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Modification of Metal Complex on the Hydrogenation of Chlorobenzene Over Polymer-Stabilized Platinum Colloidal Nanocatalyst

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The metal complex effect on the hydrogenation of chlorobenzene over a poly(N-vinyl-2-pyrrolidone)-stabilized platinum colloidal nanocatalyst (PVP-Pt) has been studied under 298 K and atmospheric pressure. The introduction of metal complexes and ligands exhibited great effect on the activity and the selectivity of the nanocatalyst. It is evidently manifested that the modification of metal complexes is not the simple sum of those of the metal central ions and the corresponding ligands.

Keywords: modification, metal complex, platinum, selective hydrogenation, chlorobenzene

Introduction

In the field of catalysis, polymer-stabilized metal colloids have shown their particular catalytic performance due to their unique chemical and physical properties as compared to either bulk metal or single metal atoms,^[1–3] and the special catalytic environment modulated by polymer stabilizers.^[4,5] It is well known that additives can markedly affect the properties of metal catalysts. The effect of metal ions has been well studied in the field of heterogeneous^[6–8] and homogeneous catalytic systems.^[9–13] Yu and Liu^[9] reviewed their group efforts on the singular modification effects of metal cations and metal complex ions on the selective catalytic hydrogenation reactions over noble metal colloidal nanocatalysts in liquid medium. They declared that metal cations exhibited more complicate effects in many selective catalytic hydrogenation reactions. Moreover, the metal complexes displayed considerable modification effects on the catalytic properties of metal colloid nanocatalysts. In recent years, Liu and colleagues^[9–16] prepared a series of polymer-stabilized platinum, palladium, and ruthenium monometallic and bimetallic colloidal nanoparticles, and studied the effect of metal complexes on metal colloids in the selective hydrogenation of various reactants.

The addition of metal complexes to the catalytic system can considerably modulate both the activity and the selectivity of the catalyst of PVP-Pt in the hydrogenation of cinnamaldehyde^[14] or halonitrobenzene.^[15,16] Feng and Liu^[14] reported that the modification of some metal complexes to the platinum nanocatalysts led to the increase in both activity and selectivity for hydrogenation of cinnamaldehyde (CAL) to cinnamyl alcohol (COL). When employing Na₃FeF₆ as the modifier, the conversion was promoted from 65.5% to 78.0% and higher selectivity (75.0%) to COL was obtained. While the neat platinum nanoparticles served as the catalyst, only moderate conversion of CAL and low selectivity (17.7%) to COL were obtained. Otherwise by introducing Ni(bpy)₃Cl₂ to the catalytic system, the modification changed the main product to hydrocinnamaldehyde (HCAL) with a selectivity of 97.3%. Yang et al.^[15] reported the effect of metal complex on hydrogenation of *o*-chloronitrobenzene (CNB) over polyvinylpyrrolidone-stabilized platinum nanocatalysts (PVP-Pt). The addition of metal complexes Ni(AcAc)₂ and Na[Co(AcAc)₃] showed favorable effect on the selectivity to *o*-chloroaniline (*o*-CAN; 76.2% and 76.5%, respectively) and the activity (0.72 and 0.83 mol H₂/(mol Pt s), respectively). On the other hand, the highest selectivity to *o*-CAN (94.0%) was achieved in the complex Ni(en)₃Cl₂ modified PVP-Pt catalyst system, though the activity was lowered to 0.16 mol H₂/(mol Pt s). They also found that Cu(en)₂Cl₂, Zn(en)₂Cl₂, and Na₃[Fe(SCN)₆] acted as poisons and caused the PVP-Pt catalyst to lose all the activity. It should be pointed out that the metal complex modification effect varies greatly with the nanocatalysts and the substances to be hydrogenated. Tu et al.^[16] disclosed that the same metal complex exhibited

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different modification effects on the hydrogenation of CNB with different chloro position relative to the nitro group. For example, Ni(en)₃Cl₂ had the most favorable effect on the selectivity of *o*-, *m*-, *p*-CNB to their corresponding CAN products, while Mn(en)Cl₂ had the most inferior effect among the metal ethylenediamine complexes. In the PVP-stabilized ruthenium colloid (PVP-Ru) catalyst system,^[17] the addition of Zn(II)-diamine complexes led to a significant increase in the activity, while the selectivity for *o*-CAN maintained at ~100%. Especially, a rate enhancement more than 30 times over neat PVP-Ru was achieved in the presence of Zn(trien)Cl₂. It was verified that the incorporation of Zn(II) complexes of multi-amines changed the reaction kinetics. It is generally believed that the interaction between the metal complexes and metal nanoparticles may alter the electronic density of metal nanoparticle's active sites, which in turn affects its catalytic performances. In conclusion, the mechanism of metal complex effect is much more complicated than metal cation effect.

