Study of a Ru-La/ZrO$_2$ Catalyst Prepared by Precipitation Method for Selective Hydrogenation of Benzene to Cyclohexene

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Abstract: A Ru-La/ZrO$_2$ catalyst was prepared by the precipitation method, in which Ru was an active component, La was a promoter and ZrO$_2$ was a dispersant. Comparing with the catalyst prepared by the chemical reduction method, the Ru-La/ZrO$_2$ exhibited higher activity and better selectivity. At 140 °C and hydrogen pressure of 5 MPa, the C$_6$H$_{10}$ selectivity reached 70% at a C$_6$H$_6$ conversion of 35% for a reaction time was 5 min and the total La/Ru loading was 10%. Textural parameters of the catalyst were obtained by physical adsorption, BET surface area and specific pore volume measurements. The catalyst sample gave a BET area of 41 m$^2$/g and a specific pore volume of 1.1 cm$^3$/g, and the most probable pore distribution was located at 5 to 10 nm. H$_2$-TPR measurements showed that ruthenium oxide could be reduced to its metallic state at about 403 K. XRD determinations indicated that ruthenium and lanthanum were highly dispersed on the zirconia. A significant advantage of the Ru-La/ZrO$_2$ catalyst is that it can be used directly in its unreduced state for the selective hydrogenation of benzene.

Key words: selective hydrogenation, benzene, cyclohexene, Ru-La/ZrO$_2$, precipitation

1. Introduction

Cyclohexene as an important intermediate product is widely used in chemical productions. The process of selective hydrogenation of benzene to cyclohexene has been an important research topic in green chemistry owing to its atomic economy and clean production [1]. In order to attain greater economic benefits, researchers are searching for a new catalytic system that is high in activity and selectivity, simple in technology, and low in cost. In this respect, some progresses have been acquired. Ruthenium has been found to be the most effective catalyst in benzene selective hydrogenation [2]. The addition of organic substances and inorganic salts in the aqueous medium could increase the yield and selectivity for cyclohexene [3,4]. Nagahara and co-workers have reported a kind of unsupported Ru-Zn catalysts in the presence of an aqueous solution of ZnSO$_4$ with suspended ZrO$_2$, and they obtained 80% in cyclohexene selectivity [5]. Supported ruthenium catalysts such as Ru/γ-Al$_2$O$_3$, Ru-Zn/ZrO$_2$ and Ru/ZnO-La$_2$O$_3$ etc. were also reported to have cyclohexene yields comparable to those of unsupported ruthenium [7–10]. Recently, some new supported amorphous ruthenium boride catalysts prepared via chemical reduction have been developed, resulting in high cyclohexene selectivities [11–13]. Previously we have prepared Ru-Zn-B/ZrO$_2$ and Ru-Fe-B/ZrO$_2$ catalysts for benzene selective hydrogenation [14–16]. In addition, amorphous alloy Ru-La-B/ZrO$_2$ catalysts have been employed in pilot scale tests, and they exhibited potentialities for industrial application [17]. With the objective of developing novel catalysts

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with superior catalytic properties, we have investigated a series of supported Ru-based catalysts. In this paper, we report on a novel Ru-La/ZrO$_2$ catalyst prepared by the precipitation method, using sodium hydroxide as the precipitant. This Ru-La/ZrO$_2$ catalyst not only exhibited superior catalytic properties, but also could be used directly in benzene selective hydrogenation without the need of any reduction.

2. Experimental

2.1. Catalyst preparation

The Ru-La/ZrO$_2$ catalyst was prepared via the following procedures. 2.5 g nanosized zirconia (ToYo, Japan, surface area 34.2 m$^2$/g) as the support was added to 30 ml of a mixed aqueous solution of RuCl$_3$·xH$_2$O and LaCl$_3$·xH$_2$O (0.05 mol/L). The resulting solution was agitated for 30 min, then 20 ml of aqueous sodium hydroxide solution (0.45 mol/L) was added drop by drop. After the agitation was continued for another 40 minutes, the precipitate was aged, filtered and the catalyst precursor was obtained. The above precursor was dried for 1.0 h at 353 K and reduced for 6.0 h in a still pipe heater at 573 K under hydrogen atmosphere by means of a temperature programmer, then it was cooled down to room temperature, oxidized for 5 minutes in air, weighted and kept in water.

The Ru-La-B/ZrO$_2$ catalyst was prepared by an aqueous NaBH$_4$ solution, which was added drop by drop to the RuCl$_3$·xH$_2$O and LaCl$_3$·xH$_2$O mixed aqueous solution containing suspended zirconia, as has been reported elsewhere [16].

