

SYNTHESIS OF POLYMER-STABILIZED PLATINUM/RUTHENIUM BIMETALLIC COLLOIDS AND THEIR CATALYTIC PROPERTIES FOR SELECTIVE HYDROGENATION OF CROTONALDEHYDE*

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Abstract Polymer-stabilized platinum/ruthenium bimetallic colloids (Pt/Ru) were synthesized by polyol reduction with microwave irradiation and characterized by TEM and XPS. The colloidal nanoparticles have small and narrow size distributions. Catalytic performance of the Pt/Ru colloidal catalysts was investigated on the selective hydrogenation of crotonaldehyde (CROL). A suitable amount of the added metal ions and base can improve the selectivity of CROL to crotyl alcohol (CROL) remarkably. The catalytic activity and the selectivity are dependent on the compositions of bimetallic colloids. Thereinto, PVP-stabilized 9Pt/1Ru colloid with a molar ratio of metals Pt:Ru = 9:1 shows the highest catalytic selectivity 77.3% to CROL at 333 K under 4.0 MPa of hydrogen.

Keywords: Platinum/ruthenium bimetallic colloid; Microwave irradiation; Polyol reduction; Selective hydrogenation; Crotonaldehyde.

INTRODUCTION

Nanosized metal colloids and clusters have received increasing attention in recent decades because of their particular chemical and physical properties^[1]. Their use in catalysis field is one of the important applications due to their high surface area and high surface energy^[2–5]. Studies on bimetallic nanosized colloids are of wide interest comparing with those on monometallic colloids since the addition of a second metal has great effects on the activity and selectivity of bimetallic catalysts. Many reports have focused on the preparation and characterization of bimetallic colloids and their catalytic application in reactions^[6–14]. Toshima *et al.*^[10–12, 15, 16] investigated the hydrogenation of olefins using polymer-stabilized platinum/palladium and palladium/gold bimetallic colloids. Liu *et al.*^[3, 4] reported the syntheses of polymer-stabilized rhodium/platinum, rhodium/gold and palladium/gold bimetallic colloids and their catalytic activities on hydrogenation of olefins. Furthermore, for bimetallic colloids comprising light metal and noble metal, palladium/copper and palladium/nickel bimetallic colloids were obtained by polyol reduction^[6, 8, 17]. Platinum/cobalt colloids were prepared and they exhibited good catalytic performance on selective hydrogenation of cinnamaldehyde^[9, 18].

As reported, conventional supported Pt/Ru bimetallic catalyst obtained by high temperature hydrogen reduction and cation exchange method had quite different catalytic performances from supported platinum particles and ruthenium particles in selective hydrogenation of cinnamaldehyde, which revealed the synergistic effect of Pt/Ru bimetallic particles^[19]. Recently, Pt/Ru bimetallic catalysts were extensively investigated for

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methanol electrooxidation in direct oxidation methanol fuel cell application^[20–22]. A higher efficiency for methanol oxidation at more negative potentials was obtained with Pt/Ru catalysts comparing with Pt catalysts. Ru₁₀Pt₂ bimetallic nanoparticles anchored with the pores of mesoporous silica were reported for the conversion of muconic acid to adipic acid, and found to be superior in the selectivity to other bimetallic and monometallic catalysts^[23]. However, there are only a few reports on the synthesis of ruthenium-containing colloids^[24–26]. Liu *et al.*^[24] reported the preparation of poly(*N*-vinyl-2-pyrrolidone) (PVP)-stabilized Pt/Ru bimetallic colloids by NaBH₄ reduction and their application in hydrogenation of *o*-chloronitrobenzene. Results showed that Pt/Ru colloids are more stable than ruthenium colloids and their activities are two orders of magnitude greater than that of ruthenium colloid. Toshima *et al.*^[26] synthesized Pt/Ru clusters by alcohol reduction and the Pt/Ru bimetallic cluster showed more active features as catalysts in hydrogen generation reaction than the platinum and ruthenium monometallic clusters. In our previous reports, platinum and ruthenium precursors could be reduced to zero-valent metals completely by polyol reduction with microwave irradiation, and thus we could obtain stable PVP-stabilized platinum colloid and ruthenium colloid^[27, 28].

