Contents lists available at SciVerse ScienceDirect



Journal of Molecular Catalysis A: Chemical



journal homepage: www.elsevier.com/locate/molcata

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

Hai-Jie Sun, Ying-Ying Dong, Shuai-Hui Li, Hou-Bing Jiang, Yuanxin Zhang, Zhong-Yi Liu*, Shou-Chang Liu

College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, Henan, China

ARTICLE INFO

Article history: Received 8 October 2012 Received in revised form 1 December 2012 Accepted 3 December 2012 Available online 11 December 2012

Keywords: Benzene Cyclohexene Ru La Selective hydrogenation

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 ZnSO₄ 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]. ZnSO₄ 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 ZnSO₄ 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/ZrO₂ catalyst in the presence of ZnSO₄. Liu et al. [5] utilized ZnSO₄ as a modifier and achieved a cyclohexene yield of 53.8% over a Ru-Ce/SBA-15 catalyst. Liu et al. [22] used ZnSO₄ and CdSO₄ as co-modifiers and obtained a cyclohexene yield of 57% over a Ru-La/SBA-15 catalyst. Sun et al. [9,10] employed ZnSO₄ 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 ZnSO₄ as the reaction modifier [12]. It has been accepted that the promoter and ZnSO₄ 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 ZnSO₄ in the slurry to form a ZnSO₄·3Zn(OH)₂·7H₂O salt during hydrogenation. The ZnSO₄·3Zn(OH)₂·7H₂O 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

^{*} Corresponding author. Tel.: +86 371 67783384. E-mail address: liuzhongyi@zzu.edu.cn (Z.-Y. Liu).

^{1381-1169/\$ -} see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.molcata.2012.12.001

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 RuCl₃·H₂O and a desired amount of LaCl₃·nH₂O were dissolved in 400 ml H₂O 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 4h 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 LaCl₃ · nH₂O 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

N₂ 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 K α (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 SiO₂/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_2O containing a share of Ru–La catalyst (comprising 1.8 g Ru) and 49.2 g of $ZnSO_4$ · $7H_2O$. 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 I | Ru crystallite sizes of | f Ru–La(x) and | $1 \operatorname{Ru}-\operatorname{La}(x) \operatorname{AH}$. |
|-----------------|------------------|-------------------------|----------------|----------------------------------------------------------------|
|-----------------|------------------|-------------------------|----------------|----------------------------------------------------------------|

| Sample | BET surface area (cm²/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 $60 \,^{\circ}$ 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 $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ 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 $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ 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 ZnSO₄ and H₂O to form an insoluble $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ salt, which was shown in reaction (1). Moreover, the amount of the formed $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ salt increased with the loading



Fig. 1. N2 adsorption-desorption isotherms of (a) Ru-La(x) catalysts and (b) Ru-La(x) AH as well as pore size distribution of (c) Ru-La(x) catalysts and (d) Ru-La(x) AH.

of La(OH)3.

$$2La(OH)_3 + 4ZnSO_4 + 3H_2O \rightarrow (Zn(OH)_2)_3(ZnSO_4)(H_2O)_3\downarrow$$
$$+ La_2(SO_4)_3$$
(1)

Table 1 also shows when the La/Ru molar ratio was below 0.30, the crystallite sizes of Ru–La(x) catalyst and Ru–La(x) AH were in range of 4.4–4.7 nm, indicating the promoter La(OH)₃ had little effect on the crystallite sizes of Ru catalyst and the crystallites of Ru–La(x) catalysts had changed little during the hydrogenation process under the reaction condition of high agitation. The crystallite sizes of Ru–La(0.30) and Ru–La(0.30) AH significantly decreased to 3.6 nm and 3.8 nm respectively. This probably was due to the dispersion effect of abundant La(OH)₃ in Ru–La(0.30) catalyst on the Ru crystallites.

