

The metal complex effect on the selective hydrogenation of *m*- and *p*-chloronitrobenzene over PVP-stabilized platinum colloidal catalysts

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Abstract

The metal complex effect on the hydrogenation of *m*-chloronitrobenzene and *p*-chloronitrobenzene (CNB) over poly-vinylpyrrolidone-stabilized platinum colloidal catalysts (PVP-Pt) has been studied under 303 K and atmospheric pressure. The introduction of metal complexes to the catalytic system has great effect on the activity and the selectivity of the catalyst. On the addition of the complexes $\text{Co}(\text{AcAc})_3^-$ and $\text{Ni}(\text{en})_3^{2+}$ to the hydrogenation of *m*-CNB, the selectivities to *m*-chloroaniline (CAN) were increased from 82.2% to 95.5% and $> 99.9\%$, while the activities were 0.88 and 0.18 mol $\text{H}_2/\text{mol Pt s}$ (the neat PVP-Pt catalyst with 0.69 mol $\text{H}_2/\text{mol Pt s}$), respectively. With iron(III) 8-hydroxyquinoline (8-HQ) complex $\text{Fe}(\text{8-HQ})^{2+}$ as a modifier, the highest selectivity of *p*-CNB to *p*-CAN ($> 99.9\%$) was obtained, even though its activity was decreased from 1.11 to 0.56 mol $\text{H}_2/\text{mol Pt s}$. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Platinum colloid; Metal complex effect; Hydrogenation; Colloidal catalyst; Chloronitrobenzene

1. Introduction

Hydrogenation of haloaromatic nitro compounds to the corresponding haloaromatic amine is an important reaction in the application field of dyes, drugs, herbicides and pesticides. It is always accompanied by some hydrogenolysis of the carbon–halogen bond. Depending on the halogen and its position relative to nitro group in the aromatic system, dehalogenation can vary from negligible to 100%. The more reactive the aromatic halogen, the greater the loss. Among

heterogeneous and homogeneous catalysts, platinum-based catalysts are particularly attractive for minimizing dehalogenation combined with a fast hydrogenation rate of the nitro group [1–7]. In order to tune the catalytic system to achieve high yields of the desired products (haloanilines), many approaches 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 additive (promoters and inhibitors) [8–10].

Polymer-stabilized metal colloids have showed their particular catalytic performance due to their high surface area of metal particles [11–13] and special catalytic environment mod-

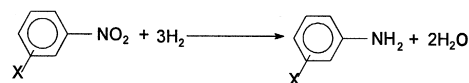
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ulated by polymer stabilizer [14,15]. Polyvinylpyrrolidone (PVP)-stabilized platinum colloids have been investigated as the catalyst in hydrogenation of *o*-chloronitrobenzene (CNB) to *o*-chloroaniline (CAN) [16]. The effect of metal ions on the PVP-Pt catalytic system has been observed. The introduction of Ni^{2+} can improve the activity and the selectivity of the platinum colloid-catalyzed hydrogenation of *o*-CNB to *o*-CAN. Moreover, the metal complexes have revealed their considerable modulation [17,18]. The adding of $\text{Ni}(\text{en})_3^{2+}$ can enhance the selectivity to *o*-CAN from 46.0% to 94.0% with 100% conversion [18]. The complex effect exists objectively and it has a universal significance. To know better the complex effect and its relation with reaction substrates, we made further investigations. *m*-CNB and *p*-CNB have the similar structure as *o*-CNB only with different chloro position relative to nitro group. Here, we describe the results on the hydrogenation of *m*-CNB, *p*-CNB over PVP-Pt colloidal catalysts modified by metal complexes, in which *m*-CAN and *p*-CAN are expected as aim products with high selectivity. Metal complex effects on CNB with different chloro position to nitro group were compared.

2. Experimental

The PVP-Pt was synthesized as reported in a previous paper [19]. Hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 0.0311 g, 6.0×10^{-5} mol) was dissolved in 25.4 ml distilled water, PVP (0.3334 g, 3.0×10^{-3} mol as monomeric unit) was then added to the solution as a stabilizing polymer and 30 ml methanol was added to the solution. NaOH solution (0.1 M, 4.6 ml) was dropped into the solution while vigorously stirring. The mixed solution was refluxed for 2 h and formed a transparent dark-brown colloid. The water–methanol solvent was evaporated on a rotavap. Then, the PVP-Pt residue was redissolved in methanol as a catalyst prior to hydrogenation. The particles of PVP-Pt colloid were



Scheme 1.

mainly in the range of 0.6–1.8 nm with an average diameter of 1.1 nm [19].