Selective catalytic hydrogenation of α , β -unsaturated aldehyde to its corresponding unsaturated alcohol has attracted many industrial and scientific interests in recent years. The hydrogenation of C=C bond is thermodynamically more favorable than the hydrogenation of C=O bond. Therefore, many attempts have been made to improve the selectivity of unsaturated aldehyde to unsaturated alcohol. For the selective hydrogenation of crotonaldehyde (CRAL), it is difficult to achieve high selectivity of crotyl alcohol (CROL) because there is no steric hindrance just like a phenyl group in cinnamaldehyde. In our present study, we describe PVP-stabilized Pt/Ru bimetallic colloids synthesized by microwave irradiation and ethylene glycol reduction, which are characterized by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The as-synthesized PVP-stabilized Pt/Ru colloids were investigated as catalysts on the selective hydrogenation of CRAL. Reaction conditions were optimized to improve the selectivity to CROL.

EXPERIMENTAL

Materials and Instruments

Poly(*N*-vinyl-2-pyrrolidone) (PVP, $M_w = 40000$) was supplied by Fluka. Crotonaldehyde and crotyl alcohol were Acros products and were redistilled under reduced pressure before use. Other reagents were obtained from Beijing Chemicals Corporation and were of analytical grade. Hydrogen (H₂) with a purity of 99.999% was supplied by Beijing Gases Factory.

TEM was performed by using a Hitachi-9000NAR apparatus. Specimens were prepared by placing a drop of the colloidal dispersion on a copper grid covered with a perforated carbon film and then evaporating the solvent. The particle diameters were measured from the magnified photographs. The particle size distribution histograms were obtained on the basis of the measurement of about 300 particles. XPS were recorded on an ESCALAB 220i-XL (VG, Inc.) photoelectron spectrometer using Mg K α radiation. The vacuum of the chamber was kept at 2×10^{-8} Pa. All binding energy values were referred to carbon ($C_{1s} = 284.6$ eV). Specimens were prepared via immobilization of metallic colloids on SiO₂^[29].

Preparation of PVP-stabilized Pt/Ru Bimetallic Colloids

PVP-stabilized Pt/Ru bimetallic colloids were prepared following the procedure reported in Ref. [28]. For example, in a 100 mL flask, hexachloroplatinic acid (H₂PtCl₆·6H₂O), ruthenium chloride (RuCl₃·*n*H₂O) and PVP (the molar ratio of PVP to metals is 50 and the content of Ru in RuCl₃·*n*H₂O was measured according to the method in Ref. [30]) were dissolved in 40 mL ethylene glycol. The flask was put in the cavity of a microwave oven (Galanz, 750 W, 2450 GHz). The mixed solution became homogeneous after stirring and then was heated for 40 s by microwave irradiation at the maximum power output. During reaction, the color of the solution turned from dark-red to dark-brown, indicating the formation of PVP-stabilized Pt/Ru bimetallic colloidal dispersion. Ethylene glycol in the dispersion was removed by ultrafiltration. The residue was redissolved in ethanol and the obtained solution was designated as Pt/Ru bimetallic colloid that could be used as catalyst in the selective hydrogenation of CRAL.

Selective Hydrogenation of CRAL

Hydrogenation of CRAL was carried out in a 100 mL stainless steel autoclave. The reaction solution contained 0.50 g CRAL, 0.20 g iso-butanol (as an internal standard for gas chromatography), 10 mL PVP-Pt/Ru dispersion (containing 1.0×10^{-5} mol of metals), 15 mL ethanol, 5 mL water, NaOH aqueous solution and metal chloride. Reaction products were analyzed by gas chromatography. The detected products were CROL, butanol, and butanal.

