Modification mechanism of Sn^{4+} for hydrogenation of p-chloronitrobenzene over PVP-Pd/γ-Al_2O_3

Qiong Xu [a,b], Xin-Mei Liu [a], Jun-Ru Chen [a], Rui-Xiang Li [a,*], Xian-Jun Li [a,*]

[a] *Key Laboratory of Green Chemistry and Technology, Ministry of Education, Department of Chemistry, Sichuan University, Chengdu, Sichuan 610064, PR China*
[b] *Department of Chemistry, Shaanxi Technology University, Hanzhong, Shaanxi 723000, PR China*

Abstract

PVP-Pd (1.5 wt.%)/γ-Al_2O_3 was prepared and used as a catalyst for the hydrogenation of p-chloronitrobenzene (p-CNB) to form p-chloroaniline (p-CAN), so that a serious dehalogenation reaction was happened. However, the catalytic property of this catalyst was remarkably affected by some metal cationic additives. Especially, when Sn^{4+} was introduced into the reaction system, the activity of the catalyst was not only promoted, but the dehalogenation reaction was also greatly suppressed. The average rate of hydrogenation increased from 1.28 mol H_2/mol Pd s on PVP-Pd/γ-Al_2O_3 catalyst to 1.96 mol H_2/mol Pd s on the PVP-Pd-Sn^{4+}/γ-Al_2O_3 catalyst (molar ratio of Pd to Sn = 1:1), and the selectivity for p-CAN increased from 66.8 to 96.6%. The dehalogenation reaction was completely restrained as the molar ratio of Sn^{4+} to Pd was up to 5. The great promotion role of Sn^{4+} could be owing to the interaction between Sn^{4+} and $-NO_2$ group of the substrate. The combination of Sn^{4+} with oxygen in $-NO_2$ increased the polarity of N=O bond. The increase of the polarity of N=O benefited the activated dihydrogen to attack the N=O bond, and the hydrogenation was accelerated. At the same time, the increase of the polarity of N=O bond caused the more lone pair electron of p orbital on chlorine atom to dislocate to phenyl ring, so C—Cl bond was strengthened and the polarity of C—Cl was weakened. Furthermore, these were unfavorable for the activated dihydrogen to attack C—Cl bond and the hydrogenation selectivity was greatly improved.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Hydrogenation; p-Chloronitrobenzenes; p-Chloroaniline; Palladium catalyst; Modification

1. Introduction

Hydrogenation of halonitroaromatic compounds to form haloaromatic amine is an important reaction in the fields of dyes, drugs, herbicides and pesticides. Because of the environmental impact associated with the use of hydrochloric acid in Bechamp's reaction, selective hydrogenation of halonitroaromatic compunds over a supported metal catalyst is now preferred. Raney nickel [1–3], platinum or modified platinum catalysts [1,3–12] are the most widely use for the high-yield synthesis of p-CAN from p-CNB. However, Raney nickel suffers the disadvantage of being pyrophoric, and platinum is very expensive. Ruthenium, rhodium and iridium are more selective for this reaction [1,5,12–16], but their catalytic activities are

generally lower. The addition of a metal ion modifier could considerably modulate both the activity and the selectivity of a catalyst for the hydrogenation of halonitroaromatic compound. Liu investigated the influence of metal cations Fe^{3+}, Ni^{2+} and Co^{2+} on the supported platinum colloids catalyst. It was found that Co^{2+} increased both the activity and the selectivity, Fe^{3+} decreased the activity of Pt/PS (PS = poly(styrene-*co*-divinylbenzene) catalyst, Ni^{2+} increased the selectivity but the activity decreased. Obviously, these metal cations displayed the different modification roles for the hydrogenation reaction [17].

A supported palladium catalyst showed a high catalytic activity for the hydrogenation of halonitroaromatics, but the selectivity to form haloaniline was generally lower because of a serious dehalogenation reaction [12,18]. In order to tune catalytic property of catalyst to achieve a high yield of haloaniline, the selective poisoning of catalyst with some compounds containing sulphur, nitrogen and phosphorus is also successful [1–3,6]. Many other approaches have been also developed, such as alloying [7,18], controlling the metal particle disper-

sion [19] and using metal/support interaction [8] and bimetallic synergic effect [4,20]. Especially, introducing some specific promoters and inhibitors into the reaction system is an effective method [21–25]. For example, the catalytic activity and the selectivity for p-CAN were improved over Pd/AC catalyst if iron powder or iron salt as co-catalyst was added into the reaction system [26]. In spite of that a great effort has been made to improve the selectivity for the hydrogenation of halonitroaromatic compounds, the dehalogenation is very difficult to be effectively inhibited and the role mechanism of promoter is not clear.

In this paper, the effect of metal cationic additives on the selective hydrogenation of p-CNB to p-CAN over PVP-Pd/γ-Al$_2$O$_3$ was investigated. It was found that Sn^{4+} played an excellent promoting role for both the hydrogenation activity of p-CNB and the selectivity of forming p-CAN. Based on our experimental results, the modification mechanism of Sn^{4+} ion for PVP-stabilized Pd/γ-Al$_2$O$_3$ was proposed.

2. Experimental

PVP (average molecular weight 40,000) was from BASF. Other reagents (A.R) were purchased from Shanghai Chemicals. Pure hydrogen (99.99%) was from Chengdu Gases Factory.