Chlorinated organic compounds are important organic intermediates and solvents in chemical industry, agricultural chemistry, and medical chemistry.^[18] Compared with aliphatics, chlorinated aromatic compounds in which the C-Cl bond has a much higher bond strength are generally more resistant to dechlorination.^[19] In order to modulate the catalytic hydrodechlorination (HDC) to achieve high yields of the desired products (cyclohexane), many approaches have been explored by the preparation of bimetallic or supported catalysts and the use of specific additives (promoters and inhibitors). Liu et al.^[20] studied the catalytic HDC of chlorobenzene over Pd nanoparticles supported on carbon nanofibers and found promising HDC performance. Zhu et al.^[21] studied HDC of chlorobenzene with 1–3 chlorine atoms on nanoscale Pd/Fe catalysts at room temperature; chlorinated benzenes could be completely reduced to benzene. Catalytic hydrodechlorination of chlorobenzene over supported palladium catalyst in buffered medium was studied, and it was found that aqueous buffer solutions preserved the catalyst morphology and the catalytic activity for up to four successive HDC reactions.^[22]

Liu et al.^[23] recently reported that nearly 100% selectivity to cyclohexane could be obtained in the HDC of chlorobenzene over a PVP-Pt colloidal nanocatalyst; however, the activity was not satisfied. The effect of metal ions on the hydrogenation of chlorobenzene over PVP-Pt colloidal catalysts was studied, and it showed that some metal cations significantly affected the catalytic performances of the colloidal nanocatalysts.^[13] High activity and high selectivity are expected to be obtained by introducing the metal complexes as modifiers on the selective hydrogenation of chlorobenzene over PVP-Pt colloidal catalysts. As far as we know, the effect of metal complexes on metal colloids in the catalytic HDC of chlorobenzene reaction has rarely been studied. To better understand the complex effect and its relation with reaction substrates, we made further investigations. Here we describe the results on the hydrogenation of chlorobenzene over PVP-Pt colloidal nanocatalysts modified by metal complexes and ligands; the

metal complex effect on the activity and the selectivity of the catalyst is investigated.

Experimental

Poly(N-vinyl-2-pyrrolidone) (PVP, average molecular weight 10,000) was purchased from Shanghai Chemicals Co., Ltd., China. Hexachloroplatinic acid (H₂PtCl₆·6H₂O) of analytical grade was supplied by Beijing Chemicals Co., Ltd. Hydrogen (H₂) with a purity of 99.999% was supplied by an extra-pure hydrogen generator HA-300. Chlorobenzene was distilled before use. Other reagents of analytical grade were supplied by Qingdao Chemicals Co. and were used directly.

The PVP-Pt was synthesized as reported in a previous paper.^[23] Hexachloroplatinic acid (H₂PtCl₆·6H₂O, 0.052 g, 1.00 × 10⁻⁴ mol) was dissolved in a mixed solution of 30 mL methanol and 30 mL water, PVP (0.222 g, 2.00 × 10⁻³ mol as monomeric unit) was then added to the solution as a stabilizer. The vigorous stirring was maintained all the time during the synthesis. The reaction mixture was refluxed for 3 h and led to a homogeneous dark-brown solution of colloidal platinum nanoparticles. The colloid was evaporated to dryness with a rotated evaporator under reduced pressure below 60°C. The resulting solid residues were redispersed in methanol with a definite concentration as the catalyst. The particles in PVP-Pt sol were mostly distributed in the range of 2.3–5.6 nm with an average diameter of 3.63 nm.^[23]

Metal complexes were formed *in situ* by mixing a metal salt with a corresponding ligand at a proper molar ratio according to the reported method.^[14–16] For example, Ni(en)(NO₃)₂ was prepared by mixing Ni(NO₃)₂·6H₂O (32.6 mg, 0.112 mmol) with ethylenediamine (6.75 mg, 0.112 mmol) in methanol. For the sake of simplicity, only metal complexes with stepwise stability constant^[24,25] *k*₁ higher than *ca.* 10⁵ were selected for test.

