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Role of boron species in the hydrogenation of *o*-chloronitrobenzene over polymer-stabilized ruthenium colloidal catalysts

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Abstract

The role of boron species in selective hydrogenation of *o*-chloronitrobenzene (*o*-CNB) over polymer-stabilized ruthenium colloids has been studied. Of the two kinds of boron species (boride and borate) present in ruthenium colloids prepared by NaBH₄ reduction, it was verified that only borate had a significant effect on the hydrogenation of *o*-CNB, while boride performed as a spectator. When metal cations were added into ruthenium colloidal catalyst system as modifiers, respectively, we observed that the synergetic effect between borate and metal cations occurred in these systems. It is suggested that metal complex ions were formed between the metal cations and borate ions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogenation; Ruthenium colloid; *o*-Chloronitrobenzene; Boron species

1. Introduction

Metal catalysts-containing boron species, generally called metal boride, have been studied extensively in some reactions [1–4]. Their catalytic properties are highly dependent upon the preparation method. The activity and selectivity of NiB and CoB, for instance, can be altered significantly by varying the amount of metal-associated boron [5–7]. Paul et al. [8] first reported the use of NiB prepared from nickel salt and NaBH₄ as hydrogenation catalysts. Narasimhan's group has published several papers about mixed metal boride catalyst, Ru-Sn-B, which was prepared by reducing metal salts with NaBH₄ [9–12]. It was reported that Ru-Sn-B/Al₂O₃ performed better in selective hy-

drogenation of fatty acid esters to fatty alcohols than Ru-Sn/Al₂O₃ prepared by H₂ reduction. It had been proved that boron species incorporated via NaBH₄ reduction played an important role in enhancing the activity and selectivity in this reaction. The role of boron probably lies in changing the electron charge distribution around ruthenium, thereby enhancing its catalytic activity. Such a correlation was suggested earlier in the case of nickel boride catalysts by Schreifels et al. [13], based on X-ray photoelectron spectroscopic studies. However, there still existed different views on the role of boron species present in metal catalysts. Pouilloux [14] reported that the catalyst without boron prepared by sol-gel method performed same as the catalyst prepared by Narasimhan's method.

Nanoscope metal clusters or colloids, owing to their unique chemical and physical properties as compared to bulk metal and/or single metal atoms, have received intense attraction in academia and

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industries, especially in catalysis [15,16]. Recently, we have prepared polyvinylpyrrolidone (PVP)-stabilized ruthenium colloidal nanoclusters (designated as PVP-Ru/B) by reducing $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ with NaBH_4 in $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ mixed solvents with the presence of PVP. PVP-Ru/B was extremely high selective for *o*-CAN in the hydrogenation of *o*-CNB [17,18]. XPS characterization showed that two kinds of boron species were present in PVP-Ru/B, i.e. boride and borate [17]. Role of boron species was once reported on the basis of the different catalytic performance between PVP-Ru/B and PVP-Ru colloids prepared by H_2 reduction [18], however the particle dimension of those catalysts was totally different from each other. In present study, we have succeeded in preparing PVP-Ru colloid by polyol reduction under microwave irradiation, the newly prepared PVP-Ru was free of boron with particle dimension similar to PVP-Ru/B [19]. As reported in literatures [9,10,17], borate species incorporated in supported catalyst was hard to be thoroughly washed out owing to the strong adsorption ability of inorganic support, so it is difficult to clarify which boron species affect the performance of boron-containing metal catalysts. On the contrary, borate species present in Ru colloid dispersion can be easily removed via ultra-filtration and successive wash with distilled water. Thus, PVP-stabilized ruthenium colloid system can serve as a good model to investigate the effect of boron species on the catalytic performance of boron-containing metal catalysts.

2. Experimental

2.1. Materials and instruments

Ruthenium chloride hydrate ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$) was used as purchased. PVP (average MW 40,000) was purchased from Fluka Co. Sodium borohydride (NaBH_4) was purchased from Sigma Co. Hydrogen gas (H_2) with a purity of 99.999% was supplied by Beijing Gases Factory. *o*-CNB was re-crystallized in 95% ethanol before use. Other analytical reagents were supplied by Beijing Chemicals.