RESULTS AND DISCUSSION

Characterization of PVP-stabilized Pt/Ru Bimetallic Colloids

A series of PVP-stabilized Pt/Ru bimetallic colloids were prepared by varying the amount of the metal precursors. According to the varying molar ratio of platinum to ruthenium in the preparation system, the obtained bimetallic colloids were named as 9Pt/1Ru, 4Pt/1Ru, 7Pt/3Ru, 3Pt/2Ru, 1Pt/1Ru, 2Pt/3Ru, and 1Pt/4Ru (the number denotes the molar ratio in the bimetallic colloids). All these colloidal dispersions had good stability for several months. 7Pt/3Ru and 1Pt/1Ru samples were chosen arbitrarily for TEM observation. Their TEM microphotographs and size distribution histograms are shown in Fig. 1. It can be seen from Fig. 1 that the bimetallic colloids have small particle sizes and good dispersity. The average diameter of 7Pt/3Ru and 1Pt/1Ru is 1.6 nm and 1.5 nm, respectively, while standard deviation is 0.37 nm and 0.35 nm.

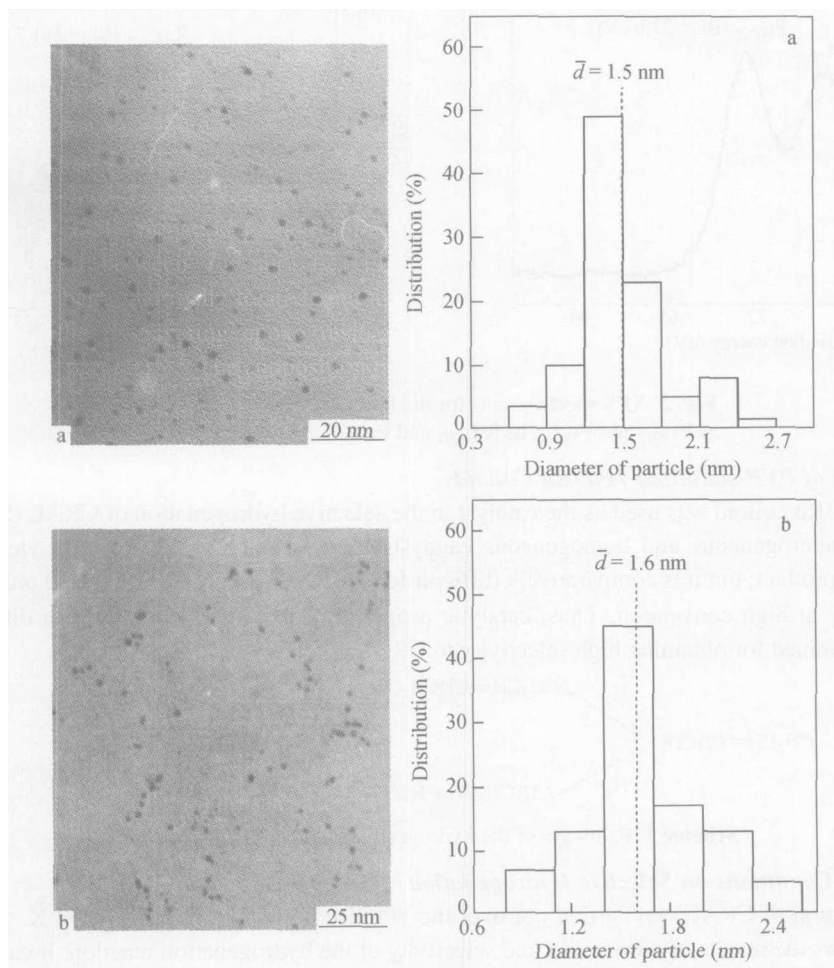


Fig. 1 TEM microphotographs (left) and the corresponding particle size distribution histograms (right) of PVP-stabilized bimetallic colloids
a) 1Pt/1Ru; b) 7Pt/3Ru

