Metal complex effect on the hydrogenation of *o*-chloronitrobenzene over polymer-stabilized colloidal ruthenium clusters

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Abstract

Effect of metal complex on hydrogenation of *o*-chloronitrobenzene (*o*-CNB) over poly-vinylpyrrolidone stabilized ruthenium colloid (PVP-Ru) has been studied in methanol media under 320 K and 4.0 MPa. The addition of Zn(II) complexes of diamines to PVP-Ru catalyst system leads to significant increase in the activity of PVP-Ru, while the selectivity for *o*-chloroaniline (*o*-CAN) maintained ~100%. Especially, rate enhancement more than 30 times that over neat PVP-Ru has been achieved in the presence of Zn(trien)Cl$_2$. It was verified that the incorporation of Zn(II) complexes of multi-amines changed the reaction kinetics. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrogenation of halonitroaromatics to the corresponding haloanilines is important in the chemistry of dyes, drugs, herbicides and pesticides. With a variety of catalysts (e.g. Pd, Pt, Ni, Rh), hydrogenation of halonitroaromatics to the corresponding haloanilines is always accompanied by some hydrogenolysis of the carbon–halogen bond. However, it was found that ruthenium was highly selective although its activity was very low [1]. In order to achieve high yields of haloanilines, many approaches have been developed either by dedicated preparation of the catalysts (alloying [2], controlling the metal particle dispersion [3]

and metal-support interaction [4], etc.) or the use of specific additives (promoters, inhibitors) [5–7].

Nanoscopic metal clusters, owing to the unique chemical and physical properties as compared to either bulk metal or single metal atom, have received intense renewed attraction especially in catalysis [8–10]. In recent years, our group have prepared a series of polymer-stabilized monometallic and bimetallic colloidal clusters. Employing poly-vinylpyrrolidone (PVP) stabilized ruthenium colloids prepared by NaBH$_4$ reduction as catalysts, it was found that nearly 100% selectivity to *o*-chloroaniline (*o*-CAN) could be obtained with activity of only 2.8×10^{-4} mol H$_2$/mol Ru s [11]. Compared to that over monometallic ruthenium colloid, an extremely high activity was achieved in the hydrogenation of *o*-CNB over PVP-Ru/Pt or PVP-Ru/Pd bimetallic colloid [12], but resulting in a remarkable loss in selectivity for *o*-CAN. Further-

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more, by adding Co^{2+} to PVP-Ru/Pt catalyst system, an activity of two orders of magnitude higher than that of PVP-Ru colloid with ~100% selectivity to o-CAN was achieved. Similarly, metal ion effect had been reported in many homogenous catalytic systems of metal clusters [11–15]. However, the effect of metal complexes on metal colloids has rarely been studied up to now, though we once reported that the incorporation of metal complexes can considerably modulate both the activity and the selectivity of PVP-Pt in the hydrogenation of cinnamaldehyde [16] or halonitrobenzene [17,18]. In present study, we aim to further clarify the metal complex effect in more extensive metal catalyst system. Because PVP-Ru catalyst system is relatively simple in the selective hydrogenation o-CNB, i.e. the product is exclusively o-CAN, it is convenient for us to investigate the metal complex effect. In present study, we have optimized the performance of PVP-Ru and obtained high yield of o-CAN in the selective hydrogenation of o-CNB by adding metal complexes. Here, we report the preliminary results.

2. Experimental

The PVP stabilized ruthenium colloids, which were designated as PVP-Ru, were prepared by polyol reduction as reported in [19]. The ethylene glycol solution of PVP-Ru colloid was first precipitated with anhydrous acetone, precipitates were washed with acetone and then dried under vacuum, re-dispersed in methanol to form a thoroughly homogeneous dispersion prior to use.

Metal complexes were formed in situ by mixing a metal salt (usually the chloride) with a corresponding ligand at a proper molar ratio according to the reported method [16]. For example, $Zn(en)_2Cl_2$ was prepared by mixing $ZnCl_2$ (15.3 mg, 0.112 mmol) with ethylenediamine (13.5 mg, 0.224 mmol) in methanol. For the sake of simplicity, only metal complexes with stepwise stability constant [20,21] k_1 more than ca. 10^5 were selected for test.

