Selective hydrogenation of *o*-chloronitrobenzene over polymer-stabilized ruthenium colloidal catalysts

Manhong Liu, Weiyong Yu, Hanfan Liu *

Polymer Chemistry Laboratory, Institute of Chemistry, Chinese Academy of Sciences and China Petro-Chemical Corporation, Beijing 100080, China

Abstract

The selective hydrogenation of *ortho*-chloronitrobenzene (*o*-CNB) to *ortho*-chloroaniline (*o*-CAN) was accomplished without dehalogenation over finely dispersed polyvinylpyrrolidone-stabilized ruthenium colloids (PVP–Ru). The influence of experimental parameters on reaction was also investigated. It was observed that some metal cations added to the system increased the activity while the selectivity remained constant. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogenation; Ruthenium colloid; *o*-Chloronitrobenzene; *o*-Chloroaniline

1. Introduction

The hydrogenation of halonitroaromatics to the corresponding haloanilines over many metallic catalysts, such as palladium, platinum and Raney nickel, has been well-studied. Though palladium is most active in hydrogenation of halonitrobenzene, it causes more dehalogenation [1]. Platinum seems to be the best catalyst for minimizing dehalogenation combined with a fast rate of reduction of the nitro group. To improve selectivity, the catalytic performances of platinum can be influenced by alloying [2], by metal/support interaction [3] or by the use of specific additives (promoters or inhibitors) in the reaction medium [1,4]. Due to its low activity, the ruthenium catalysts are not well-docu-

mented for this reaction. Tijani et al. [5] studied the behavior of some supported ruthenium catalysts in relation to the preparation conditions, metal particle size and alloying effect. It was found that ruthenium was very selective and the rate of reaction expressed per surface metal atom was affected by either ruthenium dispersion or by alloying ruthenium with a second metal. But in such ruthenium-catalyzed reactions, the conversion of the substrate hardly reached 30%.

Because of their unique chemical and physical properties as compared to their bulk metal or single metal atoms, nanoscopic metal clusters or colloids have been attracting many researchers, especially in the field of catalysis. Many metal colloids have been successfully prepared, such as platinum [6–8], rhodium [9], palladium [7,8,10], gold [11–13], etc. Their successful application in catalytic reactions has also been

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* Corresponding author. Tel: +86-10-62554487; Fax: +86-10-62569564; E-mail: caoming@public.east.cn.net

proved by the hydrogenation of various alkenes [14–16], the selective hydrogenation of cinnamaldehyde [17–19] and *o*-chloronitrobenzene [20], the hydration of acrylonitrile [21,22], the photochemical evolution of hydrogen [23] and the enantioselective hydrogenation of alkyl pyruvate [24–26]. To the best of our knowledge, polymer-stabilized ruthenium colloid has not yet been achieved, to say nothing of its use in catalytic reaction.

In this paper, we report the hydrogenation of *o*-chloronitrobenzene over a series of polymer-stabilized ruthenium colloid dispersions. The effects of experimental parameters, such as temperature, hydrogen pressure, the concentration of catalyst and metal cations added were also investigated.

2. Experimental

2.1. Materials and instrument

PVP (av. MW 40,000) was purchased from BASF. Sodium borohydride ($NaBH_4$) was provided by Sigma. Hydrogen (H_2) with a purity of 99.999% was supplied by Beijing Gases Factory. Other reagents were of analytical grade supplied by Beijing Chemicals. *o*-CNB was recrystallized in 95% ethanol and *o*-CAN was distilled before use. TEM photographs were taken by using a Hitachi-9000NAR electron microscope.