Hydrogenation of chlorobenzene was carried out at 298 K under 0.1 MPa of hydrogen.^[23] The reaction solution typically contained 1.00 mmol chlorobenzene, 10.0 mL PVP-Pt colloidal dispersion (containing 2.50 × 10⁻⁵ mol Pt), and 0.078 g 1-octane (as an internal standard for GC analysis). The total reaction solution volume was 30.0 mL with methanol as a solvent. The reaction solution was placed in a three-neck flask equipped with a magnetic stirrer and the temperature was maintained by a thermostatic water bath. After H₂ was charged several times to replace the air in the flask, the mixture was stirred vigorously and the HDC reaction started. The hydrogenation reaction rate was calculated by the uptake rate of hydrogen. Chemical analysis of the products was analyzed by GC with an AC-10 column. Reactants and products were identified by comparison with authentic samples.

Results and Discussion

The hydrogenation of chlorobenzene was studied in methanol at 298 K under 0.1 MPa of hydrogen over PVP-Pt colloidal catalyst. The hydrogenation products determined by GC-MS analysis were benzene and cyclohexane. Benzene was the

intermediate product. Thereby, benzene was immediately found in the beginning of the reaction, and started to convert to cyclohexane at the same time. No other by-products were detected by GC-MS. Table 1 summarizes the experimental results of the influence of metal complexes, metal ions, and ligands on the hydrogenation of chlorobenzene over PVP-Pt colloidal catalyst. It can be seen from Table 1 that the complexes composed of the same central metal ion with different ligands (entries 14 and 19; 16 and 25; 21 and 23) and the different central metal ions with the same ligand (entries 14–17; 19–21; 23–25) exert distinct influences on the catalytic properties. It is evidently manifested 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 both.

From Table 1 it can be seen that an activity of 9.30 mol H₂/(mol Pt h) was achieved when employing neat PVP-Pt colloids as a catalyst. It also can be observed that the modification effect of various metal cations on the PVP-Pt catalytic system. The addition of metal cations Cr³⁺ (entry 2) and Ni²⁺ (entry 6) caused subtle loss in activity, while Cr³⁺ had an inhibiting effect on the selectivity to cyclohexane. Metal cation Co²⁺ (entry 5) had inferior influence on the hydrogenation of chlorobenzene in both the activity and the

selectivity. Cation Fe³⁺ (entry 4) hindered the rate of hydrogenation. Moreover, Mn²⁺ (entry 3) and Zn²⁺ (entry 7) acted as poisons to lose all the activity of PVP-Pt colloidal nanocatalysts.

It is well known that ligands as additives can markedly affect the properties of metal catalysts. In some reactions, some ligands as modifiers accelerated the reaction rate by 1–2 orders of magnitude, which was called “ligand-acceleration phenomenon” by Jacobsen et al.^[26] Yan et al.^[17] found that the introduction of some ligands, especially ethylenediamine (en), obviously promoted the activity of PVP-Ru without any loss in selectivity for *o*-CAN. In the enantioselective hydrogenation of ethyl pyruvate at low concentration of cinchonidine, the addition of achiral tertiary amines (ATA) strongly increased both the rate of the reaction and the enantioselectivity.^[27] They all reported that ligand-acceleration reaction enhanced the reaction rate and changed the selectivity. In order to obtain high catalytic activity and selectivity, some ligands were introduced into the hydrogenation of chlorobenzene reaction. The ligands of bipyridyl (bpy) and diethylenetriamine (den) depressed the selectivity of chlorobenzene to cyclohexane. This indicates that bpy and den can suppress the hydrogenation of benzene but accelerate the

Table 1. The effect of metal complexes on the hydrogenation of chlorobenzene over PVP-Pt nanocatalyst^a

