Chem. Res. Chin. Univ., 2015, 31(4), 615—620 doi: 10.1007/s40242-015-4382-1

Effect of Lanthanum on Catalytic Performance of Ru/Al_2O_3 Catalyst for Hydrogenation of Esters to Corresponding Alcohols

ZHANG Lei, ZHENG Xiaojuan and LI Ruixiang*

Key Lab of Green Chemistry and Technology, Ministry of Education, Department of Chemistry, Sichuan University, Chengdu 610064, P. R. China

Abstract Ru-La/γ-Al_2O_3 catalyst was prepared by impregnation method and characterized by temperature programmed reduction(TPR), transmission electron microscopy(TEM), X-ray photoelectron spectra(XPS), Brunauer-Emmett-Teller(BET), X-ray diffraction(XRD), and NH_3-temperature programmed desorption(NH_3-TPD). NH_3-TPD revealed that the strong acidic centers in γ-Al_2O_3 are not the major factor to cause the hydrolysis of esters to acids in the hydrogenation of esters. The results of TPR and TEM indicate that the appropriately added lanthanum results in the good dispersion of ruthenium and the easy reduction of ruthenium oxide on Ru-La/γ-Al_2O_3, which could promote the catalytic activity of Ru-La/γ-Al_2O_3 for the hydrogenation of methyl propionate to propanol. When the amount of lanthanum added in the catalyst was up to 9%(mass fraction), 4%Ru-9%La/γ-Al_2O_3 catalyst gave a conversion of methyl propionate of 98.1% and a selectivity of 94.8% to propanol at a reaction temperature of 180 °C and a hydrogen pressure of 5.0 MPa.

Keywords Ruthenium; Lanthanum; Alumina; Methyl propionate; Hydrogenation; Propanol

1 Introduction

Alcohols are generally obtained by hydrogenating aldehydes, ketones[1,2], esters[3—6]. Because of the weak polarity and intrinsic steric hindrance of carboxylic group[7], the hydrogenation of carboxylic acids and esters is very difficult. For instance, the hydrogenation of esters over copper-based catalysts, which are widely used in industry[8], is carried out at a high temperature of 200—300 °C and a high hydrogen pressure of 20—30 MPa. Therefore, to develop an active catalyst system for the hydrogenation of esters to the corresponding alcohols under a mild condition is of great importance in research as well as in industry. Recently, some catalysts containing a noble metal(Rh, Ru, Pd, etc.) and a second metal as a promoter(Sn, Zn, etc.) are used for the hydrogenation of esters to alcohols under relatively mild conditions[6,9,10]. Among these catalysts, ruthenium-based catalysts, especially Ru-Sn or Ru-Sn-B[4], show a good activity and selectivity for the hydrogenation of esters. For example, ethyl acetate could be hydrogenated into ethanol over Ru-Sn/SiO_2[11], methyl oleate could be hydrogenated into oleyl alcohol over Ru-Sn-B/Al_2O_3[12—14], and ethyl lactate could be hydrogenated into 1,2-propanediol(1,2-PDO) over Ru-Sn-B/Al_2O_3[15]. Besides, the catalytic performance of Ru-Sn catalyst for the hydrogenation of 1,4-cyclohexanedicarboxylic acid (CHDA) to 1,4-cyclohexanedimethanol(CHDM) could be further improved by introducing Pt[16]. The promotional effect of a second metal for the hydrogenation of esters exhibits not only in heterogeneous catalysis, but also in homogeneous catalysis. For example, after $Re_2(CO)_{10}$, $Mo(CO)_6$ and $W(CO)_6$ are added in $Ru(acac)_3$ and $Ru_3(CO)_{12}$ respectively, the catalytic performance of Ru for the hydrogenation of esters is obviously improved[17]. Although the introduction of a second metal can greatly improve the catalytic performances of ruthenium-based catalysts, the hydrogenations are still performed at a temperature higher than 200 °C and a hydrogen pressure of 5.0 MPa, and the selectivity to the corresponding alcohol is generally lower than 80%. Hence, it is still a challenge to improve the activity and selectivity of a catalyst for the hydrogenation of esters to corresponding alcohols. Rare earth elements are widely used in the field of catalysis[18—20], but there has been no report on using a rare earth element to modify the performance of a catalyst for the hydrogenation of esters to alcohols. In this work, we investigated the effect of La on the hydrogenation performance of Ru-based catalyst. The aim of this work is to study how lanthanum affect the Ru-based catalyst in ester hydrogenation.