2.2. Preparation of polymer-stabilized ruthenium colloids

Method for preparation of the polyvinyl-pyrrolidone-stabilized finely dispersed Ru colloids was described elsewhere [27]. In short, the procedure is as follows: polyvinyl-pyrrolidone and ruthenium(III) chloride were dissolved in a methanol–water mixed solvent to form a tangerine to dark-brown solution. The requisite amount of aqueous sodium borohydride was then added quickly. Vigorous stirring

was maintained at all time. After stirring the solution for several hours a homogeneous dark-brown solution of colloidal ruthenium was obtained, that is, a PVP-stabilized colloidal dispersion of ruthenium. They were evaporated to dryness with rotated evaporator under reduced pressure at $\sim 35°C$. The resulting solid residues were re-dispersed in methanol with a definite concentration, giving a thoroughly homogeneous dispersion prior to the reaction.

2.3. Chemical analysis

Chemical analysis was carried out by means of inductively coupled plasma optical emission spectroscopy (ICP). The spectrometer used was a Spex 1702 scanning ICP spectrometer.

Chloride content was determined by silver chloride.

Along with the sample of catalyst Ru3 simply obtained by rotary evaporation, which preparation conditions were listed in Table 1, the same colloid dispersion was ultra-filtered, washed by 6 portions of 60 mL of distilled water, dried under vacuum at room temperature and was assigned as washed-Ru3.

2.4. X-ray photoelecton spectroscopy (XPS)

The XPS spectra were obtained with a ES-CALAB 220I-XL (VG) photoelectron spectrometer using monochromatic $MgK\alpha$ X-ray (1253.6 eV). Binding energies were referred to as C1s (285.0 eV).

The sample for XPS determination was prepared similar to the literature [28,29] with washed-Ru3.

2.5. Catalytic tests

Hydrogenation of *o*-CNB was carried out in a 100 mL stainless steel autoclave with a Teflon tube to avoid metal contamination. Typically, 1.0 mmol substrate, 0.125 g *n*-decanol (as an internal standard for GC), 8.0 mL PVP–Ru dispersion (containing 1.82×10^{-2} mmol Ru

Table 1
Hydrogenation of *o*-CNB with different PVP–Ru colloids[a]

Catalyst	Preparation condition		d^c (nm)	σ^d (nm)	Conversion (%)	Selectivity[e] (%)		
	PVP:Ru	NaBH$_4$:Ru				*o*-CAN	AN	NB
Ru1	5	10	1.76	0.72	94.1	98.9	0	1.1
Ru2	10	10	1.41	0.61	100	> 99.9	0	0
Ru3	20	10	1.38	0.51	100	> 99.9	0	0
Ru31[b]	20	10	1.38	0.51	100	> 99.9	0	0
Ru4	50	10	1.31	0.43	100	> 99.9	0	0
Ru5	20	5	1.39	0.47	100	> 99.9	0	0
Ru6	20	20	1.28	0.47	100	> 99.9	0	0
Ru7	20	50	1.32	0.49	100	96.6	3.4	0

[a] Reaction conditions are mentioned below.
Extra PVP was added to keep the molar ratio of PVP to Ru = 50:1 except Ru31.
P_{H2} = 4.0 MPa.
T = 320 K.
V = 15 mL.
o-CNB: 1 mmol.
Ru: 1.87×10^{-2} mmol.
Reaction time = 4 h.
[b] Reaction time = 3 h.
[c] Particle average diameter.
[d] Standard deviation.
[e] *o*-CAN = *o*-chloroaniline, AN = aniline, NB = nitrobenzene, no other products detected by GC.

and more PVP added to make the molar ratio of monomeric unit of PVP to ruthenium in reaction was 50:1), totalling 15.0 mL methanol used as the reaction solvent. The reaction mixture was stirred vigorously under 4.0 MPa hydrogen at 320 K. Chemical analysis of the products was performed by gas chromatography equipped with a FID detector and a DC-710 column.

3. Results and discussion

3.1. Characterization of polymer-stabilized ruthenium colloids

The PVP–Ru colloids were characterized by TEM and XPS.

