

# Hydrogenation of *o*-chloronitrobenzene over polymer-stabilized palladium–platinum bimetallic colloidal clusters

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## Abstract

Hydrogenation of *o*-chloronitrobenzene (*o*-CNB) has been studied in methanol at 303 K and atmospheric pressure over polyvinylpyrrolidone-stabilized palladium–platinum (PVP-Pd/Pt) bimetallic colloidal clusters. The catalytic properties for the hydrogenation of *o*-CNB to *o*-chloroaniline (*o*-CAN) are found to depend on the metal composition of the bimetallic clusters. All the bimetallic clusters are more active than both PVP-Pd and PVP-Pt monometallic clusters. The highest activity (1.81 mol H<sub>2</sub>/mol M s) is obtained when PVP-Pd/Pt (1/2) is used as catalyst. The best selectivity to *o*-CAN (77.5%) is achieved in PVP-Pd/Pt (1/3) catalytic system, which is much higher than those of PVP-Pt and PVP-Pd monometallic colloidal clusters. The addition of the metal cations to the system can considerably affect the catalytic properties of the bimetallic clusters. The modification behavior of metal cations also depends both on the composition of PVP-Pd/Pt bimetallic clusters and the nature of metal cations. For the PVP-Pd/Pt (1/3) bimetallic clusters, when introducing Cr<sup>3+</sup> and Co<sup>2+</sup>, the high activity (0.96 and 1.03 mol H<sub>2</sub>/mol M s) and the better selectivity (91.5 and 91.4%) compared with those of the neat PVP-Pd/Pt (1/3) catalysts (1.03 mol H<sub>2</sub>/mol M s and 77.5%) are obtained, respectively. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Pd/Pt bimetallic colloid; Metal ion modifier; Hydrogenation; *o*-Chloronitrobenzene

## 1. Introduction

Polymer-stabilized colloidal metal clusters have attracted much attention in recent years because of their great difference from metal atoms and bulk metals in size and structure, being a bridge between homogeneous catalysis and heterogeneous catalysis [1,2]. Bimetallic catalysts have been studied to discover the rela-

tionship between catalytic activity and the metal structure [3]. Of bimetallic or multi-metallic catalyst, the activity and selectivity are greatly influenced by the electronic and conformational properties of its components as well as its composition and the geometric factors involved at the metal surface. Many investigations have focused on bimetallic catalysts to clarify the correlation of the catalytic behavior or electronic structure with alloy composition. Many types of stable bimetallic sols with narrow particle size distribution, such as platinum–copper [4], plat-

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inum–rhodium [5], rhodium–gold [5], palladium–copper [6], palladium–gold [7], palla-

dium–nickel [8], platinum–cobalt [9], etc., were obtained by refluxing alcoholic solution of