2 Experimental

2.1 Materials

Support γ-Al_2O_3(calcined at 500 °C for 4 h, 160 mesh) was purchased from Shanxi Cosmetic Research Institute and $RuCl_3{\cdot}xH_2O$ from Kunming Precious Metals, China. Other chemicals, methyl propionate(C. P. grade), propionic acid(A. R.

---

*Corresponding author. E-mail: liruixiang@scu.edu.cn

Received October 13, 2014; accepted January 4, 2015.

Supported by the National Natural Science Foundation of China(No.21072138).

grade), ethyl acetate(A. R. grade), ethyl lactate(A. R. grade), methyl laurate(A. R. grade), $LaCl_3\cdot7H_2O$(A. R. grade), $NaBH_4$ (A. R. grade) and solvents(A. R. grade), were used as accepted. The purity of H_2 was higher than 99.99%.

2.2 Catalyst Preparation

2.2.1 Preparation of La/γ-Al_2O_3

γ-Al_2O_3 was impregnated with an aqueous solution of $LaCl_3\cdot7H_2O$, then dried at 120 °C for 24 h, and calcined at 350 °C for 3 h.

2.2.2 Preparation of Ru-La/γ-Al_2O_3(I)

La/γ-Al_2O_3 was impregnated with an aqueous solution of $RuCl_3$(Ru concentration 5.9 mg/mL) for 8 h, and the mixture was reduced with an aqueous solution of $NaBH_4$(B/Ru=20, molar ratio) under vigorous agitation at room temperature. The solid was filtered, washed with distilled water, and dried at 60 °C for 8 h to get the catalyst.

2.2.3 Preparation of Ru-La/γ-Al_2O_3(II)

γ-Al_2O_3 was co-impregnated with an aqueous solution containing $RuCl_3$ and $LaCl_3$, and then reduced by $NaBH_4$. The filtrate was collected to determine the content of metals in the catalyst by ICP, and the Ru loading was about 4.0%(mass fraction).

2.3 Hydrogenation Test

The hydrogenation of methyl propionate was carried out in a 60-mL stainless steel autoclave. A desired amount of catalyst, methyl propionate, and water were charged to the reactor. The autoclave was flushed with pure hydrogen four times, and then fed to a desired pressure. After the designated temperature was reached, the mixture was stirred at a stirring rate of 1500 r/min, and the reaction timing began. The products were analyzed by gas chromatography(Agilent GC-6890) with an FID detector(detector temperature was 280 °C) and an SE-30 supelco column(30 m×0.25 mm×0.25 μm).