Fig. 3(a) and (b) displays that both of Ru–La(0.14) catalyst and Ru–La(0.14) AH were consist of spherical and ellipsoidal crystallites. Fig. 3(c) and (d) shows that the Ru crystallite sizes of Ru–La(0.14) catalyst and Ru–La(0.14) AH were mainly distributed around 4.2 nm, which was consistent with the XRD results. Only lattice fringes of the (101) plane of the metallic Ru with an average spacing of 0.21 nm was detectable on the images of Ru–La(0.14) catalyst and Ru–La(0.14) AH. This might be due to the uniform dispersion of La(OH)₃ on Ru–La(0.14) catalyst and of the (Zn(OH)₂)₃(ZnSO₄)(H₂O)₃ salt on Ru–La(0.14) AH [5,27].

It has been extensively reported that the presence of Zn in Ru catalysts could significantly enhance the selectivity to cyclohexene of the Ru catalyst [15–18,26,27]. However, there were different opinions about the valence of Zn. Wang et al. [16] characterized the Ru–Zn/m–ZrO₂ catalyst by XPS and found that the Zn $2p_{3/2}$ BE of

the Zn in the catalyst was close to that of metallic Zn. Thus they suggested that the Zn²⁺ cations chemisorbed could be reduced to metallic Zn by the hydrogen atoms that spilled from the surface of the Ru catalyst. Yuan et al. [17] and He et al. [18] also indicated the Zn atoms could be introduced into the Ru-based catalyst by the reduction of Zn²⁺ according to the XPS results. However, Struijk et al. [6] indicated that the Zn^{2+} of the adsorption of $ZnSO_4$ could not be reduced on the surface of Ru catalyst also on the basis of the XPS results. But the assessment of the oxidation state of Zn from the binding energy of the Zn $2p_{3/2}$ level is not very useful due to the close appearance on XPS of the transitions corresponding to Zn(II) and metallic Zn [28]. This drawback can be overcome using the Zn LMM Auger transition, as the Auger shift between Zn(II) and metallic Zn is higher than 4.6 eV [29]. Fig. 4 shows the AES Zn LMM spectra of Ru-La(0.14) AH at the different sputtering time (0 min, 0.5 min and 1 min). As can be seen, the Kinetic energies (KEs) of Zn LMM of Ru-La(0.14) AH at the depth of 0 nm, 4.5 nm 9 nm were 983.7 eV, 983.7 eV and 983.6 eV respectively, these contributions being previously assigned to oxidized Zn [30,31]. This finding suggested that the Zn was present on the surface of Ru-La(0.14) AH mainly as oxidized Zn even under the reaction conditions of 150 °C and H₂ pressure of 5.0 MPa, which was in accordance with that the Zn on the surface of Ru-La(0.14) AH presented in the form of the $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ salt. Unfortunately, AES measurements did not allow discerning any additional contribution from metallic Zn (commonly appearing in the 991-995 eV range). Moreover, Table 2 shows that the pH values of the aqueous solutions after hydrogenation in the presence of ZnSO₄ at room temperature were around 6.0, indicating the acidity of aqueous phase due to the hydrolysis of ZnSO₄. It is well known that increasing temperature



Fig. 2. XRD patterns of Ru-La(x) catalysts and Ru-La(x) AH.



Fig. 3. TEM images of (a) Ru-La(0.14) and (b) Ru-La(0.14) AH as well as their Ru crystallite size distribution.

favors the hydrolysis. This means that the acidity of liquid phase is much higher at the reaction temperature of 423 K due to the increase of hydrolysis degree of ZnSO₄. As we know, it is difficult for the metallic Zn to exist in the acid solution, which is consistent with no clear evidences of the presence of metallic Zn on the surface of Ru catalysts observed in the AES results.

Table 2 gives the composition of Ru-La(x) AH. As can be seen, only trace amounts of La were detected on Ru-La(x) AH, indicating



Fig. 4. AES Zn LMM spectra of Ru-La(0.14) AH.

that almost all the La(OH)₃ in the catalyst had reacted with ZnSO₄ in the slurry to form the $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ salt. Especially, this also implied that the promoter La(OH)₃ could not enter into the Ru lattices and mainly existed on the Ru surface. The molar ratios of Zn/Ru and S/Ru increased with the loading of La(OH)₃, suggesting the increment of the $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ salt in consistent with the XRD results. The insoluble $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ salt was readily chemisorbed on the surface of the Ru particles. Based on these, the structures of Ru–La(x) catalyst and Ru–La(x) AH were sketched as shown in Fig. 5. Therefore, $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ salt chemisorbed on the surface of Ru particles might directly influence the performance of Ru catalyst.