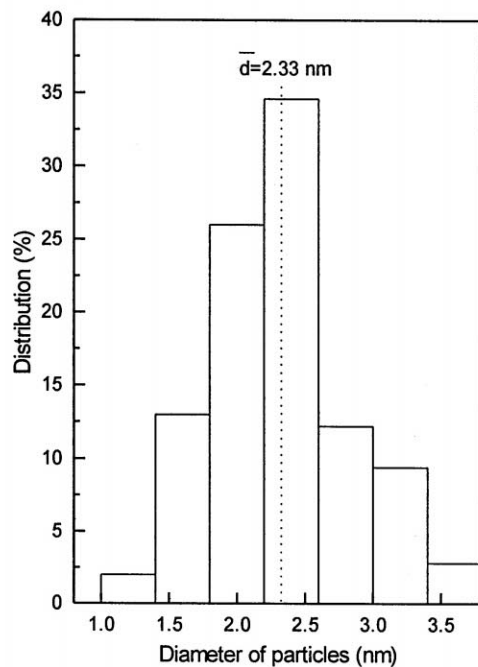
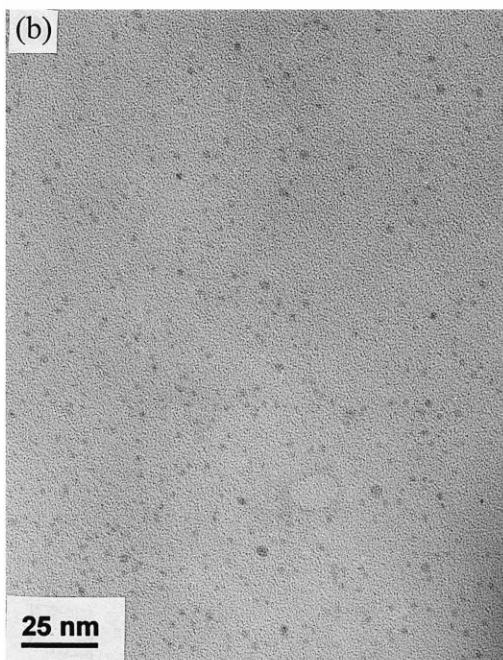
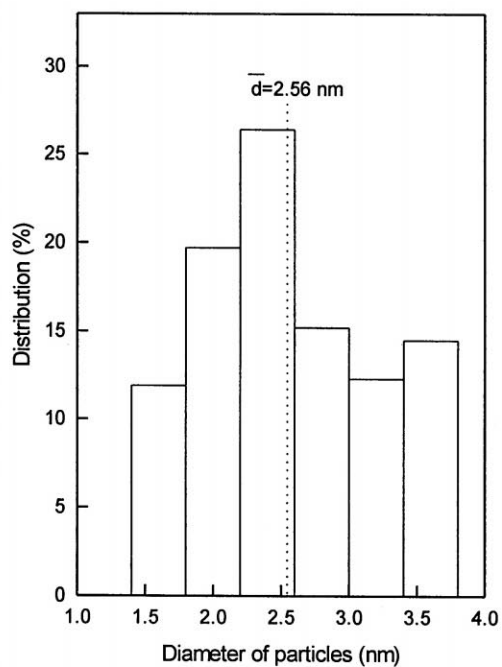
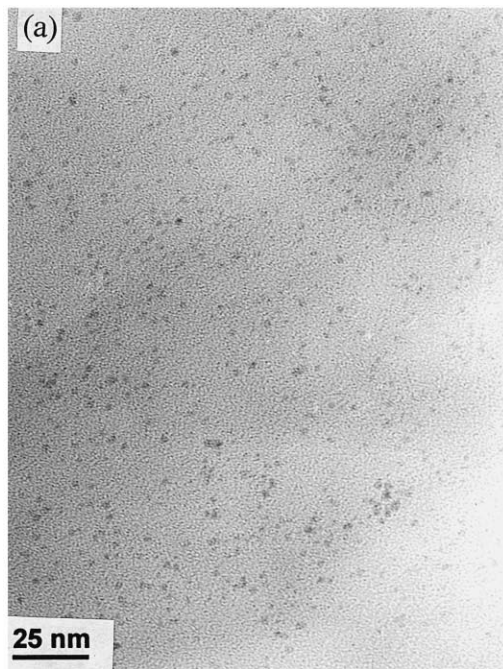


Fig. 1. The TEM photograph of PVP-Pd/Pt bimetallic colloidal clusters (left: enlarged photo; right: particle size distribution): (a) PVP-Pd/Pt (4/1); (b) PVP-Pd/Pt (3/1); (c) PVP-Pd/Pt (1/2); (d) PVP-Pd/Pt (1/3).

