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Characterization and study on performance of the Ru–La–B/ZrO_2 amorphous alloy catalysts for benzene selective hydrogenation to cyclohexene under pilot conditions

Shou Chang Liu*, Zhongyi Liu, Zheng Wang,
Yongmei Wu, Peng Yuan

Department of Chemistry, Zhengzhou University, Zhengzhou 450052, PR China

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Abstract

Various characterizations of Ru–La–B/ZrO_2 catalysts were carried out by means of XRD, TEM, SEAD, XPS and N_2-physisorption, and the activity and selectivity of the catalysts were measured. XRD results showed that Ru–La–B/ZrO_2 catalysts were considerable stable and no significant peaks corresponding to Ru crystal were observed for the catalysts treated below 673 K and ran for 500 h under pilot conditions. The study on N_2-physisorption showed that with extending of the reaction time the most probable pore diameters, specific surface areas and pore volumes became smaller supposed to be relative to the adsorption of substances in the reaction mixture and to be one of the reasons for decreasing of the activity and selectivity of the catalysts. XPS showed that ruthenium exists in metallic state; lanthanum exists in La^{3+} or in metallic state. One of the most remarkable features of Ru–La–B/ZrO_2 catalysts is the high activity and good selectivity for benzene selective hydrogenation to cyclohexene. On the other hand, the catalysts can be regenerated and have a long life under pilot conditions.

Keywords: Ru–La–B/ZrO_2 amorphous catalyst; Benzene selective hydrogenation; Pilot conditions

1. Introduction

Since cyclohexene as a reaction intermediate in the hydrogenation of benzene on a nickel film was first detected by Anderson [1], great progress of the studies on benzene selective hydrogenation to cyclohexene has been made. In 1965, Anderson and Hartog [2] obtained the maximum cyclohexene yield of only 2% with ruthenium catalyst and aliphatic alcohols catalyst modifiers in the liquid phase hydrogenation of benzene at ambient temperature and pressure. In 1972, a fateful step forward was made by Drinkard [3] because the highest cyclohexene yield of 30% was established by using ruthenium chloride as a catalyst precursor and carried out the reaction in an autoclave in which a number of additives were added to an alkaline water solution. In 1989, Asahi Chemical Industry Co. Ltd. [4] has developed a technology for a highly selective hydrogenation reaction, and succeeded in the commercialization of a new production process for producing cyclohexanol from benzene through cyclohexene. In recent years, numerous patents and papers have been published on the benzene selective hydrogenation [5–15]; most of them were described and summarized in the paper of Struijk [6,7]. Recently, some amorphous alloy attracts more and more attentions due to its high activity and selectivity in many hydrogenation reactions and its environmentally friendly preparation process, and Ru–B amorphous alloy catalysts have been employed in the benzene selective hydrogenation [16–24], but there is no report on its application in industry in the literature. We have developed an amorphous alloy Ru–La–B/ZrO_2 catalyst with high activity and high selectivity to cyclohexene. Considering thermodynamically metastable character of amorphous alloy, we deposited the amorphous alloys on ZrO_2 and added lanthanum as promoter to improve their thermal stability and catalytic properties. In the present work, various characterizations of the Ru–La–B/ZrO_2 were carried out by means of XRD, TEM, SEAD, XPS and N_2-physisorption and the activity and selectivity of the catalysts on

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* Corresponding author. Tel.: +86 371 67763706; fax: +86 371 67763706.
E-mail address: liushouchang@zzu.edu.cn (S.C. Liu).

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selective hydrogenation of benzene were measured under pilot conditions.

2. Experimental

2.1. Catalyst preparation

The Ru–La–B/ZrO_2 catalyst sample was prepared in the following procedures. A desired amount of zirconia was added to the 50 mL $RuCl_3$ and $LaCl_3$ solution (0.05 mol/L) with stirring for 30 min, then 50 mL $NaBH_4$ solution (0.5 mol/L) was added drop by drop to the above solution (mass ratio Ru/ZrO_2 = 10–20% and La/Ru = 1–5%). The agitation was continued for 5 min and then stopped. The black precipitate was kept in liquor solution for a while and then filtrated, washed thoroughly with distilled water until neutrality, and the amorphous alloy Ru–La–B/ZrO_2 catalyst was obtained.

2.2. Catalytic test

The selective hydrogenation of benzene was carried out in a 1 L autoclave. Two hundred and eighty millilitres of H_2O, 19.6 g $ZnSO_4\cdot 7H_2O$ and 4 g catalyst were introduced. Then the autoclave was sealed and filled with H_2 for more than four times to exclude air. Initially the stirring rate was fixed at 600 rpm and the H_2 pressure was kept at 3.0 MPa. When the temperature rose up to 413 K, 140 mL benzene was charged into the reactor. After this, the stirring rate was elevated to 1000 rpm, the H_2 pressure was elevated to 5.0 MPa, and the reaction was considered to start. The reaction process was monitored by taking small amount of reaction mixture at intervals, and followed by a gas chromatograph equipped with FID analyzing the products. The quantification of the benzene, cyclohexene and cyclohexane was made using calibration curves.

