

Letter

# The metal complex effect on metal clusters in liquid medium

Hongxia Feng, Hanfan Liu \*

*PCLCC*<sup>1</sup>, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China

Received 2 January 1997; accepted 15 May 1997

## Abstract

The metal complex effect on platinum clusters has been studied in the homogeneous liquid-phase hydrogenation of cinnamaldehyde (CAL) at 303 K and 4.0 MPa. The addition of metal complexes to the polymer-stabilized colloidal platinum cluster can considerably modulate both the activity and selectivity of the catalyst. When the neat platinum cluster was served as the catalyst, only moderate conversion (65.5%) of CAL and low selectivity (17.7%) to cinnamyl alcohol (COL) were obtained. However, the conversion was promoted to 78.0% and higher selectivity (75.0%) to COL was obtained, when employing  $\text{Na}_3\text{FeF}_6$  as the modifier; otherwise by introducing  $\text{Ni}(\text{bpy})_3\text{Cl}_2$  to the catalytic system, the conversion was remarkably enhanced to 82.1% and surprisingly the main product was not COL but hydrocinnamaldehyde (HCAL) with the selectivity of 97.3%. © 1997 Elsevier Science B.V.

**Keywords:** Hydrogenation; Colloidal platinum clusters; Metal complex; Cinnamaldehyde

## 1. Introduction

The chemistry and physics of metal clusters or colloids are presently attracting great and diverse interest because of the special position of these species at the interdisciplinary domain between the molecular and metallic states [1–7]. This kind of nanoscale materials are expected to play a significant role in future both in the fundamentally scientific and applied fronts. With regard to the application of metal colloids or clusters to catalysis, many researches have been

performed with the monometallic as well as bimetallic cluster catalysts for various reactions [8–14]. However, a few papers reported the effect of metal cations on the homogeneous catalytic systems of neat clusters; none have investigated the influence of metal complexes on such system. Our group recently reported that the modification of some metal cations to the platinum cluster led to the increase in both activity and selectivity for hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL) [15], and for hydrogenation of *o*-chloronitrobenzene to *o*-chloroaniline [16]. From a broad sense of modifiers, we pursue an extensive research on the influence of metal complex on the colloidal metal clusters. To our knowledge, this is the first observation on the influence of metal complexes on the metal cluster catalyst.

\* Corresponding author. Tel.: +86-10-62554487; fax: +86-10-62569564; e-mail: huangsl@infor3.icas.ac.cn

<sup>1</sup> PCLCC: Polymer Chemistry Laboratory, Chinese Academy of Sciences and China Petro-Chemical Corporation.

## 2. Experimental

The polyvinylpyrrolidone-stabilized platinum cluster catalyst (designated as PVP–Pt) was prepared as in our previous report [15].

Metal complexes were formed in situ by mixing a metal salt (mostly the chloride) with a corresponding ligand at a proper molar ratio except  $K_4Fe(CN)_6$  and  $NaBF_4$  which were directly used as purchased. For the sake of simplicity, only metal complexes with stepwise stability constants [17,18]  $k_1$  above ca.  $10^5$  were selected for test and reaction temperature was decreased to 303 K to lower the possible dissociation of the complex.

Hydrogenation of CAL was proceeded in a 150 ml stainless steel autoclave. The reaction solution contained 20 ml EtOH, 1.000 g CAL ( $7.576 \times 10^{-3}$  mol), 1.000 g tetradecanol (as an internal standard for gas chromatography), 10

ml PVP–Pt dispersion (containing Pt  $1.125 \times 10^{-5}$  mol, PVP  $5.625 \times 10^{-4}$  mol monomeric unit, 5 ml  $H_2O$  and 5 ml  $CH_3OH$ ) and a suitable amount of metal complexes,  $H_2$  was charged several times to replace air and the final pressure of  $H_2$  was 4.0 MPa. The reaction was conducted at 303 K for 2 h. Reaction products were analyzed by a Shangfen model-103 gas chromatograph equipped with a FID detector and PEG-20000 column, reactant and products were identified by the comparison with authentic samples.

