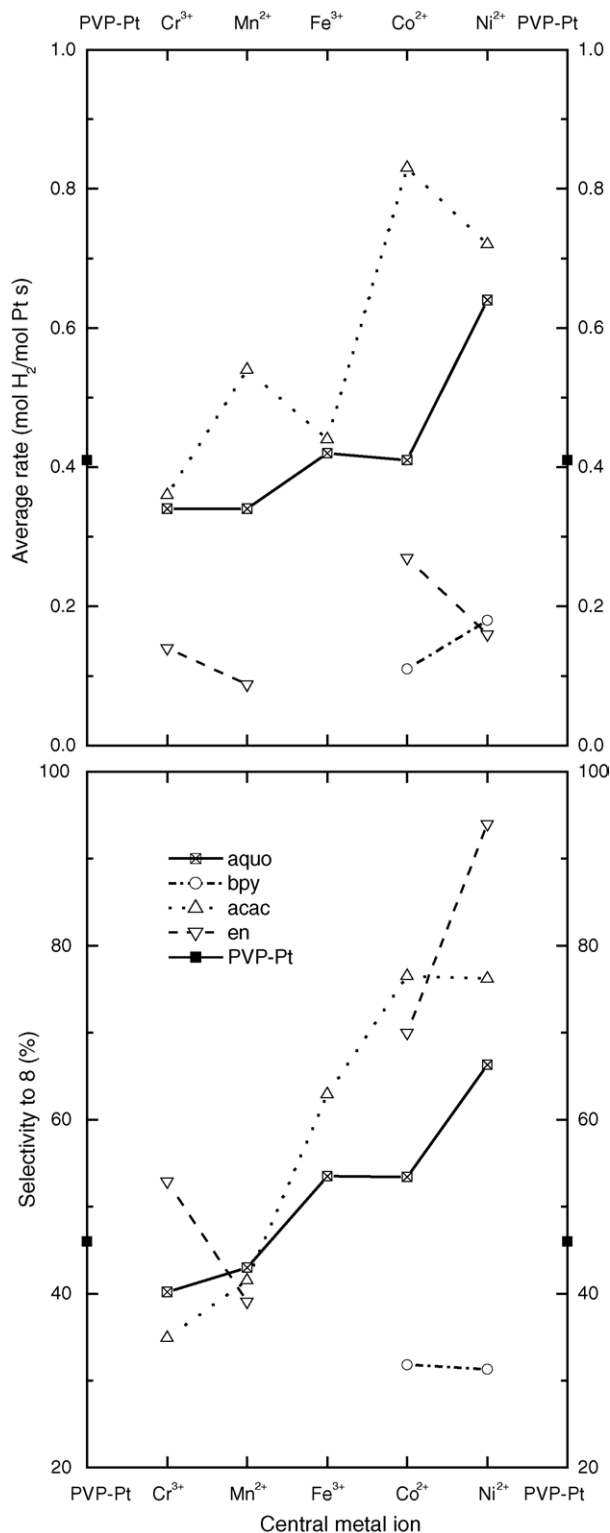


Fig. 18. Metal complex ion effect on the selective hydrogenation of **7** to **8** over PVP-Pt. Reaction conditions:  $4.80 \times 10^{-6}$  mol PVP-Pt colloid,  $1.00 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC) and  $4.80 \times 10^{-6}$  mol metal complex; 0.1 MPa H<sub>2</sub> and 303 K (the whole volume was 15.0 mL, MeOH).