Before comparing the selectivity over these catalysts, Carberry number (Ca) and Wheeler–Weisz number ($\eta \varphi^2$) were calculated

Table 2

Composition of Ru-La(x) AH and pH values of liquid phase at room temperature after hydrogenation.

| Catalyst | La/Ru AH ^c | Zn/Ru AH ^c | S/Ru AH ^c | pH value ^d |
|--------------------------|-----------------------|-----------------------|----------------------|-----------------------|
| Ru(0) ^a | 0 | 0.0313 | 0.0026 | 5.53 |
| Ru-La(0.14) ^a | 0.0017 | 0.2542 | 0.0163 | 6.18 |
| Ru-La(0.19) ^a | 0.0018 | 0.3885 | 0.0381 | 6.35 |
| Ru-La(0.30) ^a | 0.0032 | 0.5789 | 0.0673 | 6.37 |
| Ru-La(0.14) ^b | 0.1427 | 0 | 0 | 6.99 |

^a In the presence of 0.6 mol/L ZnSO₄.

^b In the absence of 0.6 mol/L ZnSO₄.

^c Determined by XRF.

d Measured by pH meter.



Fig. 5. Structure sketches of Ru-La(x) catalyst and Ru-La(x) AH.

according to previous works [32]. It was found that Carberry numbers and Wheeler-Weisz numbers were smaller than 0.05 and 0.1 respectively, indicating that external mass transport limitation and pore diffusion limitation could be neglected. This indicates that the reaction was always under kinetic control. Fig. 6(a) and (b) shows that the activity decreased and the selectivity to cyclohexene of the catalysts increased with the molar ratio of La/Ru in the presence of ZnSO₄. Fig. 6(c) shows the maximum yield of cyclohexene increased with the increment of the molar ratio of La/Ru in the presence of ZnSO₄, and then declined at higher doping amounts of La, with the optimal La/Ru molar ratio being 0.14. Ru–La(0.14) catalyst gave the highest cyclohexene yield of 59.5%, which was among the best results reported so far [5,12,22]. However, Ru-La(0.14) catalyst gave the poorest selectivity of 2.3% and the weakest yield of 1.9% in the absence of ZnSO₄, suggesting that the promoter La(OH)₃ alone could not enhance the selectivity to cyclohexene and the cyclohexene yield of Ru catalyst. This indicated that the chemisorbed $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ salt formed by La(OH)_3 reacting with ZnSO_4 played a key role in improving the selectivity to cyclohexene of the Ru catalyst.

Based on the previous works, the roles of the chemisorbed (Zn(OH)₂)₃(ZnSO₄)(H₂O)₃ salt on Ru surface might be attributed to one or a combination of the following reasons. Firstly, the chemisorbed (Zn(OH)₂)₃(ZnSO₄)(H₂O)₃ salt was rich in crystal water. Therefore, the salt chemisorbed on the surface of the catalvst caused Ru catalyst to be surrounded by a firm stagnant water layer, as shown in Fig. 5. The existence of the stagnant water layer on the surface of the catalyst could accelerate the desorption and hinder the re-adsorption of cyclohexene for further hydrogenation to cyclohexane due to the very low solubility of cyclohexene [33], resulting in the improvement of the selectivity to cyclohexene. Secondly, the Zn^{2+} of the chemisorbed $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ salt can selectively cover the most reactive sites of the catalyst, which can reduce the active sites for the chemisorption of cyclohexene and suppress the further hydrogenation of cyclohexene to cyclohexane [6,16,26,27]. Struijk et al. [6] suggested the salts which act as the effective additive should have enough absorbability on Ru to cover 50% Ru active sites. Finally, the Zn²⁺ of the chemisorbed $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ salt could form loosely bound adducts with cyclohexene, which could stabilize the formed cyclohexene on the surface of Ru catalyst and improve the selectivity to cyclohexene of Ru catalyst [5,16,22]. Therefore, increasing the loading of $La(OH)_3$ increased the formation of the $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_5$ salt, resulting in the decrease of activity and the increase of the selectivity to cyclohexene of Ru catalyst. Above all, the chemisorbed $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ salt formed by La(OH)_3 reacting with ZnSO₄ in the slurry directly enhanced the selectivity to cyclohexene of Ru catalyst.