2.4 Characterization

The content of each of the metals in all the catalysts was determined by inductively coupled plasma(ICP, IRIS Intrepid). X-ray diffraction(XRD) pattern was recorded on a PHILIPHS X'Pert MPD with Cu $K\alpha$ as a radiation at a voltage of 50 kV and a current of 40 mA. Samples were scanned in a 2θ range of 20°—110° at a rate of 0.1°/s. Transmission electron microscopy (TEM) images were obtained on a JEM-1200EX microscopy at an acceleration voltage of 100 kV. BET surface areas of the catalysts were measured on an auto adsorption/desorption analyzer(ZXF-6, Northwest Chemical Industry) at a relative pressure(p/p_0) ranged from 0.05 to 0.3; X-ray photoelectron spectra(XPS) were recorded on a Kratos XSAM800 spectrometer with Al $K\alpha$ X-ray radiation(1215 eV), operated at 15 mA and 12 kV. The vacuum of the analysis chamber was 6.7×10^{-7} Pa during data acquisition. All the binding energy values were referenced to the C_{1s} peak of contaminant carbon at 284.6 eV. NH_3-temperature programmed desorption(NH_3-TPD) measurement was performed with the reported method[21]. It was carried out in a micro-reactor with a GC-15A thermal conductivity detector(TCD, Shimadzu). Prior to the measurement, 100 mg of sample was flushed with argon of 15 mL/min and activated by heating at 400 °C(at a heating rate of 8 °C/min) for 1 h. After the catalyst was cooled to 40 °C, the adsorption of ammonia was carried out at an ammonia flowing rate of 50 mL/min for 1 h and the desorption of ammonia by heating the sample cell from 40 °C to 800 °C at a rate of 8 °C/min and an argon flowing rate of 15 mL/min. Temperature programmed reduction (TPR) experiments were performed in a laboratory-made apparatus consisted of a gas supply system, a quartz tubular micro-reactor, and a thermal conductivity detector. The catalyst of 100 mg was flushed at a N_2 flowing rate of 25 mL/min and activated at 400 °C(heating rate of 8 °C/min) for 1 h. Then the reduction of the catalyst was performed with a mixture gas of H_2 and N_2(the ratio of hydrogen to nitrogen was 5%, mass fraction) at a flowing rate of 25 mL/min, and the reduction temperature increased from 70 °C to 600 °C at a rising rate of 8 °C/min.

3 Results and Discussion

3.1 Characterization of Catalysts

XRD patterns of 4%Ru-9%La/γ-Al_2O_3(I), which was calcined at 200, 350 and 550 °C, respectively, are shown in Fig.1. Except the diffraction peaks of γ-Al_2O_3, no peaks corresponding to Ru, RuO, and RuO_2 were observed. The results indicate that ruthenium was all highly dispersed on γ-Al_2O_3[22,23].

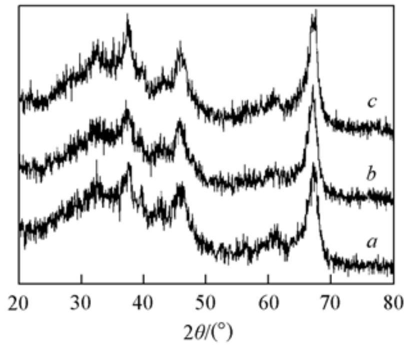

Fig.1 XRD patterns of 4%Ru-9%La/γ-Al_2O_3(I) catalyst calcined at 200 °C(*a*), 350 °C(*b*) and 550 °C(*c*)

TEM images of the catalysts with different loading of lanthanum prepared with different methods, are presented in Fig.2. Among those of the four catalysts, the Ru particles in 4%Ru-9%La/γ-Al_2O_3(I), which are homogeneously distributed on the surface of the support, show the smallest mean size[2—3 nm, Fig.2(C)]. However, the Ru particles(larger than 4 nm) in the other three catalysts[Fig.2(A), (B) and (D)] are obviously larger than those in 4%Ru-9%La/γ-Al_2O_3(I). The result reveals that appropriately added La could effectively improve the dispersion of Ru. For the catalyst 4%Ru-9%La/γ-Al_2O_3(I), the preferential supported La could occupy the strong adsorption sites on the surface of γ-Al_2O_3, so the dispersion of Ru in 4%Ru-9%La/γ-Al_2O_3(I) was much better than that in 4%Ru-9%La/γ-Al_2O_3(II)[Fig.2(D)], which was prepared by co-impregnating with the aqueous solution of $LaCl_3$ and $RuCl_3$.