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 [20]. For example, $\text{Ni}(\text{en})_3^{2+}\text{Cl}_2$ was prepared by mixing $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (26.7 mg, 0.112 mmol) with ethylenediamine (20.1 mg, 0.336 mmol) in methanol. In our experiments, only metal complexes with stepwise stability constants k [21,22] above ca. 10^5 were selected.

Catalytic hydrogenation of *m*-CNB or *p*-CNB was conducted in a 30-ml flat-bottom flask. Reaction temperature was kept constant at 303 K by an external circulation of a thermostat. The catalyst (PVP-Pt, 4.8×10^{-6} mol Pt) in methanol solution with metal complex was activated under hydrogen with magnetic stirring at 303 K for 30 min. After activation, 2.0 ml of the reactant solution (0.5 M *m*-CNB or *p*-CNB in methanol) was charged to the flask to start the reaction; the total volume of the catalytic system was 15.0 ml. The reaction rate was measured by the uptake of hydrogen. The reaction was stopped at the theoretical uptake of hydrogen according to the reaction equation in Scheme 1 (3 mol H_2 /mol CNB). Chemical analysis of the products was performed by gas chromatography (Beifen SQ-204), equipped with a FID detector and DC-710 column. Reactants 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

The hydrogenation of CNB is a complicated process, and many by-products are involved. It follows the reaction pathways described in the

literature [5]. Our purpose is to achieve high selectivity to CAN without the hydrogenolysis of the C–Cl bond (Scheme 1).

Table 1 and Table 2 list the experimental results of the influence of metal complexes, metal ions and ligands on the hydrogenation of *m*-CNB and *p*-CNB over PVP-Pt colloidal catalysts, respectively. It can be seen clearly that the effect of the metal complexes is different from both the metal central ions and the ligands, and it is not the sum of the effects of them. From Table 1, we can see that the metal cations Cr^{3+} ,

Table 1

Results of the hydrogenation of *m*-CNB over PVP-Pt colloidal clusters^a

Entry	Catalyst	Va (mol H ₂ / mol Pt s)	Selectivity (%) ^b		
			<i>m</i> -CAN	AN	NB
1	PVP-Pt	0.69	82.2	5.8	/
2	PVP-Pt-CrCl ₃	0.44	84.5	5.2	/
3	PVP-Pt-MnCl ₂	0.55	66.9	3.4	/
4	PVP-Pt-FeCl ₃	0.39	93.0	/	/
5	PVP-Pt-CoCl ₂	0.48	87.5	/	/
6	PVP-Pt-NiCl ₂	0.63	85.4	/	/
7	PVP-Pt-bpy	0.12	72.1	/	/
8	PVP-Pt-Co(bpy) ₃ ²⁺	0.11	60.4	/	/
9	PVP-Pt-Ni(bpy) ₃ ²⁺	0.13	66.1	/	/
10	PVP-Pt-H(AcAc)	0.54	71.9	2.3	/
11	PVP-Pt-Cr(AcAc) ₃	0.33	67.4	/	/
12	PVP-Pt-Mn(AcAc) ₂	0.51	60.9	1.9	/
13	PVP-Pt-Fe(AcAc) ₃	0.41	82.0	/	/
14	PVP-Pt-Co(AcAc) ₃	0.88	95.5	/	/
15	PVP-Pt-Ni(AcAc) ₂	0.42	83.9	/	/
16	PVP-Pt-en	0.052	62.8	/	/
17	PVP-Pt-Cr(en) ₃ ³⁺	0.042	68.9	/	/
18	PVP-Pt-Mn(en) ₂ ²⁺	0.058	37.6	/	/
19	PVP-Pt-Co(en) ₂ ²⁺	0.22	92.3	/	/
20	PVP-Pt-Ni(en) ₂ ²⁺	0.18	> 99.9	/	/
21	PVP-Pt-(8-HQ)	0.46	78.3	4.4	/
22	PVP-Pt-Mn-(8-HQ) ⁺	0.32	74.4	3.0	/
23	PVP-Pt-Fe-(8-HQ) ²⁺	0.17	80.0	/	/
24	PVP-Pt-Co-(8-HQ) ⁺	0.25	65.6	/	/
25	PVP-Pt-Ni-(8-HQ) ⁺	0.40	81.7	/	/
26	PVP-Pt-Fe-(8-HQ) ₂ ⁺	0.16	58.0	/	/
27	PVP-Pt-Fe-(8-HQ) ₃	0.16	46.3	/	/