Transmission electron microscopy (TEM) photographs were taken by using a Hitachi-9000NAR electron microscope. TEM samples were prepared by

placing a drop of colloid dispersion onto a copper grid covered with a perforated carbon film, followed by natural evaporation of solvent. The average particle diameter and standard deviation were calculated by counting about 250 particles from the enlarged photographs. UV–VIS spectrum was recorded on a TU-1201 UV–VIS recording spectrophotometer.

2.2. Preparation of polymer-stabilized ruthenium colloids

PVP-Ru/B was prepared as described in literature [17]. For the sake of comparison, PVP-Ru/B colloidal dispersion was ultra-filtered, washed with distilled water for several times until the final filtrate was free from Cl^- by AgCl test, the resultant colloids were designated as PVP-Ru/B'. The ruthenium colloids without boron were prepared by ethylene glycol reduction as reported in literature [19] and were designated as PVP-Ru.

All colloids were generally dried by rotary evaporation and re-dispersed in methanol prior to use.

2.3. Chemical analysis

Chemical composition of the catalysts was analyzed by means of inductively coupled plasma optical emission spectroscopy (ICP) (Spex 1702 scanning ICP spectrometer). Chloride content was determined by silver chloride. The solid sample was prepared by evaporating solvent via rotary evaporation under vacuum at 308 K.

2.4. X-ray photoelectron spectroscopy (XPS) measurements

XPS spectra were recorded with an ESCALAB 220I-XL (VG) photoelectron spectrometer using monochromatic Mg $\text{K}\alpha$ X-ray (1253.6 eV). Binding energy referred to C 1s (285.0 eV).

XPS sample for PVP-Ru/B was prepared by immobilization of PVP-Ru/B colloidal dispersions via a reported method [20,21], followed by successive wash with distilled water and dried under vacuum. XPS sample for PVP-Ru/B' was prepared by ultra-filtration and successive wash of PVP-Ru/B, followed by immobilization of the resultant PVP-Ru/B' colloidal dispersion via the same method.

Caution: care should be taken to prevent explosion of the dry boron-containing sample prepared by NaBH_4 reduction in air, which was reported by Cusumano [22].

2.5. Catalytic tests

Hydrogenation of *o*-CNB was carried out in a 100 ml stainless autoclave with a Teflon tube to avoid metal contamination. The reaction solution contained 1.0 mmol substrate, 0.125 g *n*-decanol (as GC internal standard), and 8.0 ml ruthenium colloid dispersion (containing 1.82×10^{-5} mol Ru). Total reaction solution volume was 15.0 ml, methanol as a solvent. The reaction vessel was replaced three times with high purity hydrogen gas and finally was kept H_2 pressure of 4.0 MPa at 320 K. The reaction mixture was stirred vigorously for a certain 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

3.1. Characterization of PVP-stabilized ruthenium colloids

TEM measurement is a useful method by which the colloid particle size and size distribution can be directly revealed. As exhibited in Fig. 1, PVP-Ru/B colloid and PVP-Ru colloid are of similar size and size distribution, with particle dimension 1.35 ± 0.45 and 1.40 ± 0.48 nm, respectively.

XPS spectra (Ru $3d_{5/2}$ at 280.2 eV, Ru $3p_{1/2}$ and Ru $3p_{3/2}$ at 484.1 and 462.0 eV, respectively) of PVP-Ru/B verified that the ruthenium particles were in a zero oxidation state in accordance with the literature [23]. As shown in Fig. 2, B 1s spectrum of PVP-Ru/B showed two signals at 188.1 and 192.3 eV, the former is assigned to boride (B^{3-}), while the latter corresponds to borate (B^{3+}) [5,9,17,24]. However, B 1s spectrum of PVP-Ru/B' only showed one signal at 188.1 eV, i.e. ruthenium-associated boron, namely boride. From the XPS results, we confirmed that borate produced from NaBH_4 reduction can be thoroughly removed from Ru colloid catalysts via ultra-filtration and successive wash with dis-

tilled water. Furthermore, the boride content on the PVP-Ru/B' surface can be determined by XPS measurement, thereby the atomic ratio of B to Ru = 0.066:1.