Definition

$$\text{Benzene conversion } (C_{\text{BZ}}) = \frac{\text{mole of reacted benzene}}{\text{mole of inital benzene}} \times 100,$$

$$\text{Cylohexene selectivity } (S_{\text{HE}}) = \frac{\text{mole of cyclohexene formed}}{\text{mole of converted benzene}} \times 100,$$

$$\text{Cyclohexene yield } (Y_{\text{HE}}) = \frac{\text{mole of cyclohexene formed}}{\text{mole of initial benzene}} \times 100$$

The catalyst activity and selectivity is given by γ_{40} and S_{40}, respectively. γ_{40} means that the mass of converted benzene by 1 g catalyst per hour when the conversion of benzene is at 40%, it is a general industrial target of evaluating catalytic activity. S_{40} is the cyclohexene selectivity when the benzene conversion is at 40%. The benzene conversion and the cyclohexene selectivity were plotted as a function of time, respectively. S_{40} would be obtained from this plot. γ_{40} is given by

$$\gamma_{40} = \frac{V\rho_{\text{BZ}}C_{\text{BZ}}}{t_{40}M_{\text{Cat}}} \qquad (1)$$

V is the volume of benzene (ml), ρ_{BZ} the density of benzene (0.88 g/mL), C_{BZ} the conversion of benzene (40 mol%), t_{40} reaction time (h) at 40 mol% benzene conversion and M_{Cat} is the mass of active component Ru in the catalyst (g).

2.3. Pilot experiment of Ru–La–B/ZrO_2 catalysts

A reaction slurry comprising of 170 L H_2O, 1.35 kg Ru–La–B/ZrO_2 catalyst, 1.35 kg ZrO_2 and 17 kg $ZnSO_4\cdot 7H_2O$ was charged into a reaction autoclave. Then the autoclave was sealed and the air was flushed out by nitrogen for a period of time. Next, the hydrogen pressure was kept at 4.0–4.5 MPa after hydrogen replacing the nitrogen. Before starting of the hydrogenation, the initial stirring rate was fixed at 350 rpm. The circulation flux of the slurry was maintained 130–150 kg/h, and then the temperature was raised at a rate of 80 K/h. When the desired reaction temperature of 413 K was achieved, the autoclave was running for 10–22 h in the absence of reactants to pretreat the catalyst and then the benzene was charged with circulation flux of 40–45 kg/h immediately. At the same time, the stirring rate was elevated to 450 rpm, the hydrogen pressure was elevated to 5.0 MPa, and the hydrogenation reaction started. In the reaction process, the product mixture continuously outflow from the autoclave through an overflow weir and entered a sedimentation equipment where the oil phase was separated and the water phase containing the catalysts was circulated back into the autoclave by a slurry circulation pump. An interface of oil phase and water phase in the sedimentation equipment was kept at 60–75%. The reaction process was autocontrolled by a computer, and activities and selectivities of the catalysts were monitored by taking small amount of reaction mixture at intervals through the product thief hatch, and followed by gas chromatograph equipped with FID analyzing the products. The analysis of product was the same as mentioned in Section 2.2.

The target of pilot tests was designed that the benzene conversion is 20 mol% and the cyclohexene selectivity is 60% in a single autoclave.

2.4. Characterization

The compositions of the Ru–La–B alloy were determined by ICP-AES (Thermal Elemental IRIS Intrepid).

The phases of the Ru–La–B/ZrO_2 catalyst were determined by X-ray diffraction (XRD) using Cu Kα radiation ($\lambda = 0.15418$ nm), the tube voltage was 40 kV and the tube current was 40 mA, respectively.

The surface morphology of active component on the ZrO_2 and the particle size were observed by a high-resolution transmission electron microscope (HRTEM, JEM 2011), an accelerating voltage of 100 kV was used for it. The amorphous character of the catalysts was verified by selected-area electron diffraction (SAED).

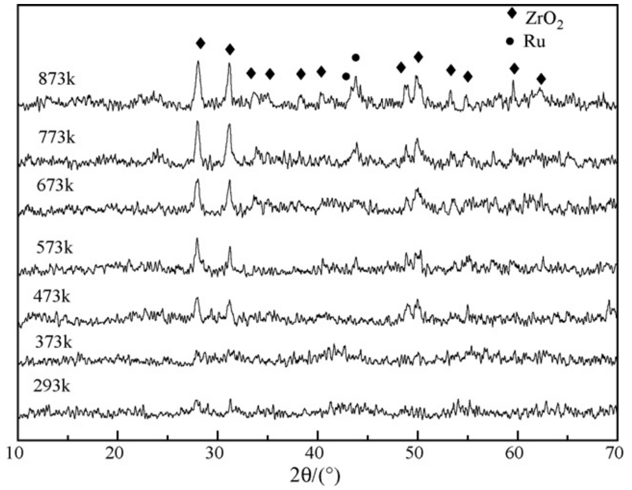

Fig. 1. XRD patterns of Ru–La–B/ZrO_2 catalysts treated at different temperatures.

X-ray photoelectron spectroscopy (XPS) analysis was carried out on a PHI 1600 ESCA system by using Al Kα radiation (1486.6 eV) at a base pressure of 10^{-8} Torr.

The texture character of the catalyst was determined by N_2-physisorption at 77 K on a Micromeritics TriStar 3000 apparatus.

3. Results and discussion

3.1. XRD of Ru–La–B/ZrO_2 catalysts

Figs. 1 and 2 are the XRD patterns of Ru–La–B/ZrO_2 catalysts treated at different temperatures and run for different reaction time under pilot conditions, respectively.