^aReaction conditions: PVP-Pt: 3.0×10^{-4} mol Pt/l; Pt: ML_x^{n+} = 1 (in molar ratio); *n*-C₁₀H₂₁OH: internal standard; *m*-CNB: 0.067 mol/l; solvent: CH₃OH 15.0 ml; reaction temperature: 303 K; *P*_{H₂}: 0.1 MPa. Conversions above are all 100%.

^bSelectivity measured by GC; some products with high boiling point could not be determined by GC analysis; AN: aniline; NB: nitrobenzene.

Table 2

Results of the hydrogenation of *p*-CNB over PVP-Pt colloidal clusters^a

Entry	Catalyst	Va (mol H ₂ / mol Pt s)	Selectivity (%)		
			<i>p</i> -Can	AN	NB
1	PVP-Pt	1.11	68.8	5.6	/
2	PVP-Pt-CrCl ₃	0.80	54.8	4.4	/
3	PVP-Pt-MnCl ₂	0.55	70.6	4.8	/
4	PVP-Pt-FeCl ₃	0.68	65.6	/	/
5	PVP-Pt-CoCl ₂	0.31	73.6	/	/
6	PVP-Pt-NiCl ₂	0.46	78.1	/	/
7	PVP-Pt-bpy	0.15	59.8	2.6	/
8	PVP-Pt-Co(bpy) ₃ ²⁺	0.17	50.8	1.7	/
9	PVP-Pt-Ni(bpy) ₃ ²⁺	0.27	30.4	0.9	/
10	PVP-Pt-H(AcAc)	1.03	59.7	2.8	/
11	PVP-Pt-Cr(AcAc) ₃	0.60	42.8	0.9	/
12	PVP-Pt-Mn(AcAc) ₂	0.51	38.9	1.6	/
13	PVP-Pt-Fe(AcAc) ₃	0.27	74.1	/	/
14	PVP-Pt-Co(AcAc) ₃	0.95	67.3	0.6	/
15	PVP-Pt-Ni(AcAc) ₂	0.28	64.7	/	/
16	PVP-Pt-en	0.072	71.4	/	/
17	PVP-Pt-Cr(en) ₃ ³⁺	0.074	17.7	/	/
18	PVP-Pt-Mn(en) ₂ ²⁺	0.076	35.6	/	/
19	PVP-Pt-Co(en) ₂ ²⁺	0.13	67.4	1.9	/
20	PVP-Pt-Ni(en) ₂ ²⁺	0.17	74.8	0.8	4.5
21	PVP-Pt-(8-HQ)	0.45	78.0	7.8	/
22	PVP-Pt-Mn-(8-HQ) ⁺	0.30	67.8	6.4	/
23	PVP-Pt-Fe-(8-HQ) ²⁺	0.56	> 99.9	/	/
24	PVP-Pt-Co-(8-HQ) ⁺	0.70	86.6	5.3	1.8
25	PVP-Pt-Ni-(8-HQ) ⁺	0.68	79.8	0.5	/
26	PVP-Pt-Fe(8-HQ) ₂ ⁺	0.38	59.7	/	/
27	PVP-Pt-Fe(8-HQ) ₃	0.38	54.7	/	/

^aReaction conditions of the hydrogenation of *p*-CNB are similar to those of *m*-CNB. Conversions above are all 100%.