Table 1 lists the chemical composition of the PVP-Ru/B and PVP-Ru/B' colloidal catalysts analyzed by ICP. The data in Table 1 clearly show that PVP-Ru/B' is free of Na^+ , Cl^- , and very little amount of boron species, i.e. boride as demonstrated by XPS. The atomic ratio of B in boride to Ru = 0.067:1, which is very close to the surface concentration determined from XPS measurement. This result also implied that boron atoms in boride are homogeneously dispersed in the ruthenium colloidal particles.

3.2. Role of boron species in the hydrogenation of *o*-CNB

The time-course of *o*-CNB over PVP-Ru/B and PVP-Ru were investigated. As shown in Fig. 3, the conversion of *o*-CNB over both kinds of ruthenium colloids increases linearly with time, showing a zero order with respect to the concentration of *o*-CNB, which is in agreement with the literature [18]. However, it was obviously shown that the average reaction rate of *o*-CNB over PVP-Ru/B was about two-fold of that over PVP-Ru. Meanwhile, both catalysts have high selectivity to *o*-CAN as demonstrated by GC. As PVP-Ru/B and PVP-Ru colloids are of similar particle size and size distribution, size effect on the catalytic performance can be ruled out. Furthermore, Na^+ and Cl^- have been proved to be spectator ions in present work (entry seven in Table 2) and former works [25,26]. On the basis of above facts, we presumed that the difference in activity between both ruthenium colloids might be attributed to the effect of boron species.

To clarify which boron species played the role in enhancing the reaction rate, hydrogenation of *o*-CNB over PVP-Ru/B, PVP-Ru/B' as well as PVP-Ru were conducted. As shown in the Table 2, the activity of PVP-Ru/B (entry two) was about two times that of PVP-Ru/B' (entry three) while PVP-Ru/B' performed nearly same as PVP-Ru (entry one) did, although PVP-Ru/B' contained a definite amount of boride. It revealed that borate in PVP-Ru/B dispersion can promote the reaction rate, while boride associated

