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Modification of metal complex on hydrogenation of o-chloronitrobenzene over polymer-stabilized platinum colloidal clusters

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Abstract

The effect of metal complex on hydrogenation of o-chloronitrobenzene (CNB) over poly-vinylpyrrolidone-stabilized platinum clusters (PVP-Pt) has been studied in methanol at 303 K and atmospheric pressure. The addition of metal complexes to the catalytic system can considerably modulate both the activity and the selectivity of the catalyst. A low activity (0.41 mol H_2/mol Pt s) and low selectivity (42.6%) were obtained when the neat PVP-Pt colloidal clusters were used as a catalyst. Upon the addition of the complexes $Ni(AcAc)_2$ and $Na[Co(AcAc)_3]$, the better selectivity to o-chloroaniline (o-CAN) were promoted to 76.2% and 76.5%, and the higher activities (0.72 mol H_2/mol Pt s and 0.83 mol H_2/mol Pt s) were obtained, respectively. On the other hand, when the complex $Ni(en)_3Cl_2$ was introduced as a modifier, the highest selectivity to o-CAN (94.0%) was achieved, though the activity was lowered to 0.16 mol H_2/mol Pt s. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Hydrogenation of halonitroaromatics to the corresponding haloanilines is important in the chemistry of dyes, drugs, herbicides and pesticides. Among heterogeneous and homogeneous catalysts, platinum-based catalysts are particularly attractive for minimizing dehalogenation combined with a fast rate of reduction of the nitro group [1–7]. Catalytic systems for achieving high yields to the desired products (haloanilines) have been developed either by dedicated preparation of the catalyst (alloying [5], controlling the metal particle dispersion [6] and metal/support interaction [7], etc.), or by the use of specific additives (promoter, inhibitor) such as bases or other electron donating compounds [8–10], the interaction of which with the metal particles modify the electronic properties of the catalyst [11].

The effect of metal ions on metal catalysts has been well studied in the field of heteroge-

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neous catalysis [12–15]. For metal colloid systems, we reported that the addition of Co^{2+} can significantly improve the activity and the selectivity to unsaturated alcohol in the hydrogenation of α,β-unsaturated aldehyde [16,17], and the introduction of Ni^{2+} to the platinum colloid-catalyzed hydrogenation of *o*-chloronitrobenzene (*o*-CNB) can enhance the activity and the selectivity to *o*-chloroaniline (*o*-CAN) at the same time [18]. However, the study on the metal complex effect is rather scarce. We recently reported that the metal complex can considerably modulate both the activity and the selectivity of colloidal poly-vinylpyrrolidone-stabilized platinum clusters (PVP-Pt) catalysts in the hydrogenation of cinnamaldehyde [19]. It remains unknown whether such unusual modification of metal complex to metal colloidal clusters is merely a special case or of universal significance. Here we describe the results on the modification of metal complexes on the hydrogenation of *o*-CNB over PVP-Pt colloidal clusters, in which the N=O double bond was expected to be reduced without the hydrogenolysis of the C–Cl bond.
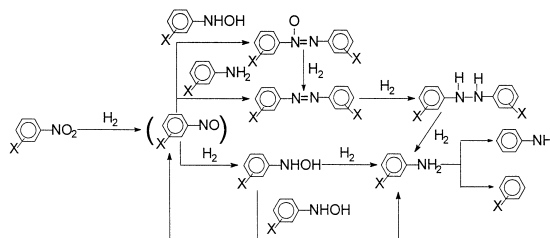
2. Experimental

The PVP-Pt was prepared as reported in a previous paper [16]. Hexachloroplantinic acid ($H_2PtCl_6 \cdot 6H_2O$, 0.293 g, 5.65×10^{-4} mol) was dissolved in 140 ml distilled water, PVP (3.12 g, 2.81×10^{-2} mol as monomeric unit) was then added to the solution as a stabilizing polymer and 180 ml methanol was added to the solution. Forty millilitres of 0.1 M NaOH solution was dropped to the solution while vigorously stirring. The mixed solution was refluxed for 2 h and resulted to a transparent dark brown colloid. The water–methanol solvent was evaporated on a Rotavap. The residue was redispersed in methanol as the catalyst designated as PVP-Pt. The particles in PVP-Pt sol were mostly distributed in the range of 1.3–1.9 nm with an average diameter of 1.55 nm [18].