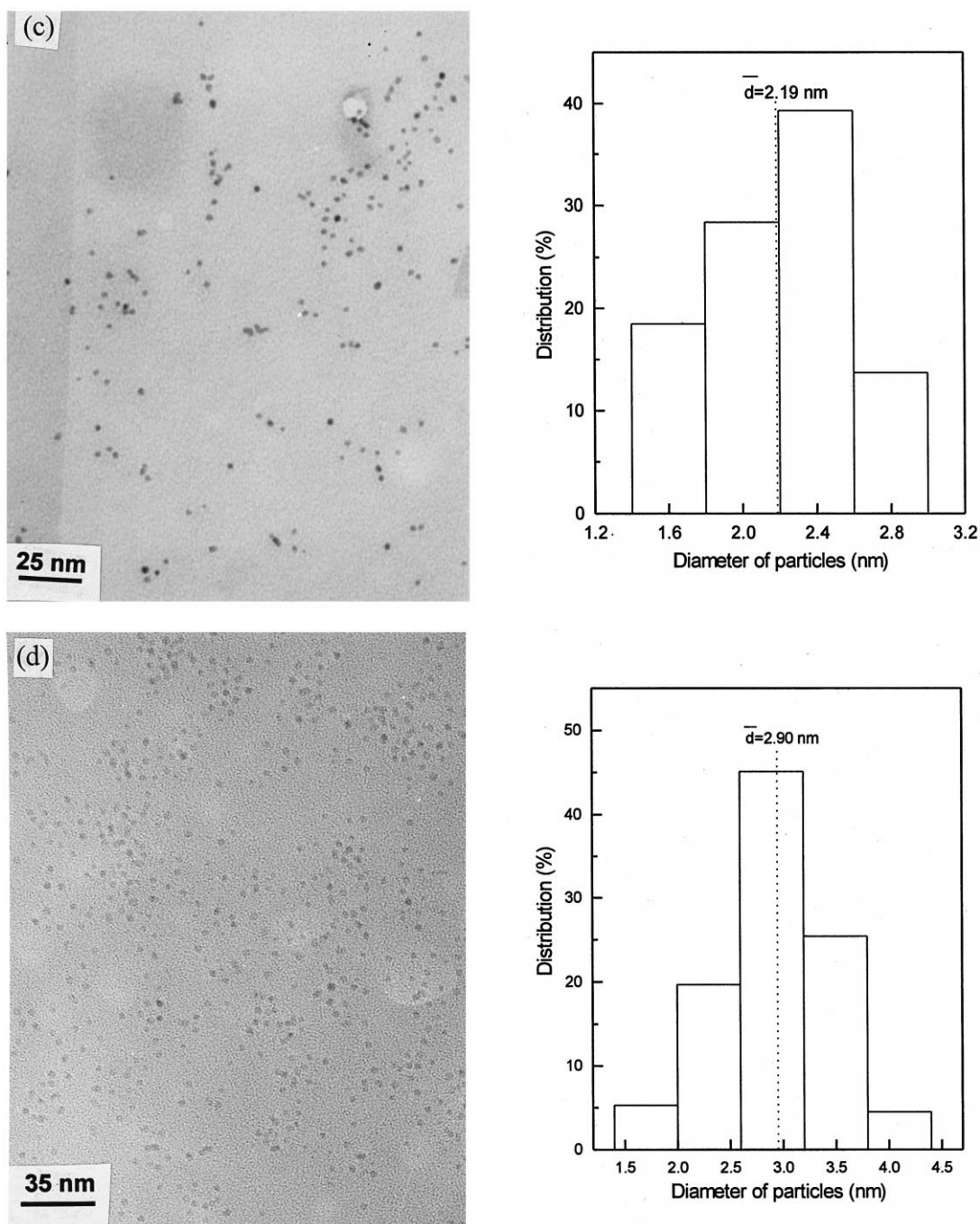


Fig. 1 (continued).

mixed metal ions of interest in the presence of a stabilizing polymer. Some papers have reported the synthesis, characterization, and the catalytic properties in the hydrogenation of cycloocta-

1,3-diene of the polymer-stabilized palladium-platinum bimetallic clusters [10–14].

Haloaromatic amines are important intermediates in the chemistry of dyes, drugs and pesti-

cides. Selective hydrogenation of halonitroaromatic compounds to the corresponding haloamines over the metal catalyst is preferred compared to the Bechamp's procedure without the environmental impact. Greenfield and Dovell [15], Bond and Webster [16] and Kosak [17,18] have reviewed the relevant literature on the catalytic properties of the supported metal catalysts. Coq et al. [19–21] have studied the behavior of the platinum catalyst in relation with the size of the metal particles for monometallic Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, with the effect of the support and the metallic precursors over supported-platinum catalysts, and with the influence of alloy in PtM/Al<sub>2</sub>O<sub>3</sub> (M = Sn, Pb, Ge, Al, Zn) bimetallic catalysts.