Fig. 6. (a) Benzene conversion and (b) cyclohexene selectivity as well as (c) cyclohexene yield over Ru–La(*x*) catalysts. Reaction conditions: a share of Ru–La(*x*) catalyst, 49.2 g of ZnSO₄·7H₂O, 280 ml of H₂O, 140 ml of benzene, reaction temperature of 150 °C, H₂ pressure of 5.0 MPa and stirring rate of 1400 r/min.



Fig. 7. Benzene conversion, cyclohexene selectivity and cyclohexene yields at 10 min as well as the maximum cyclohexene yield in 25 min over Ru–La(0.14) catalyst in the five reuse times. Reaction conditions: a share of Ru–La(x) catalyst, 49.2 g of ZnSO₄·7H₂O, 280 ml of H₂O, 140 ml of benzene, reaction temperature of 150°C, H₂ pressure of 5.0 MPa and stirring rate of 1400 r/min.

Fig. 7 shows that the benzene conversion were stable above 60%, and the selectivity to cyclohexene and cyclohexene yields were kept above 77% and 48% respectively in the first reused times. Moreover, the maximum cyclohexene yields stabilized above 59%. Although the benzene conversion slightly decreased to 56.5%, the selectivity to cyclohexene and cyclohexene yield were as high as 83.7% and 57.5%. All of these suggested that Ru catalyst modified by the $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_5$ salt had a good reusability and a excellent stability.

4. Conclusion

Results confirmed 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 a insoluble $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ salt. The $(Zn(OH)_2)_3(ZnSO_4)(H_2O)_3$ salt chemisorbed on Ru surface could significantly improve the selectivity to cyclohexene of Ru catalyst. Ru–La(0.14) catalyst gave a maximum cyclohexene yield of 59.5%. Besides, Ru–La(0.14) catalyst had a good reusability and an excellent stability. All of these indicated that some of the promoters themselves could not enhance the selectivity and the activity of the catalysts. However, they could react with the reaction modifiers to form new substances. These substances could significantly improve the selectivity and the activity of the catalysts. This finding may open a new avenue for selectivity and activity enhancement for other reactions.

Acknowledgments

This work was supported by the National Nature Science Foundation of China (21273205), the Innovation Found for Technology Based Firms of China (10C26214104505) and the Scientific Research Foundation of Graduate School of Zhengzhou University.