The preparation conditions of Ru colloids together with the corresponding average particle diameter and standard deviation (σ) determined by TEM (Fig. 1) are summarized in Table 1. It was observed that the particle size and size distribution tended to become smaller and narrower with the increase of the molar ratio of

PVP to Ru. When the molar ratio of PVP to Ru was 5:1, the largest particle size (1.76 nm) and the widest size distribution (σ = 0.72 nm) among these Ru colloids could be obtained. The size and size distribution changed a little in the range of PVP:Ru = 10:1–50:1 (1.3–1.4 nm with σ = 0.4–0.6 nm).

Table 2 gives the chemical composition of the catalysts, it can be deduced from the data that only less than 0.77% of boride associated with ruthenium (boride/Ru < 0.067 in atomic ratio). The XPS spectra (Ru 3d$_{5/2}$ at 280.6 eV, Ru 3p$_{1/2}$ and 3p$_{3/2}$ at 483.1 eV and 462.0 eV, respectively) of washed-Ru3, verified that the ruthenium colloidal particles were in a zero oxidation state in accordance with the literature [30,31]. The B1s spectrum of washed-Ru3 showed a small signal located at 188.5 eV, in addition to the one at 191.6 eV with nearly the same intensity. The former is assigned to the boride which associated with ruthenium [30,32], while the latter corresponds to borate (B^{3+}) derived from the oxidation of borohydride.
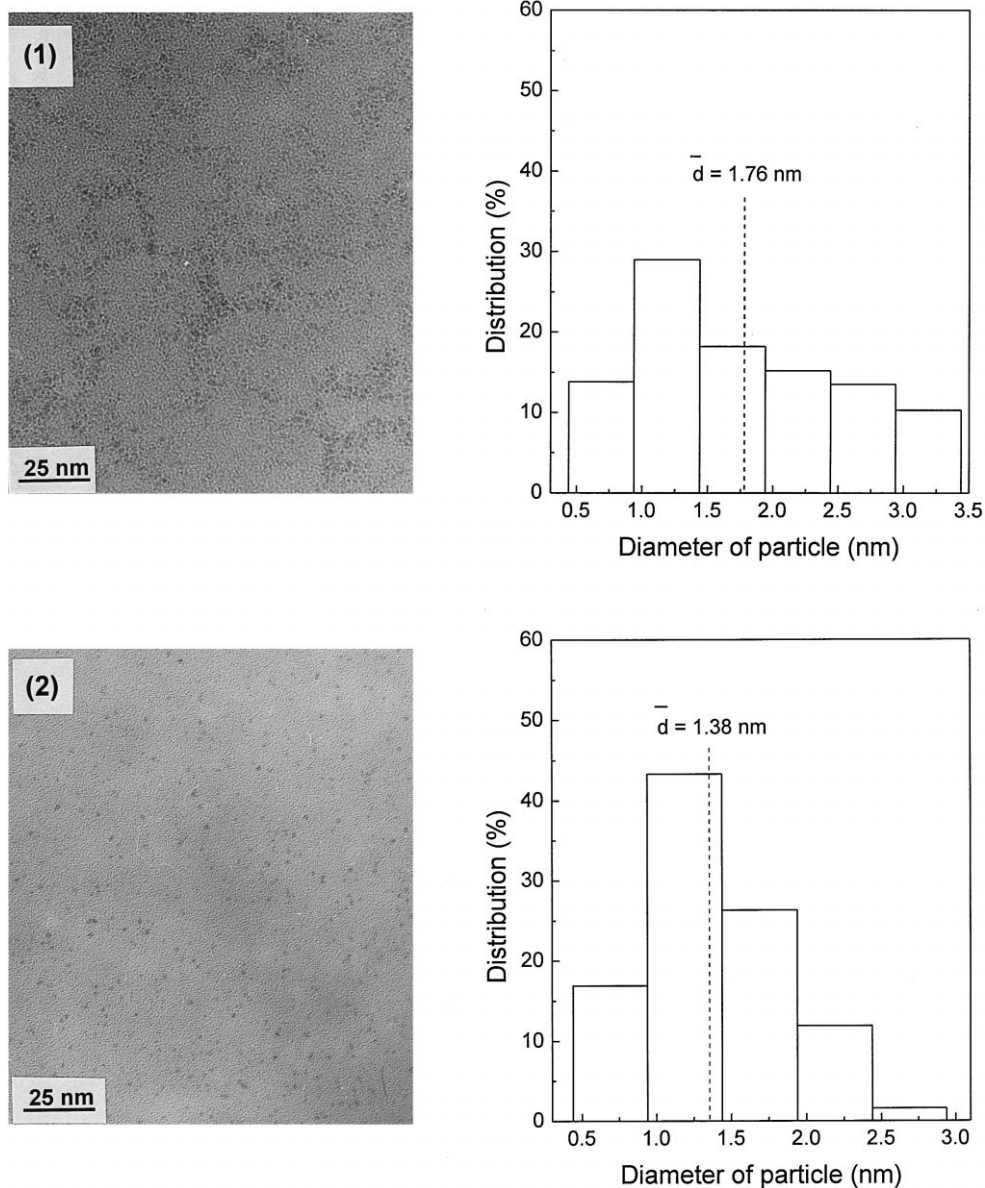
Fig. 1. Electron micrographs (left) and the corresponding particle size distribution histograms (right) of the PVP-stabilized ruthenium dispersions (1) Ru1 (2) Ru3.

