The role of La in improving the selectivity to cyclohexene of Ru catalyst for hydrogenation of benzene

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ABSTRACT

Ru–La catalysts with different La/Ru molar ratios were prepared by co-precipitation. Characterizations revealed that the promoter La existed as $La(OH)_3$ on the Ru surface. The $La(OH)_3$ itself could not enhance the selectivity to cyclohexene of Ru catalyst. However, the $La(OH)_3$ could react with $ZnSO_4$ in slurry to form an insoluble $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ salt. The chemisorbed $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ salt on Ru surface played a key role in improving the selectivity to cyclohexene of Ru catalyst. Ru–La catalyst with the optimum La/Ru molar ratio of 0.14 gave a maximum cyclohexene yield of 59.5%. Besides, Ru–La(0.14) catalyst had a good reusability and an excellent stability.

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1. Introduction

Cyclohexene is commercially important for the production of adipic acid, nylon 6, nylon 66 and many other fine chemicals [1–4]. Selective hydrogenation of benzene to cyclohexene is superior due to inexpensive products, lower amounts of undesirable products and simplified operation, compared with traditional methods, such as dehydrogenation of cyclohexane, dehydration of cyclohexanol, and the Birch reduction [5]. However, it is difficult to obtain a high yield of cyclohexene through this route, because cyclohexane, the complete hydrogenation product, is thermodynamically more favorable.

It has been proved that the addition of one or two reaction modifiers to the reaction system is one of the simplest methods to enhance the selectivity to cyclohexene of Ru catalysts. Various substances have been used as the reaction modifiers including inorganic salts [6], organic compounds [7–10], and ionic liquids [11]. $ZnSO_4$ has been regarded as the best modifiers [12]. It has been also found the modification of Ru catalysts with the promoters such as Fe [13,14], Zn [15–18], Co [19], Cu [20], Ba [21], La [22–24], Ce [4], and K [25] by the co-precipitation method, the impregnation method, or the chemical reduction method could enhance the selectivity to cyclohexene. Specially,

the combination of the promoters and the reaction modifier $ZnSO_4$ could remarkably improve the selectivity to cyclohexene of the Ru catalysts. Liu et al. [23,24] obtained a cyclohexene yield of 53% over a Ru–La–B/ZrO_2 catalyst in the presence of $ZnSO_4$. Liu et al. [5] utilized $ZnSO_4$ as a modifier and achieved a cyclohexene yield of 53.8% over a Ru–Ce/SBA-15 catalyst. Liu et al. [22] used $ZnSO_4$ and $CdSO_4$ as co-modifiers and obtained a cyclohexene yield of 57% over a Ru–La/SBA-15 catalyst. Sun et al. [9,10] employed $ZnSO_4$ and amines (or alcohols) as co-modifiers and got a cyclohexene yield of above 60% over a Ru–Zn catalyst. Asahi Chemical has industrialized the process of selective hydrogenation of benzene to cyclohexene using a Ru catalyst and $ZnSO_4$ as the reaction modifier [12]. It has been accepted that the promoter and $ZnSO_4$ were acting respectively. For example, Liu et al. [5] suggested that the Ce(III) species could enhance the hydrophilicity of the catalyst and denote some electrons to metallic Ru, which increased the selectivity to cyclohexene of Ru/SBA-15 catalyst. On the other hand, they proposed that the Zn^{2+} of $ZnSO_4$ could form adducts with cyclohexene and hinder the readsorption of cyclohexene, which suppressed the raid consecutive hydrogenation of cyclohexene and improved the selectivity to cyclohexene of the catalyst.

However, we found that a large part of the promoter Zn in Ru–Zn catalyst existed as ZnO. The ZnO on catalyst surface could react with $ZnSO_4$ in the slurry to form a $ZnSO_4 \cdot 3Zn(OH)_2 \cdot 7H_2O$ salt during hydrogenation. The $ZnSO_4 \cdot 3Zn(OH)_2 \cdot 7H_2O$ salt played a key role in improving the selectivity to cyclohexene [26,27]. Thus there was a question what the roles of the other promoters were. In

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this work, we prepared Ru–La catalysts with different La/Ru molar ratios by a simple co-precipitation method. The optimum La/Ru molar ratio was determined to be 0.14, on which a cyclohexene yield of 59.5% was obtained. Moreover, Ru–La(0.14) catalyst had a good reusability and an excellent stability. The role of the promoter La in improving the selectivity to cyclohexene of Ru catalyst was investigated.

2. Experimental

2.1. Catalyst preparations

Ru–La catalysts were prepared according to the following procedure. 9.75 g RuCl$_3 \cdot$H$_2$O and a desired amount of LaCl$_3 \cdot n$H$_2$O were dissolved in 400 ml H$_2$O with agitation. To the stirred solution, 200 ml of a 10% NaOH solution was added instantaneously and the resulting mixture was agitated for an additional 4 h at 353 K. This black precipitate was dispersed in 400 ml of a 5% NaOH solution and charged into a 1 L autoclave lined the Teflon. Hydrogen was introduced into the autoclave to raise the total internal pressure to 5 MPa and the reduction was conducted at 423 K and at 800 r/min stirring rate for 3 h. The reaction mixture was cooled and the obtained black powder was washed with water until neutrality, subsequently vacuum-dried and the desired Ru–La catalysts were obtained. The catalyst was divided into two shares, one share was used for activity test and the other was used for catalyst characterization. This method ensured that the catalysts with different La contents had the same Ru contents (about 1.8 g Ru). The monometallic Ru catalyst was denoted as Ru(0) catalysts. The amounts of LaCl$_3 \cdot n$H$_2$O were adjusted to give the catalysts with different La contents which were denoted as Ru–La(x) catalysts, where x denoted the La/Ru molar ratio measured by X-ray fluorescence (XRF).