XPS is a useful method to determine the valent state of species. XPS spectrograms of 7Pt/3Ru colloids are shown in Fig. 2. Binding energies of $\text{Pt}_{4f7/2}$ and $\text{Ru}_{3p3/2}$ are 71.0 eV and 461.7 eV, respectively. They are in good agreement with those of metallic platinum and ruthenium^[31]. It is indicated that the metal precursors ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$) have been reduced to the zero-valent metallic platinum and ruthenium, in other words, the bimetallic colloidal particles are in zero oxidation state. Ruthenium has high solubility — more than 79% (atom number) in platinum, and the corresponding X-ray diffraction analysis has been reported^[32, 33]. Moreover, it has been proven that PVP-stabilized Pt/Ru colloid has an alloy structure^[24]. So, no further analysis is made to ascertain the alloy phase of Pt/Ru colloid in the present work. XPS is also an effective technique for revealing the chemical composition of surface layer of a solid. Liu *et al.*^[4] utilized XPS to deduce the metal distribution in the bimetallic colloid of PVP-Pd/Au from the intensities of XPS peaks and the relative sensitivity factors of the elements. From the peak areas of Pt_{4f} and Ru_{3p} , surface composition of 7Pt/3Ru colloid is calculated to be Pt:Ru = 6.1:1, which indicates that platinum is enriched on the surface of the bimetallic particles. In the view of thermodynamics, when components have different surface free energies in one solid, the component that has lower surface free energy has tendency to be enriched on the surface of the solid. Surface free energy of Pt and Ru are 1865 mN/m and 2250 mN/m, respectively^[34]. Therefore, it is reasonable to suggest that platinum has the tendency to be enriched on the surface of Pt/Ru bimetallic colloidal particles.

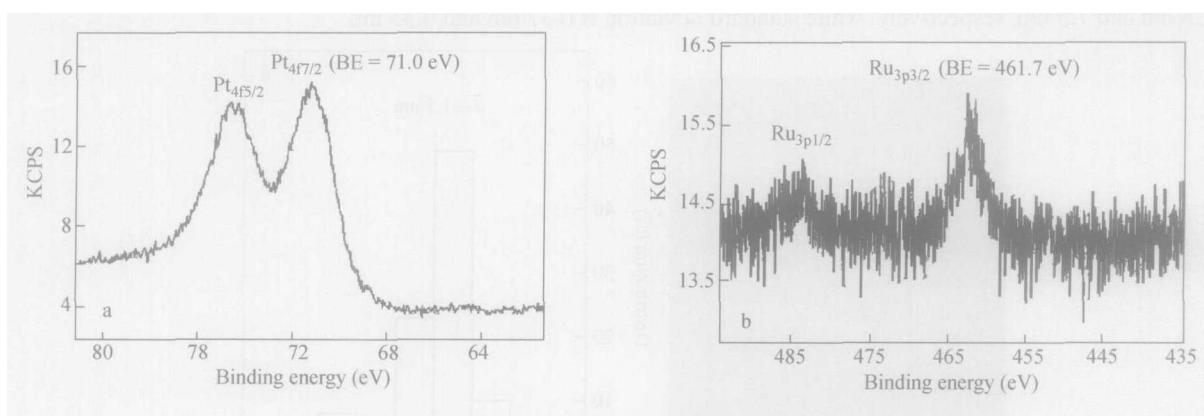
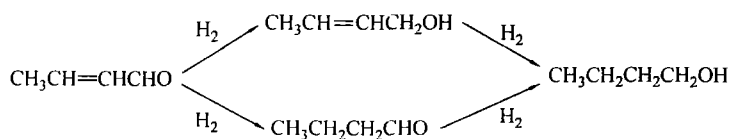


Fig. 2 XPS spectrograms for the PVP-7Pt/3Ru colloid
a) $\text{Pt}_{4f7/2}$ and $\text{Pt}_{4f5/2}$; b) $\text{Ru}_{3p3/2}$ and $\text{Ru}_{3p1/2}$

Catalytic Properties of PVP-stabilized 7Pt/3Ru Colloids

PVP-stabilized 7Pt/3Ru colloid was used as the catalyst in the selective hydrogenation of CRAL (Scheme 1). It is easy for ordinary heterogeneous and homogeneous catalysts to reduce the $\text{C}=\text{C}$ bond to yield butanol and butanal as the main product; but it is comparatively difficult for them to reduce the $\text{C}=\text{O}$ bond only to get CROL with high selectivity at high conversion. Thus, catalytic properties of the 7Pt/3Ru colloid in different reaction conditions were examined for obtaining high selectivity to CROL.



