

Modification of metal cations to metal clusters in liquid medium

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The modification of some metal cations to polymer-protected colloidal platinum clusters leads to remarkable increases in both selectivity and activity in homogeneous liquid-phase selective hydrogenation of cinnamaldehyde to cinnamyl alcohol.

Nanoscale metal clusters, because of their substantial differences from metal atoms and bulk metals in size and structure, have attracted increasing attention especially in the field of catalysis.¹ Owing to the thermodynamic instability of metal clusters, studies have mainly focused on reactions conducted under mild conditions, such as hydrogenation of monoenes or dienes² and hydration of acrylonitrile³ near or at ambient conditions. For the same reason, few papers have reported the influence of additives to the homogeneous catalytic systems of neat metal clusters. However, it is well known that additives, such as ions, can markedly affect the catalytic properties of supported metal catalysts.⁴ Liao and coworkers⁵ recently reported that the selectivity to *p*-chloroaniline can be remarkably increased by adding an equimolar amount of RuCl₃ to a PVP-PdCl₂ [PVP = poly(*N*-vinyl-2-pyrrolidone)] catalytic system for hydrogenation of *p*-chloronitrobenzene. It is common knowledge that an increase in the selectivity of a catalyst by incorporating additives causes a decrease in activity. However, in the selective hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL) catalysed by polymer-protected colloidal platinum clusters, considerable increases in both the selectivity and the activity were observed when employing metal cations as modifiers. To the best of our knowledge, this is the first example of a homogeneous metal catalytic system in which both the selectivity and the activity of a cluster catalyst can be greatly enhanced by the addition of suitable metal cations and here, we report our preliminary results.

Polymer-protected colloidal platinum clusters were prepared by a reported method^{2a} in the form of dark-brown homogeneous dispersions (designated as PVP-Pt). TEM observation showed that the average diameter of PVP-Pt was 1.1 nm with a narrow size distribution in the range 0.6–1.8 nm with $\sigma = 0.30$ nm.

Hydrogenation of CAL was carried out in a 150 ml stainless-steel autoclave. The reaction solution contained 40 ml EtOH, 1 mg NaOH, 1.000 g CAL (7.576×10^{-3} mol), 1.000 g tetradecanol (as an internal standard for gas chromatography), 20 ml PVP-Pt dispersion {containing Pt (2.249×10^{-5} mol), PVP [1.125×10^{-3} mol (monomeric unit)], 10 ml H₂O and 10 ml MeOH} and metal salt added, H₂ was charged several times to replace air and the final pressure of H₂ was 4.0 MPa. The hydrogenation reaction was performed at 333 K for 1.5 h. The reaction products were periodically analysed by gas chromatography.

There are two competitive hydrogenation reactions starting from CAL (Scheme 1). Ordinary heterogeneous catalysts can easily reduce C=C double bonds to yield hydrogenated cinnamaldehyde as the main product [Scheme 1, reaction (ii)]. However, it is a challenging task to reduce the C=O double bond without reduction of the C=C double bond [Scheme 1, reaction (i)].

Under the reaction conditions employed, when using neat PVP-Pt alone as a catalyst, 37.5% conversion of CAL with

12.0% selectivity for COL was observed. However, upon introducing Fe³⁺ or Co²⁺ into the catalytic system, the activity was enhanced to 120%, and the selectivity for COL increased to 98.5% (Table 1).

Maximum selectivity (99.7%) was achieved using Co²⁺ as a modifier to the PVP-Pt system; at a Co²⁺: Pt molar ratio of 1:3 conversion reached 82.1% (Fig. 1).

It was found that CoCl₂·6H₂O and Co(NO₃)₂·6H₂O led to the same activity and selectivity (see Fig. 1) in a wide region from 1:20 to 20:1 molar ratio Co²⁺: Pt in the reaction system. This indicated that non-strongly coordinating anions (not, however, strongly coordinating anions such as CN⁻, SCN⁻, F⁻ etc.) acted merely as spectator ions. The mechanism for this unusual modification of metal cations in the performance of PVP-Pt