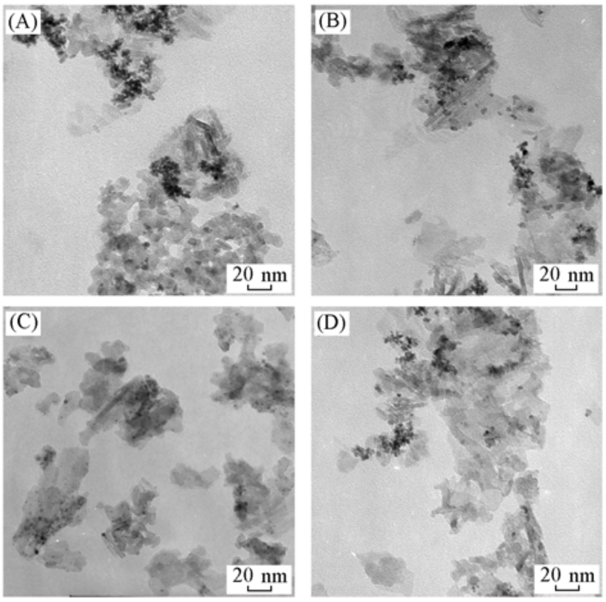

Fig.2 TEM images of 4%Ru/γ-Al_2O_3(A), 4%Ru-3%La/γ-Al_2O_3(I)(B), 4%Ru-9%La/γ-Al_2O_3(I)(C) and 4%Ru-9%La/γ-Al_2O_3(II)(D)

TPR characterization of the catalysts is shown in Fig.3. In Fig.3 curve *a*, the reduction peak at 197 °C can be attributed to the reduction of ruthenium oxide[24]. When the addition amount of lanthanum was 3%, the reduction temperature of ruthenium oxide increased from 197 °C[25] for the monometallic Ru catalyst to 261 °C for 4%Ru-3%La/γ-Al_2O_3(I) and the reduction peak intensity of ruthenium oxide became weak(Fig.3 curve *b*). Obviously, the reduction of Ru(III) to Ru(0) becomes difficult in this case. When lanthanum loading increased to 9%(Fig.3 curve *c*), a new reduction peak of ruthenium oxide appeared at 140 °C besides the major reduction peak at 195 °C[25]. The new reduction peak revealed the formation of some new active species in this catalyst. While the addition amount of lanthanum was beyond 9%(Fig.3 curve *d*), the reduction of ruthenium oxide became difficult and the reduction temperature increased to 230 °C. Compared with 4%Ru-9%La/γ-Al_2O_3(I) calcined at 350 °C(Fig.3 curve *c*), the reduction of ruthenium oxide in 4%Ru-9%La/γ-Al_2O_3(I) calcined at 650 °C(Fig.3 curve *f*) was more difficult, and not only was its TPR peak of ruthenium obviously weakened, but also the reduction temperature of ruthenium oxide rose from 140 °C to 180 °C. Furthermore, the catalyst 4%Ru-9%La/ γ-Al_2O_3(II) showed a weak reduction peak of ruthenium oxide at a higher temperature of 229 °C(Fig.3 curve *e*). The above results revealed that not only the dispersion of ruthenium in 4%Ru-9%La/γ-Al_2O_3(I) calcined at 350 °C was the best, but also the reduction of ruthenium was the easiest.

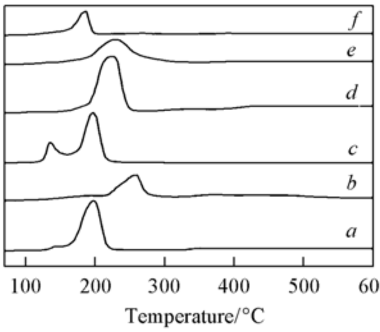

Fig.3 TPR profiles of the catalysts

a. 4%Ru/γ-Al_2O_3; *b*. 4%Ru-3%La/γ-Al_2O_3(I); *c*. 4%Ru-9%La/γ-Al_2O_3(I), calcined at 350 °C; *d*. 4%Ru-13%La/γ-Al_2O_3(I); *e*. 4%Ru-9%La/γ-Al_2O_3(II); *f*. 4%Ru-9%La/γ-Al_2O_3(I), calcined at 650 °C.