As shown in Figs. 1 and 2, when the catalyst was treated at the temperatures below 673 K or ran for 512 h at a temperature of 413 K, no significant change in the XRD patterns was found and no distinct peaks corresponding to Ru phase were seen though the content of Ru in the catalyst was up to 15 wt.%. Only the diffraction peaks attributed to monoclinic zirconia were observed. However, in Fig. 1 the most intensive peak corresponding to (1 0 1) crystalline plane of metallic Ru appeared when the catalyst was heated at above 773 K, and the intensity of the crystallized Ru peaks increased gradually with the increase of treating temperatures from 773 to 873 K, indicating the occurrence of the crystallization of Ru–La–B amorphous alloy. Those suggest that Ru–La–B alloy is highly dispersed on ZrO_2 and the Ru–La–B/ZrO_2 catalyst is considerable stable below 773 K and under the pilot conditions, which might be attributed to the structure effect of La and to dispersing effect of ZrO_2 for the ruthenium active component. Adding a small amount of lanthanum could result in deformation and irregularity of crystal lattice of the ruthenium since La has a larger atomic radius than that of Ru (r_{La} = 187.0 pm, r_{Ru} = 132.5 pm). Meanwhile, the dispersing effect of ZrO_2 makes Ru–La–B amorphous alloy uniformly dispersed, and the interaction between the alloy and the ZrO_2 makes ruthenium atoms remove difficultly, thus restraining the conglomeration and crystallization of Ru–La–B amorphous alloys [26].

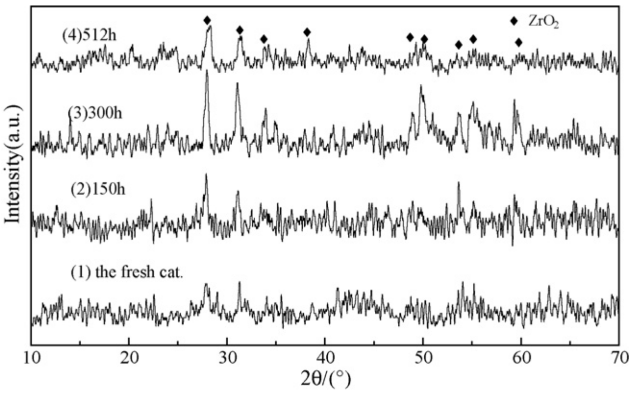

Fig. 2. XRD patterns of Ru–La–B/ZrO_2 catalysts run for different reaction time under pilot conditions.

3.2. TEM and SAED picture of Ru–La–B/ZrO_2 catalysts

Fig. 3 is the TEM and SAED pictures of Ru–La–B/ZrO_2 catalysts run for different time under pilot conditions at 413 K, respectively.

Fig. 3a–c are the TEM pictures, the light gray circular or elliptic flakes are ultrafine ZrO_2 crystallites, and the black particles on the ZrO_2 are the active components comprising Ru–B and La amorphous alloys with the aid of EDX analysis. Fig. 3a′–c′ are the SAED pictures corresponding to a–c, respectively, which are the way employed in confirming the structure of amorphous alloy. From Fig. 3a–c, it can be seen that, the Ru–La–B components are well dispersed on ZrO_2 matrix and statistical results show the particle diameters ranging from 3 to 6 nm, and the particle sizes of both Ru–La–B and ZrO_2 become larger with extending of the reaction time. From Fig. 3a′–c′, the catalysts, especially the fresh one, display a number of diffraction circles which are the typical amorphous character of Ru–La–B/ZrO_2 catalysts, and some small white spots on the circles, especially for the sample run for 512 h, appeared with extending of the reaction time. Those suggest that the conglomeration and the crystallization process of the nanosized amorphous alloy catalysts occur spontaneously and slowly under the pilot conditions.

3.3. Texture character of Ru–La–B/ZrO_2 catalysts

Table 1 and Fig. 4 show the texture character of Ru–La–B/ZrO_2 catalysts run for different time.

From Table 1, it can be seen that the specific surface areas vary from about 38–30 m^2/g, and the pore volumes vary from 0.20 to

Table 1
The specific surface areas and pore volumes of Ru–La–B/ZrO_2 catalysts run for different time

No.	Running time (h)	BET surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)
a	0	37.7	0.20
b	300	36.9	0.16
c	512	29.4	0.16