2.2. Catalytic activities test

The selective hydrogenation of benzene was carried out in a WDF-0.25 autoclave. The slurry consisted of 50 ml H$_2$O, 7.2 g ZnSO$_4$·7H$_2$O and 0.5 g catalyst. 29 ml benzene was introduced when the reaction temperature rose up to 413 K and the reaction was considered to start. The final reaction conditions were: temperature 413 K, hydrogen pressure 5.0 MPa, and stirring rate of 1000 r/min. The reaction process was monitored by taking small amounts of the reaction mixture at 5, 10 and 15 min for gas chromatograph analysis using a TCD detector, from which the benzene conversion and the cyclohexene selectivity at different reaction time could be calculated.

2.3. Catalyst characterization

The texture of the catalyst was measured with an NOVA-2000 adsorption apparatus by means of nitrogen physisorption at 77 K. X-ray diffraction (XRD) patterns was recorded on a Rigaku Dmax-3B powder diffraction-meter with Cu K$_\alpha$ radiation. Catalyst reducibility was determined by temperature-programmed reduction (TPR) with a TP-5000 adsorption apparatus equipped with a thermal conductivity detector (TCD). The samples were heated up to 573 K at a rate of 10 K/min in a gas stream of 10% hydrogen in argon.

3. Results and discussion

3.1. Activity and selectivity of the catalyst

The results of benzene conversion and cyclohexene selectivity at different reaction time during the hydrogenation of benzene over the catalysts with different mass ratio of lanthanum to ruthenium are shown in Table 1.

### Table 1. Effect of different La/Ru ratios on C$_6$H$_6$ conversion and C$_6$H$_{10}$ selectivity

<table>
<thead>
<tr>
<th>m(La/Ru)/%</th>
<th>Benzene conversion (%)</th>
<th>Cyclohexene selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5 min</td>
<td>10 min</td>
</tr>
<tr>
<td>5</td>
<td>40.33</td>
<td>61.05</td>
</tr>
<tr>
<td>8</td>
<td>42.45</td>
<td>53.72</td>
</tr>
<tr>
<td>10</td>
<td>34.98</td>
<td>48.51</td>
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<tr>
<td>12</td>
<td>48.78</td>
<td>61.43</td>
</tr>
<tr>
<td>14</td>
<td>49.43</td>
<td>73.20</td>
</tr>
<tr>
<td>Ra-La-B/ZrO$_2$</td>
<td>26.67</td>
<td>45.09</td>
</tr>
</tbody>
</table>

Reaction conditions: 413 K, 5 MPa H$_2$, 29 ml C$_6$H$_6$, 50 ml H$_2$O, 7.2 g ZnSO$_4$, 0.5 g cat, 1000 r/min
From Table 1, it can be seen that all the catalysts exhibited high catalytic activities. The conversions of benzene reached 30%–50% after 5 minutes of reaction, which were 20% higher than that on the amorphous alloy catalyst prepared by chemical reduction under the same reaction conditions, as compared to the last row of the data in Table 1.

The superior activity of the Ru-La/ZrO	extsubscript{2} catalyst is attributed to a higher dispersion of the active components. Different from the Ru-La-B/ZrO	extsubscript{2} catalyst prepared by chemical reduction, the Ru	extsuperscript{3+} in Ru-La/ZrO	extsubscript{2} catalyst prepared by precipitation was deposited and dispersed on zirconia with NaOH and the active phase of the catalyst was formed via calcination and reduction. On the other hand, the Ru	extsuperscript{3+} in the catalyst prepared by chemical reduction was reduced and deposited on the zirconia in aqueous solution by NaBH	extsubscript{4}, and the active phase of the catalyst was formed directly. The active components of the former have higher dispersion and utilization after reduction due to the fact that the Ru-La/ZrO	extsubscript{2} precursors are existing in a colloidal state. For benzene consecutive hydrogenation, the time corresponding to maximum yields of intermediate cyclohexene is the optimal residence time of benzene. Usually, the residence time of benzene can be shortened if the catalyst has a superior activity. On the other hand, passivation of the catalyst, an operation in which the catalyst was pretreated for a period of time with aqueous salt solution in the absence of benzene under reaction conditions, would stabilize the structure and change the sedimentation properties of the catalyst. Meanwhile, hydrogen adsorbed on the catalyst surface would lead to distinct diminishing of the activity and enhancing of the selectivity. It has been reported that the activity would be lowered by 10% and the selectivity would be increased by 10% after the catalyst was passivated for 22 h [1]. Our studies have indicated that when the catalyst containing 10% La/Ru was passivated, then a 25% initial conversion and a selectivity up to 80% could be obtained. Therefore, it can be concluded that the superiority of Ru-La/ZrO	extsubscript{2} catalyst lies in its higher activity and its modifiable selectivity.