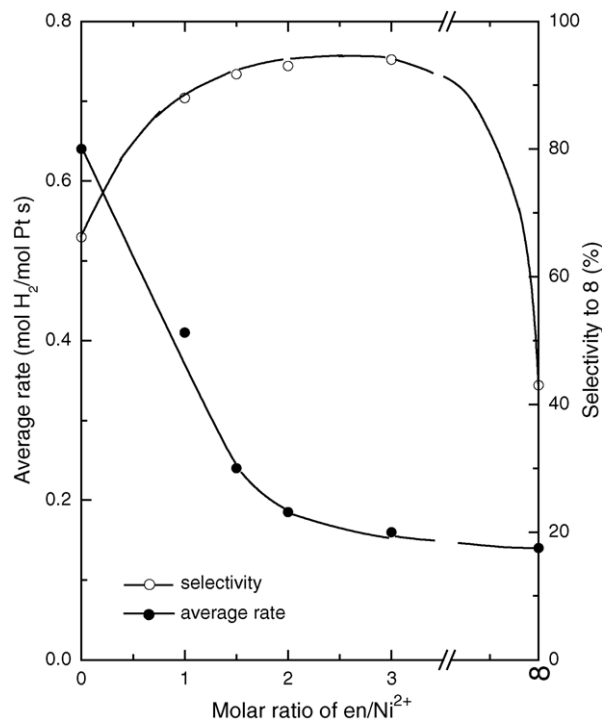


Fig. 19. Influence of the molar ratio of en/Ni<sup>2+</sup> in the selective hydrogenation of **7** to **8** over PVP-Pt. Reaction conditions:  $4.80 \times 10^{-6}$  mol PVP-Pt colloid,  $1.00 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC) and  $4.80 \times 10^{-6}$  mol metal complex; 0.1 MPa H<sub>2</sub> and 303 K (the whole volume was 15.0 mL, MeOH).

Table 21

The effect of Zn(II)–amine complex ions on the hydrogenation of **7** to **8** over PVP-Ru colloidal nanocatalyst<sup>a</sup>

No.	Catalytic system <sup>b</sup>	Relative average rate	Selectivity to <b>8</b> <sup>c</sup> (%)
1	PVP-Ru	1.00	>99.9
2	PVP-Ru-ZnCl <sub>2</sub>	0.768	>99.9
3	PVP-Ru-pn	6.04	>99.9
4	PVP-Ru-Zn(pn) <sub>2</sub> Cl <sub>2</sub>	7.68	>99.9
5	PVP-Ru-en	9.11	>99.9
6	PVP-Ru-Zn(en) <sub>2</sub> Cl <sub>2</sub>	15.9	>99.9
7	PVP-Ru-Zn(en)Cl <sub>2</sub>	6.67	89.0
8	PVP-Ru-den	12.1	>99.9
9	PVP-Ru-Zn(den) <sub>2</sub> Cl <sub>2</sub>	31.1	83.0
10	PVP-Ru-Zn(den)Cl <sub>2</sub>	16.3	97.0
11	PVP-Ru-trien	18.2	>99.9
12	PVP-Ru-Zn(trien) <sub>2</sub> Cl <sub>2</sub>	36.4	>99.9
13	PVP-Ru-Zn(trien)Cl <sub>2</sub>	18.0	>99.9
14	PVP-Ru-tetren	17.6	>99.9
15	PVP-Ru-Zn(tetren)Cl <sub>2</sub>	21.2	79.4

<sup>a</sup> Reaction conditions:  $1.87 \times 10^{-5}$  mol PVP-Ru colloid,  $1.00 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC); 4.0 MPa H<sub>2</sub> and 320 K (the whole volume was 15.0 mL, MeOH).

<sup>b</sup> Metal complexes were prepared in situ by mixing a metal salt with a corresponding ligand at a proper molar ratio; the molar ratio of metal complex:Pt = 1:1; pn = 1,3-propanediamine, en = ethylenediamine, den = diethylenetriamine, trien = triethylenetetramine, tetren = tetraethylenepentamine.

<sup>c</sup> The other products included aniline, nitrobenzene, *o*-chlorophenylhydroxylamine, *o*-chloronitrosobenzene, chlorobenzene, azo- and azoxy-dichlorobenzenes.