Metal complexes were formed in situ by mixing a metal salt (usually the chloride) with a ligand at a proper molar ratio according to the reported method [19,20]. For example, $Ni(en)_3Cl_2$ was prepared by mixing $NiCl_2 \cdot 6H_2O$ (26.7 mg, 0.112 mmol) with ethylenediamine (20.1 mg, 0.336 mmol) in methanol. For the sake of simplicity, only metal complexes with stepwise stability constants [21,22] k_1 above ca. 10^5 were selected for the test.

Catalytic hydrogenation of *o*-CNB was conducted in a 30 ml flat-bottom flask. Reaction temperature was kept constant at $\pm 0.1°C$ by an external circulation of a thermostat. The catalyst (PVP-Pt, 4.8×10^{-6} mol Pt) with the metal complex was activated under hydrogen with magnetic stirring at 303 K for 40 min. After activation, 2.0 ml of the reactant solution (0.5 M *o*-CNB in methanol) was charged to the flask; the total volume of the catalytic system was 15.0 ml. The reaction rate was measured by the uptake of hydrogen. Chemical analysis of the products was performed by gas chromatography (Shangfen model 103), equipped with a FID detector and DC-710 column. Reactants and products were identified by comparison with authentic samples. n-$C_{14}H_{30}$ was used as an internal standard.

3. Results and discussion

The hydrogenation of halonitrobenzene follows the reaction pathways described in the literature [5], as shown in Scheme 1.

Scheme 1. Pathways of the hydrogenation of halogenated nitrobenzene.

Table 1 lists the experimental results of the influence of metal complexes, metal ions and ligands on the hydrogenation of o-CNB over PVP-Pt colloidal catalyst. Although the results were diverse for the complexes composed of the same central metal ion with different ligands (entries 7, 8, 15, 20–23) and of the different central ions with the same ligand (entries 7 and 9; 11–15; 17–20 and 22–25), it is evidently manifested that the influence of the complexes is not the sum of those of the metal central ions and the ligands. As reported in the literature [18], the metal cations Fe^{3+}, Co^{2+} and Ni^{2+} exert favorable influence on both activity and the selectivity of the reaction, while the Cr^{3+}, Mn^{2+} ions modulate only slightly the perfor-

mance of the catalyst. From the data listed in Table 1, it can be seen that metal bipyridine complexes exert inferior influences on the hydrogenation in both activity and selectivity, while the metal acetylacetonate complexes show a more favorable effect in comparison with the metal cations. On the other hand, the metal ethylenediamine complexes result in a decrease in the hydrogenation rate but an increase in the selectivity to o-CAN. It is obvious as indicated in Fig. 1. The other complexes, such as $Cu(en)_2Cl_2$, $Zn(en)_2Cl_2$ and $Na_3[Fe(SCN)_6]$ (entries 24, 25, and 26) caused the PVP-Pt catalyst to lose all the activity.

With respect to the nickel(II) ethylenediamine complexes, different complex ions ex-

Table 1
The effect of metal complexes on the hydrogenation of o-CNB over PVP-Pt colloidal clusters[a]