Table 1 also shows that the cyclohexene selectivities were about 70% at 40% benzene conversion for all the precipitated catalysts. Moreover, in contrast to the amorphous alloy catalyst prepared by chemical reduction, they all have similar selectivities at the same benzene conversion. The superior selectivity of the Ru-La/ZrO	extsubscript{2} catalyst is regarded to depend on its chemical compositions and preparation conditions, and is attributed to the promoting effect of the lanthanum. This can be explained as that the lanthanum, being a light rare earth element, has larger atomic radius (La 187.3 pm, as compared with Ru of 132.5 pm) and the property of easy-denoting of electrons. Thus, addition of lanthanum to the catalyst would result in a deformation of the ruthenium crystal lattice, so that both the atomic geometric configuration and the atomic distance of ruthenium are changed, which would lead to a modification of the electronic properties and an alternation of the structure and characteristics of the active centers.

In addition, Table 1 shows that the catalyst with 10%La/Ru attained a maximum cyclohexene selectivity at the same benzene conversion. This will be discussed in the following section of 3.3.

In order to investigate in more detail the relationship among the macroscopic properties, the microscopic structure and the preparation conditions of the Ru-La/ZrO	extsubscript{2} catalyst, it was studied by means of XRD, BET surface area, total pore volume, distribution of pore size and H\textsubscript{2}-TPR measurements.

### 3.2. XRD measurements

Figure 1 presents the XRD patterns of Ru based catalysts prepared by different methods. Figure 1(1) shows the XRD pattern of pure ruthenium prepared by precipitation. There exist three obvious diffraction peaks at 2θ of 38.1°, 41.4° and 43.9°, which are all attributed to metallic ruthenium. As can be seen in Figure 1(2), only one broaden diffraction peak is observed at 2θ of 43.9° on the XRD pattern of the Ru-La-B catalyst prepared by chemical reduction before hydrogenation, which is attributed to the typical diffraction of amorphous alloy. This is in good agreement with those reported in the literature [12]. However, in Figure 1(3) the peaks corresponding to ruthenium crystallites appeared after hydrogenation, indicating crystallization of the Ru-La-B amorphous alloy. Figure 1(4) and 1(5) show the XRD patterns of the Ru-La/ZrO	extsubscript{2} catalyst prepared by precipitation before and after hydrogenation, respectively. Only diffraction peaks of monoclinic zirconia can be observed. Even though the loading of ruthenium was up to 15%, no distinct peaks corresponding to ruthenium crystallites can be seen in the patterns, indicating that the active component of the ruthenium was highly dispersed on zirconia. Evidently, comparing with the amorphous alloy catalyst, the Ru-La/ZrO	extsubscript{2}
catalyst prepared by precipitation has a more stable structure. This is one of the striking features of this catalyst.

Figure 1. XRD patterns of Ru based catalysts prepared by different methods
(1) XRD pattern of pure Ru prepared by precipitation method,
(2) XRD pattern of Ru-La-B catalyst prepared by the chemical reduction method before hydrogenation, (3) XRD pattern of Ru-La-B catalyst prepared by the chemical reduction method after hydrogenation, (4) XRD pattern of Ru-La/ZrO₂ catalyst prepared by the precipitation method before hydrogenation, (5) XRD pattern of the Ru-La/ZrO₂ catalyst prepared by precipitation method after hydrogenation

3.3. Textural determination

Table 2 shows the BET surface areas and specific pore volumes of the Ru-La/ZrO₂ catalysts prepared by precipitation. Figure 2 shows the pore size distribution of the Ru-La/ZrO₂ catalysts with different La/Ru ratios.

Table 2. The BET surface areas and specific pore volumes of Ru-La/ZrO₂ catalysts

<table>
<thead>
<tr>
<th>m(La/Ru)/%</th>
<th>BET surface area (m²/g)</th>
<th>Specific pore volume (cm³/g) (p/p₀=0.99)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>40.53</td>
<td>0.1121</td>
</tr>
<tr>
<td>8</td>
<td>38.24</td>
<td>0.0915</td>
</tr>
<tr>
<td>10</td>
<td>41.33</td>
<td>0.1084</td>
</tr>
<tr>
<td>12</td>
<td>40.36</td>
<td>0.1113</td>
</tr>
<tr>
<td>14</td>
<td>38.38</td>
<td>0.0737</td>
</tr>
</tbody>
</table>

Figure 2. Variation of pore size distribution of Ru-La/ZrO₂ catalysts with different La/Ru ratios

It can be seen from Table 2 that catalysts with different La/Ru ratios have a mean BET surface area of 40 m²/g and a mean specific pore volume of 0.1 cm³/g, and the catalyst with 10% La/Ru has slightly larger BET surface area than that of the others.