Hydrogenation of o-CNB was carried out in a 100 ml stainless autoclave with a Teflon tube to avoid metal contamination. The reaction solution typically contained 1.0 mmol substrate, 0.125 g n-decanol (as an internal standard for GC analysis), and 8.0 ml ruthe-
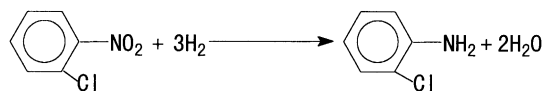
Scheme 1.

nium colloid dispersion (containing 1.87×10^{-5} mol Ru). Total reaction solution volume was 15.0 ml with methanol as a solvent. The reaction vessel was replaced three times with high purity hydrogen gas and finally kept H_2 pressure to 4.0 MPa at 320 K. The reaction mixture was stirred vigorously for a period time. Chemical analysis of the products was performed by gas chromatography equipped with a FID detector and a DC-710 packed column.

3. Results and discussion

The hydrogenation of choloronitrobenzene is a complicated process and many by-products were involved, it follows the reaction pathways described in [2]. Our purpose is to achieve high yield of o-chloroaniline without hydrogenolysis of C–Cl bond. The stoichiometric reaction scheme of o-CNB is shown in Scheme 1.

As described in introduction, we once reported that the PVP-stabilized ruthenium colloids prepared by $NaBH_4$ reduction were highly effective in favor of the selectivity for o-CAN [11]. However, recently it was found in our group that the boron species (borate such as $Na_2B_4O_7$, etc.) soluble in so-prepared Ru colloid dispersion can enhance the activity of the catalysts in hydrogenation of o-CNB [22]. In addition, it was also suggested that the metal complex ions of borate were formed and resulted in significant rate enhancement in this reaction when adding metal cations into the Ru colloid dispersion containing boron species. Taking the effect of boron species into account, in present study PVP-stabilized neat ruthenium colloids ($d = 1.40$ nm, $\delta = 0.48$ nm) prepared by polyol reduction [19] were employed as catalysts, which is free of boron species.

Table 1 lists the experimental results of the hydrogenation of o-CNB over PVP-Ru colloid catalyst in the presence of some metal complexes, metal ions or ligands. When employing neat PVP-Ru colloids as catalyst, an activity of 1.12×10^{-4} mol H_2/mol Ru s

Table 1
Hydrogenation of o-CNB over modified-PVP-Ru catalyst system[a]

Entry	Catalyst system	Reaction rate × 10^4 (mol H_2/mol Ru s)	Selectivity for o-CAN (%)
1	PVP-Ru	1.12	>99.9
2	PVP-Ru-FeCl$_3$	1.01	>99.9
3	PVP-Ru-CoCl$_2$	0.82	>99.9
4	PVP-Ru-ZnCl$_2$	0.86	>99.9
5	PVP-Ru-NiCl$_2$	0.74	>99.9
6	PVP-Ru-2en[b]	10.2	>99.9
7	PVP-Ru-bpy	1.45	>99.9
8	PVP-Ru-Hacac	1.23	>99.9
9	PVP-Ru-8-HQ	1.67	>99.9
10	PVP-Ru-Ni(en)$_2$Cl$_2$	4.15	>99.9
11	PVP-Ru-Co(en)$_2$Cl$_2$	3.27	>99.9
12	PVP-Ru-Zn(en)$_2$Cl$_2$[c]	17.8	>99.9
13	PVP-Ru-Co(bpy)$_3$Cl$_2$	1.82	>99.9
14	PVP-Fe(acac)$_3$	1.81	>99.9
15	PVP-Ru-Co(8-HQ)$_2$	1.2	>99.9

[a] Reaction conditions: $P_{H_2} = 4.0$ MPa, $T = 320$ K, $V = 15$ ml, o-CNB: 1.0 mmol, Ru: 1.87×10^{-2} mmol, the molar ratio of modifier to Ru: 1:1, reaction time: 120 min bpy: bipyridyl, en: ethylenediamine, acac: acetylacetonate, 8-HQ: 8-hydroxylquiline.

[b] Reaction time: 30 min.