Recently, we have extensively studied the modification of metal cations and metal complexes on the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes and *o*-chloronitrobenzene (*o*-CNB) over polymer-stabilized platinum [22–26] and ruthenium clusters [27]. The addition of the metal ions and metal complexes modifiers to the catalytic system can considerably modulate both the activity and the selectivity of the colloidal catalysts. It is meaningful to investigate such modification of metal cations on the bimetallic cluster catalysts. Here we report the experimental study on the selective hydrogenation of *o*-CNB to *o*-chloroaniline (*o*-CAN) catalyzed by a Pd–Pt bimetallic cluster system as well as the modification of metal cations on it.

## 2. Experimental

PVP (average molecular weight: 40,000) was purchased from BASF. *o*-CNB was recrystallized in 95% ethanol before use. Other reagents were of analytical grade supplied by Beijing Chemicals Hydrogen (H<sub>2</sub>) source with purity 99.999% was supplied by extra-pure hydrogen generator DCH-III.

Transmission electron microscopy (TEM) photographs were taken by using a Hitachi-9000NAR instrument. Specimens were prepared

by placing a drop of the colloid dispersion upon a copper covered with a perforated carbon film and then evaporating the solvent. The particle diameters were measured from the enlarged photographs. The particle size distribution histograms were obtained on the basis of the measurement of about 250 particles.

The method used to prepare the PVP-stabilized palladium–platinum bimetallic clusters was similar to the reported procedure [10]. For example, in a 100-ml flask, palladium (II) chloride (PdCl<sub>2</sub>: 5.37 mg, 0.030 mmol) was dissolved in 30-ml ethanol by stirring for 10 h, resulting in a light turbid yellow solution. Hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub> · 6H<sub>2</sub>O: 5.18 mg, 0.010 mmol), an amount of PVP (185 mg, 1.66 mmol as monomeric unit) as a stabilizing polymer was dissolved in 30-ml water, mixed the two solutions and stirred at room temperature for 0.5 h. The mixture was refluxed for 1.5 h to get a dark-brown homogeneous dispersion. The dispersion was evaporated by a Rotavap, and then the residue was redispersed in methanol as the catalyst designated as PVP-Pd/Pt (3/1) (number in parentheses stands for the atomic ratio of the metals). Other PVP-stabilized Pd/Pt bimetallic colloidal samples with different atomic ratio were obtained by varying the molar ratio of H<sub>2</sub>PtCl<sub>6</sub> · 6H<sub>2</sub>O to PdCl<sub>2</sub> with keeping the total amount of both metals constant (0.040 mmol).

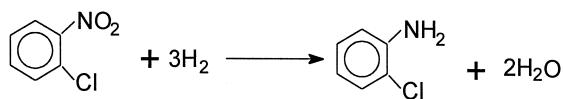
Catalytic hydrogenation of *o*-CNB was conducted in a 30-ml flat-bottom flask; the reaction temperature was kept constant by external circulation of a thermostat within  $\pm 0.1^\circ\text{C}$ . The catalyst (PVP-Pd/Pt,  $4.80 \times 10^{-6}$  mol (Pd + Pt)) with metal salt (as chloride) was activated under hydrogen with magnetic stirring at 303 K for 40 min. After activation, 2.0 ml of the reactant solution (1.0 mmol in methanol) then was charged to the flask; the total volume of the catalytic system was 15.0 ml. The hydrogenation reaction rate was measured by the uptake of the hydrogen. Chemical analysis of the products was performed by gas chromatography (Beifen SQ-204), equipped with a FID detector and

DC-710 column. Reactant and products were identified by comparison with authentic samples,  $n\text{-C}_{10}\text{H}_{21}\text{OH}$  was used as an internal standard.

