

RESEARCH NOTE

The Effect of Boron on Selective Benzene Hydrogenation to Cyclohexene over Ruthenium Boride Powders

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The partial hydrogenation of benzene to cyclohexene is of great synthetic and industrial interest (1). Since the first benzene-selective hydrogenation of an Ni film was reported in 1957 (2), various catalysts have been designed to improve the hydrogenation selectivity (3–5). Among them, the Ru-based catalysts, such as Ru powder, Ru black, and Ru powder deposited onto a support, have been studied thoroughly, and many require high-temperature activation and/or reduction. Non-heat-treated catalysts may be expected to have different catalytic properties. In recent years, chemically prepared amorphous metal–boride powders have attracted much attention due to the combination of their ultrafine size and amorphous structure, which can lead to potential applications (6–8). Obviously, the properties of the powders will mainly be determined by the atomic ratio of metal to boron, so much effort has been devoted to preparing such metal borides as CoB, NiB, and FeB with a widest possible composition range by altering preparation conditions (7–11). However, comparatively few studies (12, 13) have been carried out concerning the preparation aspects of ruthenium–boride (Ru–B). It has been reported that the temperature, which will greatly affect the nucleation conditions, and thereby the composition of the metal borides, is a very important factor in the preparation of metal borides (10). In this work, the regulation of boron content over a wider range through altering preparation temperature is reported. In a previous paper (13), it was demonstrated that ruthenium boride catalysts are highly selective in the partial hydrogenation of benzene to cyclohexene compared with catalysts without boron. Evidently, the high selectivity toward cyclohexene is related to the boron associated with ruthenium. To further understand the promotional effect of boron on the benzene-selective hydrogenation to cyclohexene, the dependence of cyclohexene selectivity on the ruthenium-associated boron is also reported in this study.

The amorphous Ru–B powders were prepared by dropwise addition of 0.1 mol dm⁻³ aq. RuCl₃ (15 ml) to 1 mol

dm⁻³ KBH₄ (10 ml) within about 5 min under strong agitation at -7, 1, 8, 19, 30, and 40°C. The black precipitate was washed thoroughly with a large amount of distilled water, followed by an ethanol rinse, and soaked in 99% ethanol for the characterization and activity test. The ruthenium metal without boron was also prepared by complete reduction of ruthenium trichloride in flowing hydrogen at 673 K, and XRD measurement confirmed that the sample as prepared is crystalline ruthenium metal.

The X-ray diffraction (XRD) patterns were collected by a Rigaku Dmax-3C powder diffractometer using Ni-filtered Cu K α radiation (0.15418 nm). The X-ray tube was operated at 35 kV and 20 mA. BET surface areas were measured by nitrogen adsorption at 77 K on a Micrometrics ASAP-2000 adsorption apparatus. Hydrogen chemisorption measurements were carried out at room temperature in a TPR/TPD 2900 Micromeritics apparatus. The number of exposed metal sites was evaluated using a pulse method, and assuming H/Ru = 1 (14). Prior to the measurement, the samples were pretreated *in situ* at 573 K in a flow of Ar for 2 h. The results of X-ray photoelectron spectroscopy (XPS) were obtained on a VG ESCALAB MKII photoelectron spectrometer using Mg K α radiation (10 kV and 30 mA). The base pressure in the analyzing chamber was maintained on the order of 10⁻⁹ Torr. The spectrometer was operated at 20 eV pass energy. The sample was mounted quickly onto a grid attached to a sample holder in the pretreatment chamber, keeping the powder soaked in 99% ethanol to minimize the oxidation of the powder by air. After evacuating the ethanol, the sample was transferred *in situ* to the analyzing chamber. Quantification of the XPS spectra was carried out taking the peak area ratios of Ru 3d_{5/2} and B 1s. The areas were estimated by resolving the curves, assuming Gaussian peak shapes, and were corrected using cross sections reported by Scofield (15).

The selective hydrogenation of benzene over amorphous Ru–B powders was carried out in a 500-ml stainless autoclave with a magnetic stirrer. After 1.5 g ZnSO₄ · 7H₂O was dissolved in 100 ml distilled water, the as-prepared Ru–B

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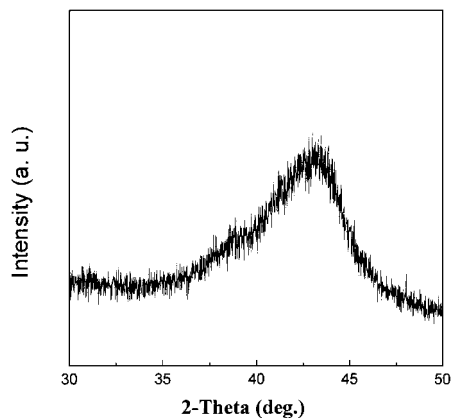


FIG. 1. XRD pattern of an Ru-B powder reduced at a temperature of 8°C by KBH_4 solution.

powder and 35 ml benzene were introduced. Then the autoclave was sealed and filled with H_2 more than three times to exclude air. The final reaction conditions were 423 K, 4.0 MPa of hydrogen pressure, and 1000 rpm stirring rate to exclude diffusion effects. The reaction process was monitored by taking small amounts of the reaction mixture at intervals and carrying out gas chromatograph analysis on an instrument equipped with a TCD detector.