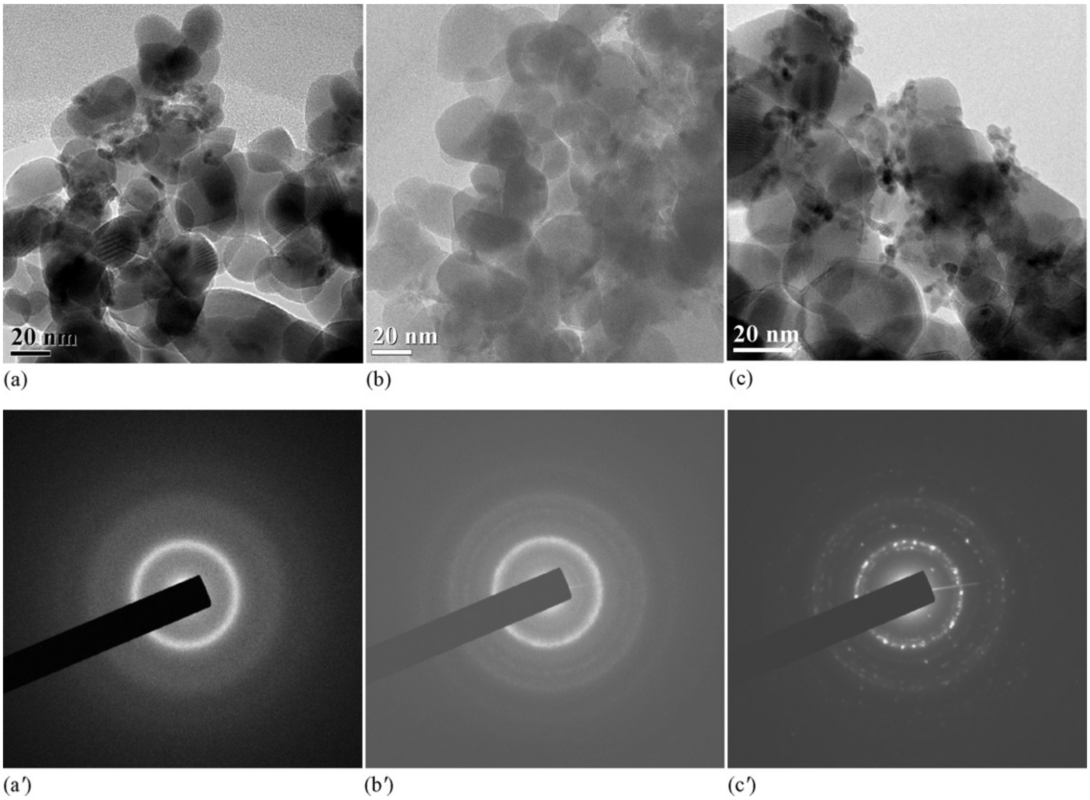

Fig. 3. TEM and SEAD pictures of Ru–La–B/ZrO_2 catalysts run for different time. (a) TEM of the fresh catalyst, (b) TEM of the catalyst run for 300 h, (c) TEM of the catalyst run for 512 h. (a′) SEAD of the fresh catalyst, (b′) SEAD of the catalyst run for 300 h, (c′) SEAD of the catalyst run for 512 h.

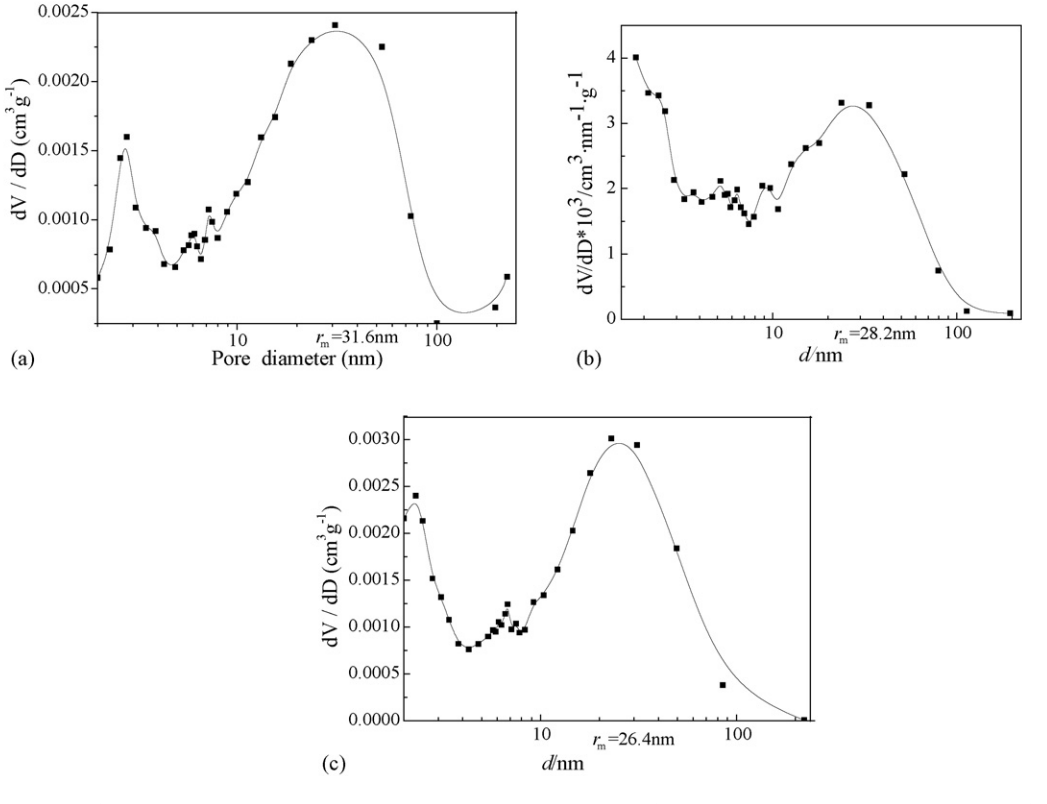

Fig. 4. The differential curves of pore size distribution of the Ru–La–B/ZrO_2 catalysts run for different time in the pilot conditions. (a) The fresh catalyst, (b) the catalyst run for 300 h, (c) the catalyst runs for 512 h.

Table 2
The compositions of Ru–La–B/ZrO_2 catalysts in the atomic ratio

Catalyst sample	Composition
a (the fresh Ru–La–B/ZrO_2 catalyst)	$Ru_{18.14}La_{0.08}B_{18.86}/ZrO_2$
b (the catalyst run for 300 h)	$Ru_{17.26}La_{0.05}B_{13.26}Zn_{0.35}Fe_{0.13}/ZrO_2$
c (the catalyst run for 512 h)	$Ru_{16.73}La_{0.01}B_{12.64}Zn_{0.27}Fe_{0.14}/ZrO_2$

0.16 cm^3/g with different reaction time. From Fig. 4, it can be observed that the pore size distributions of the catalysts are from 10 to 100 nm, and mainly nearby 30 nm. For the fresh catalyst, the most probable pore diameter is about 31.6 nm, and for the catalysts run for 300 and 512 h the most probable pore diameters are about 28.2 nm and about 26.4 nm, respectively. These results show that in the reaction process, the specific surface areas, the pore volumes, and the most probable pore diameters of the catalysts decreased, which might be relative to the adsorption of substances in the reaction mixture and might be one of the reasons for decreasing of the catalyst activity and selectivity.