### 3. Results and discussion

TEM is a conventional method to give detailed information about the shapes, mean size and size distribution of colloidal dispersions. The TEM photographs and the corresponding particle size distribution histograms of some PVP-Pd/Pt bimetallic clusters are shown in Fig. 1. The average diameter and the standard deviation of platinum particles are listed in Table 1. It can be seen from Fig. 1 and Table 1 that the sizes of the bimetallic particles are small and with a narrow distribution. The results of TEM elucidate that the bimetallic clusters are in alloying state compared to the results reported in the literature [10].

The stoichiometric reaction involved in hydrogenation of *o*-CNB is:



In this process, it is desirable to achieve selective hydrogenation to *o*-CAN without dehalogenation. The hydrogenation of halonitrobenzenes follows the formal reaction pathways described elsewhere [20,23]. During the hydrogenation catalyzed by PVP-Pd/Pt bimetallic clusters, the only products which can be determined by GC analysis are *o*-CAN, aniline (AN), and nitrobenzene (NB). The other by-products are not detected by GC, including *o*-chloronitrosobenzene (*o*-CNSB), azobenzene and azoxydichloronitrobenzene (AOCB).

The dependence of the activity and the selectivity of the PVP-Pd/Pt bimetallic clusters upon the metal compositions is shown in Fig. 2.

Table 1

The average diameter and the standard deviation of PVP-Pd/Pt bimetallic colloidal clusters

Sample	Average diameter (nm)	Standard deviation (nm)
PVP-Pd	2.74	0.59
PVFP-Pd/Pt (4/1)	2.56	0.39
PVP-Pd/Pt (3/1)	2.33	0.40
PVP-Pd/Pt (2/1)	2.31	0.38
PVP-Pd/Pt (1/1)	2.17	0.31
PVP-Pd/Pt (1/2)	2.19	0.33
PVP-Pd/Pt (1/3)	2.90	0.39
PVP-Pd/Pt (1/4)	1.68	0.30
PVP-Pt	2.52	0.34

It can be seen from Fig. 2b that the activities (average rates) of all the bimetallic colloids are much higher than those of the PVP-Pd and PVP-Pt monometallic clusters. The highest catalytic activity (1.70 mol  $\text{H}_2$ /mol M s) is achieved in the range of Pd/Pt = 2/1–Pd/Pt = 1/2 bimetallic clusters, which is about three-fold higher than those by the palladium and platinum monometallic colloids. Furthermore, the results in Fig. 2c indicate that the selectivity also depends on the composition of the PVP-Pd/Pt bimetallic clusters. The selectivity to *o*-CAN of the bimetallic clusters increases slowly with the increase of platinum content and enhances abruptly to the maximum Pt/Pd = 3/1 (77.5%), which is much higher than those of the monometallic palladium (38%) and platinum (63%) clusters, respectively, then the selectivity decreases. The ionization potential of palladium (8.34 eV) is known to be smaller than that of platinum (9.0 eV) [28]. Thus, the electronic interaction between platinum and palladium atoms results in the platinum atoms being rich in electron density. This kind of synergic effect in electron density would favor the platinum atom on the surface to the selective hydrogenation of N=O double bond of the bimetallic catalysts [29,30].

The addition of metal cations into the PVP-Pd/Pt bimetallic catalytic system can improve both the activity and the selectivity to *o*-CAN. In the previous paper [23], we have reported