[c] Reaction time: 35 min.

was achieved. The addition of several metal cations caused subtle loss in activity. However, the introduction of some ligands especially ethylenediamine (en) obviously enhanced the activity of PVP-Ru without any loss in selectivity for o-CAN, it appeared to be a ligand acceleration reaction. Interestingly, an excellent rate enhancement was achieved upon employing metal complexes as modifiers. In the cases of complexes of en, the activities of so-modified PVP-Ru were all enhanced in varying degree. Particularly for Zn(en)$_2$Cl$_2$, the activity increased by about fifteen times than that of unmodified PVP-Ru and got up to 1.78×10^{-3} mol H_2/mol Ru s. At the same time, Co(bpy)$_3$Cl$_2$, Fe(acac)$_3$ only moderately improved the reaction rate, while the Co(8-HQ)$_2$ performed as a spectator. From above results it was found that different metal complexes performed very distinctly. Furthermore, it is evidently manifest that the modification of metal complexes is not the simple sum of those of the metal central ions and the corresponding ligands.

It was clearly shown in Table 1 that ethylenediamine and its Zn(II) complex exhibited excellent rate enhancement effect in the selective hydrogenation of

Table 2
Effect of Zn(II) complexes of multi-amine ligands on selective hydrogenation of o-CNB over PVP-Ru[a]

Entry	Catalyst system	Average rate × 10^4 (mol H_2/mol Ru s)	Conversion (%)[b]	Selectivity (%) o-CAN	Others[c]
1	PVP-Ru	1.12	21.6 (120)	>99.9	–
2	PVP-Ru-ZnCl$_2$	0.86	16.6 (120)	>99.9	–
4	PVP-Ru-2pn	6.77	65.3 (60)	>99.9	–
5	PVP-Ru-2en	10.2	98 (60)	>99.9	–
6	PVP-Ru-2den	13.5	66.4 (30)	>99.9	–
7	PVP-Ru-2trien	20.4	100 (30)	>99.9	–
8	PVP-Ru-tetren	19.7	97.0 (30)	>99.9	–
9	PVP-Ru-Zn(pn)$_2$Cl$_2$	8.6	83.0 (60)	>99.9	–
10	PVP-Ru-Zn(en)$_2$Cl$_2$	29.5	100 (20)	89.0	11.0
11	PVP-Ru-Zn(en)$_2$Cl$_2$	17.8	100 (35)	>99.9	–
12	PVP-Ru-Zn(en)Cl$_2$	7.47	72.0 (60)	>99.9	–
13[d]	PVP-Ru-Zn(den)$_2$Cl$_2$	34.8	84.0 (30)	83.0	17.0
14	PVP-Ru-Zn(den)Cl$_2$	18.3	100 (35)	97.0	3.0
15[d]	PVP-Ru-Zn(trien)$_2$Cl$_2$	40.8	100 (30)	>99.9	–
16	PVP-Ru-Zn(trien)Cl$_2$	20.2	100 (30)	>99.9	–
17	PVP-Ru-Zn(tetren)Cl$_2$	23.7	81.5 (20)	79.4	20.6

[a] Reaction conditions same as in Table 1; pn: 1,3-propanediamine, en: ethylenediamine, den: diethylenetriamine, trien: triethylenetetramine, tetren: tetraethylenepentamine.

[b] Data in parentheses are the given reaction time in minutes.

[c] Others refer to several by-products except AN and NB.

[d] The amount of Ru used was 9.35×10^{-6} mol.

o-CNB. With respect to this significant results, we applied more multi-amine ligands and their Zn(II) complexes to the reaction. The experimental results were listed in Table 2. To our surprise, all selected complexes considerably elevated the activity of PVP-Ru in a varying degree while remaining high selectivity for o-CAN. Particularly in the case of $Zn(trien)_2Cl_2$ (entry 15), the activity of so-modified PVP-Ru increased by 30 times more than that of the unmodified PVP-Ru. Moreover, it was worthy to notice that the activity of the Zn(II) complexes-modified PVP-Ru was apparently dependent on the stability constant of metal complexes, namely the rate enhancement grew greater with the coordination constants. The first stepwise coordination constants of the Zn(II) complexes of the selected multi-amine ligands were listed as follows: $k_{1\,tetren} = 4 \times 10^{15}$, $k_{1\,trien} = 1 \times 10^{12}$, $k_{1\,den} = 1 \times 10^9$, $k_{1\,en} = 8 \times 10^5$, $k_{1\,pn} = 5.2 \times 10^5$ [23]. These data revealed the strong coordination ability of these multi-amines, namely Zn(II) complexes of multi-amines are easily formed. In order to further avoid the effect of free ligands, the Zn(II) complexes with molar ratio of Zn(II) to ligand of 1:1 was tested. As a result, the obvious rate enhancement were also observed (entry 12, 14, 16, 17). Based on above experimental results, it was suggested that metal complex indeed improved the reaction rate. Despite Zn^{2+} caused a decrease in the activity of PVP-Ru, the incor-