Figure 2 shows three kinds of pore sizes for the Ru-La/ZrO₂ catalysts with different La/Ru ratios: (1) Some micropores below 2 nm width are attributed to the intrinsic pores of zirconia, which have no contribution to the activity and selectivity for the selective hydrogenation of benzene in spite of its promoting effect on the BET surface area and the specific pore volume. This is because no active components can enter into these pores during the preparation process, and there are no active centers on its internal surface. (2) Some mesopores with a pore size of 10 nm are produced by the interaction between the ZrO₂ and the active components during the preparation process, and they are the main sources of the BET surface area and the specific pore volume, and they are the main reaction spots because of the locating of many active centers inside them. (3) Some macropores with pore size of 45 nm are probably corresponding to interstices among the particles. They exhibit the largest diameters, but they have little impact on the BET surface area and the specific pore volume. These macropores are just like the external surface of the particles, and may have a certain influence on the activity and selectivity of the catalyst. As shown in Figure 2, when
the La/Ru ratio of the catalyst is 1:9, the mesopores of 5 to 10 nm represent a typical normal distribution, which means that these pores occupy a larger proportion of the total pores, and their sizes are homogeneously distributed.

In short, the textural parameters mentioned above all have effects on the activities and the selectivities of the catalysts. It is known that the catalysts with larger surface areas could offer more active sites, while those with larger mean pore sizes would be beneficial for rapid diffusion of the intermediate cyclohexene from the pores, thus avoiding further hydrogenation of cyclohexene to cyclohexane [16]. And the homogeneous distribution of the mean pore size is favored to the utilization of the surface area and the specific pore volume. That could be one of the reasons for the catalyst containing 10%La/Ru to have better activity and superior selectivity.

3.4. H$_2$-TPR studies of reduction behaviors of Ru-La/ZrO$_2$ catalysts

Figure 3 show the H$_2$-TPR profiles of Ru-La/ZrO$_2$ precursors with a 10%La/Ru loading, dried at 353 K in air and calcined at 473 K for 1 h.

![Figure 3. H$_2$-TPR profile of Ru-La/ZrO$_2$ precursor dried at 313 K (a) and calcined at 473 K (b)](image)

Figure 3(a) shows three peaks, corresponding to the reduction of Ru$_2$O$_3$, Ru(OH)$_3$ or Ru$_2$O$_3$·3H$_2$O, and RuO$_2$. The catalyst precursors existed mainly as Ru(OH)$_3$ or Ru$_2$O$_3$·3H$_2$O. Generally, Ru$^{4+}$ can be oxidized or reduced easily. After eliminating the water adsorbed on the Ru precursor by drying at 353 K, it may be completely dehydrated to Ru$_2$O$_3$ and deeply oxidized to RuO$_2$ due to its high dispersion on ZrO$_2$. The first TPR peak with a maximum at about 382 K is attributed to the reduction of Ru$_2$O$_3$, indicating the easier reduction and the less amount of Ru$_2$O$_3$. The second peak with a maximum at about 388 K corresponds to the reduction of Ru(OH)$_3$ or Ru$_2$O$_3$·3H$_2$O, and the higher reduction temperature than that of the first peak suggests that the reduction of the hydroxide or the hydrate oxide include the process of water loss and reduction, thus needing more energy. In addition, the larger peak area indicates the existence of comparatively larger amount of Ru(OH)$_3$ or Ru$_2$O$_3$·3H$_2$O in the precursor. The third peak with a maximum at about 402 K is assigned to the reduction of RuO$_2$, which is difficult to be reduced. From its passivative peak shape, we assume that the reduction of RuO$_2$ may be carried out in two steps: the Ru$^{4+}$ is first reduced to Ru$^{3+}$, and then the Ru$^{3+}$ is reduced to Ru$^{0}$. The reactions corresponding to the three reduction peaks can be illustrated in Figure 3(a) as follows:

$$Ru_2O_3 + 3H_2 \rightarrow 2Ru + 3H_2O \quad (1)$$
$$Ru_2O_3·3H_2O + 3H_2 \rightarrow 2Ru + 6H_2O \quad (2)$$
$$RuO_2 + 2H_2 \rightarrow Ru + 2H_2O \quad (3)$$