NH_3-TPD profiles of the catalysts are presented in Fig.4. For Ru/γ-Al_2O_3(Fig.4 curve *a*), the spectrum shows two desorption peaks in a low temperature region of 160—425 °C and a high temperature region of 478—780 °C, respectively. It indicates the existence of two acid sites(strong and weak acid sites)[26], especially, the existence of lots of strong acid centers on Ru/γ-Al_2O_3. After La was introduced into the catalyst, the peak of NH_3 in the high temperature region was sharply weakened and that in the low temperature was obviously strengthened. Moreover, the desorption temperature of NH_3 decreased with the increase of La loading in Fig.4 curves *a*, *c* and *d*. These results suggest that the strong acid sites of the catalyst were neutralized by base La_2O_3 and transformed into the weak acidic centers. Especially, the desorption peak in the high temperature region in Fig.4 curve *d* almost disappeared and the peak in the low temperature region also weakened. Therefore, the acid intensity of acid sites in 4%Ru-9%La/γ-Al_2O_3(I) was the weakest among those of the investigated catalysts. In addition, the desorption temperature and desorption peak area in the low temperature region in Fig.4 curve *b* were higher than those in Fig.4 curve *d*. The result indicates that the acid intensity of those of 4%Ru-9%La/γ-Al_2O_3(I) calcined at 200 °C was stronger and the weak acid centers was more than those of 4%Ru-9%La/γ-Al_2O_3(I) calcined at 350 °C. In other words, the increase of the calcination temperature promoted the interaction between the acid center and base La_2O_3.

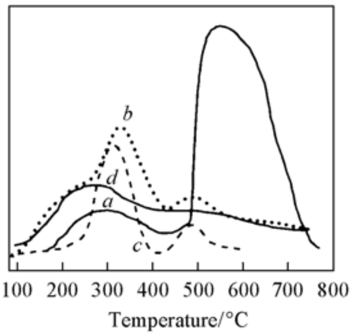

Fig.4 NH_3-TPD profiles of the catalysts

a. 4%Ru/γ-Al_2O_3; *b*. 4%Ru-9%La/γ-Al_2O_3(I) calcined at 200 °C; *c*. 4%Ru-3%La/γ-Al_2O_3(I) calcined at 350 °C; *d*. 4%Ru-9%La/γ-Al_2O_3(I) calcined at 350 °C.

BET results are summarized in Table 1. It was noticeable that S_{BET} and pore volume increased with increasing the lanthanum content from 3% to 9%, but decreased when the Lanthanum content was beyond 9%. 4%Ru-9%La/γ-Al_2O_3(I) had the maximum S_{BET} and pore volume. Its structure characters are almost consistent with the results reported by Subramanian[27,28].

Fig.5 shows the XPS spectra for 4%Ru-9%La/γ-Al_2O_3(I) reduced by $NaBH_4$. As the peak of $Ru_{3d_{3/2}}$ was covered by

Table 1 Effect of La content on 4%Ru-La/γ-Al_2O_3(I) for the hydrogenation of methyl propionate[a]

