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ARTICLE

Preparation of Ru-[bmim]BF_4 Catalyst Using $NaBH_4$ as Reducing Agent and Its Performance in Selective Hydrogenation of Benzene

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Abstract: A Ru-[bmim]BF_4 catalyst was prepared in a mixture of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) and H_2O using $NaBH_4$ as a reducing agent. The Ru-[bmim]BF_4 catalyst showed higher selectivity for cyclohexene than a catalyst reduced by $N_2H_4 \cdot H_2O$ because of the influence of boron. When Ru-[bmim]BF_4 was reused, higher activity and lower selectivity were obtained because the number of Ru active sites increased through leaching of the ionic liquid. The used catalyst also contained ZnOHF formed in the reaction between F^- and $ZnSO_4$, which was an additive in the reaction. Under the influence of the ionic liquid as a template, ZnOHF grew along the (001) direction and exhibited rod-like morphology.

Key words: ruthenium; 1-butyl-3-methylimidazolium tetrafluoroborate; sodium borohydride; zinc hydroxyfluoride; benzene; selective hydrogenation

Selective hydrogenation of benzene is a way to produce cyclohexene and has been the focus of both industrial and academic researchers because of its atom economy and inexpensive raw materials [1–6]. However, cyclohexane is more readily obtained during hydrogenation of benzene than cyclohexene. To increase the selectivity for cyclohexene, Ru-based catalysts as well as H_2O are used. $ZnSO_4$ is also added to increase the hydrophilicity of the catalyst. This limits readsorption of cyclohexene onto the catalyst surface through its low solubility in H_2O. As a result, further hydrogenation is prohibited and the selectivity for cyclohexene increases.

In recent years, ionic liquids (ILs), as a novel kind of solvent, medium and catalyst, have been widely used in organic synthesis, catalysis, extraction, and material preparation. ILs are expected to act as an effective reaction medium or additive in selective hydrogenation of benzene. Rossi et al. [2] prepared Ru(0) nanoparticles from a RuO_2 precursor in imidazolium IL 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) for selective hydrogenation of benzene. The cyclohexene (65%) was obtained when benzene conversion was only 0.3%. Silveira et al. [3] and Liu et al. [4] prepared Ru-based catalysts in ILs [bmim]PF_6 and [beim]Cl, respectively. However, cyclohexene was only obtained with high selectivity at low rates of conversion. Schwab et al. [5] investigated the influence of several kinds of ILs as additives on the selective hydrogenation of benzene. They indicated that some ILs, such as [B3MPyr][DCA], could enhance the hydrophilicity of the Ru catalyst and adsorb onto its surface. This reduced the catalytic activity of Ru, allowing more cyclohexene to be obtained. However, they also observed that high selectivity for cyclohexene of ~60% appeared only in the initial stage of the reaction; in other words, at low benzene conversion. When hydrogenation was continued, the obtained cyclohexene could be readsorbed onto the Ru active sites and further hydrogenated to cyclohexane.

We prepared Ru-[bmim]BF_4 catalyst in a mixture of [bmim]BF_4 and H_2O using $N_2H_4 \cdot H_2O$ as a reductant [6]. Over this catalyst, 12.2% benzene was converted into cyclohexene

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with a selectivity of 40.5%. It was also found that a Ru-carbene metal complex formed through the interaction between imidazolium cations and Ru particles under alkaline conditions. Although the abovementioned Ru-[bmim]BF_4 catalyst achieved better results than other analogous catalysts [2–5], it was unable to match the performance of traditional Ru-Zn catalysts. There are a number of possible ways to improve the catalytic performance of Ru-[bmim]BF_4 that require further investigation.

Sun et al. [7] prepared Ru-Fe-B/ZrO_2 for selective hydrogenation of benzene using $NaBH_4$ as a reductant. They achieved a selectivity for cyclohexene of up to 80% after 54% benzene conversion. The high selectivity for cyclohexene was attributed to the boron in the catalyst. In this paper, a Ru catalyst was prepared in a mixture of [bmim]BF_4 and H_2O using $NaBH_4$ as a reductant. The performance of the resulting catalyst for selective hydrogenation of benzene is determined, and the change of the catalyst during the reaction is also discussed.