Entry	Catalytic system	Average rate (mol H_2/mol Pt s)	Conversion of o-CNB (%)[b]	Selectivity (%)		
				o-CAN	NB	AN
1	PVP-Pt	0.41	100 (27.0)	46.0	1.3	–
2	PVP-Pt–Mn^{2+}	0.34	100 (32.5)	43.0	4.4	5.2
3	PVP-Pt–Fe^{3+}	0.42	95.5 (26.4)	53.5	trace	10.8
4	PVP-Pt–Co^{2+}	0.41	83.9 (27.0)	53.4	1.1	1.4
5	PVP-Pt–Ni^{2+}	0.64	100 (17.5)	66.2	–	–
6	PVP-Pt–3bpy	0.15	80.0 (73.8)	35.2	4.6	–
7	PVP-Pt–$Ni(bpy)_3^{2+}$	0.18	83.9 (61.5)	31.3	2.2	–
8	PVP-Pt–$1.5Ni(bpy)_2^{2+}$	0.32	92.5 (34.6)	50.0	4.3	–
9	PVP-Pt–$Co(bpy)_3^{2+}$	0.11	64.2 (100.5)	31.8	–	–
10	PVP-Pt–$H(AcAc)$	0.52	100 (21.2)	48.3	7.9	–
11	PVP-Pt–$Mn(AcAc)_2$	0.54	100 (20.5)	41.5	2.9	–
12	PVP-Pt–$Cr(AcAc)_3$	0.36	86.9 (31.4)	34.9	4.0	–
13	PVP-Pt–$Fe(AcAc)_3$	0.44	100 (25.3)	62.9	6.9	–
14	PVP-Pt–$Co(AcAc)_3^-$	0.83	100 (13.4)	76.5	1.5	–
15	PVP-Pt–$Ni(AcAc)_2$	0.72	100 (15.6)	76.2	–	–
16	PVP-Pt–en	0.14	100 (77.4)	43.0	24.1	–
17	PVP-Pt–$Mn(en)^{2+}$	0.088	100 (126.7)	39.1	22.8	–
18	PVP-Pt–$Cr(en)_3^{3+}$	0.14	92.1 (77.2)	52.9	9.7	–
19	PVP-Pt–$Co(en)^{2+}$	0.27	100 (41.1)	70.0	1.7	–
20	PVP-Pt–$Ni(en)^{2+}$	0.41	100 (27.3)	88.0	–	–
21	PVP-Pt–$Ni(en)_{1.5}^{2+}$	0.23	100 (47.9)	91.7	2.3	–
22	PVP-Pt–$Ni(en)_2^{2+}$	0.20	96.2 (55.5)	93.0	–	–
23	PVP-Pt–$Ni(en)_3^{2+}$	0.16	100 (68.4)	94.0	–	–
24	PVP-Pt–$Cu(en)_2^{2+}$	0	–	–	–	–
25	PVP-Pt–$Zn(en)_2^{2+}$	0	–	–	–	–
26	PVP-Pt–$Fe(SCN)_6^{3-}$	0	–	–	–	–

[a]Reaction conditions: PVP-Pt: 3.0×10^{-4} mol Pt/l; Pt:ML_x^{n+} in molar ratio; n-$C_{14}H_{30}$: internal standard; o-CNB: 0.067mol/l; solvent: CH_3OH 15.0 ml; reaction temperature: 303 K; P_{H_2}: 0.1 MPa.
[b]Conversion measured by GC, the value in parentheses was the time for a given conversion.
[c]Selectivity measured by GC, o-CNB: o-chloronitrobenzene; o-CAN: o-chloroaniline; NB: nitrobenzene; AN: aniline.
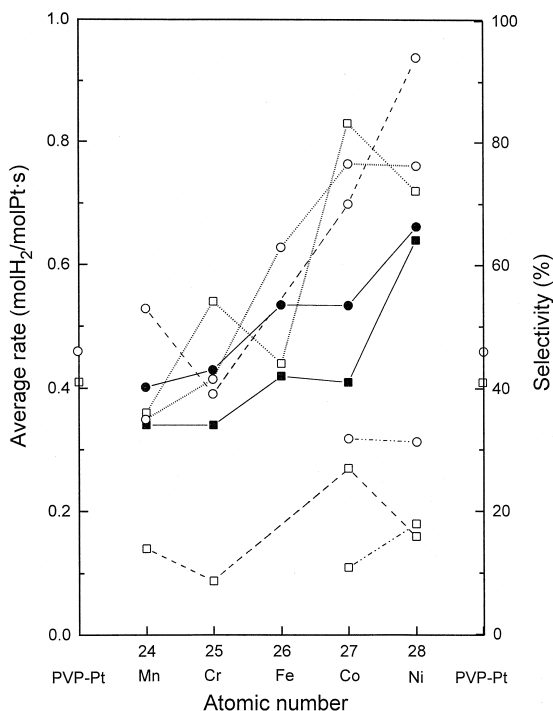
Fig. 1. The modification of metal complexes on the hydrogenation of o-CNB over PVP-Pt colloidal clusters (solvent: methanol, $v = 15.0$ ml, $T = 303$ K, $P_{H_2} = 0.1$ MPa). (Average rate: square; selectivity: circle. ——— metal cation, —— ·· —— bpy complex, · · · AcAc complex, - - - en complex.)