Entry	Catalytic system	Average rate (mol H ₂ /[mol Pt h])	Conversion of chlorobenzene (%)	Selectivity (%)	
				Cyclohexane	Benzene
1	PVP-Pt	9.30	77.5	66.0	34.0
2	PVP-Pt-Cr ³⁺	8.40	70.0	38.1	62.0
3	PVP-Pt-Mn ²⁺	0	0	—	—
4	PVP-Pt-Fe ³⁺	3.51	29.2	58.2	41.8
5	PVP-Pt-Co ²⁺	4.60	38.4	33.4	66.6
6	PVP-Pt-Ni ²⁺	8.64	72.0	56.4	43.6
7	PVP-Pt-Zn ²⁺	0	0	0	0
8	PVP-Pt-bpy	10.13	84.4	55.3	44.7
9	PVP-Pt-den	10.57	88.1	54.2	45.8
10	PVP-Pt-trine	8.49	70.7	46.1	62.9
11	PVP-Pt-tetren	7.54	62.8	33.2	66.8
12	PVP-Pt-Py	10.30	85.9	62.5	37.5
13	PVP-Pt-en	9.96	83.0	64.8	35.2
14	PVP-Pt-Cr(en) ₃ (NO ₃) ₃	7.17	59.7	40.4	59.6
15	PVP-Pt-Co(en)(NO ₃) ₂	6.03	50.2	41.6	58.4
16	PVP-Pt-Ni(en)(NO ₃) ₂	5.54	46.2	34.7	65.3
17	PVP-Pt-Zn(en) ₂ (NO ₃) ₂	0	0	—	—
18	PVP-Pt-Hacac	10.90	90.9	68.4	31.6
19	PVP-Pt-Cr(acac) ₃ (NO ₃) ₃	9.18	76.5	56.0	44.0
20	PVP-Pt-Mn(acac) ₂ Cl ₂	0.32	2.6	100.0	0.0
21	PVP-Pt-Fe(acac) ₃ (NO ₃) ₃	3.48	29.0	30.8	69.2
22	PVP-Pt-8-HQ	6.35	52.9	34.6	65.4
23	PVP-Pt-Fe(8-HQ)(NO ₃) ₃	2.83	23.6	14.2	85.8
24	PVP-Pt-Co(8-HQ)(NO ₃) ₂	6.63	55.2	32.3	67.7
25	PV-Pt-Ni(8-HQ)(NO ₃) ₂	8.40	70.0	77.5	22.5

en = ethylenediamine; 8-HQ = 8-hydroxylquinoline; acac = acetylacetonate; bpy = bipyridyl; den = diethylenetriamine; trine = triethylenetetramine; tetren = tetraethylenepentamine; Py = pyrrole.

^aReaction conditions: P_{H₂} = 0.1 MPa, T = 298 K, V = 30 mL, chlorobenzene: 1 mmol, Pt: 2.5 × 10⁻⁵ mol, the molar ratio of the modifier to Pt was 1:1, reaction time: 10 h.

hydrogenation of chlorobenzene at the same time (the average rate of reaction were observed up to 10.13 and 10.57 mol H₂/[mol Pt h], respectively). Acetylacetonate (acac) favorably raised both the activity and the selectivity greatly (the average reaction rate was improved from 9.30 to 10.90 mol H₂/(mol Pt h), and the selectivity to cyclohexane was increased from 66.0% to 68.4%, respectively). It also can be seen that the ligand of 8-hydroxyquinoline (8-HQ) exerted inferior influences on the hydrogenation in both activity and selectivity, while the pyrrole (Py) resulted in an increase in the hydrogenation rate with a decrease of the selectivity to cyclohexane. Further study on the hydrogenation of chlorobenzene over PVP-Pt modified by ethylenediamine (en) and multiamine ligands showed that the amines ligands had different modification effects compared with the neat PVP-Pt which indicated evidently in Figure 1.

Obviously different results were obtained by the multi-amine ligands (en, den, trine, tetren) with the increase of the number of -NH₂ from 2 to 5. The conversions of chlorobenzene over PVP-Pt-en and PVP-Pt-den catalytic systems were much higher than that of PVP-Pt. When the number of -NH₂ increased to 3, the conversions were evidently decreased and lower than that of PVP-Pt at 5 h reaction time, which indicated that the activity of PVP-Pt catalysts modified by multi-amine ligands were different with the number of -NH₂. After 5 h, the conversion of chlorobenzene over PVP-Pt-en system (containing 2 -NH₂) was 76.1%, which was the highest conversion, while the conversion of chlorobenzene over PVP-Pt-tetren system (containing 5 -NH₂) was 51.4%. From the previous results, it is unquestionable that the conversion of chlorobenzene decreased obviously with the increase of the number of -NH₂. Owing to the interaction of Pt with multi-amine ligands, the electronic density of the platinum active site is closely related to the number of -NH₂, which in turn affects the catalytic performance. It was reported that there were different situations about this phenomenon in different reaction system. However, in Yan et al.'s^[17] paper, multi-amine ligands considerably elevated the activity of PVP-Ru