References

- W.T. Wang, H.Z. Liu, T.B. Wu, P. Zhang, G.D. Ding, S.G. Liang, T. Jiang, B.X. Han, J. Mol. Catal. A: Chem. 355 (2012) 174–179.
- [2] W. Xue, Y. Song, Y.J. Wang, D.D. Wang, F. Li, Catal. Commun. 11 (2009) 29–33.
 [3] H.J. Sun, W. Guo, X.L. Xiao, Z.H. Chen, Z.Y. Liu, S.C. Liu, Chin. J. Catal. 32 (2011)
- [4] J.B. Ning, J. Xu, J. Liu, F. Lu, Catal. Lett. 109 (2006) 175–180.
- [5] J.L. Liu, L.J. Zhu, Y. Pei, J.H. Zhuang, H. Li, H.X. Li, M.H. Qiao, K.N. Fan, Appl. Catal. A: Gen. 353 (2009) 282–287.
- [6] J. Struijk, R. Moene, T.V.D. Kamp, J.J.F. Scholten, Appl. Catal. A: Gen. 89 (1992) 77–102.
- [7] E.V. Spinacé, J.M. Vaz, Catal. Commun. 4 (2003) 91–96.
- 8] G.Y. Fan, R.X. Li, X.J. Li, H. Chen, Catal. Commun. 9 (2008) 1394–1397.
- [9] H.J. Sun, Z.H. Chen, W. Guo, X.L. Zhou, Z.Y. Liu, S.C. Liu, Chin. J. Chem. 29 (2011) 369–373.
- [10] H.J. Sun, Y.J. Pan, H.X. Wang, Y.Y. Dong, Z.Y. Liu, S.C. Liu, Chin. J. Catal. 33 (2012) 610–620.
- [11] F. Schwab, M. Lucas, P. Claus, Angew. Chem. Int. Ed. 50 (2011) 1–5.
- [12] H. Nagahara, M. Ono, M. Konishi, Y. Fukuoka, Appl. Surf. Sci. 121–122 (1997) 448–451.
- [13] J.W. da-Silva, A.J.G. Cobo, Appl. Catal. A: Gen. 252 (2003) 9-16.
- [14] H.J. Sun, C. Zhang, P. Yuan, J.X. Li, S.C. Liu, Chin. J. Catal. 29 (2008) 441-446.
- [15] S.C. Hu, Y.W. Chen, Ind. Eng. Chem. Res. 40 (2001) 6099-6104.
- [16] J.Q. Wang, Y.Z. Wang, S.H. Xie, M.H. Qiao, H.X. Li, K.N. Fan, Appl. Catal. A: Gen. 272 (2004) 29–36.
- [17] P.Q. Yuan, B.Q. Wang, Y.M. Ma, H.M. He, Z.M. Cheng, W.K. Yuan, J. Mol. Catal. A: Chem. 301 (2009) 140–145.
- [18] H.M. He, P.Q. Yuan, Y.M. Ma, Z.M. Cheng, W.K. Yuan, Chin. J. Catal. 30 (2009) 312-318.
- [19] G.Y. Fan, W.D. Jiang, J.B. Wang, R.X. Li, H. Chen, X.J. Li, Catal. Commun. 10 (2008) 98–102.
- [20] H.Z. Liu, S.G. Liang, W.T. Wang, T. Jiang, B.X. Han, J. Mol. Catal. A: Chem. 341 (2011) 35-41.
- [21] J. Bu, J.L. Liu, X.Y. Chen, J.H. Zhuang, S.R. Yan, M.H. Qiao, H.Y. He, K.N. Fan, Catal. Commun. 9 (2008) 2612–2615.
- [22] J.L. Liu, Y. Zhu, J. Liu, Y. Pei, Z.H. Li, H. Li, H.X. Li, M.H. Qiao, K.N. Fan, J. Catal. 268 (2009) 100–153.
- [23] S.C. Liu, Z.Y. Liu, Z. Wang, Y.M. Wu, P. Yuan, Chem. Eng. J. 139 (2008) 157–164.
 [24] S.C. Liu, Z.Y. Liu, Z. Wang, S.H. Zhao, Y.M. Wu, Appl. Catal. A: Gen. 313 (2006)
- 49–57.
- [25] L. Ronchin, L. Toniolo, Catal. Today 66 (2001) 363-369.
- [26] H.J. Sun, X.D. Zhang, Z.H. Chen, X.L. Xiao, W. Guo, Z.Y. Liu, S.C. Liu, Chin. J. Catal. 32 (2011) 224–230.
- [27] H.J. Sun, H.X. Wang, H.B. Jiang, S.H. Li, S.C. Liu, Z.Y. Liu, X.M. Yuan, Appl. Catal. A: Gen. (2012), http://dx.doi.org/10.1016/j.apcata.2012.10.016.
- [28] B. Peplinski, W.E.S. Unger, I. Grohmann, Appl. Surf. Sci. 62 (1992) 115-129.
- [29] W.L. Dai, Q. Sun, J.F. Deng, D. Wu, Y.H. Sun, Appl. Surf. Sci. 177 (2001) 172–179.
 [30] J. Silvestre-Albero, J.C. Serrano-Ruiz, A. Sepúlveda-Escribano, F. Rodríguez-
- Reinoso, Appl. Catal. A: Gen. 292 (2005) 244–251.
- [31] E.V. Ramos-Fernándze, A.E.P. Ferreira, A. Sepúlveda-Escribano, F. Kapteijn, F. Rodríguez-Reinoso, J. Catal. 258 (2008) 52–60.
- [32] S.C. Hu, Y.W. Chen, Ind. Eng. Chem. Res. 36 (1997) 5153-5159.
- [33] J. Struijk, M. d'Angremond, W.J.M. Lucas-de Regt, J.J.F. Scholten, Appl. Catal. A: Gen. 83 (1992) 263-295.