2.2. Catalyst characterization

N$_2$ physisorption was determined on a Quantachrome Nova 100e apparatus at 77 K. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method, and the pore size distributions were obtained by the Barrett–Joyner–Halenda (BJH) method according to the desorption branches. X-ray diffraction (XRD) patterns were acquired on a PANalytcal X'Pert PRO instrument using Cu Kα (λ = 1.541 Å) with scan range from 5° to 90° at a step of 0.03°. The crystallite sizes of metallic Ru in the catalysts were estimated from the strongest peak broading at 44.0° using the Scherrer equation. Transmission electron micrographs (TEM) and energy dispersion scanning (EDS) were observed on a JEOL JEM-2100 instrument using an accelerating voltage of 200 kV. Auger Electron Spectroscopy (AES) and sputter profiles were taken on a ULVAC PHI-700 Nano-canning Auger system with on-axis scanning argon ion gun and CMA energy analyzer. The energy resolution ratio was 0.1%. The background pressure of analysis room was less than 5.2×10^{-7} Pa. The standard sample was SiO$_2$/Si. The sputtering rate was 9 nm/min. The La/Ru molar ratios and the compositions of Ru–La(x) catalysts after hydrogenation were measured by X-ray fluorescence (XRF) on a Bruker S4 Pioneer instrument.

2.3. Activity test

The selective hydrogenation of benzene was performed in a 1 L autoclave lined the hastelloy. The autoclave was charged with 280 ml of H$_2$O containing a share of Ru–La catalyst (comprising 1.8 g Ru) and 49.2 g of ZnSO$_4 \cdot$7H$_2$O. Then heating commenced with H$_2$ pressure of 5 MPa and stirring rate of 800 r/min. 140 ml of benzene was fed and the stirring rate was elevated to 1400 r/min to exclude the diffusion effect when the temperature reached 150 °C.

Table 1
Physicochemical properties and Ru crystallite sizes of Ru–La(x) and Ru–La(x) AH.

Sample	BET surface area (cm^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	Ru crystallite size (nm)
Ru(0)	59	0.18	10.63	4.7
Ru–La(0.14)	52	0.15	11.67	4.5
Ru–La(0.19)	53	0.15	10.96	4.7
Ru–La(0.30)	57	0.17	10.89	3.6
Ru(0) AH	56	0.16	10.44	4.5
Ru–La(0.14) AH	55	0.14	9.13	4.4
Ru–La(0.19) AH	52	0.16	9.76	4.7
Ru–La(0.30) AH	43	0.09	8.72	3.8

The reaction products were monitored by taking a small amount of the reaction mixture every 5 min and analyzed using a GC-1690 Gas Chromatograph with FID detector. After the reaction the organic was removed and the solid sample was vacuum-dried at 60 °C for characterization. The sample after reaction corresponding to Ru–La(x) catalyst was denoted as Ru–La(x) AH, where AH stood for After Hydrogenation. The monometallic Ru catalyst after hydrogenation was denoted as Ru(0) AH.

The reusability and stability of Ru–La(0.14) catalyst were investigated according to the following procedures. At the end of the first reaction, the autoclave was cooled down and the organic phase was separated. The slurry containing the catalyst was recycled in accordance with the above hydrogenation procedures without any addition.

3. Results and discussion

Fig. 1(a) and (b) shows that Ru–La(x) catalysts and Ru–La(x) AH all showed the type-IV adsorption properties. All the closed hysteresis loops were of type H3, according to IUPAC classification. Fig. 1(c) and (d) shows that most of the pores of Ru–La(x) catalysts and Ru–La(x) AH were mainly distributed in the range of 2–50 nm. Besides, there were some macropores in the range of 60–120 nm in these catalysts. Table 1 shows that BET surface areas, pore volumes and pore diameters of Ru–La(x) catalysts slightly changed with the increase of the molar ratios of La/Ru, indicating that the addition of La could not alter the texture structure of the catalysts. The BET surface areas, pore volumes and pore diameters of Ru–La(x) AH generally decreased with the increase of the molar ratios of La/Ru. Combined with the characterization results, it is proposed that the (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ salt formed in hydrogenation might block some of the pores of the catalysts, which resulted in the decrease of the BET surface areas, pore volumes and pore diameters of Ru–La(x) AH.

Fig. 2(a) shows that all the Ru–La(x) catalysts showed the diffraction peaks of metallic Ru (JCPDS 01-070-0274), indicating the Ru in the catalysts mainly existed as metallic Ru. Besides, the diffraction peaks of La(OH)$_3$ (JCPDS 00-006-0585) were present in the XRD patterns of Ru–La(x) catalyst, indicating the promoter La mainly existed as La(OH)$_3$. Moreover, the intensity of the diffraction peaks of La(OH)$_3$ increased with the molar ratio of La/Ru, indicating the increment of the La(OH)$_3$ contents. Fig. 2(b) shows that all the Ru–La(x) AH gave the diffraction peaks of metallic Ru. Besides, the diffraction peaks of the (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ salt (JCPDS 00-078-0247) were clearly observed on Ru–La(x) AH. Moreover, the intensity of the diffraction peak at 11.2° of this salt increased with the molar ratios of La/Ru, indicating the increase of its amount. Interestingly, the diffraction peaks of La(OH)$_3$ disappeared. All of these indicated that the promoter La(OH)$_3$ on the surface of the catalyst had reacted with the reaction modifier ZnSO$_4$ and H$_2$O to form an insoluble (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ salt, which was shown in reaction (1). Moreover, the amount of the formed (Zn(OH)$_2$)$_3$(ZnSO$_4$)(H$_2$O)$_3$ salt increased with the loading