Fe^{2+} , Co^{2+} and Ni^{2+} show favorable effect on the selectivity of *m*-CNB to *m*-CAN, while the Mn^{2+} ion has a bad effect on the selectivity. Metal bipyridine complexes have inferior influences on the hydrogenation of *m*-CNB in both activity and selectivity. The acetylacetonate complexes with the different metal central ions have different effects. It should be pointed out that the introduction of $\text{Co}(\text{AcAc})_3^-$ can improve both the activity and the selectivity greatly (the average rate of reaction is improved from 0.69 to 0.88 mol H₂/mol Pt s, and the selectivity to *m*-CAN is from 82.2% to 95.5%, respectively). The hydrogenation rate of *m*-CNB decreased obviously with the introduction of the

metal ethylenediamine complexes. However, when Co(en)Cl_2 , $\text{Ni(en)}_3\text{Cl}_2$ are added to the hydrogenation system, the high selectivity to *m*-CAN was observed with 92.3% and > 99.9%, respectively. In addition, the metal 8-hydroxyquinoline (abbreviated as 8-HQ) complexes have inferior influences on the selectivity of the hydrogenation. In Table 2, the influence of metal complexes on the hydrogenation of *p*-CNB with PVP-Pt colloidal catalyst was also listed. The metal bipyridine complexes caused decrease both in the activity and the selectivity of the hydrogenation of *p*-CNB. The metal acetylacetonate complexes and the metal ethylenediamine complexes with various metal central ions show their different effect on the system of PVP-Pt-catalyzed *p*-CNB selective hydrogenation. Many metal 8-HQ complexes exert favorable effect on the selectivity considerably. With Fe(8-HQ)^{2+} introduced, the selectivity to *p*-CAN rise to > 99.9%. Therefore, by optimizing the metal complex as the modifier, the selective hydrogenation of CNB over PVP-Pt catalyst can achieve high selectivity to CAN.

Fig. 1 and Fig. 2 show the comparison of metal complex effects on the hydrogenation of *o*-CNB, *m*-CNB and *p*-CNB over PVP-Pt col-

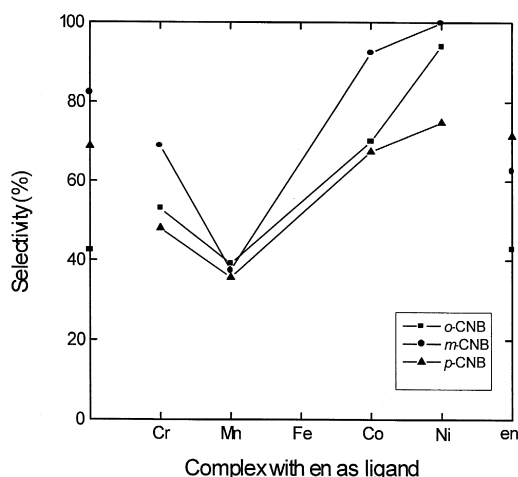


Fig. 1. The metal ethylenediamine complex effect on the selectivity hydrogenation of *o*-, *m*- and *p*-CNB (the metal complexes are $\text{Cr(en)}_3\text{Cl}_3$, Mn(en)Cl_2 , Co(en)Cl_2 and $\text{Ni(en)}_3\text{Cl}_2$ successively).

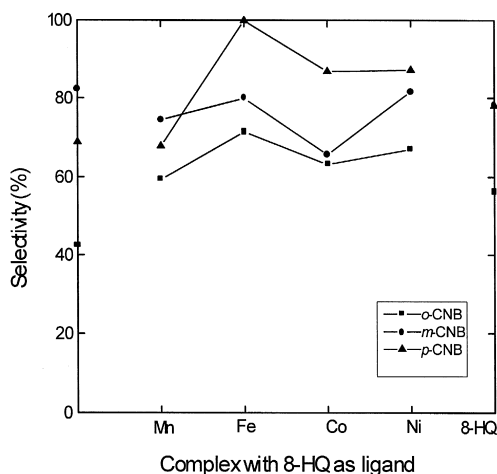


Fig. 2. The metal 8-HQ complex effect on the selectivity hydrogenation of *o*-, *m*- and *p*-CNB (the metal complexes are Mn(8-HQ)Cl , Fe(8-HQ)Cl_2 , Co(8-HQ)Cl and Ni(8-HQ)Cl successively).