2.1. Preparations of catalysts

PVP-Pd/γ-Al$_2$O$_3$ (Catalyst **I**): It was prepared as the method in literature [18]. PVP (45.1 mg) as a stabilizing agent was dissolved in a mixture solvent (40 mL) of water and ethanol (volume ratio = 1:9). 1.50 mL PdCl$_2$·2H$_2$O solution (1.41×10^{-4} mol, the molar ratio of monomeric unit of PVP to palladium = 3) was added to above PVP solution with vigorous stirring. After the mixed solution was refluxed for 3 h, a dark colloid solution was formed. Then 1.0 g γ-Al$_2$O$_3$ was added to the cooled colloid solution and the mixture solution was continued to stir at room temperature for 24 h. Afterwards, the solid substance PVP-Pd/γ-Al$_2$O$_3$ was filtrated, washed with distilled water two times and dried under vacuum at 60 °C for 10 h. The content of palladium determined by ICP was 1.5 wt.% in PVP-Pd/γ-Al$_2$O$_3$.

PVP-Pd-Sn^{4+}/γ-Al$_2$O$_3$ (Catalyst **II**): SnCl$_4$ and PdCl$_2$ (Sn^{4+}/Pd = 1 in molar ratio) were simultaneously added into the mixture solvent (40 mL) of water and ethanol containing PVP. The other procedures were the same as catalyst **I**.

Catalyst **III**: SnCl$_4$ and PdCl$_2$ (Sn^{4+}/Pd = 0.05 in molar ratio) were simultaneously added into the mixture solvent (40 mL) of water and ethanol containing PVP. The other procedures were the same as catalyst **I**.

Catalyst **IV**: Catalyst **I** was impregnated in ethanol solution of SnCl$_4$ (Sn^{4+}/Pd = 1 in molar ratio) at room temperature for 12 h. At the end of impregnation, the solvent was removed and dried under vacuum at room temperature for 5 h.

Catalyst **V**: Catalyst **I** was impregnated in ethanol solution of SnCl$_4$ (Sn^{4+}/Pd = 1 in molar ratio) at room temperature for 12 h. At the end of impregnation, the solvent was removed and dried under vacuum at 60 °C for 5 h.

2.2. Catalytic hydrogenation

Selective hydrogenation of p-CNB was carried out in a 60 mL stainless steel autoclave with a thermocouple and a magnetic stirring bar. The solution containing 0.0177 g PVP-Pd/γ-Al$_2$O$_3$ (Pd 2.5×10^{-6} mol), 0.3939 g p-CNB (2.5×10^{-3} mol), 2.5×10^{-6} mol metal ion and 5.0 mL ethanol was introduced into the autoclave. The autoclave was purged by pure hydrogen for five times to replace air, and then was pressurized to 1.0 MPa. When the autoclave was heated to the desired temperature, the stirrer was turned on and the reaction time was accounted. At the end of reaction, the autoclave was immersed in an ice-water bath to quench the reaction.

2.3. Analysis

The reaction products were analyzed by GC-960 equipped with a FID detector and SE-30 capillary column. The oven temperature was 160 °C, injector temperature 240 °C and detector temperature 260 °C. Reactants and products were identified by comparison with authentic samples. High-Resolution TEM (HRTEM) images were obtained on a Philips TECNAI F-30 FEG instrument at an accelerating voltage of 300 KV. The XPS spectra were obtained with a XSAM800 photoelectron spectrometer using monochromatic Mg Kα X-ray 1486.6 eV and binding energies were referred to as C1s 284.8 eV.

3. Results and discussion

3.1. Modifications of supported palladium catalyst with metal cations

The effect of different metal cations (added as chlorides) on hydrogenation of p-CNB over PVP-Pd was listed in Table 1. The data showed that Li$^+$, Ca^{2+} and Co^{2+} definitely enhanced the activity but the selectivity slightly decreased. The additions of Mg^{2+}, Fe^{3+}, Fe^{2+} and Ni^{2+} were obviously unfavorable for both the catalytic activity and the selectivity. Sn^{2+} enhanced the

Table 1
Effects of metal cations on selective hydrogenation of p-CNB over catalyst **I**

Entry	Metal cations	Conversion (%)	Selectivity (%)			
			p-CAN	p-CNSB	AN	Others
1	None	58.7	64.3	0	35.7	0
2	Li$^+$	73.1	61.7	0	38.3	0
3	Ca^{2+}	74.0	62.0	0	38.0	0
4	Sn^{4+}	74.4	96.6	0	3.4	0
5	Sn^{2+}	68.7	85.9	2.4	11.7	0
6	Co^{2+}	68.4	60.0	2.3	37.7	0
7	Mg^{2+}	47.0	53.2	0	46.8	0
8	Fe^{3+}	39.8	46.0	0	54.0	0
9	Fe^{2+}	49.7	60.3	0	39.7	0
10	Ni^{2+}	40.6	60.1	0	39.9	0

Reaction conditions: p-CNB: 2.5×10^{-3} mol; catalyst **I**, 0.0177 g (Pd 2.5×10^{-6} mol); metal cations were directly added into reaction solution and M^{n+}/Pd was 1.0 (molar ratio); temperature, 323 K; P_{H_2}, 1.0 MPa; time, 20 min; solvent, ethanol 5.0 mL.