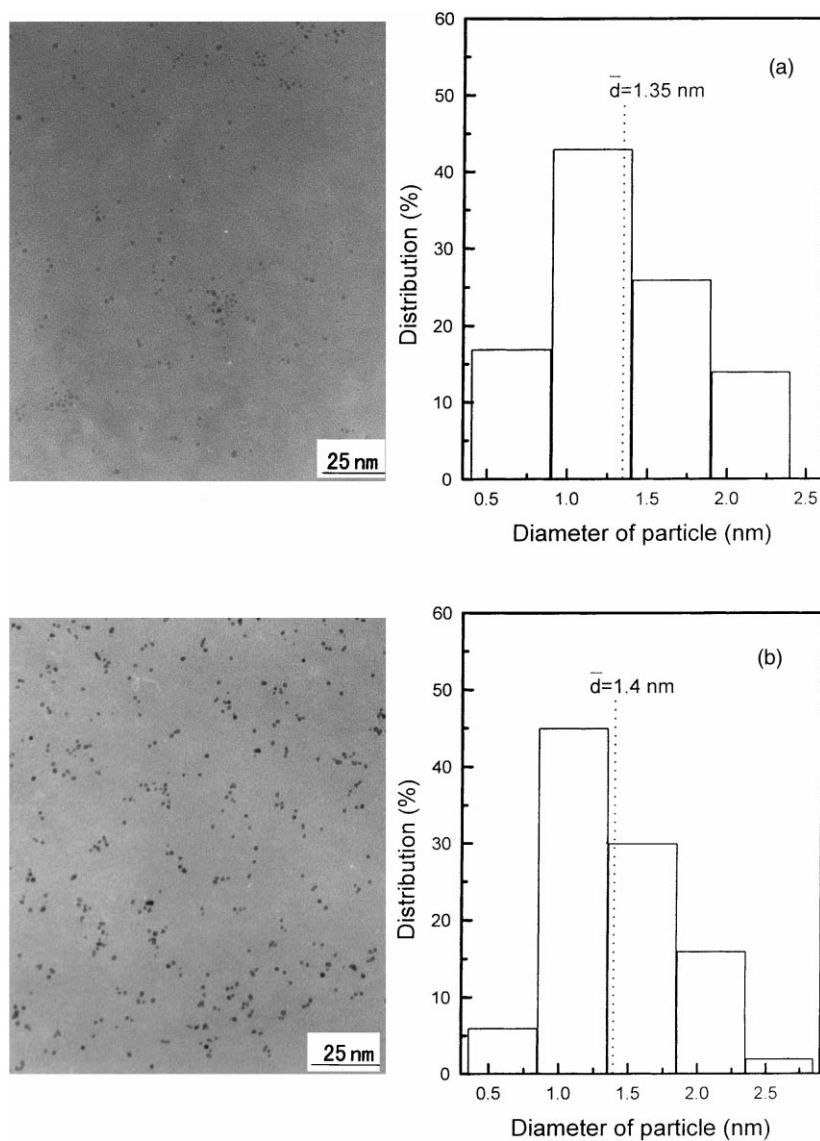


Fig. 1. TEM photographs (left) with the corresponding particle size histograms (right) of the ruthenium colloidal clusters: (a) PVP-Ru/B; (b) PVP-Ru.

with ruthenium had no effect on the hydrogenation of *o*-CNB. This can be further verified by adding 4.55×10^{-5} mol of $\text{Na}_2\text{B}_4\text{O}_7$ into PVP-Ru/B' or PVP-Ru catalyst system, whereas the boron content in $\text{Na}_2\text{B}_4\text{O}_7$ was equivalent to that in PVP-Ru/B. As a result, the activity of the $\text{Na}_2\text{B}_4\text{O}_7$ -modified PVP-Ru/B' (entry four) or $\text{Na}_2\text{B}_4\text{O}_7$ -modified PVP-Ru (entry five) resembles that of PVP-Ru/B (entry two). Fur-

thermore, filtrate resulted from the preparation of PVP-Ru/B' were dried via rotary evaporation. The activity of PVP-Ru increased and closely reached that of PVP-Ru/B after the solid residue was added into PVP-Ru catalytic system as additives (entry six). It can be deduced that borate caused the rate enhancement. Borate ions (such as $\text{B}_4\text{O}_7^{2-}$ etc.) are inorganic ligand, so the rate enhancement may