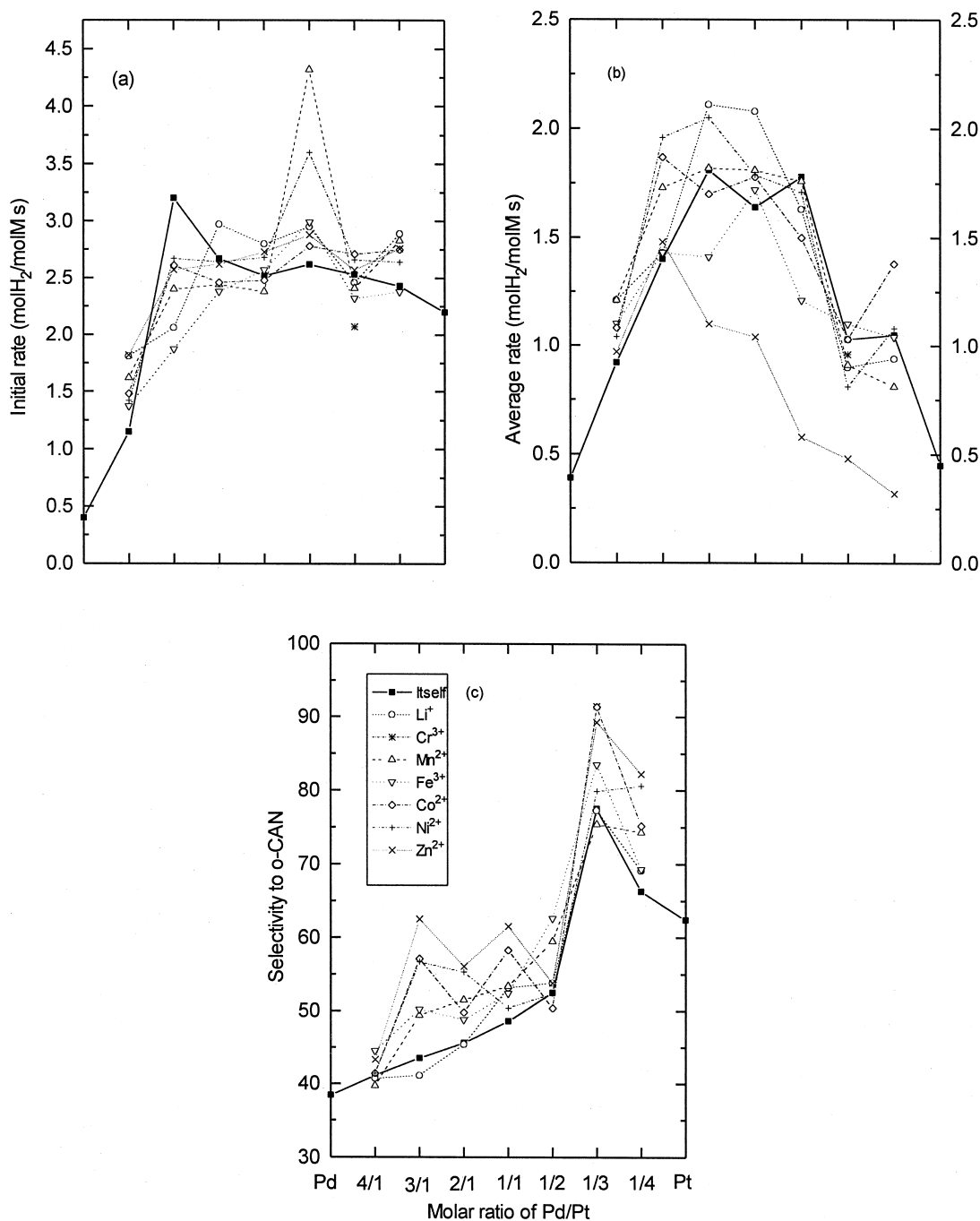


Fig. 2. The effect of metal cations on the hydrogenation of *o*-CNB over PVP-Pd/Pt bimetallic colloidal clusters: (a) initial rate; (b) average rate; (c) selectivity to *o*-CAN.

that the metal cations, such as Li<sup>+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Zn<sup>2+</sup>, have significant effect on both the activity and the selectivity of

PVP-Pt cluster catalysts. We pursued an extensive survey on the influence of these metal cations on the selective hydrogenation of *o*-CNB

over PVP-Pd/Pt bimetallic clusters with different composition. The experimental results are summarized in Fig. 2.