## 3. Results and discussion

The catalytic hydrogenation results are summarized in Table 1. From the data listed in the table, it can be seen that the complexes composed of the same central metal ion with differ-

Table 1

The influence of metal complexes on hydrogenation of cinnamaldehyde catalyzed by the colloidal cluster PVP–Pt catalyst<sup>a</sup>

Entry	Catalytic system <sup>b</sup>	Average rate <sup>c</sup> / mol CAL (mol Pt h) <sup>-1</sup>	Conversion of CAL <sup>c</sup> (%)	Selectivity <sup>c</sup> (%)	
				COL	HCAL
1	PVP–Pt	220.6	65.5	17.7	82.3
2	PVP–Pt–FeCl <sub>3</sub>	267.8	79.5	62.0	36.9
3	PVP–Pt–NaBF <sub>4</sub>	220.6	65.5	24.4	75.4
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	24.3
6	PVP–Pt–Fe(gly) <sub>3</sub>	253.9	75.4	34.9	64.0
7	PVP–Pt–Fe(sal) <sub>3</sub>	207.1	61.5	44.4	54.3
8	PVP–Pt–K <sub>4</sub> Fe(CN) <sub>6</sub>	223.4	66.3	15.4	82.3
9	PVP–Pt–Al(AcAc) <sub>3</sub>	188.6	56.0	25.0	74.8
10	PVP–Pt–Cr(AcAc) <sub>2</sub> Cl	276.8	82.2	19.7	80.3
11	PVP–Pt–Fe(AcAc) <sub>3</sub>	233.1	69.2	58.8	40.8
12	PVP–Pt–Co(AcAc) <sub>2</sub>	268.1	79.6	30.4	68.0
13	PVP–Pt–Ni(AcAc) <sub>2</sub>	230.7	68.5	25.5	72.5
14	PVP–Pt–Cu(AcAc) <sub>2</sub>	236.4	70.2	16.4	83.6
15	PVP–Pt–Ce(AcAc) <sub>3</sub>	253.0	75.1	18.6	81.0
16	PVP–Pt–Co(bpy) <sub>3</sub> Cl <sub>2</sub>	241.8	71.8	25.1	74.5
17	PVP–Pt–Ni(bpy) <sub>3</sub> Cl <sub>2</sub>	276.6	82.1	3.6	97.3
18	PVP–Pt–Ni(gly) <sub>2</sub>	266.1	79.0	22.2	77.8
19	PVP–Pt–Zn(gly) <sub>2</sub>	214.6	63.7	26.7	72.9
20	PVP–Pt–NaF	143.1	42.5	15.3	84.1

<sup>a</sup> Metal complexes were prepared in situ by mixed a metal salt a corresponding ligand at a proper molar ratio except  $K_4Fe(CN)_6$  and  $NaBF_4$  which were directly used as purchased; the molar ratio of metal complexes: Pt = 1:20.

<sup>b</sup> AcAc = acetylacetonate; bpy = bipyridyl; gly = glycinate; sal = salicylate.

<sup>c</sup> CAL = cinnamaldehyde; COL = cinnamyl alcohol; HCAL = hydrocinnamaldehyde; and no 3-phenylpropan-1-ol can be detected.

ent ligands (entries 5–8,11; 12,16; 13,17,18) or the different central metal ions with the same ligand (entries 3–5; 9–15; 16,17; 6,18,19) exert the distinct influences on the catalytic reaction. For example, iron complexes:  $\text{Na}_3\text{FeF}_6$  (entry 5),  $\text{Fe}(\text{gly})_3$  (entry 6) substantially enhanced both the activity and selectivity to COL, while  $\text{Fe}(\text{sal})_3$  (entry 7),  $\text{Fe}(\text{AcAc})_3$  (entry 11) remarkably increased the selectivity to COL with slightly influencing the activity, however,  $\text{K}_4\text{Fe}(\text{CN})_6$  (entry 8) acted merely as a spectator. The complexes with the same ligand, assume a similar role. For the acetylacetonate complexes, upon introducing  $\text{Cr}(\text{AcAc})_2\text{Cl}$  (entry 10), or  $\text{Ce}(\text{AcAc})_3$  (entry 15), the activity was considerably enhanced compared with the neat Pt cluster catalyst, whereas the selectivity was slightly changed; however  $\text{Ni}(\text{AcAc})_2$  (entry 13) enhanced both the activity and selectivity in moderation. For the bipyridyl complexes,  $\text{Co}(\text{bpy})_3\text{Cl}_2$  (entry 16) exerted a moderate effect, despite  $\text{Co}^{2+}$  was the best promoter in our previous system [15], but when using  $\text{Ni}(\text{bpy})_3\text{Cl}_2$  (entry 17) as a modifier, the conversion was markedly promoted to 82.1%, and surprisingly the main product was not COL but HCAL with the selectivity of 97.3%. Furthermore,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  were known as poisons for the platinum cluster catalyst, while by formation of complexes  $\text{Cu}(\text{AcAc})_2$  (entry 14) with ligand acetylacetonate and  $\text{Zn}(\text{gly})_2$  (entry 19) with ligand glycinate, both activity and selectivity were slightly fluctuated compared with the neat Pt cluster. So it provides us with an effective procedure: by adding the proper ligand the deactivity of some metal ions can be diminished. Another point is that although many and diverse metal complexes were surveyed, none of the complexes was found to exhibit such a substantial increase in both the activity and selectivity of a cluster catalyst as by adding  $\text{Fe}^{3+}$  or  $\text{Co}^{2+}$  cations as reported before [15]. It should be noted, however, the previous results with the metal cations were the optimized ones obtained by adding sodium hydroxide and others, with proper molar ratio of metal cation to