3.2. Selective hydrogenation of o-CNB over ruthenium colloids

The results of hydrogenation of *o*-CNB over the Ru colloid catalysts are also listed in Table 1. First of all, the amount of PVP used in the preparation of PVP–Ru colloids is different, and extra PVP was added to reaction system till the molar ratio of monomeric unit of PVP to ruthenium (PVP:Ru) was 50:1. Almost the same results could be achieved except the Ru1 catalyst in selective hydrogenation of *o*-CNB to *o*-CAN over these Ru colloid dispersions. With these catalysts (Ru2–Ru4), the reactions were accomplished in 4 h with satisfactory results in activity and selectivity. The conversion of *o*-

Table 2
Chemical composition of the catalysts

Sample	Composition (% by weight)			
	Ru	B	Na	Cl
Ru3	3.61	3.85	8.18	3.79
Washed-Ru3	4.35	0.033	0	0

CNB is very selective and yields o-CAN exclusively. As for the Ru1 nanocluster, the selectivity of o-CAN is a little lower than others while the conversion of o-CNB is 94.1% after 4 h reaction. Moreover, the reaction mixture was no longer homogenous and partial precipitation of metallic ruthenium was observed after the reaction. This is due to the small amount of the stabilizing polymer, PVP, in the preparation of colloidal ruthenium. This is also in agreement with TEM image (Fig. 1) which shows that the Ru1 nanoparticles has a tendency to aggregate. Our results demonstrated that the characteristics of Ru colloid catalysts were determined by the preparation conditions. Comparing the hydrogenation of o-CNB over Ru3 with that of Ru31, it can be observed that the extra addition of PVP in hydrogenation results in decrease in activity (the reaction was accomplished in 3 h over Ru31 and in 4 h over Ru3, respectively). This indicated that PVP has some inhibiting effect on the reaction. Increasing the molar ratio of sodium borohydride to ruthenium with the constant amount of PVP, four colloids (Ru3, Ru5, Ru6, and Ru7) can be achieved. TEM results showed that these Ru colloids had similar size and size distribution. Hydrogenation of o-CNB over these catalysts give rather perfect results except for Ru7 ($NaBH_4$:Ru = 50:1) in which the selectivity is lower. This may be attributed to the large amount of base generated from the hydrolysis of $NaBH_4$. It has been found that in the hydrogenation of o-CNB by PVP–Pt colloid, the addition of NaOH has limited effect on activity and selectivity [33]. To confirm this assumption, the equivalent amount of NaOH generated by excess $NaBH_4$ in Ru7

was added into the Ru6 catalytic system, almost the same selectivity of o-CAN (96.9%) and aniline (3.1%) as that of Ru7 was obtained.