Scheme 1 Pathways of the hydrogenation of crotonaldehyde

Effects of Reaction Conditions on Selective Hydrogenation

Selective hydrogenation of CRAL was carried out over the 7Pt/3Ru bimetallic colloid at 333 K, $P_{\text{H}_2} = 4.0$ MPa for 2 h. Table 1 shows the results of conversion and selectivity of the hydrogenation reaction. It can be found that the conversion of CRAL is 80.6% with 7Pt/3Ru colloid as a catalyst without any modifier, while there is no CROL formed. In the reaction system over polymer-stabilized metal colloids as catalysts, it has been reported

that the activity and the selectivity of the selective hydrogenation of α,β -unsaturated aldehyde to α,β -unsaturated alcohol could be improved by the addition of some metal cations, especially transition metal ions^[24, 35, 36]. Thus, metal salt containing Fe^{3+} , Co^{2+} or Ni^{2+} ions was added into the reaction as a modifier. The addition of Ni^{2+} ions had no effect on the selectivity to CROL while it could increase the conversion of the reaction from 80.6% to 100%. However, with Fe^{3+} and Co^{2+} ions introduced, the selectivity of CRAL to CROL increased from zero to 70.9% and 45.7%, respectively, accompanied by some decrease of the conversion. The modification may be due to the interaction of metal cations with the $\text{C}=\text{O}$ groups in the reactants. The adsorbed metal cations activate the $\text{C}=\text{O}$ bonds and thus increase the selectivity to unsaturated alcohols. In order to obtain the high selectivity to CROL, Fe^{3+} ions are used as the modifier in the following catalytic reactions.

Table 1. Selective hydrogenation of CRAL over PVP-7Pt/3Ru colloidal catalysts with different metal ions as modifier

Catalyst*	Conversion (%)		Selectivity (%)	
	CRAL	CROL	<i>n</i> -Butanal	<i>n</i> -Butanol
PVP-7Pt/3Ru	80.6	0	82.0	18.0
PVP-7Pt/3Ru- FeCl_3	55.4	70.9	19.8	9.30
PVP-7Pt/3Ru- CoCl_2	66.9	45.7	34.6	19.7
PVP-7Pt/3Ru- NiCl_2	100	0	71.2	28.8

* Molar ratio of metal cations to (Pt + Ru) is 1.0; 1.0 mg of NaOH was added to hydrogenation system.

Figures 3 and 4 show the results of hydrogenation of CRAL over 7Pt/3Ru colloidal catalyst at different reaction temperatures and pressures. We can see that the conversion of CRAL improved gradually with the rising of temperature or pressure. High temperature favors the thermodynamic interaction between reactants and catalyst, and thus causes the increase in the reaction rate. Under higher reaction pressure, more hydrogen will be dissolved in the reactive solution, which gives the possibility of high reaction conversion. However, the selectivity of CRAL to CROL had the optimum value of 70.9% at 333 K and 4.0 MPa. With higher reaction temperature and pressure beyond 333 K and 4.0 MPa, respectively, the selectivity to CROL decreases obviously. In order to have high selectivity, reaction conditions were optimized as $T = 333 \text{ K}$ and $P_{\text{H}_2} = 4.0 \text{ MPa}$.