3.4. XPS of Ru–La–B/ZrO_2 catalysts

The bulk compositions of Ru–La–B/ZrO_2 catalysts (the atomic ratio) run for different time under the pilot conditions were determined by ICP and listed in Table 2.

In Table 2b and c, Zn and Fe in the catalysts came from the adsorption of Zn^{2+} and Fe^{2+} in the reaction slurry, in which an amount of zinc sulfate was added to improve activity and selectivity of the reaction and Fe^{2+} stemmed from the reaction vessel.

Table 3 listed the electron binding energy (BE) of the elements in the catalysts run for different time in the pilot conditions, in which a is the fresh Ru–La–B/ZrO_2 catalyst, b is the catalyst run for 300 h, and c is the catalyst run for 512 h.

From Table 3, only the BE value of $Ru3d_{5/2}$ is employed during this discussion since the BE value of $Ru3d_{3/2}$ is covered by the BE value of C1s. It can be concluded from Table 3a–c that almost all ruthenium species existed in its metallic state with the binding energy of 279.3, 280.3 and 279.7 eV, respectively. For the fresh catalyst, the BE value of 279.3 eV was slightly less than the standard BE value of metallic Ru (280.1 eV) indicating the acceptance of some electrons from other elements. In the reaction process, ruthenium existed in metallic state with slight variations of BE value compared to the standard BE value of metallic Ru. The surface electronic state of boron species cannot be identified because the peak of B1s electron binding energy is totally covered by a wide peak of Zr $3d_{5/2}$ and Cl 2p which comes from the precursor $RuCl_3$. It has been reported, however, that boron species on the Ru–B amorphous alloy were in the elemental and oxidative states and some electrons transferred from B to metallic Ru, making Ru electron-enriched while B electron-deficient [17,18]. According to Table 3, for the fresh catalyst, the binding energy of La $3d_{5/2}$ is 843.1 eV which is higher than the standard BE value of elemental La (835.8 eV) indicating that La existed in La^{3+}, corresponding to La_2O_3 [26]. With the process of the reaction under hydrogen atmosphere, the BE values of La $3d_{5/2}$ were 836.1 eV(b) and 836.5 eV(c), respectively, which were slightly higher than the standard BE value of metallic La (835.8 eV), indicating that La existed in metallic state due to the reduction of hydrogen in the reaction process, and some electrons might be donated from La to ruthenium making La electron-deficient. For the used samples, the peaks of zinc and iron corresponding to Zn^{2+} and Fe^{2+} were also observed, and their BE values are listed in Table 3, which are in accordance with the results obtained by ICP.

Table 3
The electron binding energy (BE) of the elements in the catalysts run for different time

	Standard BE (eV)	(a) BE (eV)	(b) BE (eV)	(c) BE (eV)
Ru $3d_{5/2}$	280.1	279.3	280.3	279.7
La $3d_{5/2}$	835.8	843.1	836.1	836.5
$Fe2p_{3/2}$	706.7		709.2	
$Zn2p_{3/2}$	1021.5		1022.5	1022.5
C 1s	284.6	284.6	284.6	284.6
Cl 2p	198.0	198.0	198.2	198.1
$Zr3d_{5/2}$	182.2	182.2	182.2	182.2
O 1s	530.2	530.2	531.6	530.2

3.5. Activity and selectivity of the Ru–La–B/ZrO_2 catalyst

Table 4 shows the activity and selectivity of the Ru–La–B/ZrO_2 catalyst in a 1 L stirring autoclave.

Table 4
Conversion and selectivity of the Ru–La–B/ZrO_2 catalyst

t (min)	C_{BZ} (mol%)	S_{HE} (%)	Y_{HE} (mol%)
5	11.8	85.7	10.1
15	33.5	82.0	27.5
30	58.7	75.1	44.1
45	75.5	68.6	51.8
60	85.9	61.9	53.2

Run conditions: 280 mL H_2O, 140 mL C_6H_6, 4 g Ru–La–B/ZrO_2 cat (0.64 g Ru), 413 K, $p_{H2} = 5$ MPa, 1000 rpm, pretreatment for 22 h.

From Table 4, it can be seen that with the benzene conversions increasing, the cyclohexene yield achieved above 50%, and the selectivity to cyclohexene over the catalyst is beyond 85% in the initial stage. According to the method expressed in Section 2.2, it can be calculated that t_{40} is 18.6 min, S_{40} is 80.6% at the benzene conversion of 40%, and $\gamma_{40} = 248\ h^{-1}$, meaning 248 g of benzene was converted by 1 g catalyst per hour at the benzene conversion of 40%. On the other hand, if the activity is expressed in the amount of benzene (mmol) converted by 1 g of Ru per minute, it can be calculated that γ_{40} is equal to 53.0 mmol/g min. In comparison with the data reported in the literatures [25–28], it can be concluded that the Ru–La–B/ZrO_2 catalyst has high activity and good selectivity to cyclohexene, which is one of the most remarkable features of the Ru–La–B/ZrO_2 amorphous alloy catalyst.

High-performance of the Ru–La–B/ZrO_2 catalyst mainly attributed to the combination of the amorphous character, the

Table 5
The content of $Zn^{2+}$and Fe^{2+}in the reaction slurry and in the catalyst run for different time

Running time (h)	(a) In the reaction slurry		(b) In the catalyst	
	$[Zn^{2+}]$ (wt.%)	$[Fe^{2+}]$ (wt.%)	$[Zn^{2+}]$ (wt.%)	$[Fe^{2+}]$ (wt.%)
22	2.96	0.0066	2.0	0.15
82	2.83	0.035	3.32	0.78

Table 6
The comparison of the conversions and selectivities before and after washing

	5 min		10 min		15 min	
	C_{BZ} (mol%)	S_{HE} (%)	C_{BZ} (mol%)	S_{HE} (%)	C_{BZ} (mol%)	S_{HE} (%)
1.Before washing	6.5	60.4	11.4	50.2	16.5	31.4
2. After washing with H_2O	6.1	65.4	9.5	61.5	13.4	48.5
3. After washing with 0.5 M HCl	10.8	65.8	18.8	61.2	27.6	49.6
4. After washing with 2.0 M HCl	14.5	59.6	23.2	57.8	32.5	51.4
5. After washing with 1.0 M H_2SO_4	11.6	68.0	20.2	57.0	29.3	48.9

promoting effect of La and the dispersing effect of ZrO_2 on the active components.