filtration separation after the hydrogenation. It was verified that Fe^{3+} changed into Fe^{2+}, while Co^{2+} and Ni^{2+} remained during the reaction which are in accordance with the literature [17,19]. The results show that the metal ions, such as Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} cannot be reduced to the metallic state and/or form bimetallic colloids in combination with platinum. Owing to the equilibrium of step dissociation of metal complexes, there is no unitary of species but a mixture of multistep complexes at an integer molar ratio of ligand to metal, for example, at a molar ratio of bpy:$Ni^{2+} = 3$, three species of complexes, $Ni(bpy)Cl_2$, $Ni(bpy)_2Cl_2$ and $Ni(bpy)_3Cl_2$ coexisted in the reaction medium at a concentration of 7.37×10^{-7} M, 2.18×10^{-6} M and 1.63×10^{-5} M by calculation, respectively, under our experimental condition [21]. Thus, it causes the mechanism of metal complexes effect very complicated. However, it is generally believed that the interaction between metal complexes and the platinum particles may change the electronic density of the platinum active site, which in turn influences the catalytic performance. Further detailed study is needed to clear the mechanism.
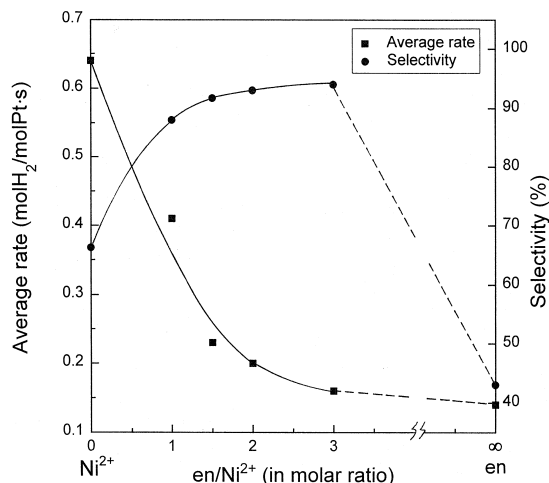
isted, such as, $Ni(en)^{2+}$, $Ni(en)_2^{2+}$, $Ni(en)_3^{2+}$, and they exerted the distinct influence on the performances of the catalyst (see Fig. 2). These results show that the behavior of metal complexes is closely related to the number of the ligands coordinated to the central metal ion. Clearly, different results were obtained at different ratios of en:Ni^{2+}, the activity was evidently decreased, whereas the selectivity to o-CAN was significantly increased with the increase in molar ratio of en:Ni^{2+} in the range of 0–3. In other words, an inverse relationship between catalytic activity and selectivity exerts by nickel(II) ethylenediamine complexes. The best yield in o-CAN (94.0%) was achieved when the $Ni(en)_3^{2+}$ complex was used as a modifier.

The real mechanism of the metal complex effect is still obscure. We analyze the oxidation state of Fe^{3+}, Co^{2+} and Ni^{2+} added by super-

Fig. 2. Hydrogenation of o-CNB over PVP-Pt catalysts with nickel(II)-ethylenediamine complex system at different molar ratio of en:Ni^{2+}. (■ Average rate; ● Selectivity.)

4. Conclusions

The addition of metal complexes to the catalytic system can considerably modulate both the activity and the selectivity to *o*-CAN on the hydrogenation of *o*-CNB over the PVP-Pt catalyst. The influence of the complexes is not the sum of those of the metal central ions and the ligands. A low activity (0.41 mol H_2/mol Pt s) and selectivity (42.6%) were obtained when the neat PVP-Pt colloidal cluster was used as a catalyst. Upon adding the complexes $Ni(AcAc)_2$ and $Na[Co(AcAc)_3]$, better selectivity to *o*-CAN (76.2% and 76.5%) with higher activities (0.72 mol H_2/mol Pt s and 0.83 mol H_2/mol Pt s) were obtained, respectively. When the complex $Ni(en)_3Cl_2$ was introduced as a modifier, the highest yield in *o*-CAN (94.0%) was achieved though the activity was lowered to 0.16 mol H_2/mol Pt s.

Acknowledgements

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