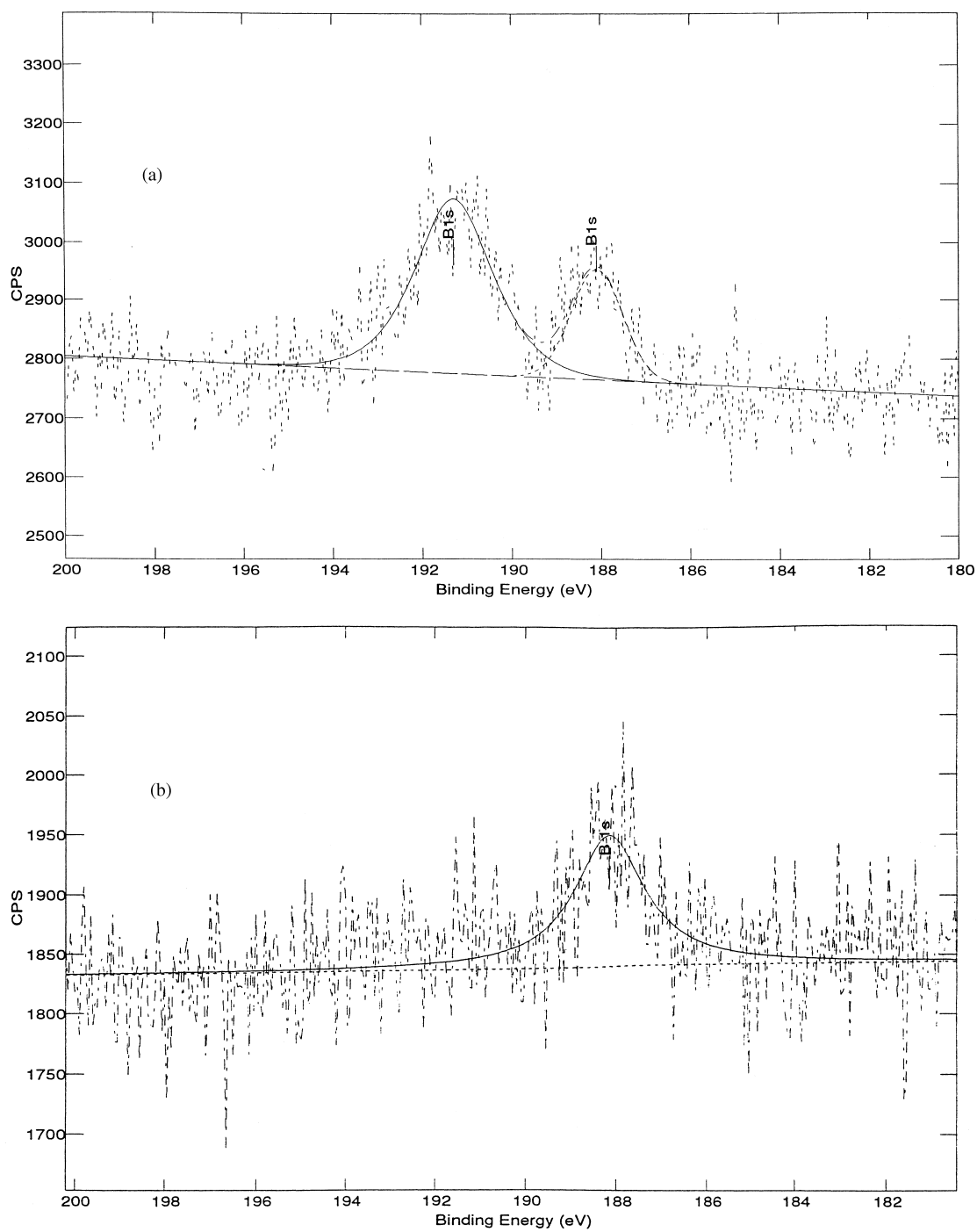


Fig. 2. X-ray photoelectron spectra of B 1s of PVP-Ru/B (a) and PVP-Ru/B' (b) colloids. The molar ratio of NaBH_4 to Ru^{3+} used in preparation = 10:1.

Table 1
Chemical composition of ruthenium colloid catalyst^a

Catalyst	Composition (wt. %)			
	Ru	B	Na	Cl
PVP-Ru/B	1.64	1.74	3.70	1.72
PVP-Ru/B'	2.37	0.018	0	0

^a Catalyst preparation condition: PVP/Ru = 50:1, NaBH₄/Ru = 10:1 (molar ratio).

be attributed to the “ligand acceleration effect” [27,28]. As both boron species always exist in supported metal catalyst, we presumed that the role of boron formerly reported might mainly be caused by borate.

3.3. Role of borate in the presence of metal cations

We once observed that the activity of PVP-Ru/B could be obviously enhanced by adding some metal cations into the system [18]. However, in present study, we do not find the same phenomenon in PVP-Ru/B' system, so we suspected that borate present in PVP-Ru/B may influence the metal cation effect. As shown in Fig. 4, curve ‘a’ showed that metal cations added in PVP-Ru/B system promoted the hydrogenation of *o*-CNB to different extents, except that Zn²⁺ and Sn²⁺ slightly inhibited the reaction. Curve ‘b’ exhibited that all selected metal cations did not promote the reaction over PVP-Ru/B' catalyst, some cations (such as Cr³⁺, Mn²⁺, Ni²⁺

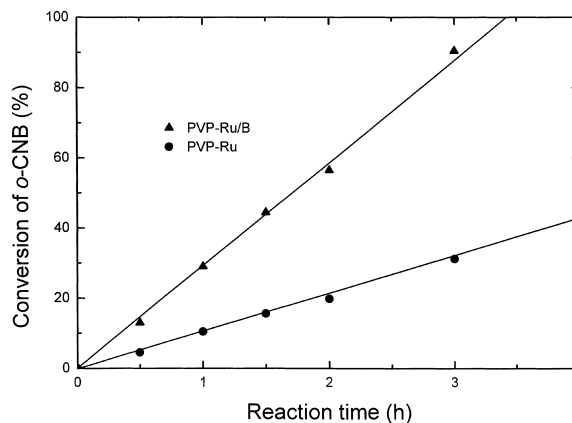


Fig. 3. Conversion of *o*-CNB over different ruthenium colloids as a function vs. reaction time.