Figure 1 shows the XRD pattern of a typical Ru-B powder sample. A broad peak centered at 2θ ca. 43° can be observed for all ruthenium boride samples. It is assigned to the amorphous state of the ruthenium-metalloid alloy (13). No distinct peaks corresponding to a crystalline phase of Ru were seen in the patterns.

Figure 2 is the Ru $3d$ spectrum of this sample and similar results can be obtained from the other samples. The results of XPS measurements show the two peaks corresponding to Ru $3d_{5/2}$ and Ru $3d_{3/2}$, respectively. Since the peak of Ru $3d_{3/2}$ overlaps with the C $1s$ peak, only the peak of

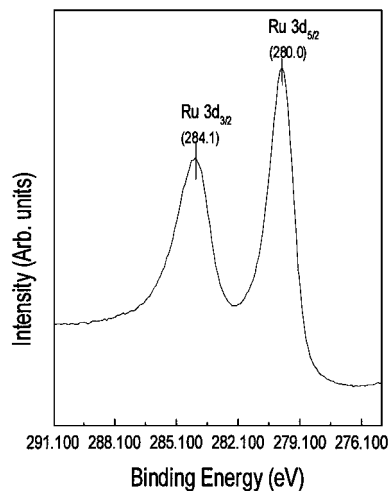


FIG. 2. XPS spectra of Ru $3d$ for an Ru-B sample reduced at a temperature of 8°C by KBH_4 solution.

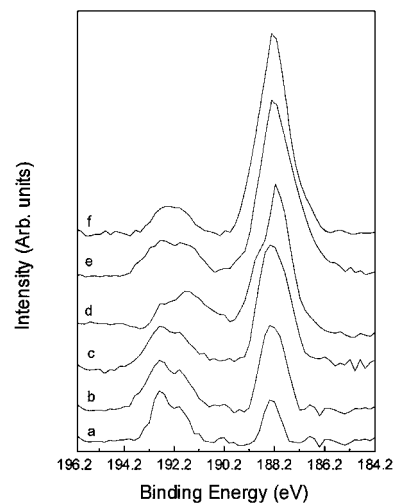


FIG. 3. XPS spectra of B $1s$ for the Ru-B powders reduced at different temperatures ($^\circ\text{C}$): (a) -7 , (b) 1 , (c) 8 , (d) 19 , (e) 30 , and (f) 40 .

Ru $3d_{5/2}$ is employed during the discussion. It is indicated from the XPS analysis of ruthenium borides that almost all the ruthenium species exist in the elementary state with the binding energy (BE) of 280.0 eV, which is in accordance with the assignment in the literature (12). Figure 3 compares the B $1s$ spectra of the amorphous Ru-B powders. As shown in this figure, the two kinds of signals whose BE values fall in the range 188.2–188.6 and 191.8–193.6 eV, respectively, exist in the B $1s$ spectrum of all these Ru-B powders. The former is ascribed to elementary boron associated with ruthenium as ruthenium boride, in line with literature assignments on NiB, CoB, PtB, and PdB catalysts (16–18), while the latter, on wet fresh Ru-B powder, mainly corresponds to borate (B^{3+}) species resulting from hydrolysis of potassium borohydride (12, 19). With regard to the elementary boron in the ruthenium borides, the binding energy as compared to its standard BE value (186.5–187.0 eV) (11) is positively shifted to 188.2–188.6 eV, as presented in Table 1. This indicates that the electron densities of ruthenium in these samples are increased by electron donation

TABLE 1
B $1s$ Binding Energies and Surface Compositions
of Ru-B Powders

Sample no.	Preparation temperature ($^\circ\text{C}$)	B $1s^a$ (eV)	Surface composition ^b (atomic ratio)
1	-7	188.5	$\text{Ru}_{98.1}\text{B}_{1.9}$
2	1	188.4	$\text{Ru}_{95.8}\text{B}_{4.2}$
3	8	188.4	$\text{Ru}_{93.3}\text{B}_{6.7}$
4	19	188.2	$\text{Ru}_{91.6}\text{B}_{8.4}$
5	30	188.5	$\text{Ru}_{89.9}\text{B}_{10.1}$
6	40	188.6	$\text{Ru}_{90.1}\text{B}_{9.9}$

^a The error in the binding energy measurements is ± 0.2 eV.

^b The content of oxidative metalloid species is subtracted from the surface content of metalloid.