In order to clarify the influence of boron species on the reaction, another ruthenium colloid was prepared. In an autoclave, a PVP-stabilized Ru colloid without boron was obtained with PVP:Ru = 20:1 (the same as Ru3) by hydrogen reduction under pressure (hydrogen pressure 4.0 MPa, 333 K, 24 h). The resultant colloid (assigned as Ru3∗) has an average diameter of 2.8 nm with a standard deviation of 0.63 nm. Three parallel hydrogenation experiments of o-CNB over Ru3∗ in 1 h were carried out under the same conditions as listed in Table 1. In the first one, without any boron in the system, the conversion is 4.5% which is much slower than that of catalyst Ru3 (26.5% conversion). In the second one, a requisite amount of sodium tetraborate was added to Ru3∗ with the molar ratio of B:Ru = 5:1, and the conversion is 47.6%. In the third one, a solution of hydrolyzed sodium borohydride ($NaBH_4$ was dissolved in water and stirred for more than 10 h) was added to the Ru3∗ system in which the molar ratio of B:Ru was also maintained as 5:1. The mixture was evaporated to dryness and then re-dispersed in methanol as a catalyst. The conversion is 63.4% over this catalyst. The selectivity of these three experiments were ∼ 100, 97.6 and ∼ 100%, respectively. These results implied that the borate (B^{3+}) other than boride which associated to the ruthenium exerted a major influence on the ruthenium catalyst system.

3.3. Influence of reaction parameters

The effect of various reaction parameters viz. o-CNB concentration, the concentration of catalyst, hydrogen pressure, and temperature on the reaction rate over Ru3 catalyst are discussed below.

The conversion of o-CNB on Ru3 was investigated as a function of time. Results presented

in Fig. 2 demonstrate that the concentration of *o*-CAN in the reaction increases linearly with time, thus showing a zero order respect to the concentration of *o*-CNB. Hence, the initial rate is the same as the average rate when the concentration of *o*-CNB is below 0.17 mol L^{-1}. According to Rode and Chaudhari [34], the initial rate of hydrogenation of *meta*-chloronitrobenzene (*m*-CNB) over Pt–S/C was observed to be zero order with *m*-CNB when the concentration of the substrate is higher than 0.28 mol L^{-1}. Below this concentration, the rate is no longer observed to be independent of *m*-CNB concentration. This indicated that the catalytic properties of Ru are different from Pt.

The hydrogenation of *o*-CNB with various concentration of Ru3 was carried out. The concentration of reactant (*o*-CNB) were analyzed at 1 h reaction time, the rate of hydrogenation was observed to be the first order dependence with catalyst concentration. This is in accordance with the result achieved by Rode and Chaudhari [34].

As illustrated in Fig. 3, it can be seen that the curve is somewhat complex. The rate of hydrogenation was observed to be raising rapidly at low hydrogen pressure ($P_{H2} < 0.5$ MPa), then, it increased slowly, and finally showed a linear dependency on hydrogen pressure. This effect of hydrogen pressure to the reaction rate is not thoroughly clear at present.

In addition, the activation energy of the reaction catalyzed by the PVP–Ru colloid was determined. The result is shown in an Arrhenius plot in Fig. 4. The apparent activation energy derived from the plot is 20.1 kJ/mol, which is slightly lower than that reported by Coq et al. [35] for the hydrogenation of *p*-chloronitrobenzene over Pt/Al$_2$O$_3$ catalyst (25.1 kJ/mol).