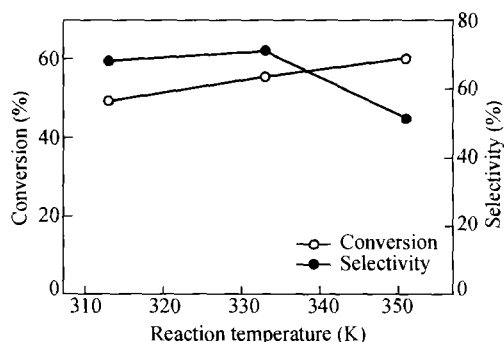


Fig. 3 Effect of temperature on the hydrogenation of CRAL over PVP-7Pt/3Ru colloidal catalyst. Reaction conditions: NaOH: 1 mg; The molar ratio of Fe^{3+} to (Pt + Ru): 1.0; Reaction pressure: 4.0 MPa; Reaction time: 2 h

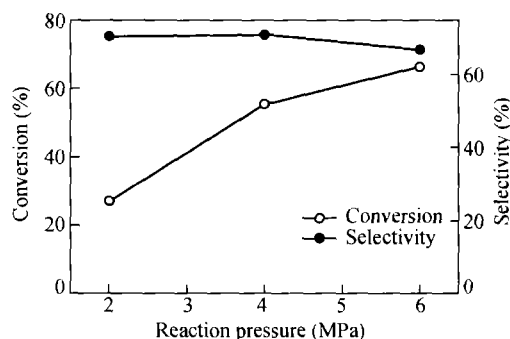


Fig. 4 Effect of pressure on the hydrogenation of CRAL over PVP-7Pt/3Ru colloidal catalyst. Reaction conditions: NaOH: 1 mg; The molar ratio of Fe^{3+} to (Pt + Ru): 1.0; Reaction temperature: 333 K; Reaction time: 2 h

Changing the amount of base NaOH in the hydrogenation reaction of CRAL, catalytic performance of 7Pt/3Ru colloid was examined. It can be seen from Fig. 5 that the selectivity to CROL was improved with the increasing amount of NaOH. When NaOH was 3.0 mg, the selectivity to CROL was 82.2%. As the amount of NaOH increased from 0 to 0.5 mg, the conversion increased from 84.3% to 92.3%. But, the conversion decreased remarkably to 55.4% with 1 mg NaOH added. Then, with more NaOH, conversion decreased gradually. Therefore, reaction conversion and selectivity could be improved by optimizing the amount of NaOH introduced into the reaction system. The above results are similar to those reported in many references^[35–38].

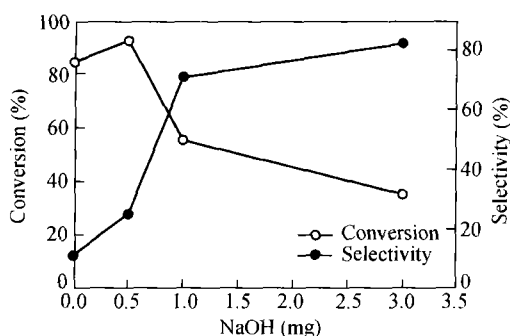


Fig. 5 Effect of the amount of NaOH on the hydrogenation of CRAL over PVP-7Pt/3Ru colloidal catalyst
Reaction conditions: Molar ratio of Fe^{3+} to (Pt + Ru): 1.0; Reaction temperature: 333 K;
Reaction pressure: 4.0 MPa; Reaction time: 2 h

Different amount of Fe^{3+} ions was added in the hydrogenation of CRAL over PVP-7Pt/3Ru colloidal catalyst. It is shown in Fig. 6 that the amount of Fe^{3+} ions has remarkable effects on the catalytic properties of 7Pt/3Ru bimetallic colloid. It should be noted that a small amount of Fe^{3+} ions can improve both the conversion and the selectivity, while more Fe^{3+} ions cause an obvious decrease in conversion and the selectivity. The highest conversion 97.7% appears at molar ratio of $\text{Fe}^{3+}/(\text{Pt}+\text{Ru}) = 0.1$, while the selectivity to CROL 70.9% appears at $\text{Fe}^{3+}/(\text{Pt}+\text{Ru}) = 1.0$ but the conversion is only 55.4%.