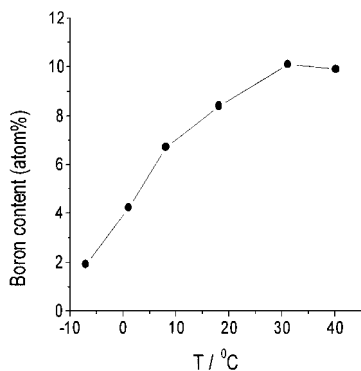


FIG. 4. Dependence of elementary boron content on reduction temperature for amorphous Ru-B powders.

from boron to ruthenium just as considered in the other metal borides (11, 16, 19). It is noteworthy that the intensity of signal corresponding to the elementary boron increases significantly with the increase of the prepared temperature of samples, whereas there seems to be very little change for that of the signals assigned to B^{3+} species. No appreciable change in the intensities of two signals can be observed as the chemical reduction temperature of samples is elevated to 30°C. The spectral changes may suggest that the boron content for amorphous Ru-B powders can be regulated over a wide range by altering the preparation temperature. Listed in Table 1 are the surface compositions estimated from the quantitative XPS analysis, in which the content of oxidized metalloid species is subtracted from the content of metalloid. According to these data, the temperature dependence of the contents of the elementary boron associated with ruthenium is shown in Fig. 4. It is evident from this plot that the content of the elementary boron is dependent on the preparation temperature of samples at least in the range -7 –30°C. On increasing the reaction temperature from -7 to 30°C, the content of elementary

boron increases from 1.9 to 10.1 atom% correspondingly, as such changed the catalytic property of the as-prepared ruthenium boride powders.

Reported in Table 2 are the activities for the selective hydrogenation of benzene. Additionally, the BET surface area and number of active ruthenium sites in the surface of the ruthenium-boride powders, as well as for a pure Ru, are also given. As shown in this table, the conversions of benzene increase from 21.0 to 56.3% with the increase of boron content from 0 to 10.1%, and on the other hand, no distinct difference can be found in the reaction rate of benzene ($\text{mol/s/m}_{\text{cat}}^2$). The interpretation of this behavior can be made by considering the surface areas and the number of surface metal sites which also increase with the increase of boron content. Therefore, the reaction rates of these samples are similar. The most representative value of catalyst activities is turnover frequency (TOF), which here is expressed as the number of benzene molecules converted per second and per surface metal site. It can be seen from Table 2 that in the case of these Ru-B powders, the turnover frequency does not change much with the alternation of the boron content, which can be considered practically constant. However, it is noted that the TOF of the pure ruthenium is greater than that of the amorphous ruthenium-boron powder.

Table 3 shows the maximum cyclohexene yields and the concomitant benzene conversions, as well as the selectivities for cyclohexene observed in the reactions of benzene-selective hydrogenation to cyclohexene over the ruthenium-boride powders with the different boron contents. It can be seen from the data in Table 3 that by varying the amount of ruthenium-associated boron from 0 to 10.1 atom%, the cyclohexene yield can be enhanced significantly from 6.3 to 30.4 mol%, and the selectivity increased from 19.4 to 50.8%. It is clear from these results that the elementary boron associated with Ru effectively promotes the yield and selectivity toward cyclohexene. In a word, the

TABLE 2

Catalytic Activity of Benzene Hydrogenation over Ru-B Powders and a Pure Ru^a

Run no.	Composition	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Number of Ru sites ($\text{g}_{\text{cat}}^{-1} \times 10^{-19}$)	Catalytic activities ^b		
				Conversion (%)	Rate $\times 10^5$ ($\text{mol s}^{-1} \text{m}_{\text{cat}}^{-2}$)	TOF (s^{-1})
1	Pure Ru	5.3	1.04	21.0	2.87	8.79
2	Ru _{98.1} B _{1.9}	10.3	3.63	28.7	2.02	3.45
3	Ru _{95.8} B _{4.2}	11.4	4.32	34.9	2.22	3.52
4	Ru _{93.3} B _{6.7}	15.1	5.68	37.0	1.77	2.84
5	Ru _{91.6} B _{8.4}	16.2	6.98	41.8	1.88	2.63
6	Ru _{89.9} B _{10.1}	17.0	8.42	50.9	2.18	2.65
7	Ru _{90.1} B _{9.9}	17.8	9.12	56.1	2.28	2.68

^a Reaction conditions: benzene (35 ml), water (100 ml), Ru-B powder (0.15 g), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (1.5 g), reaction temperature 423 K, reaction pressure 4 MPa.

^b Measured at reaction time 1 h.

TABLE 3

The Influence of B Content on the Yield and Selectivity of Selective Benzene Hydrogenation to Cyclohexene^a

Run no.	Composition	Reaction time (min)	Cyclohexene yield ^b (mol%)	Benzene conversion (%)	Cyclohexene selectivity (%)
1	Pure Ru	90	6.3	32.5	19.4
2	Ru _{98.1} B _{1.9}	55	7.1	28.1	25.3
3	Ru _{95.8} B _{4.2}	65	13.7	40.8	33.6
4	Ru _{93.3} B _{6.7}	85	21.7	55.7	39.0
5	Ru _{91.6} B _{8.4}	85	27.4	60.4	45.4
6	Ru _{89.9} B _{10.1}	75	30.4	59.9	50.8
7	Ru _{90.1} B _{9.9}	70	31.2	61.1	51.1

^a Reaction conditions are the same as those in Table 2.

^b The maximum cyclohexene yield in each run.

activity and selectivity of ruthenium borides for cyclohexene can be altered significantly by varying the amount of ruthenium-associated boron.

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