The two hydrogen consumption peaks in Figure 3(b) are assigned to the reduction of RuO$_2$. Because Ru(OH)$_3$ can be oxidized to RuO$_2$ at 423 K, so the sample after calcination at 473 K is in the form of Ru$^{4+}$. According to the above results, the first peak with the maximum at about 395 K can be attributed to the reduction of Ru$^{4+}$ to Ru$^{3+}$, and the other peak with the maximum at about 411 K is related to the reduction of Ru$^{3+}$ to metallic ruthenium. It was found that the temperature for the complete reduction of RuO$_2$ in the sample calcined at 473 K is 9 K higher than that of the sample dried at 353 K. This indicates that there is a strong interaction between RuO$_2$ and ZrO$_2$ in the sample calcined at the high temperature.

Figure 3 indicates that the reduction temperature of the Ru-La/ZrO$_2$ precursor prepared by precipitation is below 413 K, irrespective of the existence of the active component ruthenium. We suggest that the Ru-La/ZrO$_2$ precursor prepared by precipitation can possibly be used directly in the selective hydrogenation of benzene, that is, the reduction of the active component in the precursor could probably be car-
ried out in the autoclave during the heat treatment process from room temperature to 413 K. If this can be proved as feasible, the catalyst precursor would exhibit hydrogenation activity. Then, this can not only get rid of the process of calcination and reduction, but can also make the catalyst storage more convenient.

3.5. Activity and selectivity of the Ru-La/ZrO$_2$ precursors used directly in the benzene hydrogenation

According to the information offered by H$_2$-TPR, some experiments were carried out. The Ru-La/ZrO$_2$ precursors, with different La/Ru ratios, prepared by precipitation and without being washed and reduced, were used directly for the selective hydrogenation of benzene. The activities and the selectivities of these precursors are shown in Table 3.

As shown in Table 3, the Ru-La/ZrO$_2$ precursors exhibited comparatively high activities and selectivities for the selective hydrogenation of benzene. Their activities were slightly lower than those of the Ru-La/ZrO$_2$ catalysts shown in Table 1. However, their activities and selectivities were similar to that of the Ru-La-B/ZrO$_2$ catalyst prepared by chemical reduction in Table 1.

<table>
<thead>
<tr>
<th>m(La/Ru)/%</th>
<th>Benzene conversion (%)</th>
<th>Cyclohexene selectivity (%)</th>
</tr>
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<tr>
<td></td>
<td>5 min</td>
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<td>14</td>
<td>30.25</td>
<td>39.68</td>
</tr>
</tbody>
</table>

Reaction conditions are the same as in Table 1.

In view of the above results, we consider that two approaches can be taken once the catalyst precursors are prepared by precipitation. One is to obtain the catalyst by filtering, drying, calcining and reducing the precursors, and then it is used for benzene selective hydrogenation. This approach includes more steps, but the activity of the catalyst is very high. The other approach is not to wash and filter the precursors, but just eliminating the supernatant solution, and then the precursors are used directly in the reaction. This is a simpler way for the preparation of the catalyst, but the activity as well as the selectivity can still approach that of the catalyst prepared by chemical reduction.

4. Conclusions

The activity of a Ru-La/ZrO$_2$ catalyst prepared by the precipitation method is higher than that of the Ru-based amorphous alloy catalysts prepared by chemical reduction, while the selectivities of these two kinds of catalysts are almost the same at the same conversion of benzene. The catalyst with 10%La/Ru (mass ratio) exhibits a higher selectivity. XRD measurements indicate that ruthenium, the active component, and lanthanum, the promoter, are highly dispersed on zirconia. Meanwhile, the Ru-La/ZrO$_2$ catalyst possesses a more stable structure.

Investigations on the catalyst texture showed that the catalyst with 10%Ru/La has slightly larger BET surface area and a homogeneous distribution of mesopores with sizes of 5 to 10 nm. These pores are the source of BET surface area and pore volume, and are also the main locations for the reactive sites of benzene selective hydrogenation to cyclohexene.

It is demonstrated that the unreduced precursors can be used directly for selective hydrogenation of benzene, as they also exhibited better activity and selectivity. In this way, the preparation process of Ru-based catalysts for benzene selective hydrogenation by precipitation instead of by chemical reduction can be simplified.

References

1997, 121/122: 448