Ru-[bmim]BF_4 catalyst was prepared in a similar manner to that described in the literature [6] using $NaBH_4$ as a reductant instead of $N_2H_4\cdot H_2O$. A molar ratio of $NaBH_4$ to Ru of 10:1 was used. The obtained catalyst had a Ru content of 10 wt% and was named Ru-[bmim]BF_4-II. The Ru-[bmim]BF_4-II catalyst was washed thoroughly with ethanol and double distilled H_2O, and then dried at 80 °C for 12 h.

X-ray diffraction (XRD) was carried out using a Rigaku D/Max-2500 X-ray diffractometer and Cu K_α radiation at 40 kV and 100 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed with a PE PHI-1600 spectrometer with a Mg K_α source (1253.6 eV). Binding energies were calibrated with respect to the C 1*s* peaks at 284.6 eV arising from adventitious carbon. Transmission electron microscope (TEM) images were obtained with an FEI TECNOL 20 microscope.

Selective hydrogenation of benzene was carried out in a 100 ml stainless steel autoclave fitted with a magnetic stirrer. In a typical experiment, benzene, Ru-[bmim]BF_4-II catalyst and $ZnSO_4\cdot 7H_2O$ were introduced into the autoclave together with H_2O as a solvent. The autoclave was sealed and pressurized with N_2 for leak testing, then purged and the temperature was adjusted to that desired. Pressurized H_2 was then introduced into the autoclave to react with benzene. At the end of the reaction, the autoclave was cooled in an ice bath and vented. The catalyst was separated by centrifugation, and the liquid was separated into water and an oil phase. The reaction products in the oil phase were identified and quantified by capillary gas chromatography using a BAIF SP-3420 chromatograph with a 50 m × 0.25 mm PEG 20M column and flame ionization detector.

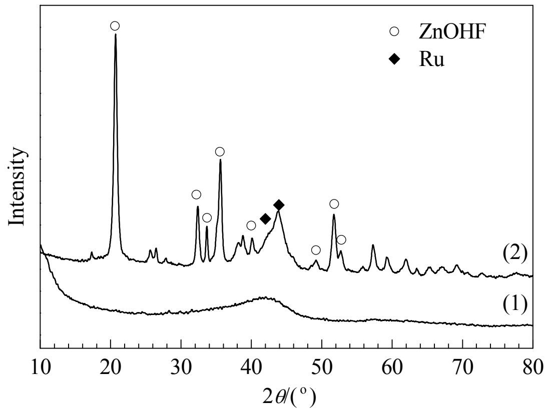

Fig. 1. XRD patterns of Ru-[bmim]BF_4-II catalysts. (1) Fresh; (2) Once-used.

Figure 1 shows an XRD pattern of the fresh Ru-[bmim]BF_4-II catalyst. A broad peak is centered at a 2θ of ~43°, which was assigned to amorphous Ru-B alloy by Liu et al. [8]. The broadness of this peak indicates the small size of the Ru particles. TEM images of Ru-[bmim]BF_4-II catalyst are presented in Fig. 2(a). A large number of Ru particles, with diameters of about 1–2 nm, are loosely aggregated with some organic compounds coating the outside. The external layer is possibly remnant IL.

Selective hydrogenation of benzene was carried out to evaluate the performance of the Ru-[bmim]BF_4-II catalyst; the

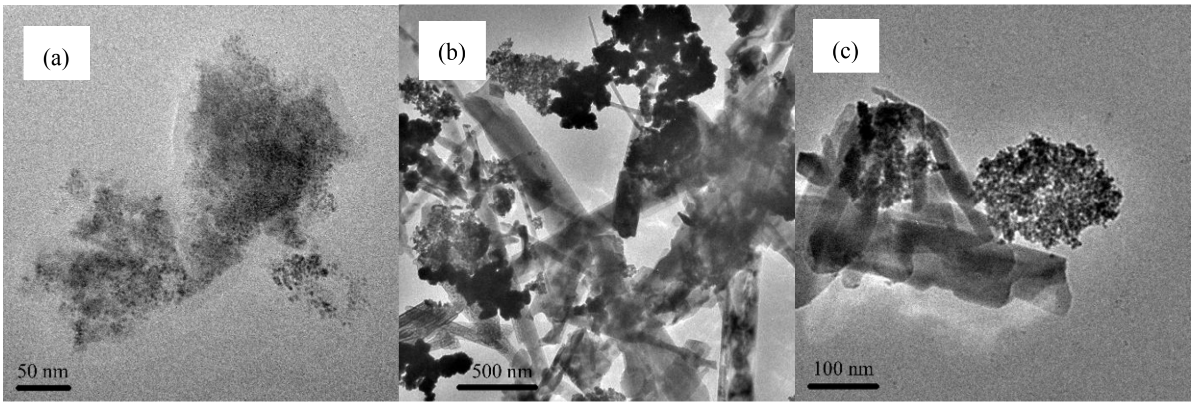

Fig. 2. TEM images of Ru-[bmim]BF_4-II catalysts. (a) Fresh; (b,c) Once-used.