in different degrees while remaining high selectivity for *o*-CAN. The activity of PVP-Ru boosted excellently with the increase of the number of -NH₂. In the presence of trine, the activity increased by about nineteen times than that of unmodified PVP-Ru and got up to 2.4×10^{-3} mol H₂/(mol Ru s); furthermore, the conversion of *o*-CNB was increased from 21.6% to 100%.

From the previous discussion, it is obvious that the hydrogenation catalyst PVP-Pt modified by different ligands have different effects on the catalytic activity and selectivity to cyclohexane. Most of ligands considerably elevated the activity of PVP-Pt (e.g., en, acac, bpy, den, Py) and some ligands increased the selectivity (en, acac, Py). It should be pointed out that the acetylacetonate and pyrrole displayed a more favorable effect comparing with the neat Pt catalyst on both activity and the selectivity to cyclohexane.

Metal complexes were formed by mixing a metal salt (usually the nitrate salt) with a corresponding ligand at a proper molar ratio. The modification effects of metal ethylenediamine, acetylacetonate and 8-HQ complexes on the hydrogenation of chlorobenzene over PVP-Pt colloidal catalyst are also listed in Table 1. It can be seen that PVP-Pt-en (entry 13) can improve the activity with slight loss in the yield of cyclohexane. However, the metal ethylenediamine complexes deactivated the PVP-Pt catalyst and resulted in a decrease in both activity and selectivity. Figure 2 shows the effect of metal ethylenediamine complexes on the selective hydrogenation of chlorobenzene over PVP-Pt catalyst. All the metal ethylenediamine complexes hindered the hydrogenation in both activity and selectivity compared with the neat PVP-Pt and PVP-Pt-en catalyst systems. Moreover, the activity and the selectivity declined with the increase of atomic number of metal central ions in the range of 24–30. Cr(en)₃(NO₃)₃ had higher activity than other metal ethylenediamine complexes (Figure 2); however it had some inhibiting effect on the reaction (the activity was only 7.17 mol H₂/[mol Pt h]). It can be seen from Table 1 that metal cation Co²⁺ showed bad effect on the activity of PVP-Pt comparing with the addition of

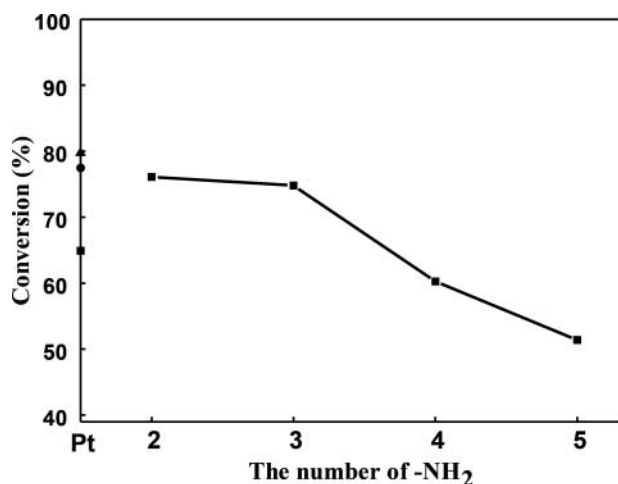


Fig 1. Hydrogenation of chlorobenzene over multi-amine ligands modified PVP-Pt nanocatalyst at 5 h reaction time.