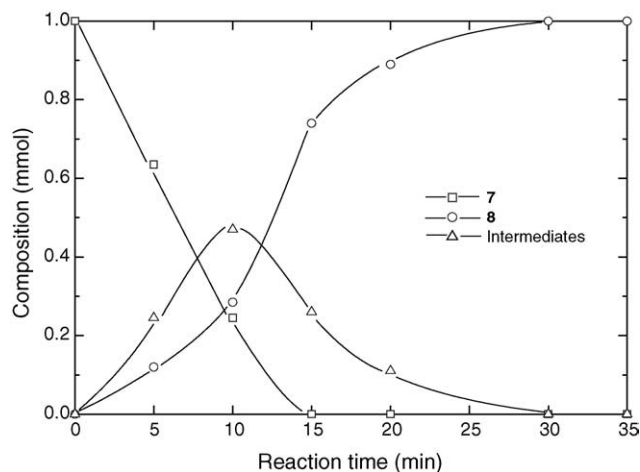


Fig. 20. Time evolution in the selective hydrogenation of **7** to **8** over  $\text{Zn}(\text{en})_2\text{Cl}_2$  modified PVP-Ru. Reaction conditions:  $1.87 \times 10^{-5}$  mol PVP-Ru colloid,  $1.87 \times 10^{-5}$  mol  $\text{Zn}(\text{en})_2\text{Cl}_2$ ,  $1.00 \times 10^{-3}$  mol **7**, 0.10 mL *n*-decanol (internal standard for GC); 4.0 MPa  $\text{H}_2$  and 320 K (the whole volume was 15.0 mL, MeOH).

plexes is not a simple sum of those of the metal central ions and the ligands, and metal complex effect is extremely effective in the selective hydrogenation of **7** over PVP-Ru nanocatalyst. Further study showed that in the presence of  $\text{Zn}(\text{en})_2\text{Cl}_2$ , the conversion of **7** was already 100% in 20 min, but the selectivity to **8** was only 89.0% at this time; the selectivity increased to 100% by extending the reaction to 35 min (Fig. 20). That meant there were some intermediates produced during the hydrogenation, which could be further converted to **8** gradually. GC-MS analysis did find two species, 2,2-azodichlorobenzene and azoxydichlorobenzene as the intermediates. Those intermediates were generally found in the catalytic system with  $\text{Zn}(\text{II})$ -multi-amine complexes, but not in the neat PVP-Ru system.

It was found that the activity increased rapidly (from 1 to 6.70) by adding very little amount of  $\text{Zn}(\text{en})_2\text{Cl}_2$  (molar ratio of  $\text{Zn}(\text{en})_2\text{Cl}_2$  to Ru = 0.02:1) to the PVP-Ru system. This is similar to the metal cation modification effect to the selective hydrogenation of **1** to **2** over PVP-Pt nanocatalyst (Fig. 2). It should be pointed out that the metal complex modification effect varies greatly with the nanocatalysts and the substances to be hydrogenated [121]. Therefore, the mechanism of metal complex effect is much more complicated than metal cation effect. However, it is generally believed that the interaction between the metal complexes and metal nanoparticles may alter the electronic density of metal nanoparticles' active sites, and hence affect the catalytic performances of metal nanocatalysts [79].

## 8. Final remarks

The metal cation (aqua metal complex ion) and metal organic complex ion effects are interesting and important. To find more efficient species and to make clear modification mechanism are the two major research objects. The former needs more tests and development of new catalytic reaction systems; the latter requires a thorough grasp of experimental data and accurate theoretical calculations.

These modification effects are also effective in supported nanocatalysts [80,122]. The primary study on the stereoselective hydrogenation of 2,3-butanedione disclosed the great increase in activity and selectivity by using metal cations and metal complexes as modifiers [123,124]. Further reading materials on preparation and application of colloidal nanoparticles may be helpful to understand the content of this paper [20,58,59,125,126].

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