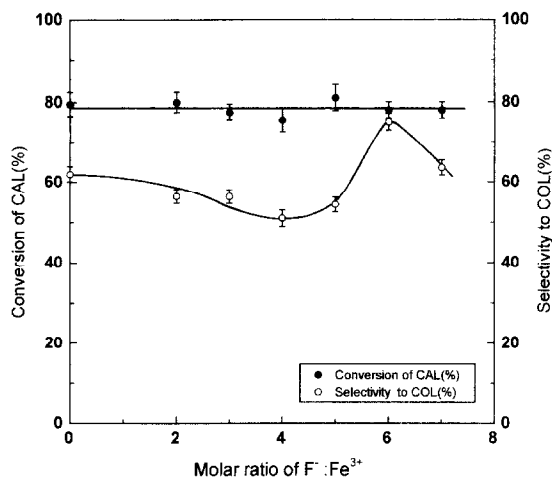


Fig. 1. Hydrogenation of CAL catalyzed by PVP–Pt cluster with ferric-fluoride complex system at different molar ratio of  $\text{F}^-:\text{Fe}^{3+}$  (●: conversion of CAL, ○: selectivity to COL).

platinum, etc. With respect to the iron complexes, if we make a comparison on the base of the same reaction condition,  $\text{Na}_3\text{FeF}_6$  complex (entry 5) showed superior result than that of  $\text{Fe}^{3+}$  cation (entry 2). It looks even more evident as shown in Fig. 1.

Obviously different results were obtained at different molar ratios of  $\text{F}^-:\text{Fe}^{3+}$ , with the increase in molar ratio of  $\text{F}^-:\text{Fe}^{3+}$  at a suitable range, the activity was nearly unchanged, yet the selectivity to COL decreased slowly first, then increased to the maximum (75.0%) at  $\text{F}^-:\text{Fe}^{3+} \sim 6$ ; when the amount of  $\text{F}^-$  to higher extends  $\text{F}^-:\text{Fe}^{3+} > 6$  in molar ratio, it decreased abruptly, this may be attributed to the inferior effect on the reaction of the free  $\text{F}^-$  ions (entry 20). Fig. 2 shows the concentration dependence of  $\text{Na}_3\text{FeF}_6$  on Pt catalyst's performance. It reaches a maximum in both activity and selectivity within a range of the metal complex: Pt ratios of 0.2–1.0.

The data mentioned above showed that the metal complexes have a different effect on the catalyst's performance from the metal cations, despite that some factors, e.g., the concentration of the distinct metal complex species, were not controlled. It is interesting to note that the