Table 2
Effect of Cl$^-$ on selective hydrogenation of p-CNB over catalyst **I**

Promoters	Conversion (%)	Selectivity (%)		
		p-CAN	p-CNSB	AN
SnCl$_4$	74.4	96.6	0	3.4
CoCl$_2$	51.6	68.7	1.3	30.0
NiCl$_2$	21.1	74.9	6.1	19.0
CaCl$_2$	39.2	63.1	2.4	34.5

Reaction conditions: p-CNB: 2.5×10^{-3} mol; catalyst **I**, 0.0177 g (Pd 2.5×10^{-6} mol); Cl$^-$, 1.0×10^{-5} mol; temperature, 323 K; P_{H_2}, 1.0 MPa; time, 20 min; solvent, ethanol 5.0 mL.

activity of catalyst a certain extent and the selectivity for p-CAN rose from 64.3 to 85.9%. Surprisingly, the introduction of Sn^{4+} ion into the reaction solution caused a significant improvement in both the activity and the selectivity. The conversion of p-CNB not only rose from 58.7 to 74.4%, but the selectivity for p-CAN also increased from 64.3 to 96.6%.

According to the reported results, Cl$^-$ in reaction solution could be adsorbed on the surface of catalyst and some special active centers were selectively poisoned [27]. It would result in the decrease of the dehalogenation activity. Because the metal cations were introduced to the reaction solution as the metal chlorides, the difference of the positive charge of metal cations would lead to the different amount of chlorine anion. In order to prove that the modification role was mainly caused by metal ions rather than by Cl$^-$, the experiments were carried out under the same concentration of Cl$^-$ (Cl$^-$:Pd = 4) rather than metal cations. The results listed in Table 2 indicated that the catalytic activities and selectivities were mainly influenced by metal cations. Furthermore, NH$_4$Cl was introduced into this system. Because NH$_4^+$ could not coordinate with the substrate and the hydrogenation product, the effect of Cl$^-$ could be clearly reflected. When the molar ratio of NH$_4$Cl to p-CNB increased from 1:1000 to 1:10, the hydrogenation activity gradually decreased with the increase of Cl$^-$ while the selectivity was not any change (Table 3). These results proved clearly that the modification role was from metal cations.

3.2. Effect of molar ratio of Sn^{4+} to Pd on hydrogenation

The effect of molar ratio of Sn^{4+} to Pd on hydrogenation of p-CNB was investigated and the results were showed in Fig. 1. Both the catalytic activity and selectivity to form p-

Table 3
Effect of addition of NH$_4$Cl on hydrogenation of p-CNB over catalyst **I**

p-CNB/NH$_4$Cl in molar ratio	Conversion (%)	Selectivity (%)		
		p-CAN	p-CNSB	AN
None	99.5	68.5	0	31.5
1000:1	86.2	68.6	0	31.4
100:1	79.0	70.9	0	29.1
10:1	68.8	68.8	0	31.2

Reaction conditions: p-CNB: 2.5×10^{-3} mol; catalyst **I**, 0.0177 g (Pd 2.5×10^{-6} mol); temperature, 323 K; P_{H_2}, 1.0 MPa; time, 50 min; solvent, ethanol 5.0 mL.

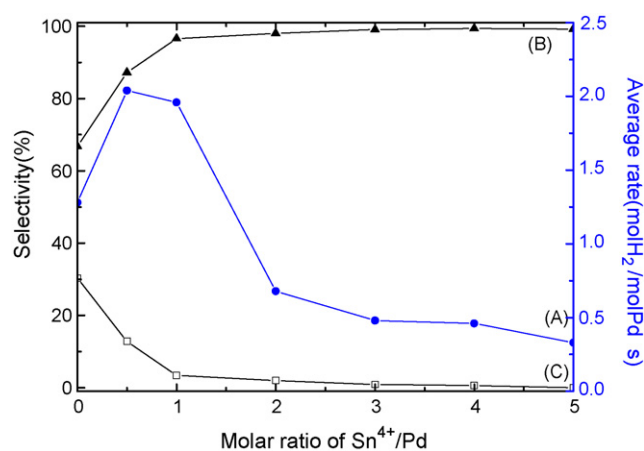Fig. 1. Effect of molar ratio of Sn^{4+} to Pd on hydrogenation of p-CNB over PVP-Pd catalyst: (A) average rate (mol H$_2$/mol Pd s); (B) selectivity to p-CAN; (C) selectivity to aniline. *Reaction conditions*: p-CNB: 2.5×10^{-3} mol; catalyst **I**, 0.0177 g (containing Pd 2.5×10^{-6} mol); temperature, 323 K; P_{H_2}, 1.0 MPa; solvent, ethanol 5.0 mL (average rates were derived from the time at close to 100% of conversion).

CAN increased with the increase of Sn^{4+} concentration when the molar ratio of Sn^{4+} to Pd was in the range of 0.0–1.0. When the molar ratio of Sn^{4+} to Pd was 1.0, the promoting role of Sn^{4+} for the catalytic activity reached a maximum, dehalogenation reaction was markedly inhibited, and the selectivity to form p-CAN increased from 66.8 to 96.6%. If the molar ratio of Sn^{4+} to Pd exceeded 1.0, the selectivity would increase further, but the activity of catalyst gradually decreased. When the molar ratio of Sn^{4+} to Pd was up to 5, dehalogenation reaction was completely inhibited. The detectable by-product was only p-CNSB of 0.8%. According to references [1,4–6,13,14,28–32], p-CNSB is an intermediate to form p-CAN, it would disappear with the extension of reaction time. To the best of our knowledge, this was the highest selectivity among all reports about the hydrogenation of halonitroaromatic compounds catalyzed by the supported palladium catalysts.