3.6. Regeneration of the Ru–La–B/ZrO_2 catalyst

In order to develop and establish a new production process for producing cyclohexene effectively from benzene based on the Ru–La–B/ZrO_2 amorphous alloy catalyst, the regeneration method has been studied in the pilot conditions in detail.

It was found that the activities of the catalysts decreased fast in the pilot conditions if the reaction vessel is not coated with Teflon. The main reason for the deactivation of the catalysts was just likely attribute to the adsorption of contaminants stemmed from the reaction vessel on the catalyst surface. Table 5 shows the content of $Zn^{2+}$and Fe^{2+} in the reaction slurry and in the catalyst run for different time.

From Table 5, it can be seen that with the process of the reaction, the concentration of Zn^{2+} decreased while the concentration of Fe^{2+} increased in the slurry comprising of water, catalysts, zinc sulfate and zirconia. On the other hand, the amount of both Zn^{2+} and Fe^{2+} in the catalysts increased. Generally, the adsorption of a suitable amount of Zn^{2+} is helpful to improving the selectivity of the catalysts. While the adsorption of Fe^{2+} on the catalyst would cover the active sites, then would result in the activity of the catalyst decreasing. So we suggest that the deactivation of the catalysts is mainly caused by the adsorption of Fe^{2+} on the catalyst surface. If the catalysts are washed by water or by diluted acid, the adsorbed Fe^{2+} on the catalyst would be wiped out and the activities of the catalysts could be recovered. Table 6 shows the comparison of the conversions and selectivities of the catalysts before and after washing with water as well as with different diluted acids.

Run conditions: 423 K, 5 MPa, 29 mL C_6H_6, 58 mL H_2O, 0.5 mol L^{-1} $ZnSO_4$, 0.5 g cat, 900 rpm, generation temperature 298 K.

From Table 6, it can be concluded that the regeneration method of washing with diluted acids is better than that of with water, the activities and selectivities of the catalysts were recovered evidently by washing with diluted acids. Table 7 shows the washed ion percent in the catalysts with different methods.

By contrast of the data in Tables 5 and 7, it can be known from Table 5 that the content of Zn^{2+} was 3.32% and Fe^{2+} was 0.78% in the catalysts run for 82 h under the pilot conditions. However, only the partial Zn^{2+} can be removed while the Fe^{2+} cannot be removed by washing with water, but all the Zn^{2+} and partial Fe^{2+} can be removed by washing with diluted acids, for instance, 3.25% Zn^{2+} was removed by washing with 0.5 mol L^{-1} HCl, which was in good accordance with the actual content 3.32% Zn^{2+} adsorbed by the catalysts; 0.58% Fe^{2+} was removed by washing with 2.0 mol L^{-1} HCl, which was lower than the actual content 0.78% Fe^{2+} adsorbed by the catalysts. From Table 6, it can be known that the method by washing with 2.0 mol L^{-1} HCl was the best; the renewed catalysts exhibited the best activity and selectivity to cyclohexene.

Fig. 5 shows the variation of benzene conversions and selectivities to cyclohexene with reaction time under the pilot conditions through partial regeneration of the catalysts.

As shown in Fig. 5, when the reaction ran for 152 h, the benzene conversion was 24.0%, and the selectivity to cyclohexene was 60.5%, which is lower than that in the initial stage. In order to recover the activity, the regeneration of the catalysts was carried out by the following procedure: firstly, taking out 10 L slurry from sample-taking mouth of the equipment, followed by washing with 2.0 mol L^{-1} HCl and filtering, about 0.2 kg catalyst (one-tenth of the total catalysts) being regenerated, then adding 10 L H_2O and 1.5 kg $ZnSO_4{\cdot}7H_2O$ to keep the composition of the slurry unchanged; finally charging the regenerated catalyst

Table 7
The washed ion percent in the catalysts with different methods

Washed ion percent in the catalysts	$[Fe^{2+}]$ (wt.%)	$[Zn^{2+}]$ (wt.%)
With H_2O	0.00	0.56
With 0.5 M HCl	0.33	3.25
With 2.0 M HCl	0.58	2.35
With 1.0 M H_2SO_4	0.40	2.50

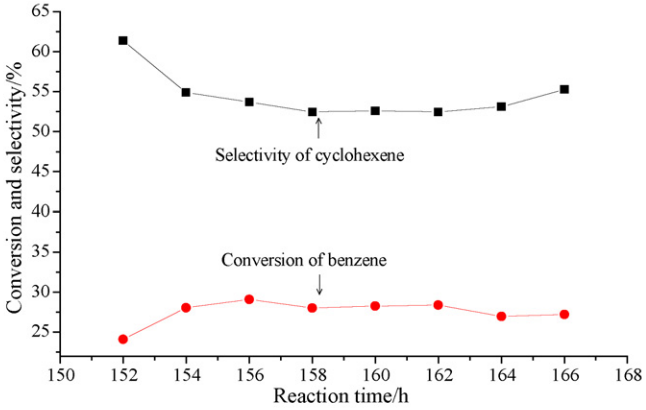

Fig. 5. The variation of the conversions and selectivities to cyclohexene with time in the pilot conditions through partial regeneration of the catalysts.

into the autoclave. The benzene conversions rose up to 30.6% after adding the regenerated catalysts, and it kept the activities above 24.0% for 14 h, which showed the regeneration method is available and effective.