loidal catalyst. Among the metal ethylenediamine complexes, $\text{Ni(en)}_3\text{Cl}_2$ has the most favorable effect on the selectivity of *o*-, *m*-, *p*-CNB to their corresponding CAN products, while Mn(en)Cl_2 has the most inferior effect. Moreover, Fe(8-HQ)^{2+} has more positive effect on the selectivity than other metal 8-HQ complexes. Thus, with the increase of atomic number of metal central ions, selectivities for the hydrogenation of *o*-, *m*- or *p*-CNB is in the profiles with similar tendency. The only discrepancy is that the extent of modification of the same metal complexes is different on these three kinds of CNB with the different substituent sites.

8-HQ is a typical chelating ligand. As far as the iron(III) 8-HQ complexes, three kinds of complexes exist: Fe(8-HQ)^{2+} , Fe(8-HQ)_2^+ and Fe(8-HQ)_3 . Seen from Fig. 3, they showed the distinct influence on the catalytic hydrogenation, obviously, Fe(8-HQ)^{2+} exerted the best favorable influence on the selectivity to CAN than Fe(8-HQ)_2^+ and Fe(8-HQ)_3 did. The activity and the selectivity declined with the increase in molar ratio of 8-HQ: Fe^{3+} in the range of 1–3. The best yield (> 99.9%) was achieved in the hydrogenation of *p*-CNB to *p*-CAN.

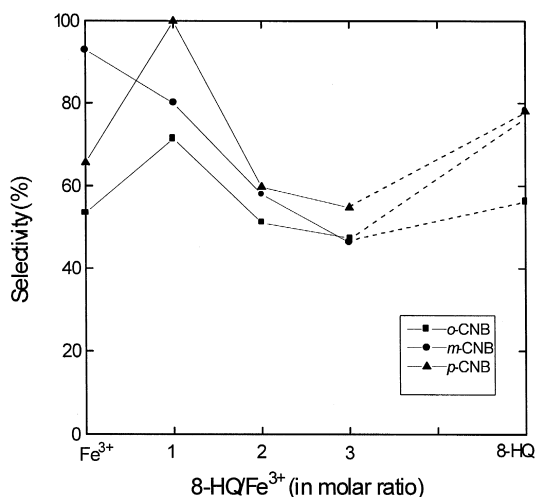


Fig. 3. Hydrogenation of *p*-CNB over PVP-Pt colloidal catalysts with iron(III) 8-HQ complex at different molar ratio of 8-HQ: Fe³⁺ as modifier.

In conclusion, metal complexes exert particular effect on the selective hydrogenation of CNB, which is different from the effect of either metal central ions or ligands. The behavior of metal complexes is closely related to the number of the ligands coordinated to the metal central ions. The same metal complex has different modification on the hydrogenation of CNB with different chloro position relative to the nitro group.

The special effect of metal complex and its universal significance over PVP-Pt catalytic reaction system [17,18] promoted us to study the real mechanism of the metal complex effect. Metal complex is composed of the metal central ion and the ligand which are a pair of electron donor–acceptor. We suspect that the complex effect is related to the interaction of metal complex with reaction substrate, reaction product or the metallic catalyst. Owing to the equilibrium of step dissociation of metal complexes, there is a mixture of multistep complexes at an integer molar ratio of ligand to metal. This causes the mechanism of metal complexes effect very complicated. 8-HQ is a chelating ligand, iron(III) 8-HQ complexes have large coordination stabil-

ity constants (K) with $10^{13.69}$ for K_1 , $10^{12.61}$ for K_2 and $10^{10.6}$ for K_3 . So, they can exist in solvent stably and the step dissociation of them is negligible. Thus, we examined the UV spectra of the mixture of *p*-CNB or *p*-CAN and iron(III) 8-HQ complex in ethanol solution, the preliminary results showed the interaction of iron(III) 8-HQ complexes with *p*-CNB and *p*-CAN. This interaction can influence the conjugated system of CNB or CAN and the interaction of metal complex with PVP-Pt catalyst may change the electron density of surface Pt atoms, which then modifies the catalytic activity of Pt colloidal catalyst and the selectivity of CNB to CAN. The further investigation is now proceeding.

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