3.3. Effect of addition method of Sn^{4+}

In order to clarify the modification roles of Sn^{4+} occurred in solution or on surface of catalyst, the addition methods of Sn^{4+} were studied. The results in Table 4 showed that the best mod-

Table 4
Effect of addition methods of Sn^{4+} on hydrogenation of p-CNB over catalyst **I**

Catalyst	Average rate (mol H$_2$/mol Pd s)	Selectivity (%)			
		p-CAN	p-CNSB	AN	Others
I	1.28	66.8	2.9	30.3	0
I*	1.96	96.6	0	3.4	0
II	1.29	82.1	0	17.9	0
III	1.31	72.7	0	27.3	0
IV	1.55	95.7	0	4.3	0
V	1.28	72.3	0	27.7	0

Reaction conditions: the same as in Table 1. Catalyst **I***, Sn^{4+} was added into reaction system directly (average rate was derived from the time at close to conversion 100%).

ification method was adding Sn^{4+} to reaction solution directly (PVP-Pd + Sn^{4+}: catalyst **I***). After the hydrogenation was completed, the mixture solution was filtered. The data of ICP analysis of the filtrate indicated that the majority of Sn^{4+} (95%) was kept in solution, and only 5% of total Sn^{4+} quantity was adsorbed on the surface of catalyst. However, when the same amount of Sn^{4+} (5%) was completely supported on PVP-Pd catalyst; the activity of catalyst and the selectivity of product were not obviously improved (catalyst **III** in Table 4). Furthermore, if Sn^{4+} (molar ratio of Pd to Sn^{4+} = 1:1) was added in the preparation proceeding of catalyst (catalyst **II**), its catalytic activity and selectivity were much lower than that of catalyst **I***. Catalyst **IV**, which was prepared by impregnation with ethanol solution of Sn^{4+} (Sn^{4+}/Pd = 1 in molar ratio), was dried at room temperature so that Sn^{4+} was protected from hydrolyzing and forming $SnO_2 \cdot xH_2O$. The selectivity of p-CAN was very close with that of catalyst **I***, but the catalytic activity was lower. The mixture solution was filtered at the end of hydrogenation. The result of ICP analysis of the filtrate showed the majority (ca. 80%) of Sn^{4+} supported on the catalyst was extracted to the reaction solution. Compared with catalyst **I**, catalyst **V**, in which Sn^{4+} could occurred hydrolysis when it was dried at 60 °C, did not obviously show change of catalytic activity and selectivity. These demonstrated that the promoting role of Sn^{4+} resulted from Sn^{4+} in solution and the Sn^{4+} adsorbed on the surface of the catalyst was unfavorable to improve the catalytic activity and selectivity.

3.4. Effect of reaction time on dehalogenation

Figs. 2 and 3 show the changes of conversion and selectivity with the reaction time in the absence of Sn^{4+} and in the presence of Sn^{4+}, respectively. They reflected that the selectivity of p-CAN was mostly not changed with the progressing of hydrogenation. After the hydrogenation completed, the dehalogenation did not continue with the extension of reaction time. In order to further understand what group of substrate occurred interaction with Sn^{4+}, chlorobenzene and nitrobenzene were used as substrates to investigate the dehalogenation reaction over catalyst **I** and catalyst **I***. However, the result showed that
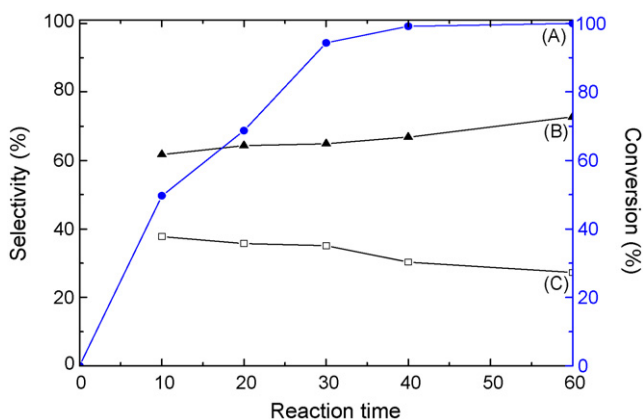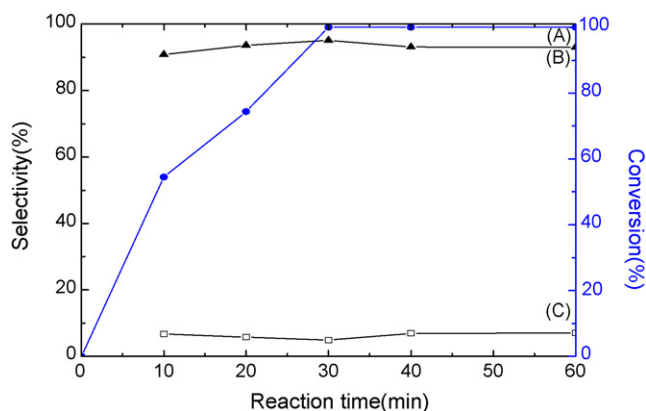

Fig. 3. Effect of reaction time on hydrogenation of p-CNB in PVP-Pd-Sn^{4+} catalytic system: (A) conversion; (B) selectivity to p-CAN; (C) selectivity to aniline. *Reaction conditions*: Sn^{4+}/Pd = 1 (in molar ratio), other conditions are the same as Fig. 2.

the dehalogenation of chlorobenzene did not occur at all in the same conditions and the hydrogenation rate of nitrobenzene was enhanced in the presence of Sn^{4+} (Table 5). This means that the presence of nitro group or the formation of −NH_2 was the main reason to lead to the breaking of C−Cl. The fact that the dehalogenation at the end of hydrogenation did not continue with the extension of reaction time reflected that the dehalogenation proceeded in parallel with the hydrogenation of nitro group.