Table 1 Catalytic Performance of Ru-[bmim]BF$_4$ for benzene selective hydrogenation

Entry	Catalyst	Benzene conversion (%)	Cyclohexene selectivity (%)
1[a]	Ru-[bmim]BF$_4$-I	56.4	19.0
2	Ru-[bmim]BF$_4$-II	49.5	34.1
3[b]	Ru-[bmim]BF$_4$-II	59.6	23.8

Reaction conditions: H_2 5.5 MPa, $v(H_2O):v(\text{benzene}) = 2:1$, $n(C_6H_6):n(\text{Ru}) = 525$, 150 °C, 30 min, $c(\text{ZnSO}_4) = 0.05$ mol/L.

[a] Ru-[bmim]BF$_4$-I catalyst was prepared using $N_2H_4 \cdot H_2O$ as reducing agent.

[b] Ru-[bmim]BF$_4$-II was reused for the second time.

results are listed in Table 1. Ru-[bmim]BF$_4$-II shows slightly lower activity than that of Ru-[bmim]BF$_4$-I catalyst, which was prepared using $N_2H_4 \cdot H_2O$ as a reductant. However, the selectivity for cyclohexene over the former catalyst is far higher than that obtained over Ru-[bmim]BF$_4$-I. This difference may be attributed to the effect of boron.

To clarify the influence of boron on catalyst performance, Ru-[bmim]BF$_4$-II was characterized by XPS (Fig. 3). Because the Ru $3d_{3/2}$ peak overlaps with that of C1s, only the Ru $3d_{5/2}$ peak is considered in the following discussion. From Fig. 3, one can see that almost all of Ru is present in its elemental state with a binding energy (BE) of 280.7 eV, which is slightly higher than that of elemental Ru (280.0 eV) reported by Liu et al. [8]. This positive shift may be assigned to the remaining [bmim]BF$_4$ on the surface of Ru. The BF_4^- anion attracts electrons strongly, which can decrease the electron density of Ru and increase the BE of inner electrons. Moreover, surface oxidation of Ru by O_2 before XPS measurement would also result in a positive shift of BE [6].

According to the BE of B 1*s* (193.5 eV), oxidized boron was present in the Ru-[bmim]BF$_4$-II catalyst [9]. These oxides may come from the hydrolysis of $NaBH_4$. Xie et al. [10] found that the presence of oxidized boron species on the surface of Ru catalyst could greatly enhance the hydrophilicity of the catalyst by interacting with water molecules through hydrogen bonding. In addition, according to the asymmetry of the B 1*s* XPS spectra, there was some elemental boron with a lower BE in the catalyst. Elemental boron would donate electrons to elemental Ru, making boron electron deficient, which also promotes water adsorption on the catalyst surface, because electron-deficient boron can readily accept the lone electron pair on the oxygen atom in a water molecule. Therefore, during selective hydrogenation of benzene, further hydrogenation of cyclohexene to cyclohexane is retarded by reducing the readsorption of cyclohexene on the hydrophilic catalyst surface.

Ru-[bmim]BF$_4$-II catalyst that had been used once was separated from the aqueous phase by centrifugation and then reused for selective hydrogenation of benzene without any further treatment. Entry 3 in Table 1 indicates that Ru-[bmim]BF$_4$-II showed low stability during the reaction, because the selectivity for cyclohexene decreased significantly when benzene conversion increased to 59.6%.

Figure 1(b) shows an XRD pattern of the Ru-[bmim]BF$_4$-II catalyst that had been used once. There are obvious differences between the patterns of the catalysts before and after reaction. The peaks corresponding to metallic Ru become strong and sharp, which indicates that Ru particles gradually increase in size because of the H_2 atmosphere in the reaction. It also indicates that the protection from the IL was weakened.

There are also some strong diffraction peaks assigned to zinc hydroxyfluoride (ZnOHF), which formed during selective hydrogenation of benzene through a reaction between [bmim]BF$_4$ and $ZnSO_4$, an additive in the selective hydrogenation of benzene. Wu et al. [11] synthesized ZnOHF nanofibers from $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ in the presence of the IL 1,2,3-trimethylimid-azolium tetrafluoroborate.