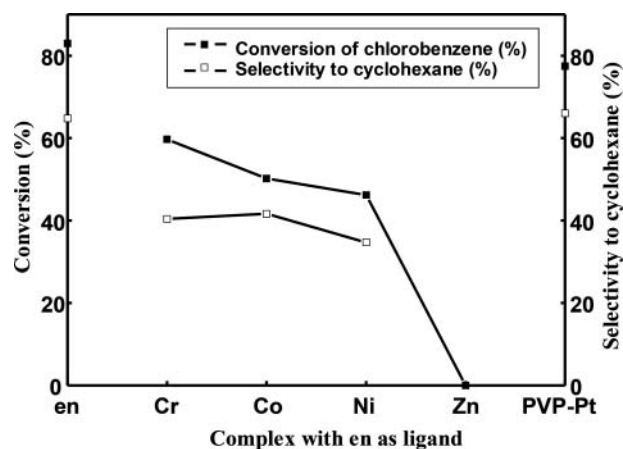


Fig 2. The metal ethylenediamine complex effect on the selective hydrogenation of chlorobenzene over PVP-Pt colloidal nanocatalyst—the metal complexes were Cr(en)₃(NO₃)₃, Co(en)(NO₃)₂, Ni(en)(NO₃)₂, and Zn(en)₂(NO₃)₂ successively. ■ = conversion of chlorobenzene, □ = selectivity to cyclohexane.

Ni^{2+} , while $\text{Co}(\text{en})(\text{NO}_3)_2$ improved both the activity and the selectivity compared to the nickel ethylenediamine complex (the average rate of reaction was improved from 5.54 to 6.03 mol H_2 /[mol Pt h], and the selectivity to cyclohexane was increased from 34.7% to 41.6%, respectively). The data mentioned above showed that metal complexes exerted particular effect on the selective hydrogenation of chlorobenzene, which is different from the effect of either metal central ions or ligands. Because Zn^{2+} caused PVP-Pt to lose all the activity, the addition of $\text{Zn}(\text{en})_2(\text{NO}_3)_2$ poisoned the catalyst seriously and hindered the hydrogenation of chlorobenzene. There were different results about zinc complexes in different reaction systems.^[15,17] In Yang et al.'s^[15] paper, $\text{Zn}(\text{en})_2\text{Cl}_2$ performed as a poison in the hydrogenation of *o*-CNB in PVP-Pt and caused the whole activity to lose. Yan^[17] reported that the incorporation of Zn (II) cation with multi-amines enhanced the activity of PVP-Ru and performed superior to ligands alone, despite Zn^{2+} causing a decrease in the activity of PVP-Ru colloidal catalyst in the hydrogenation of *o*-CNB. Particularly in the case of $\text{Zn}(\text{trien})_2\text{Cl}_2$, the activity of the as-modified PVP-Ru increased by 30 times more than that of the unmodified PVP-Ru. Our results concerning the activity of PVP-Pt modified by zinc complexes in the hydrogenation of chlorobenzene were consistent with those results reported by Yang et al.^[15] In different catalytic systems, the same metal complex had different modification on the catalytic hydrogenation reaction.

With respect to the equilibrium of step dissociation of metal complexes, there was no unitary of species but a mixture of multistep complexes coexisted in the reaction system. Take PVP-Pt- $[\text{Cr}(\text{en})_3]^{3+}$ as an example, where $[\text{Cr}(\text{en})]^{3+}$, $[\text{Cr}(\text{en})_2]^{3+}$, and $[\text{Cr}(\text{en})_3]^{3+}$ coexisted in the reaction medium in different concentrations. The mixture made the complexes effect on the catalytic activity and selectivity very complicated. In conclusion, 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 each.

In the study of ligands as modifiers, PVP-Pt-Hacac (entry 18) had the best effect on both the activity and the selectivity (the average rate of reaction was improved from 9.30 to 10.90 mol H_2 /[mol Pt h], and the selectivity to cyclohexane was increased from 66.0% to 68.4%, respectively). Metal acetylacetonate complexes had inferior influences on the hydrogenation of chlorobenzene in both activity and selectivity except that $\text{Cr}(\text{acac})_3(\text{NO}_3)_3$ performed as a spectator (Figure 3). $\text{Fe}(\text{acac})_3(\text{NO}_3)_3$ hindered the hydrogenation rate and caused the activity and selectivity decrease evidently, while $\text{Mn}(\text{acac})_2\text{Cl}_2$ (entry 20) performed as a poison (the activity fell into 0.32 mol H_2 /[mol Pt h], while the selectivity increased up to 100%). The metal cations Cr^{3+} , Mn^{2+} , and Fe^{3+} (entries 2–4) exerted inferior influences on the hydrogenation (the average rate was 8.40, 0.00, and 3.51 mol H_2 /[mol Pt h], respectively). However, upon the addition of the acac ligand, the metal complexes weakened the inferior influences of these metal cations. Yang et al.^[15] also found that the metal acetylacetonate complexes showed a more favorable effect in comparison with the metal cations. When the complex $\text{Ni}(\text{acac})_2$ was introduced as a