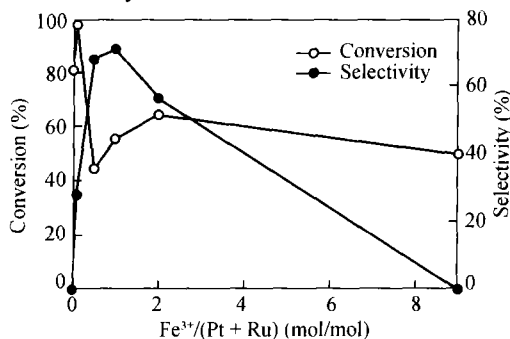


Fig. 6 Effect of the amount of Fe^{3+} ions on the hydrogenation of CRAL over PVP-7Pt/3Ru colloidal catalyst
Reaction conditions: NaOH: 1 mg; Reaction temperature: 333 K; Reaction pressure: 4.0 MPa; Reaction time: 2 h

From the above experimental results, it can be seen that the optimum reaction conditions for high conversion and selectivity of the hydrogenation of CRAL are: $T = 333$ K, $P_{\text{H}_2} = 4.0$ MPa, NaOH 1.0 mg, and $\text{Fe}^{3+}/(\text{Pt} + \text{Ru}) = 1.0$ (molar ratio).

Hydrogenation of CRAL over PVP-stabilized Pt/Ru Bimetallic Colloidal Catalysts with Different Compositions

Changing the molar ratio of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ to $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ in the preparation solution, we obtained a series of PVP-stabilized Pt/Ru bimetallic colloids with different compositions. The hydrogenation of CRAL were performed under the optimum conditions described above for 2 h. Results are shown in Fig. 7. For comparison, catalytic results of platinum and ruthenium monometallic colloids by polyol reduction were also given. With the increasing proportion of platinum in Pt/Ru colloidal catalysts, the conversion of hydrogenation increases progressively. When the molar ratio $\text{Pt}/(\text{Pt} + \text{Ru})$ of the catalyst was 0.9, conversion was at its highest 67.6%, which was slightly higher than that of the reaction over Pt monometallic colloidal catalyst. With $\text{Pt}/(\text{Pt} + \text{Ru})$ less than 0.2, the bimetallic colloidal catalyst shows no selectivity to CROL. Then, the selectivity was improved,

accompanied by an increase in the platinum amount. The notable result was that the selectivity rose abruptly to 65.7% when platinum content was 50 mol% and then increased gradually. The highest selectivity was 77.3% for 9Pt/1Ru catalyst with $\text{Pt}/(\text{Pt} + \text{Ru}) = 0.9$, which was slightly higher than the results of Pt monometallic colloidal catalyst. The lines connected from the experimental data (conversion and selectivity) of Pt colloid to Ru colloid were roughly regarded as the behavior of the physical mixture of Pt and Ru colloids with different molar ratios. In Fig. 7, although curve of the catalytic activities of Pt/Ru bimetallic colloids approaches that of the physical mixture (the dash line), its selectivity shows a large deviation from the dotted line; moreover, the catalytic activity and selectivity of the 9Pt/1Ru colloidal catalyst exhibited the highest values. In the present case, it is hard to determine if there is any synergetic effect concluding from the slightly higher activity and selectivity of the 9Pt/1Ru colloid than those of the Pt colloid. Known from the results of XPS measurement for 7Pt/3Ru bimetallic colloid, platinum atoms are enriched on the surface of bimetallic particles. So, it is easily understandable that the colloids with $\text{Pt}/(\text{Pt} + \text{Ru}) = 0.5\text{--}0.9$ have high surface platinum contents, which may be the reason that results in the similar selectivity to CROL for these bimetallic catalysts as the Pt monometallic colloid. Regardless of the reason for the high selectivity to CROL over the bimetallic catalysts that was due to the concentration of platinum on the surface of the bimetallic particles, the existence of the inner enriched ruthenium could have influence on the electron structure of the surface platinum and thus affected the catalytic performance of the bimetallic catalysts.