3.4. Influence of metal cations

The addition of metal cations can markedly increase both activity and selectivity in the hydrogenation of cinnamaldehyde and chloronitrobenzene over polymer-stabilized platinum
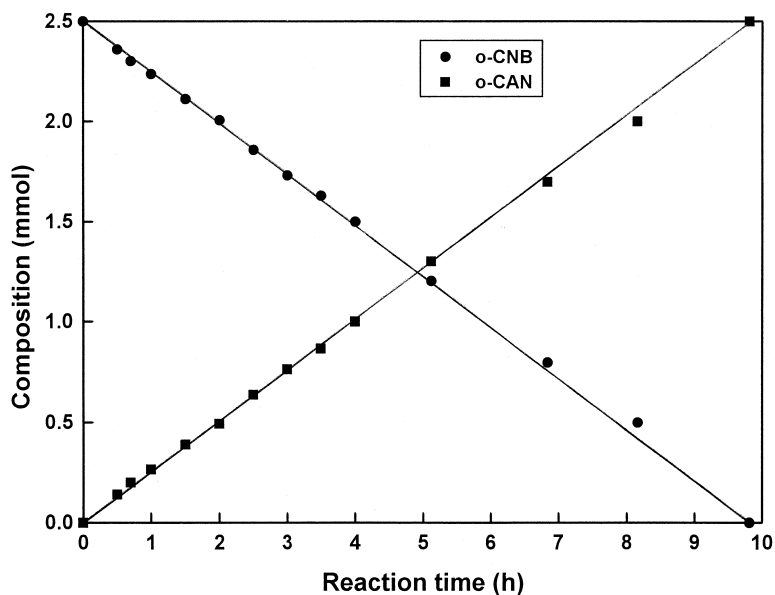

Fig. 2. Hydrogenation of *o*-CNB over Ru3 catalyst as a function of time.
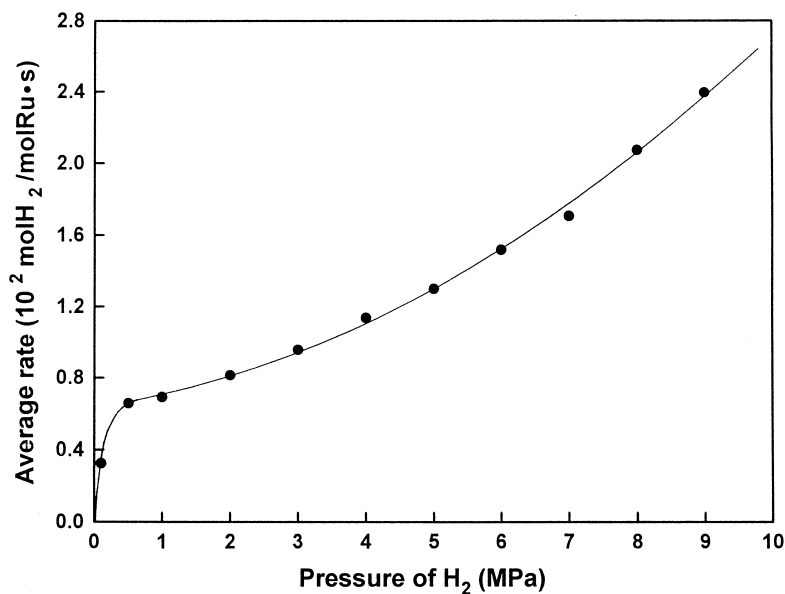
Fig. 3. Effect of H_2 pressure on the rate of hydrogenation.

colloid as reported [19,20]. The metal cation effect was also investigated in the ruthenium colloid system, results were summarized in Table 3. It can be seen from Table 3 that almost all the metal cations surveyed here can improve the activity in varying degree while maintaining the high selectivity. The maximum activity was obtained by using Fe^{3+} ion as a modifier in the
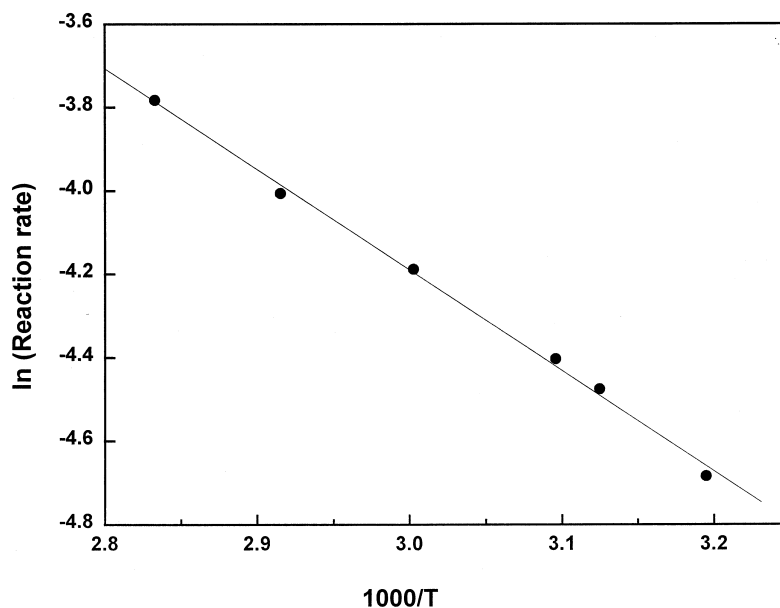