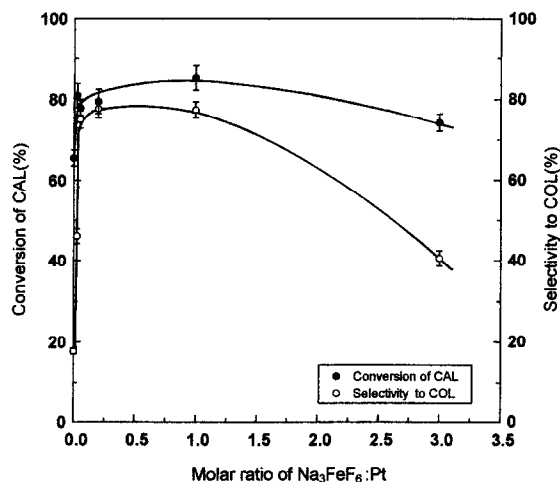


Fig. 2. Hydrogenation of CAL catalyzed by PVP-Pt- $\text{Na}_3\text{FeF}_6$  at different molar ratio of  $\text{Na}_3\text{FeF}_6$ :Pt (●: conversion of CAL, ○: selectivity to COL).

change in selectivity from saturated aldehyde to unsaturated alcohol is not apparently simply the result of poisoning the carbon-carbon double bond hydrogenation — the rates of the modified reactions are as fast as or faster than the base-case Pt catalyzed reaction, and so a true promotional effect is occurring. Gallezot et al. reported that the effect in cinnamaldehyde hydrogenation of a charcoal-supported platinum mediated by iron salt was observed to change the selectivity in favour of cinnamyl alcohol [19]. The reason for the effect given by Gallezot is that the electrophilic Fe ion on the Pt surface coordinates the aldehydic oxygen thus holding the C=O bond near the Pt surface. Although the mechanism of the metal complexes effect on the colloidal cluster catalyst looks much more complicated than the established heterogeneous catalyst system, we would prefer to take the similar explanation. Further investigations are in progress.

## Acknowledgements

Financial support of the National Natural Science Foundation of China (Contract No. 29474181) and the Fund of the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, the Chinese Academy of Sciences (Contract No. 9616) were acknowledged. This work was also supported by the Fund of the Director of the Institute of Chemistry, the Chinese Academy of Sciences.

## References

- [1] G. Schmid, *Chem. Rev.* 92 (1992) 1709.
- [2] L.N. Lewis, *Chem. Rev.* 93 (1993) 693.
- [3] K.J. Klabunde, Y.Y.X. Li, B.J. Tan, *Chem. Mater.* 3 (1991) 30.
- [4] J.M. Thomas, *Pure Appl. Chem.* 60 (1988) 1517.
- [5] K. Kimura, *Z. Phys. D: At. Mol. Cluster* 11 (1989) 327.
- [6] M.A. Marcus, M.P. Andrews, J. Zegenhagen, A.S. Bommanavar, P. Montano, *Phys. Rev. B* 42 (1990) 3312.
- [7] H. Liu, N. Toshima, *J. Chem. Soc. Chem. Commun.* (1992) 1095.
- [8] H. Hirai, N. Toshima, in: Y. Iwasawa (Ed.), *Tailored Metal Catalysts*, Reidel, Dordrecht, 1985, pp. 121–135.
- [9] C. Amiens, D. de Caro, B. Chandret, J.S. Bradley, R. Mazel, C. Roucau, *J. Am. Chem. Soc.* 115 (1993) 11638.
- [10] Y. Wang, H. Liu, Y. Jiang, *J. Chem. Soc. Chem. Commun.* (1989) 1878.
- [11] J.S. Bradley, J. Millar, E.W. Hill, M. Melchior, *J. Chem. Soc. Chem. Commun.* (1990) 705.
- [12] Y. Wang, H. Liu, *Polym. Bull.* 25 (1991) 139.
- [13] H. Liu, G. Mao, S. Meng, *J. Mol. Catal.* 74 (1992) 275.
- [14] H. Bönemann, W. Brijoux, R. Brinkmann, E. Dinjus, T. Jousen, B. Korall, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 1312.
- [15] W. Yu, H. Liu, Q. Tao, *J. Chem. Soc. Chem. Commun.* (1996) 1773.
- [16] X. Yang, H. Liu, *Appl. Catal.*, in press.
- [17] E. Martell, R.M. Smith, *Critical Stability Constants*, Plenum Press, New York, 1974.
- [18] J. Kragten, *Atlas of Metal-Ligand Equilibria in Aqueous Solution*, Ellis Horwood, New York, 1978.
- [19] D. Richard, J. Ockelford, A. Giroir-Fendler, P. Gallezot, *Catal. Lett.* 3 (1989) 53.