In comparison with the results of the monometallic colloid PVP-Pt catalyst, the influence of metal cations on the selective hydrogenation of *o*-CNB over bimetallic colloid PVP-Pd/Pt catalyst exhibits varied patterns depending on the composition of the bimetallic colloid. Fig. 2a shows the relationship between the initial rate of hydrogenation and the composition of PVP-Pd/Pt as well as the influence of metal cations. It can be found from Fig. 2a that the initial rate of the neat bimetallic colloid shows a maximum (3.2 mol H<sub>2</sub>/mol M s) at Pd/Pt = 3/1, meanwhile, the introduction of metal cations examined inhibits the reaction to an extent. Changing the composition of the bimetallic catalyst to Pd/Pt = 1/2, the addition of metal cations promotes the activity to another maximum, especially by adding Mn<sup>2+</sup>, Ni<sup>2+</sup> (to 4.3 and 3.6 mol H<sub>2</sub>/mol M s, respectively), although the activity of the neat colloid is low (2.6 mol H<sub>2</sub>/mol M s). With respect to the average rate, the profile is quite different from that of the initial rate (see Fig. 2b). The addition of Li<sup>+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup> and Mn<sup>2+</sup> enhances the average rate of the reaction, while introducing Fe<sup>3+</sup>, especially by adding Zn<sup>2+</sup> decreases the rate. Furthermore, the added metal cations exert favorable influence on the selectivity to *o*-CAN in the range of all composition of the bimetallic colloid as shown in Fig. 2c, which come to the extreme at Pd/Pt = 1/3. Upon introduction of Cr<sup>3+</sup> and Co<sup>2+</sup>, the high activity (1.03 and 0.96 mol H<sub>2</sub>/mol M s) and the best selectivity (91.4 and 91.5%) compared with those of neat PVP-Pd/Pt (1/3) bimetallic clusters are achieved, respectively.

As the results shown in Fig. 2, it can be seen that introducing metal cations considerably affect the properties of PVP-Pd/Pt bimetallic catalysts. The modification behavior is connected with the composition of the colloids and the nature of the metal cations. The positive charges of the metal cations change the surface elec-

tronic distribution of the bimetallic clusters. The metal ion Li<sup>+</sup> definitely has influence on the properties of PVP-Pd/Pt bimetallic colloids, which may be related with its very small ion radius and a high value of the positive charge to the proton number. Among these metal cations, Zn<sup>2+</sup> ions acts as a poison, which causes the selectivity to increase and the activity to decrease. This trend becomes more significant with the increase of atomic ratio of Pt/Pd of the bimetallic colloids as indicated in Fig. 2. For the other transition metal ions, such as Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup>, the electronic interaction between the metal ions and bimetallic clusters improves the catalyst surface to activate the hydrogen molecule (H<sub>2</sub>), which accelerates the rate of hydrogenation of N=O double bond. Furthermore, the coordination effect between the metal ions and amino group of the main products brings a decrease in the relative strength of adsorption between *o*-CAN and *o*-CNB [23], thus causing the selectivity to *o*-CAN and the activity of the catalytic system to increase at the same time.

Although the above discussion explains the catalytic behavior and the modification of metal cations on the activity and selectivity upon the selective hydrogenation of *o*-CNB to *o*-CAN to an extent, the mechanism of such behaviors is much more complicated, a detailed study should be carried out further.

#### 4. Conclusions

The experimental results shows that the catalytic properties of PVP-Pd/Pt bimetallic clusters for the selective hydrogenation of *o*-CNB depend on the composition of the colloids. All bimetallic clusters are more active than PVP-Pd and PVP-Pt mono-metallic clusters. The highest activity (1.81 mol H<sub>2</sub>/mol M s) is obtained over PVP-Pd/Pt (2/1) colloids and the best selectivity is achieved over PVP-Pd/Pt (1/3) colloids when the neat PVP-Pd/Pt clusters are used as catalysts. The addition of metal cations

to the catalytic system can considerably modulate both the activity and selectivity of the catalysts. The metal ion  $Zn^{2+}$  acts as a poison modification similar to the normal modifiers. Similar to those of PVP-Pt catalytic system, addition of the proper metal cations into the PVP-Pd/Pt bimetallic clusters can improve both the activity and the selectivity to *o*-CAN of the system at the same time. The modification may be related with the electronic synergic effect and the coordination effect between the metal ions and the bimetallic clusters. For PVP-Pd/Pt (1/3) bimetallic clusters as catalysts, upon introducing  $Cr^{3+}$  and  $Co^{2+}$ , the higher activity (0.96 and 1.03 mol  $H_2$ /mol M s for average rate, respectively) and the highest selectivity to *o*-CAN are obtained (91.2 and 91.3%, respectively), which are much superior to the monometallic PVP-Pt cluster system [23].