poration of Zn(II) cation with multi-amines obviously enhanced the activity of PVP-Ru and performed superior to ligands alone. Metal complex effect was shown effective in the selective hydrogenation of o-CNB over PVP-Ru colloidal cluster catalysts.

Fig. 1 demonstrated the hydrogenation of o-CNB over PVP-Ru-$Zn(en)_2Cl_2$ catalyst system at different molar ratio of $Zn(en)_2Cl_2$ to Ru. It was found that the addition of a very small amount of $Zn(en)_2Cl_2$ ($Zn(en)_2Cl_2$:Ru = 0.02:1) resulted in an abrupt increase in the activity to 7.51×10^{-4} mol H_2/mol Ru·s and in a wide molar ratio range of $Zn(en)_2Cl_2$ to Ru from 1:10 to 10:1 the activity was equal to or more than 10.4×10^{-4} mol H_2/mol Ru·s. Similar results were also observed in the cases of $Zn(den)_2Cl_2$ and $Zn(trien)_2Cl_2$, etc.

As shown in Table 2, 100% conversion of o-CNB with ∼100% of selectivity for o-CAN can be achieved in the presence of $Zn(en)_2Cl_2$ in a short reaction period (entry 11). Interestingly, when further shortening the reaction time to 20 min there resulted in ∼100% conversion of o-CNB with only 89.0% of selectivity for o-CAN (entry 10). This indicated that the presence of $Zn(en)_2Cl_2$ caused the formation of intermediates in early stage of the reaction which is not aniline or nitrobenzene. In fact, this also occurred in the cases of other complexes such as $Zn(trien)_2Cl_2$, etc. This is the common characteristic behavior of metal com-
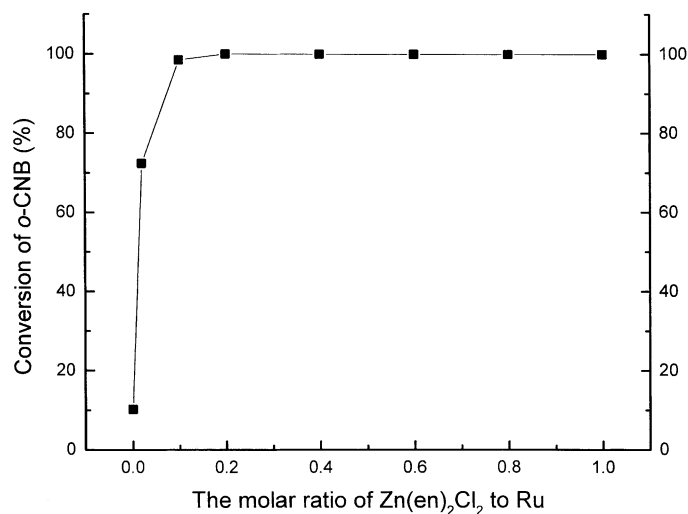

Fig. 1. Hydrogenation of o-CNB over PVP-Ru-$Zn(en)_2Cl_2$ system at different molar ratio of $Zn(en)_2Cl_2$ to Ru. Ru: 9.3×10^{-6} mol, reaction time: 1.0 h.
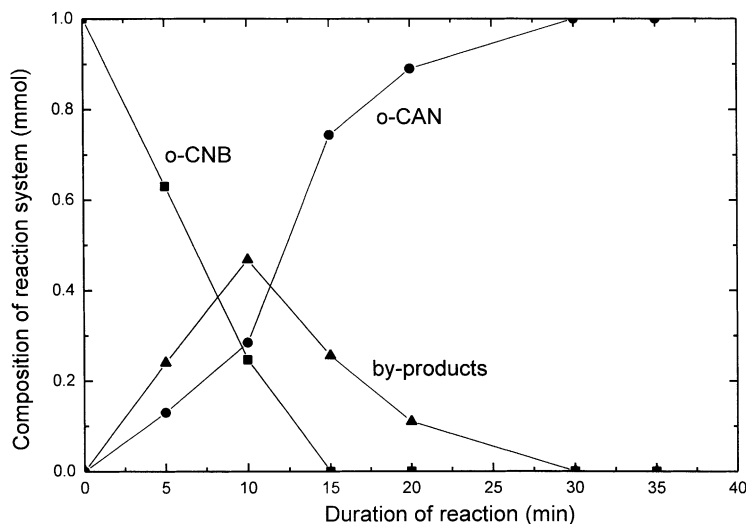
Fig. 2. Hydrogenation of *o*-CNB over PVP-Ru in the presence of Zn(en)$_2$Cl$_2$ as a function vs. reaction time. The molar ratio of Zn(en)$_2$Cl$_2$ to Ru was 1:1.