etc.) even inhibited the hydrogenation. Interestingly, when adding 4.55×10^{-5} mol of Na₂B₄O₇ into PVP-Ru/B' colloid system to keep the molar ratio of B to Ru of 10:1, the promotion effect of metal cations was recovered with the tendency similar to the case of PVP-Ru/B (see curve ‘c’, Fig. 4). Here, Na₂B₄O₇ substituted for borate in PVP-Ru/B colloid dispersion. On the basis of above results, we confirmed that a synergetic effect between borate and metal cations occurred. Formerly, metal complex effect had been observed in Pt and Ru cluster systems [29–31], we suspected that complex ions formed between metal cations and borate in the reaction solution.

Table 2
The influence of boron species present in Ru colloids on hydrogenation of *o*-CNB^a

Entry	Catalyst system	Average rate ($\times 10^4$) (mol H ₂ /mol Ru s)	Conversion (%) ^b	Selectivity for <i>o</i> -CAN (%)
1	PVP-Ru	1.16	21.0 (120)	>99.9
2	PVP-Ru/B	2.53 \pm 0.22	48.8 (120)	>99.9
3	PVP-Ru/B'	1.18	21.3 (120)	>99.9
4	PVP-Ru/B'-Na ₂ B ₄ O ₇ ^c	2.75	53.0 (120)	>99.9
5	PVP-Ru-Na ₂ B ₄ O ₇ ^c	2.5	48.1 (120)	>99.9
6	PVP-Ru-borate ^d	2.8	54.1 (120)	>99.9
7	PVP-Ru-NaCl ^e	1.13	20.5 (120)	>99.9

^a Reaction condition was described in experimental section. Ru colloid preparation condition was shown in Table 1.

^b Data in parentheses stand for the reaction time in minutes.

^c An amount of 4.55×10^{-5} mol of Na₂B₄O₇ was added to the catalyst system, where the molar ratio of B to Ru was 10:1.

^d Filtrate resulted from preparation of PVP-Ru/B' was added into PVP-Ru colloid system after being dried and being re-dissolved in methanol.

^e An amount of 9.1×10^{-5} mol of NaCl was added into PVP-Ru catalyst system.

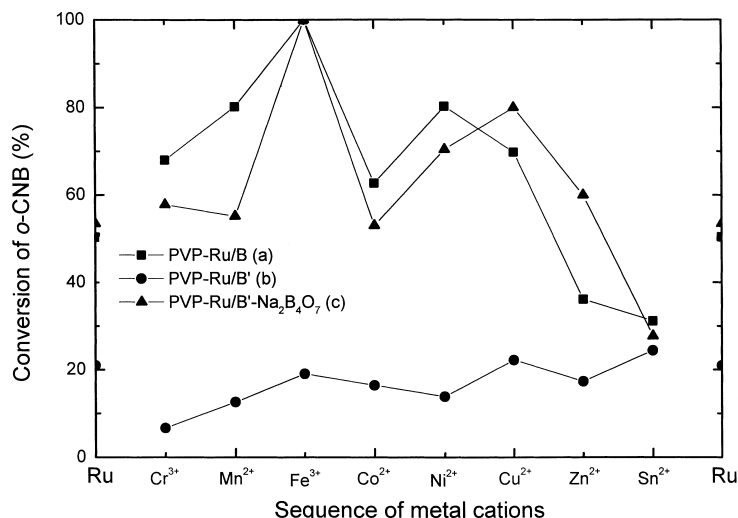


Fig. 4. Influence of borate on the hydrogenation of *o*-CNB over different ruthenium colloids in the presence of metal cations.