3.5. Modification mechanism of Sn^{4+}

HRTEM (Fig. 4) images showed that the average diameter of palladium particles in catalyst **I** was about 70 nm and was distributed in a wide range of particle size. However, the average diameter of palladium particles in catalyst **II** was about 8.0 nm with a narrow distribution in the size of particles. This reflected that Sn^{4+} introduced in PVP-Pd in the process of catalyst preparation played an important role to protecting the palladium nanoparticles from aggregating. However, whether catalyst **I** or catalyst **II** was used for the hydrogenation of p-CNB, the activities of both catalysts were not obviously different in spite of some increasing of selectivity of catalyst **II**. This result reflected that the sizes of palladium particles and the structural factors of catalyst were not main influences on the catalytic activity and selectivity.

The binding energies of Pd $3d_{5/2}$ in catalyst **I** and catalyst **IV** were 336.0 and 336.3 eV in XPS spectra (Fig. 5). It showed that the valence state of Pd was zero. Compared with the binding

Fig. 2. Effect of reaction time on hydrogenation of p-CNB over PVP-Pd catalyst: (A) conversion; (B) selectivity to p-CAN; (C) selectivity to aniline. *Reaction conditions*: same as Fig. 1.

Table 5
Effect of Sn^{4+} on hydrogenation of nitrobenzene to aniline over catalyst **I**

Entry	Conversion (%)	Selectivity (%)		
		AN	NSB	Others
Catalyst I	79.9	96.5	3.5	0
Catalyst I*	100	100	0	0

Reaction conditions: NB, 2.5 mmol; catalyst **I**, 0.0177 g (Pd 2.5 × 10^{-6} mol); temperature, 313 K; P_{H_2}, 0.5 MPa; time, 30 min; Sn^{4+}/Pd:1.0 (molar ratio); solvent, ethanol 5.0 mL.
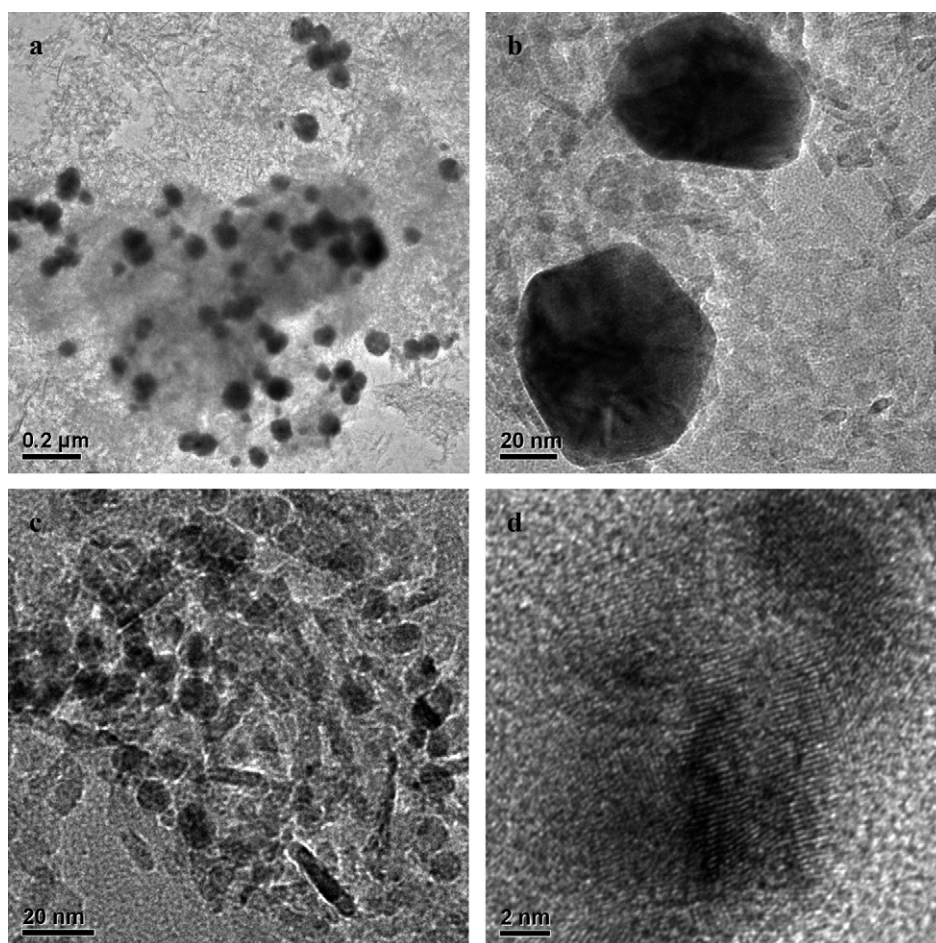
Fig. 4. HRTEM photographs of (a and b) catalyst **I** (c and d) catalyst **II** (molar ratio Sn^{4+} to Pd = 1.0).