Fig. 2(b) and (c) show TEM images of the Ru-[bmim]BF$_4$-II catalyst after one use. There are two main kinds of substance in the images. Some are agglomerations of small particles, which are presumed to be metallic Ru particles. Compared with Fig. 2(a), the Ru particles in the used catalyst are clearer because the IL protection layer is absent, which also allows the Ru particles to aggregate. The other type of substance in the image is rod-like particles with widths of up to 200 nm and lengths on the micro scale. These rod-like particles are ZnOHF.

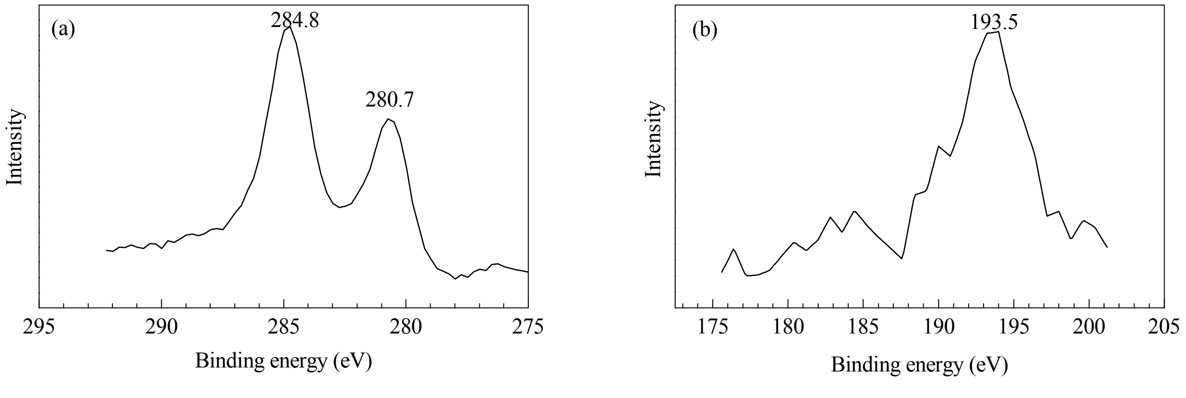

Fig. 3. XPS spectra of Ru 3*d* (a) and B 1*s* (b) for Ru-[bmim]BF$_4$-II catalyst.

XPS measurements of the used Ru-[bmim]BF_4-II catalyst revealed that the content of N on the surface decreased from 18.8% to 1.7%, which also indicated the leaching of IL from the surface of Ru-[bmim]BF_4-II.

These results all suggest that there were more exposed metallic Ru active sites in the used Ru-[bmim]BF_4-II catalyst than the fresh one. Therefore, the used catalyst exhibited higher catalytic activity and lower selectivity for cyclohexene.

Liu et al. [12] reported that when the transition metal ion was reduced by $NaBH_4$, a small amount of sodium metaborate was found in the product, which made it weakly basic. As a result, the basic Ru-[bmim]BF_4-II catalyst readily reacted with $ZnSO_4$, an additive with weak acidity, during the selective hydrogenation of benzene, producing $Zn(OH)_2$ and partly covering Ru active sites. This reduced the catalytic activity and increased the selectivity for cyclohexene. However, because of the presence of [bmim]BF_4 in this study, ZnOHF was formed in the used catalyst instead of $Zn(OH)_2$. A mechanism for the formation of ZnOHF is proposed as follows (Eqs. 1 and 2) from the work of Dai et al. [13]:

$$Zn^{2+} + F^- \rightarrow ZnF^+ \quad (1)$$

$$ZnF^+ + OH^- \rightarrow ZnOHF \quad (2)$$

First, Zn^{2+} rapidly combines with F^- from [bmim]BF_4 to form a ZnF^+ complex (Eq. (1)). Solid ZnOHF is then obtained from the reaction between ZnF^+ and OH^- (Eq. (2)), which is present from the hydrolysis of $NaBH_4$. In addition, because of hydrogen bonding and π-π stacking, the (110) plane of ZnOHF is covered by an adsorbed layer of BF_4^-, which slows the rate of growth. At the same time, [bmim]$^+$ cations align and arrange along the (110) plane driven by the coulomb coupling force, which leads to ordered growth of ZnOHF in the [001] direction to form rod-like crystals with a 1D feature.

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