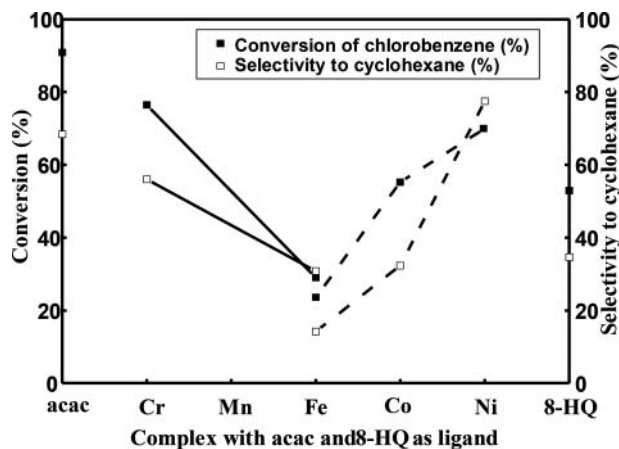


Fig 3. The metal ethylenediamine complex and metal 8-hydroxyquinoline complex effect on the selective hydrogenation of chlorobenzene over PVP-Pt colloidal nanocatalyst—the metal complexes were $\text{Cr}(\text{acac})_3(\text{NO}_3)_3$, $\text{Fe}(\text{acac})_3(\text{NO}_3)_3$, $\text{Fe}(\text{8-HQ})(\text{NO}_3)_3$, $\text{Co}(\text{8-HQ})(\text{NO}_3)_2$, and $\text{Ni}(\text{8-HQ})(\text{NO}_3)_2$, successively. ■ = conversion of chlorobenzene, □ = selectivity to cyclohexane, —acac complex, - - - = 8-HQ complex).

modifier, a better selectivity to *o*-chloroaniline and a higher activity were obtained.

Figure 3 also shows that the effect of metal 8-hydroxyquinoline complexes on the selective hydrogenation of chlorobenzene. The 8-hydroxyquinoline complexes with the different metal central ions had different effects. The hydrogenation rate of chlorobenzene and selectivity decreased obviously with the introduction of $\text{Fe}(\text{8-HQ})(\text{NO}_3)_3$ and $\text{Co}(\text{8-HQ})(\text{NO}_3)_2$. However, with $\text{Co}(\text{8-HQ})(\text{NO}_3)_2$ introduced, the activity was considerably enhanced compared to the PVP-Pt- Co^{2+} system (entry 5) whereas the selectivity was slightly changed. With respect to the PVP-Pt- Ni^{2+} (entry 6) and PVP-Pt systems, the selectivity was greatly promoted to 77.5% and the catalytic performance of the catalyst was modulated slightly when $\text{Ni}(\text{8-HQ})(\text{NO}_3)_2$ was used as a modifier. In Yan et al.'s^[17] paper, $\text{Co}(\text{8-HQ})_2$ performed as a spectator, while 8-HQ ligand enhanced the activity of PVP-Ru without any loss in the selectivity for *o*-CAN. Tu et al.^[16] reported that the metal 8-hydroxyquinoline complexes had inferior influences on the selectivity of the hydrogenation of *m*-CNB and many metal 8-HQ complexes exerted favorable effect on the selectivity of the hydrogenation of *p*-CNB considerably. They found that $\text{Fe}(\text{8-HQ})^{2+}$ exerted the best favorable influence on the selectivity to CAN than $\text{Fe}(\text{8-HQ})_2^+$ and $\text{Fe}(\text{8-HQ})_3$ did. Thus, the behavior of metal complexes was closely related to the number of the ligands coordinated to the metal central ions. They suspected that the complex effect was related to the interaction of metal complex with reaction substrate, reaction product, or the metallic catalyst.

Conclusions

In conclusion, the metal complex effect on the hydrogenation of chlorobenzene over PVP-Pt has been studied under 298 K

and atmospheric pressure. When the neat platinum nanoparticles was served as the catalyst, only 77.5% conversion and moderate selectivity to cyclohexane (65.58%) were obtained. The metal complexes and ligands employed to the catalytic system had great effect on both the activity and the selectivity of the catalyst.

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