energy of Pd $3d_{5/2}$, the binding energies of Pd in the two catalysts had a rising trend because of the interaction between palladium and supporter γ-Al_2O_3 [33]. The binding energy 486.4 eV of Sn $3d_{5/2}$ was in good agreement with Sn(IV) and other valent states of tin were not observed in XPS spectra. Thus, XPS spectra further proved that the promoting action in the hydrogenation of *p*-CNB reaction system was from Sn^{4+} rather than Sn^{2+} or Sn. Although Bacaud [34] pointed out that Sn in Pt-Sn catalyst could be reduced into Sn^{2+} and metallic Sn in H_2 atmosphere at 500 °C and they was immediately oxidized to Sn^{4+} by the protons of supporter in vacuum, Sn^{2+} was not found in the reaction solution by the experiment of mercury dichloride after the reaction finished. The low reaction temperature could be the main reason not to reduce Sn^{4+} into Sn^{2+} and Sn.

The effect of metal cation on the hydrogenation of halonitroaromatic compound is an extraordinarily complicated problem. According to the reported results, Sn^{2+} increased the reaction activity of PVP-Ru catalyst in hydrogenation of *o*-CNB to *o*-CAN [12], but Sn^{2+} poisoned the catalyst PVP-Ru-Pt and PVP-Pt [9]. Both of Sn^{2+} and Sn^{4+} increased the activity and the selectivity to desired product over PtSn/nylon and PtSn/Al_2O_3 [7,35]. Previous studies [17,36] on the modification of metal cation pointed out that there was a chemical interaction between reactant and metal cation adsorbed on the surface of catalyst.

The metal cation absorbed on the surface of catalyst was favorable for the activation of polar N=O bond in −NO_2 group, then the dissociated H atoms near the activated N=O bond attacked the N=O bond, so that the nitro group was reduced into −NH_2 group. At the same time, the interaction between metal cation in the solution and −NH_2 group of product shortened the stay time of product molecule on the surface of catalyst, so the C−Cl bond hydrogenolysis was avoided. Therefore, the activity and the selectivity of catalyst were improved. Some researchers suggested that the effect of metal cation on hydrogenation properties of supported metal catalyst could be interpreted by electronic effect and geometric effect [37,38].

In fact, our results could be not explained with the above mechanisms. Ni^{2+} and Co^{2+} could strongly coordinated with amines, but they did not inhibit the dehalogenation (Table 1). This means that to promote the desorption of product by means of the coordination of added metal ions with amine absorbed on the surface of catalyst is not really a reason to suppress the dehalogenation. When the prepared catalyst was dried at 60 °C, the $SnCl_4$ on the surface of catalyst could occur the hydrolysis and convert into $SnO_2 \cdot xH_2O$. Compared with the result catalyzed by catalyst **V** dried at 60 °C, catalyst **IV** dried under vacuum at room temperature displayed much better ability of suppressing the dehalogenation. It indicated that the modifica-
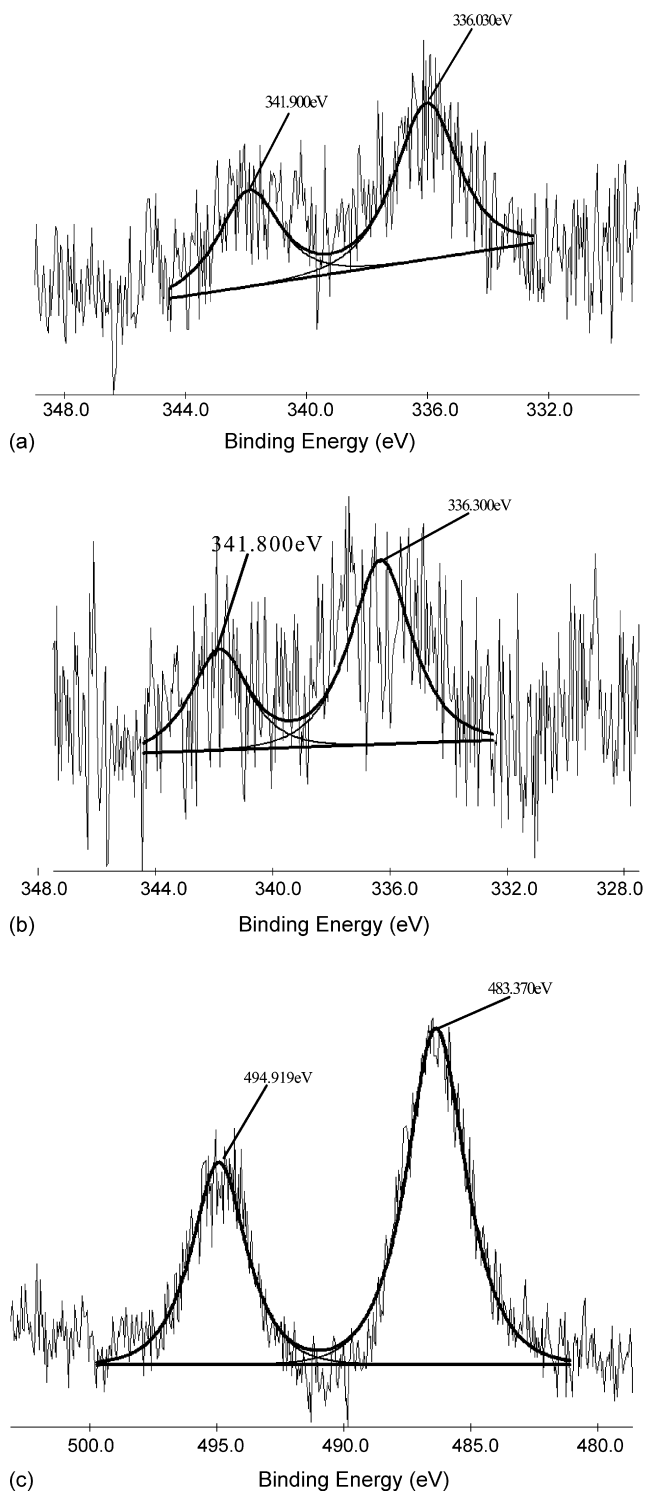
Fig. 5. (a) XPS of Pd ($3d_{3/2}$) and Pd ($3d_{5/2}$) of catalyst **I**; (b) XPS of Pd ($3d_{3/2}$) and Pd ($3d_{5/2}$) in catalyst **IV**; (c) XPS of Sn ($3d_{3/2}$) and Sn ($3d_{5/2}$) in catalyst **IV**.