UV–VIS spectra further confirmed the coordination between metal cations and ligands [32,33]. As shown in Fig. 5, an absorption peak occurred at 528 nm for the methanol solution of CoCl₂, however for the mixed solution of Na₂B₄O₇ and CoCl₂ in methanol, the peak shifted to 541 nm and the peak grew wider than the former. This result indicated that there existed interaction between Co²⁺ and borate. In addition, yellow crys-

talline precipitate was observed in the concentrated mixed solution of Na₂B₄O₇ and Co²⁺ after standing for several minutes. The precipitate was examined to contain both Co and B (molar ratio of Co:B = 1:1.03 determined by ICP) after being thoroughly washed by ethanol. Based on these facts, we reached a conclusion that Co(II) complex of borate was formed in this reaction system. Therefore, it was the metal

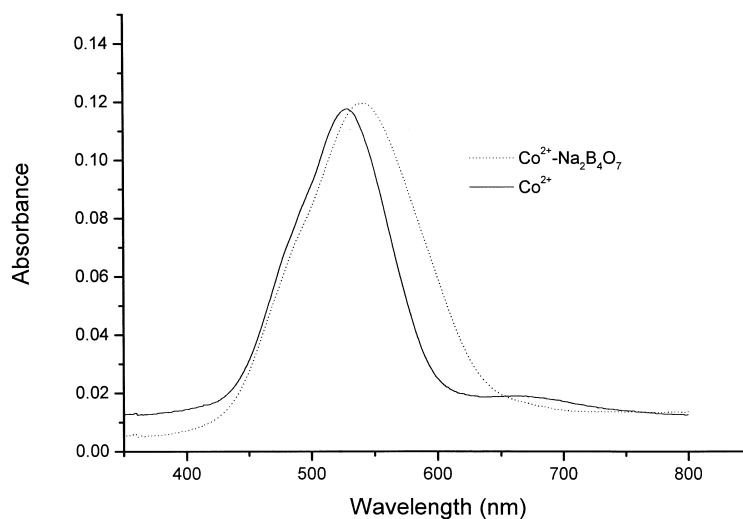


Fig. 5. UV–VIS spectra of Co²⁺ (solid) and Co²⁺–Na₂B₄O₇ (dot) in methanol (Co²⁺/B = 1:4 in molar ratio).

Table 3

Influence of Na₂B₄O₇ on hydrogenation of *o*-CNB over PVP-Ru in the presence of metal cations^a

Entry	Catalyst system	Conversion (%)	Selectivity for <i>o</i> -CAN (%)
1	PVP-Ru	21.0	>99.9
2	PVP-Ru-Fe ³⁺	19.5	>99.9
3	PVP-Ru-Cu ²⁺	3.54	>99.9
4	PVP-Ru-Na ₂ B ₄ O ₇ ^b	48.1	>99.9
5	PVP-Ru-Na ₂ B ₄ O ₇ -Fe ³⁺ ^b	100	>99.9
6	PVP-Ru-Na ₂ B ₄ O ₇ -Cu ²⁺ ^b	72.0	>99.9

^a Reaction condition was described in experimental section, reaction time is 2 h, Mⁿ⁺/Ru = 1:1.

^b An amount of 4.55 × 10⁻⁵ mol of Na₂B₄O₇ was added to the catalyst system, where B/Ru = 10:1 (molar ratio).

complex of borate that really enhanced the reaction rate.

Furthermore, the role of borate added in PVP-Ru colloidal dispersion was also investigated in the presence of metal cations. As shown in Table 3, Fe³⁺ and Cu²⁺ both inhibited the reaction and acted as poisons for the PVP-Ru system. However, when 4.55 × 10⁻⁵ mol Na₂B₄O₇ (molar ratio of B to Ru = 10:1) was added into PVP-Ru in the presence of Fe³⁺ or Cu²⁺, the conversion of *o*-CNB was considerably enhanced. Since there is no any boron species present in PVP-Ru system, the above results have further proved that the promotion effect of metal cations on the hydrogenation of *o*-CNB over PVP-Ru exclusively resulted from the metal complex effect.

4. Summary

As a model of supported metal catalyst, the catalytic performance of polymer-stabilized ruthenium colloids was studied to clarify the role of boron in hydrogenation of *o*-CNB.

The boron species present in PVP-Ru/B do affect the catalytic performance of the catalyst system. For both of the boron species, only the oxidized product (borate) exhibited a remarkable promotion effect on the reaction rate.

In the presence of metal cations, it was demonstrated that the metal complexes of borate formed in the catalytic system played a decisive role for the rate enhancement.

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