Fig. 4. The Arrhenius plot of hydrogenation of *o*-CNB over PVP–Ru cluster.

Table 3
Hydrogenation of o-CNB over PVP–Ru–MCl$_x$ system[a]

Catalytic system	Conversion (%)	Selectivity[b] (%) o-CAN
PVP–Ru	39.0	> 99.9
PVP–Ru–Fe^{3+}	62.0	> 99.9
PVP–Ru–Co^{2+}	42.1	> 99.9
PVP–Ru–Ni^{2+}	53.4	> 99.9
PVP–Ru–Li^{+}	48.5	> 99.9
PVP–Ru–Sn^{2+}	46.2	> 99.9
PVP–Ru–Zn^{2+}	36.2	> 99.9

[a]Reaction conditions are mentioned below.
P_{H2} = 4.0 MPa.
T = 320 K.
Reaction time = 1.5 h.
V = 15 mL.
Ru: 1.87×10^{-2} mmol.
PVP:Ru = 50:1.
o-CNB: 1 mmol.
M^{n+}:Ru = 1:1 (molar ratio).
[b]There were no aniline, nitrobenzene and other products detected by GC.

reaction system. This fact is different from that of the hydrogenation o-CNB over PVP-stabilized colloidal platinum catalyst in which the Ni^{2+} ions gave the best result [20]. It can be seen here that the VIII group metal ions, such as Fe^{3+}, Co^{2+} and Ni^{2+}, can modify the colloids to a certain extent. It is well-known that Sn^{2+} and Zn^{2+} usually acted as poisons to a hydrogenation metal catalyst. Indeed, the Sn^{2+} ion or the Zn^{2+} ion acted as a poison to the catalyst in the hydrogenation of o-CNB to o-CAN over PVP–Pt colloid as reported [20]. Here, it is interesting to note that the Sn^{2+} ion prompts the activity and the Zn^{2+} ion influenced little on the activity in the PVP–Ru system. A similar positive effect upon alloying Sn to Ru was reported in the hydrogenation of p-CNB to p-CAN over Ru–Sn/Al$_2$O$_3$ [5]. From the literature [5], it is known that Sn is in a zero oxidation state in Ru–Sn/Al$_2$O$_3$ catalyst which is different from that the PVP–Ru–SnCl$_2$ system in which Sn is in an ionic state. Certainly, it is hard to ascertain the valent state of Sn in the reaction system, Deshpande et al. [30] studied the ruthenium–tin boride via XPS and verified that tin existed predominantly as Sn^{2+} or Sn^{4+}.

4. Summary

This paper described the selective hydrogenation of o-CNB to o-CAN over Ru colloids:
1. Nearly 100% selectivity to o-CAN can be obtained over PVP–Ru colloids at 100% conversion of o-CNB, and the PVP–Ru colloids can survive under the hydrogenation condition at 320 K and 4.0 MPa.
2. The modification of metal cations to PVP–Ru colloid results in increasing activity.
3. The reaction was verified to be independent of the concentration of o-CNB, first order with the concentration of catalyst and complicated dependence on hydrogen pressure, respectively.

Acknowledgements

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