tion role was caused by Sn^{4+} and not by $SnO_2 \cdot xH_2O$. At the same time, the added method of Sn^{4+} gave an evidence that Sn^{4+} in solution played an important role rather than Sn^{4+} absorbed in the surface of catalyst. Therefore, we suggested that the suppression role of Sn^{4+} for dehalogenation reaction should result from the strong interaction between Sn^{4+} in solution and the
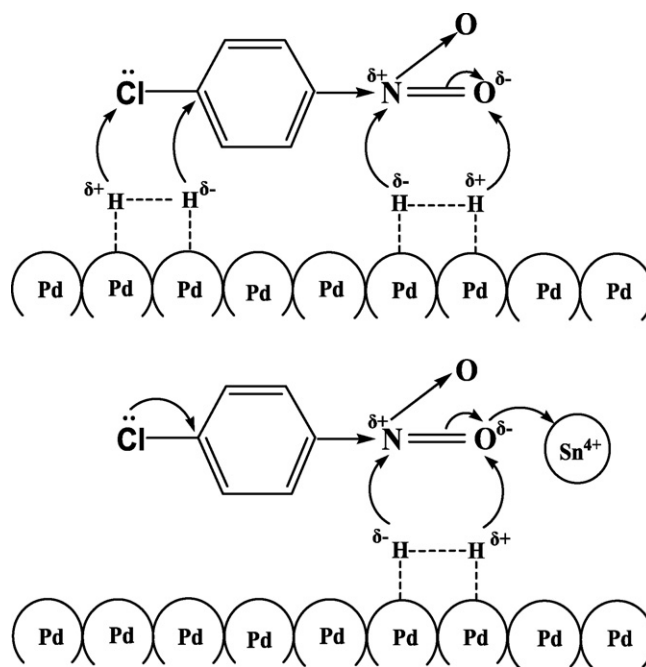

Fig. 6. Modification mechanism of Sn^{4+} ions to hydrogenation of p-CNB.

nitro group of p-CBN. Although the coordination of Sn^{4+} with $-NH_2$ can occur, the high positive charge of Sn^{4+} (hard Lewis acid) leads to that it prefers to combine with the oxygen atom (hard Lewis base) in nitro group rather than chlorine atom or nitrogen atom $-NH_2$. That the oxygen in nitro group coordinates with Sn^{4+} further increases the polarity of N=O bond. The activated dihydrogen or hydride on the surface of palladium attack easily the N=O bond polarized by Sn^{4+}. At the same time, the coordination of the nitro group in substrate molecule with Sn^{4+} enhances the electron-withdrawing ability of nitro group and induces the lone pair electron on chlorine atom transferring to phenyl ring, so that C–Cl polarity is weakened, C–Cl bond is strengthened. The both factors result in that the dehalogenation of p-CNB becomes more difficult. If the concentration of Sn^{4+} is too high, a lot of Sn^{4+} will be absorbed on the surface of catalyst and the many active centers of catalyst will be occupied, so the activity of catalyst is inhibited. According to the result in Section 3.5, the dehalogenation and the hydrogenation of nitro group proceeded simultaneously. It is consistent with a reference report [39]. The proposal mechanism was shown in Fig. 6.

4. Conclusions

The hydrogenation activity of p-CNB and the selectivity to form p-CAN over PVP-Pd/γ-Al_2O_3 were obviously promoted by the addition of Sn^{4+}. Hydrogenolysis reaction of C–Cl was completely blocked when the molar ratio of Sn^{4+} to Pd was up to 5. The modification mechanism of Sn^{4+} could be the interaction between Sn^{4+} and $-NO_2$ group of the substrate increased the polarity of N=O bond and accelerated the hydrogenation of nitro group. Because of the same reason, the polarity of C–Cl bond was decreased and the strength of C–Cl bond was increased, so that the dehalogenation reaction was greatly inhibited.

References

[1] H. Arnold, F. Dobert, J. Gaube, in: G. Ertl, H. Knozinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 5, Wiley, New York, 1997. p. 2165.