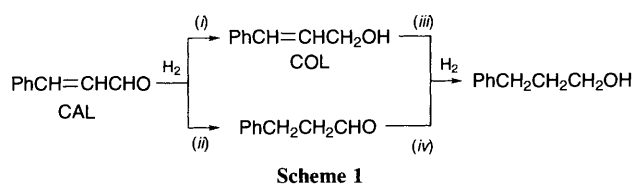


Table 1 Hydrogenation of cinnamaldehyde catalysed by PVP-Pt-MCl_x systems^a

Catalytic system	Average rate/ mol CAL (mol Pt h) ⁻¹	Conv. of CAL/%	Selectivity/% ^b		
			COL	HCAL	HCOL
PVP-Pt	84.2	37.5	12.0	80.0	8.0
PVP-Pt-NaCl	85.9	38.3	19.1	74.9	6.0
PVP-Pt-FeCl ₃	187.5	83.5	98.5	1.5	Trace
PVP-Pt-CoCl ₂	186.2	82.9	98.8	1.2	Trace
PVP-Pt-NiCl ₂	115.7	51.5	34.4	50.6	15.0
PVP-Pt-ZnCl ₂	29.2	13.0	99.8	0.2	Trace

^a Molar ratio M: Pt = 1:1. ^b HCAL = hydrocinnamaldehyde, HCOL = 3-phenylpropan-1-ol.

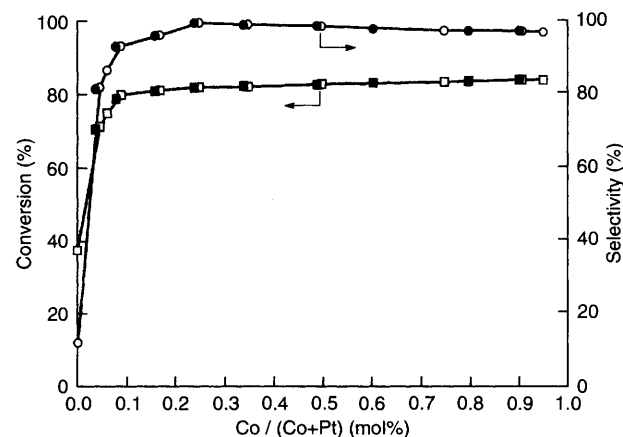


Fig. 1 Conversion of CAL (■, □) and selectivity for COL (●, ○) vs. molar percentage of Co²⁺ in the PVP-Pt catalytic system with CoCl₂·6H₂O (filled symbols) or Co(NO₃)₂·6H₂O (open symbols)

catalysts still, however, remains unclear and further investigation is in progress.

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References

- 1 G. Schmid, *Chem. Rev.*, 1992, **92**, 1709; L. N. Lewis, *Chem. Rev.*, 1993, **93**, 2693.
- 2 (a) H. Hirai, *J. Macromol. Sci., Chem.*, 1979, **A13**, 633; (b) H. Hirai, H. Chawanya and N. Toshima, *Makromol. Chem., Rapid Commun.*, 1981, **2**, 99; (c) H. Hirai, H. Chawanya and N. Toshima, *React. Polym.*, 1985, **3**, 127; (d) Y. Wang and H. Liu, *Polym. Bull.*, 1991, **25**, 139; (e) Y. Wang, H. Liu and Y. Jiang, *J. Chem. Soc., Chem. Commun.*, 1989, 1878; (f) H. Liu, G. Mao and S. Meng, *J. Mol. Catal.*, 1992, **74**, 275.
- 3 H. Hirai, H. Wakabayashi and M. Komiyama, *Chem. Lett.*, 1983, 1047; N. Toshima and Y. Wang, *Langmuir*, 1994, **10**, 4574.
- 4 B. Coq, P. S. Kumbhar, C. Moreau, P. Moreau and M. G. Warawdekar, *J. Mol. Catal.*, 1993, **85**, 215; Y. Z. Chen, S. W. Wei and K. J. Wu, *Appl. Catal. A: Gen.*, 1993, **99**, 85; U. Schröder and L. de Verdier, *J. Catal.*, 1993, **142**, 490; J. Struijk, R. Moene, T. van der Kamp and J. J. F. Scholten, *Appl. Catal. A: Gen.*, 1992, **89**, 77.
- 5 Z. Yu, S. Liao, Y. Xu, B. Yang and D. Yu, *J. Chem. Soc., Chem. Commun.*, 1995, 1155.

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