3.7. The life of the Ru–La–B/ZrO$_2$ catalyst

A 100 L reactor coated with Teflon has been used to avoid contamination by metal ions, by which the life of the catalysts was investigated under the following conditions: the circulation flux of the slurry was maintained at 140 kg/h, and the benzene circulation flux was fixed at 42 kg/h, the reaction was carried out under the temperature of 413 K, the hydrogen pressure of 4.5 MPa and the stirring rate of 450 rpm were employed. Fig. 6 shows the activities and the selectivities to cyclohexene of the catalysts when the reaction ran from 364 to 380 h.

As shown in Fig. 6, the Ru–La–B/ZrO$_2$ amorphous alloy catalyst exhibited a long life. When the catalyst ran for 380 h, the activities and the selectivities to cyclohexene of the catalysts dropped a little. After adding the regenerated catalysts (one-tenth of the total catalysts), the activities and the selectivities to cyclohexene were kept for 15 h. When the reaction ran for 396 h, regeneration was carried out again by using the same method. Fig. 7 shows the activities and selectivities of the catalysts ran from 395 to 465 h.

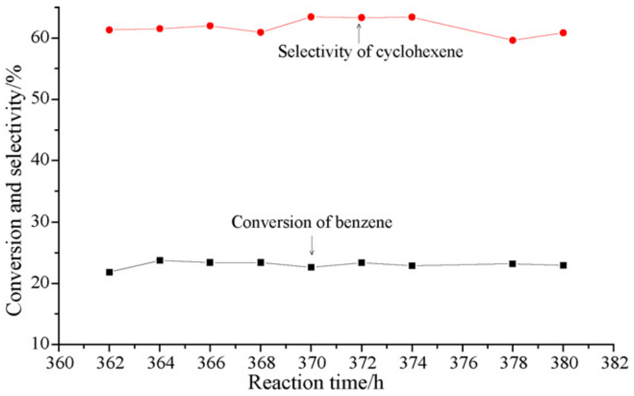

Fig. 6. The variation of benzene conversions and cyclohexene selectivities with the time from 364 to 380 h.

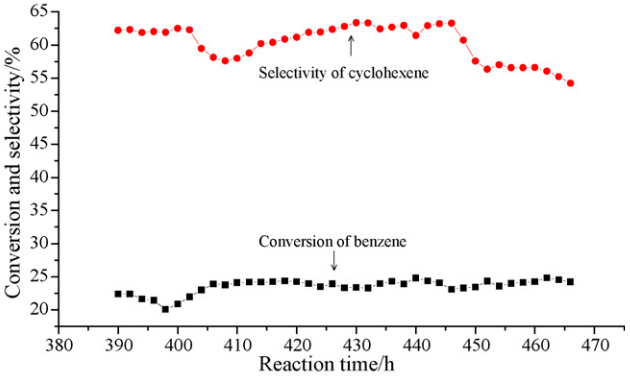

Fig. 7. The activities and selectivities of the catalysts ran from 395 to 465 h.

It was tested that the Ru–La–B/ZrO$_2$ amorphous alloy catalysts run for 512 h, although the activities and selectivities of the catalysts appeared fluctuating, the benzene conversions were stabilized above 25%. Therefore, it can be predicted that if consecutive process regeneration of the catalysts could be realized, the Ru–La–B/ZrO$_2$ amorphous alloy catalysts would run for a much longer time.

4. Conclusions

Various characterizations and measurements of the activity and selectivity of Ru–La–B/ZrO$_2$ catalysts for benzene selective hydrogenation to cyclohexene under pilot conditions show that the Ru–La–B/ZrO$_2$ catalyst has the amorphous alloy character. The amorphous alloy Ru–La–B is highly dispersed on ZrO$_2$ matrix, in which ruthenium exists in metallic state, lanthanum exists in La^{3+} or in metallic state, and boron species exist in elemental and oxidative states under reaction conditions. La and ZrO$_2$ play important roles in stabilization of the amorphous alloy structure and greatly improving the activity and selectivity of the catalysts. Under pilot conditions, the adsorption of Fe^{2+} stemmed from the reaction vessel on the catalysts is the main reason for deactivation of the catalysts. By washing with diluted acids, the catalysts can be regenerated. Ru–La–B/ZrO$_2$ catalysts not only exhibit high activity and superior selectivity to cyclohexene, but also have a long life. Therefore, it would have a good prospect for industrial applications.

References

[1] J.R. Anderson, The catalytic hydrogenation of benzene and toluene over evaporated films of nickel and tungsten, Aust. J. Chem. 10 (1957) 409–416.
[2] F. Hartog, J.H. Tebben, C.A.M. Weterings, The mechanism of benzene hydrogenation on group VIII metals, Proc. Int. Congr. Catal. 2 (1965) 1210–1221.
[3] W.C. Drinkard, Selective catalytic hydrogenation of aromatics to cycloolefins, NL Patent 7,205,832 1972.
[4] H. Nagahara, M. Konishi, Partial hydrogenation of monocyclic aromatic hydrocarbons, US Patent 4,734,536 1988.
[5] C. Schild, A. Wokaun, A. Balker, Carbon dioxide hydrogenation over nickel/zirconia catalysts from amorphous precursors: on the mechanism of methane formation, J. Phys. Chem. 95 (1991) 6341–6346.
[6] J. Struijk, J.J.F. Scholten, Selectivity to cyclohexenes in the liquid phase hydrogenation of benzene and toluene over ruthenium catalysts, as influenced by reaction modifiers, Appl. Catal. A: Gen. 82 (1992) 277–287.