[2] K. Weissermel, H.J. Arpe, Industrial Organic Chemistry, third ed., VCH, Weinheim, 1997.

[3] P.N. Rylander, in: J.R. Anderson, M. Boudart (Eds.), Catalysis-Science and Technology, vol. 4, Akademie-Verlag, Berlin, 1993, p. 1.

[4] X.L. Yang, H.F. Liu, H. Zhong, J. Mol. Catal. A Chem. 147 (1999) 55.

[5] Z.K. Yu, S.J. Liao, Y. Xu, B. Yang, D.R. Yu, J. Mol. Catal. A Chem. 120 (1997) 247.

[6] V.R. Chandrashekhar, R.V. Chaudhari, Ind. Eng. Chem. Res. 33 (1994) 1645.

[7] B. Coq, A. Tijani, F. Figueras, J. Mol. Catal. 71 (1992) 317.

[8] B. Coq, A. Tijani, R. Dutartre, F. Figueras, J. Mol. Catal. 79 (1993) 253.

[9] X.L. Yang, H.F. Liu, Appl. Catal. A Gen. 164 (1997) 197.

[10] W.X. Tu, H.F. Liu, K.Y. Liew, J. Colloid Interface Sci. 229 (2000) 453.

[11] W.X. Tu, H.F. Liu, Y. Tang, J. Mol. Catal. A Chem. 159 (2000) 115.

[12] M.H. Liu, W.Y. Yu, H.F. Liu, J.M. Zheng, J. Colloid Interface Sci. 214 (1999) 231.

[13] M.H. Liu, W.Y. Yu, H.F. Liu, J. Mol. Catal. A Chem. 138 (1999) 295.

[14] A. Tijani, B. Coq, F. Figueras, Appl. Catal. 76 (1991) 255.

[15] E. Auer, A. Freud, M. Gross, R. Hartung, P. Panster, in: F.E. Herkes (Ed.), Catalysis of Organic Reactions, Marcel-Dekker, New York, 1998, p. 551.

[16] Z.K. Yu, S.J. Liao, Y. Xu, B. Yang, D.R. Yu, J. Chem. Soc. Chem. Commun. 11 (1995) 1155.

[17] W.Y. Yu, H.F. Liu, X.H. An, X.M. Ma, Z.J. Liu, L. Qiang, J. Mol. Catal. A Chem. 147 (1999) 73.

[18] R. Kosak, in: W.H. Jones (Ed.), Catalysis in Organic Syntheses, Academic Press, New York, 1980, pp. 107–117.

[19] B. Coq, A. Tijani, F. Figueras, J. Mol. Catal. 68 (1991) 331.

[20] Z. Yu, S. Liao, Y. Xu, B. Yang, D. Yu, J. Mol. Catal. A Chem. 120 (1997) 247.

[21] H. Greenfield, F.S. Dovell, J. Org. Chem. 32 (1967) 3670.

[22] G.C. Bond, D.E. Webster, N. Y. Acad. Sci. Ann. 158 (1969) 540.

[23] J.R. Kosak, N. Y. Acad. Sci. Ann. 172 (1970) 175.

[24] X.X. Han, R.X. Zhou, X.M. Zheng, H. Jiang, J. Mol. Catal. 193 (2003) 103.

[25] X.X. Han, R.X. Zhou, G.H. Lai, B.H. Yue, X.M. Zheng, Catal. Lett. 89 (2003) 255.

[26] U.S. 5105012, 14 April 1992.

[27] B. Coq, F. Figueras, Coord. Chem. Rev. 178–200 (1998) 1753.

[28] H.U. Blaser, U. Siegrist, H. Steiner, M. Studer, in: R.A. Sheldon, H. van Bekkum (Eds.), Fine Chemicals Through Heterogeneous Catalysis, Wiley, New York, 2001, p. 389.

[29] F. Notheisz, M. Bartok, in: R.A. Sheldon, H. van Bekkum (Eds.), Fine Chemicals Through Heterogeneous Catalysis, Wiley, New York, 2001, p. 415.

[30] Y.Z. Chen, Y.C. Chen, Appl. Catal. A Gen. 115 (1994) 45.

[31] I.A. Ilchenko, A.V. Bulatov, I.E. Uflyand, V.N. Sheinker, Kinet. Catal. 32 (1991) 691.

[32] Y. An, D. Yuan, M.Y. Huang, Y.Y. Jiang, Macromol. Symp. 80 (1994) 257.

[33] R. Frank, Ph.D. Thesis, 1999.

[34] B. Bacaud, P. Bussiere, F. Figueras, J. Catal. 69 (1981) 399.

[35] S. Galvgno, A. Donato, G. Neri, R. Pietropaolo, J. Mol. Catal. 42 (1987) 379.

[36] B.J. Zuo, Y. Wang, Q.L. Wang, J.L. Zhang, N.Z. Wu, L.D. Peng, J. Catal. 222 (2004) 493.

[37] S. Galvagno, A. Donato, G. Neri, R. Poetrpaolo, J. Mol. Catal. 42 (1987) 379.

[38] X. Han, R. Zhou, G. Lai, X. Zheng, Catal. Today 93 (2004) 433.

[39] V. Kratky, M. Kralik, M. Mecarova, M. Stolcova, L. Zalibera, M. Hronec, Appl. Catal. A Gen. 235 (2002) 225.