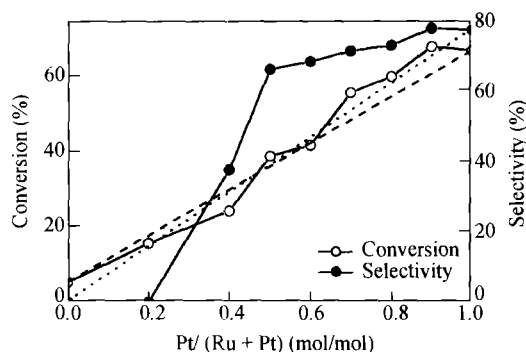


Fig. 7 Selective hydrogenation of CRAL over PVP-stabilized Pt/Ru bimetallic colloidal catalysts with different compositions

Reaction conditions: NaOH: 1 mg; Molar ratio of Fe^{3+} to $(\text{Pt} + \text{Ru})$: 1.0; Reaction temperature: 333 K; Reaction pressure: 4.0 MPa; Reaction time: 2 h

Some details will be focused on the particular catalytic properties of the Pt/Ru bimetallic colloids. As reported by Yu *et al.* [36, 38], PVP-stabilized Pt and Ru colloids have the ability to hydrogenize the $\text{C}=\text{O}$ bond in aldehyde. However, in our case of the hydrogenation of CRAL without metal cations as a modifier, the present Pt/Ru bimetallic colloidal catalysts show no selectivity to the unsaturated alcohol product CROL. The same case occurs even for the colloid with $\text{Pt}/(\text{Ru} + \text{Pt})$ less than 0.2 with the cation modifier. With regard to the effect of the metal cations, their effects in the PVP-stabilized Pt/Ru colloidal catalyst systems are different from other colloidal systems in the above references. Moreover, with the modification of Fe^{3+} ions, the selectivity to CROL over the PVP-Pt monometallic colloidal catalyst synthesized by polyol reduction (76.8%) is much higher than that over the PVP-Pt colloidal catalyst (48.9%) in Ref. [35]. With the molar ratio of $\text{Fe}^{3+}/(\text{Pt} + \text{Ru}) = 1.0$, the selectivity to CROL reaches its maximum. All of the above results indicate that the catalytic properties of Pt/Ru bimetallic colloids differ from the Pt or Ru colloids reported in the previous references. One point on the synthesis method of the colloids is to be noted. In the Refs. [36] and [38], PVP-Pt colloids were prepared by the alcohol (methanol or ethanol)-water reduction with the addition of NaOH, while PVP-Ru colloids were obtained by NaBH_4 reduction. Some reaction residues (such as: salts, boron species) still remained in the colloid. In our preparation of the Pt/Ru colloids, ethylene glycol was used as solvent as well as a reducing agent and the obtained products were handled by an ultrafilter, which could give pure Pt/Ru colloidal catalysts and solvent

ethanol. Different from conventional supported metal particles by high temperature reduction, PVP-stabilized metal colloidal particles were prepared in a mild reaction condition, which probably resulted in unmaturing particles with surface crystal defects. Therefore, for different preparation systems, the formed colloidal particles have slightly differences in surface crystal morphology, which will cause different catalytic performances of colloidal catalysts.

The achieved high selectivity to CROL 77.3% over the 9Pt/1Ru bimetallic colloidal catalyst is better than most of the published results in catalytic hydrogenation^[39–43]. Compared with PVP-stabilized platinum catalyst, Pt/Ru bimetallic catalyst has an advantage of lower cost with the metal Ru included.

CONCLUSION

PVP-stabilized Pt/Ru bimetallic colloidal dispersions can be obtained by ethylene glycol reduction with microwave irradiation. They are stable for more than several months. TEM results show that they have small particles sizes and narrow size distributions. XPS characterization of PVP-stabilized 7Pt/3Ru reveals that platinum is enriched on the surface of the bimetallic particles. A suitable amount of Fe^{3+} ions or NaOH can remarkably improve the selectivity to CROL in the selective hydrogenation of CRAL over the Pt/Ru bimetallic colloids. Catalytic properties of the Pt/Ru colloids vary on their composition. When the molar ratio of Pt/(Pt+Ru) is above 0.5, Pt/Ru colloidal catalysts have good reaction activity and high selectivity to CROL. The selectivity is the highest with 77.3% over 9Pt/1Ru colloid in the presence of modifiers.

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