[7] J. Struijk, M. d'Agremond, W.J.M. Lucas-de Regt, Partial liquid phase hydrogenation of benzene to cyclohexene over ruthenium catalysts in the presence of an aqueous salt solution. i. preparation, characterization of the catalyst and study of a number of process variables, Appl. Catal. A: Gen. 83 (1992) 263–295.

[8] H. Nagahara, M. Ono, M. KOnishi, Partial hydrogenation of benzene to cyclohexene, Appl. Surf. Sci. 121/122 (1997) 448–451.

[9] L. Ronchin, L. Toniolo, Selective hydrogenation of benzene to cyclohexene catalyzed by Ru supported catalysts: influence of the alkali promoters on kinetics, selectivity and yield, Catal. Today 66 (2001) 363–369.

[10] E.V. Spinace, J.M. Vaz, Liquid-phase hydrogenation of benzene to cyclohexene catalyzed by Ru/SiO_2 in the presence of water–organic mixtures, Catal. Commun. 4 (2003) 91–96.

[11] J.Q. Wang, P.J. Guo, S.R. Yan, Colloidal RuB/$Al_2O_3 \cdot xH_2O$ catalyst for liquid phase hydrogenation of benzene to cyclohexene, J. Mol. Catal. A: Chem. 222 (2004) 229–234.

[12] S.P. Lee, Y.W. Chen, Nitrobenzene hydrogenation on Ni–P, Ni–B and Ni–P–B ultrafine materials, J. Mol. Catal. A: Chem. 152 (2000) 213–223.

[13] R.B. Zhang, F.Y. Li, N. Zhang, Benzene hydrogenation over amorphous NiB/bentonite catalyst and promoting effect of Nd, Appl. Catal. A: Gen. 239 (2003) 17–23.

[14] X.F. Chen, H.X. Li, W.L. Dai, Selective hydrogenation of cinnamaldehyde to cinnamyl alcohol over the Co–La–B/SiO_2 amorphous catalyst and the promoting effect of La-dopant, Appl. Catal. A: Gen. 253 (2003) 359–369.

[15] R.B. Zhang, Q.J. Shi, F.Y. Li, The effects of rare earths on supported amorphous NiB/Al_2O_3 catalysts, Appl. Catal. A: Gen. 205 (2001) 279–284.

[16] W.J. Wang, M.H. Qiao, S.H. Xie, Selective hydrogenation of cyclopentadiene to cyclopentene over an amorphous NiB/SiO_2 catalyst, Appl. Catal. A: Gen. 163 (1997) 101–109.

[17] Y. Chen, Chemical preparation and characterization of metal–metalloid ultrafine amorphous alloy particles, Catal. Today 44 (1998) 3–16.

[18] S.H. Xie, M.H. Qiao, H.X. Li, A novel Ru–B/SiO_2 amorphous catalyst used in benzene-selective hydrogenation, Appl. Catal. A: Gen. 176 (1999) 129–134.

[19] Z. Liu, S.H. Xie, B. Liu, Benzene-selective hydrogenation to cyclohexene over supported ruthenium boride catalysts prepared by a novel method, New J. Chem. 23 (1999) 1057.

[20] J.F. Deng, H.X. Li, W.J. Wang, Progress in design of new amorphous alloy catalysts, Catal. Today 51 (1999) 113–125.

[21] H.X. Li, W.J. Wang, H. Li, Crystallization deactivation of Ni–P/SiO_2 amorphous catalyst and the stabilizing effect of silica support on the Ni–P amorphous structure, J. Catal. 194 (2000) 211–221.

[22] S.C. Liu, G. Luo, H.R. Wang, Studies on operation conditions for liquid phase selective hydrogenation of benzene to cyclohexene over Ru–M–B/ZrO_2 catalyst, J. Catal. Chin. 23 (2002) 317–320.

[23] S.C. Liu, Y.Q. Guo, X.L. Yang, Kinetic equations for liquid-phase selective hydrogenation of benzene to cyclohexene, J. Catal. Chin. 24 (2003) 42–46.

[24] Y.J. Hou, Y.Q. Wang, F. He, Effects of lanthanum addition on Ni–B/γ-Al_2O_3 amorphous alloy catalysts used in anthraquinone hydrogenation, Appl. Catal. A: Gen. 259 (2004) 35–40.

[25] S.C. Hu, Y.W. Chen, Partial hydrogenation of benzene to cyclohexene on ruthenium catalysts supported on La_2O_3–ZnO binary oxides, Ind. Eng. Chem. Res. 36 (1997) 5153–5159.

[26] S.C. Hu, Y.W. Chen, Effect of preparation on Ru–Zn ultrafine catalysts in partial hydrogenation of benzene, Ind. Eng. Chem. Res. 40 (2001) 3127–3132.

[27] J.Q. Wang, Y.Z. Wang, S.H. Xie, M.H. Qiao, H.X. Li, K.N. Fan, Partial hydrogenation of benzene to cyclohexene on a Ru–Zn/*m*-ZrO_2 nanocomposite catalyst, Appl. Catal. A: Gen. 272 (2004) 29–36.

[28] S.C. Hu, Y.W. Chen, Partial hydrogenation of benzene on Ru–Zn/SiO_2 catalysts, Ind. Eng. Chem. Res. 40 (2001) 6099–6104.