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### References

- [1] G. Schmid, Chem. Rev. 92 (1992) 1709.  
 [2] L.N. Lewis, Chem. Rev. 93 (1993) 2693.

- [3] J.H. Sinfelt, Acc. Chem. Res. 20 (1987) 134.  
 [4] N. Toshima, Y. Wang, Langmuir 10 (1994) 4574.  
 [5] Y. Wang, H. Liu, Polym. Bull. 25 (1991) 139.  
 [6] J.S. Bradley, E.W. Hill, C. Klein, B. Chaudret, A. Duteil, Chem. Mater. 5 (1993) 254.  
 [7] H. Liu, G. Mao, S. Meng, J. Mol. Catal. 74 (1992) 275.  
 [8] N. Toshima, P. Lu, Chem. Lett. (1996) 729.  
 [9] W. Yu, Y. Wang, H. Liu, W. Zheng, J. Mol. Catal. A: Chem. 112 (1996) 105.  
 [10] N. Toshima, K. Kushihashi, T. Yonezawa, H. Hirai, Chem. Lett. (1989) 1769.  
 [11] N. Toshima, T. Yonezawa, M. Harada, K. Asakura, Y. Iwasawa, Chem. Lett. (1990) 815.  
 [12] N. Toshima, T. Yonezawa, K. Kushihashi, J. Chem. Soc. Faraday Trans. 89 (1993) 2537.  
 [13] N. Toshima, M. Hirada, T. Yonezawa, K. Kushihashi, K. Asakura, J. Phys. Chem. 95 (1991) 7448.  
 [14] M. Harada, K. Asakura, Y. Ueki, N. Toshima, J. Phys. Chem. 96 (1992) 9730.  
 [15] H. Greenfield, F.S. Dovell, J. Org. Chem. 32 (1967) 3670.  
 [16] G.C. Bond, D.E. Webster, N.Y. Ann. Acad. Sci. 158 (1969) 540.  
 [17] J.R. Kosak, N.Y. Ann. Acad. Sci. 172 (1970) 175.  
 [18] J.R. Kosak, in: W.H. Jones (Ed.), Catalysis in Organic Synthesis, Academic Press, New York, 1980, pp. 107–117.  
 [19] B. Coq, A. Tijani, F. Figueras, J. Mol. Catal. 68 (1991) 331.  
 [20] B. Coq, A. Tijani, F. Figueras, J. Mol. Catal. 71 (1992) 317.  
 [21] B. Coq, A. Tijani, R. Dutatre, F. Figueras, J. Mol. Catal. 79 (1993) 253.  
 [22] W. Yu, H. Liu, Q. Tao, Chem. Commun. (1996) 1773.  
 [23] X. Yang, H. Liu, Appl. Catal. A 164 (1997) 197.  
 [24] H. Feng, H. Liu, J. Mol. Catal. A 126 (1997) L5.  
 [25] W. Yu, H. Liu, M. Liu, Q. Tao, J. Mol. Catal. A 138 (1999) 273.  
 [26] X. Yang, Z. Deng, H. Liu, J. Mol. Catal. A, in press.  
 [27] M. Liu, W. Yu, H. Liu, J. Mol. Catal. A 138 (1999) 295.  
 [28] R.C. Weast (Ed. in Chief), CRC Handbook of Chemistry and Physics, 70th edn., CRC Press, Boca Raton, FL, 1989–1990, pp. E80–E81.  
 [29] P. Gallezot, D. Richard, Catal. Rev. 40 (1998) 81.  
 [30] W. Yu, M. Liu, H. Liu, X. An, Z. Liu, X. Ma, J. Mol. Catal. A 142 (1999) 161.