plexes composed of Zn^{2+} and multi-amines ligands. This can further be revealed in Fig. 2.

Fig. 2 showed the reaction composition variation with the reaction time in the presence of Zn(en)$_2$Cl$_2$. It can be seen that by-products were formed in the early stage and gradually disappeared with the reaction further going until wholly converting to *o*-CAN by the end. This phenomenon did not exist in the same reaction over neat PVP-Ru [11]. Considering the reaction pathways described in [2], it can be deduced that the by-products may be some intermediates, which can be further hydrogenated to form *o*-CAN. GC-MS analyses also revealed that the by-products were composed of intermediates such as 2,2-azodichlorobenzene, azoxydichlorobenzene.

As shown in Scheme 2, it was well known that there are three steps of hydrogenation for this reaction. Comparing the performance of PVP-Ru and Zn(en)$_2$Cl$_2$-modified PVP-Ru, it was supposed that the incorporation of Zn(en)$_2$Cl$_2$ perhaps accelerated the first step of hydrogenation from *o*-CNB to

o-chloronitrosobenzene (*o*-CNSB), while in the case of PVP-Ru the first step of hydrogenation is the rate-determining step, namely $k_1 \ll k_2 k_3$. The real mechanism of the metal complex effect is still obscure. Owing to the equilibrium of step dissociation of metal complexes, there is no unitary of species but a mixture of multi-step complexes. For example, at a molar ratio of bpy: Ni^{2+} = 3, three species of Ni(bpy)Cl$_2$, Ni(bpy)$_2$Cl$_2$, Ni(bpy)$_3$Cl$_2$ coexisted in the reaction medium in different concentration. In addition, the effect of Zn(en)$_2$Cl$_2$ on the hydrogenation of *o*-CNB varied with the catalysts. For example, Zn(en)$_2$Cl$_2$ performed as a poison in PVP-Pt cluster system, namely the addition of Zn(en)$_2$Cl$_2$ caused whole loss in activity [17]. In an earlier study [18], we once found that the same metal complex has different modification on the hydrogenation of CNB with different chloro position relative to the nitro group, UV-spectra showed the interaction of metal complex with substrate (CNB) and products (CAN). Thus, the mechanisms of metal complex effect are rather
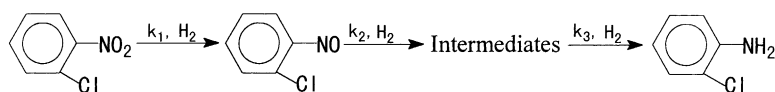
Scheme 2.

complicated. However, it is generally believed that the interaction between metal complex and ruthenium cluster particles may change the electronic density of ruthenium active site, which in turn influence the catalytic performance [17]. Further mechanism research is in progress.

4. Summary

In conclusion, compared to the activity of neat PVP-Ru colloid catalyst, the addition of metal complexes to the catalytic system enhanced its activity to different extent while the selectivity remained constant. It was shown that the rate enhancement resulted from the incorporation of metal complexes is not the simple sum of those of the corresponding metal central ions and the ligands. Upon the addition of the complexes composed of Zn^{2+} and nitrogen-containing ligands, the activity was promoted by more than one order of magnitude. The presence of $Zn(en)_2Cl_2$, etc. changed the reaction kinetics. Metal complex effect was shown effective in the hydrogenation of *o*-CNB over PVP-Ru catalysts.

Acknowledgements

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