La_2O_3/γ-Al_2O_3 mass ratio(%)	S_{BET}/($m^2\cdot g^{-1}$)	Pore volume/($cm^3\cdot g^{-1}$)	Average pore diameter/nm	Conversion(%)	Selectivity(%)		
					1-PO[b]	PA[c]	TREF[d]
0	127.6	0.23	3.2	61.1	94.2	5.2	0.6
3	131.2	0.26	3.4	68.4	93.7	6.0	0.3
5	142.7	0.28	3.3	82.8	96.5	2.8	0.7
7	159.6	0.32	3.2	93.9	92.8	4.8	2.4
9	175.0	0.36	3.2	98.1	94.8	3.4	1.8
11	171.4	0.34	3.3	96.2	89.3	8.3	2.4
13	163.8	0.34	3.3	94.8	90.3	8.5	1.2

a. Reaction conditions: 0.1 mL of methyl propionate; 2.0 mL of H_2O; temperature, 180 °C; hydrogen pressure, 5.0 MPa; 4%Ru-La/γ-Al_2O_3(I) catalyst, 52.6 mg; reaction time, 10 h; *b*. 1-propanol; *c*. propionic acid; *d*. transesterification.

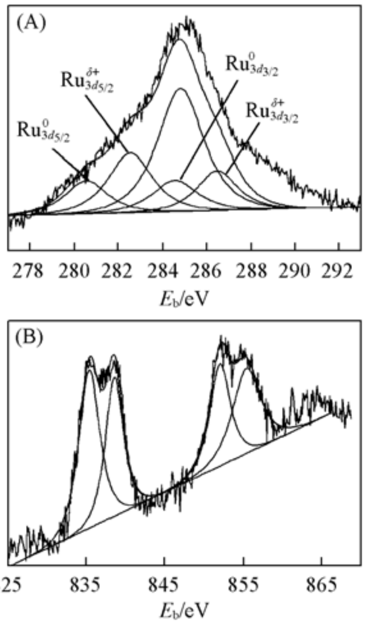

Fig.5 XPS spectra of the Ru_{3d}(A) and La_{3d}(B) in 4%Ru-9%La/γ-Al_2O_3(I) catalyst reduced by $NaBH_4$

the peak of C_{1s}, the peak of $Ru_{3d_{5/2}}$ was employed to determine the oxidation state of ruthenium. In Fig.5(A), two Ru species were detected in the $NaBH_4$ reduced catalyst. One is Ru(0) with a binding energy of 280.53 eV[29,30], the other is the electron-deficient species $Ru^{\delta+}$ at 282.53 eV[31]. In Fig.5(B), the electron binding energy of $La_{3d_{5/2}}$ at 835.3 eV is the value corresponding to La^{3+}[32], indicating that lanthanum still exists in La^{3+} in the sample.

3.2 Effect of La Content in the Catalysts on the Hydrogenation

Methyl propionate was used as the model compound, the performances of the above catalysts were investigated with the results summarized in Table 1. It was seen that although 4%Ru/γ-Al_2O_3 showed a good selectivity of 94.2% at 180 °C and 5.0 MPa, it gave a low conversion of 61.1%. Interestingly, the conversion of methyl propionate over Ru-La/γ-Al_2O_3(I) increased gradually with the increase of lanthanum loading. When the mass ratio of La_2O_3 to γ-Al_2O_3 was up to 9%, the conversion reached a maximum value of 98.1% and the selectivity to propanol was close to 95%. If the mass ratio of La_2O_3 to γ-Al_2O_3 was over 9%, the conversion and selectivity began to decrease. To our knowledge, a conversion of methyl propionate of 98.1% and a propanol selectivity of 95% over 4%Ru-9%La/γ-Al_2O_3(I) under this mild conditions are better than the reported results over Pd/ZnO at 300 °C for the hydrogenation of methyl propionate[29]. Luo *et al.*[18] found that the addition of Sn in RuB/γ-Al_2O_3 obviously improved the dispersion of ruthenium and avoided the aggregation of ruthenium. RuSnB/γ-Al_2O_3 gave a high yield of 1,2-propanediol in the hydrogenation of ethyl lactate. Guo *et al.*[33] also reported that La_2O_3 could promote the reduction of NiO, and improved the activity of Ni for the hydrogenation of *m*-dinitrobenzene. In this case, lanthanum seemed to play a similar role as above tin. According to the characterization results of TPR and TEM, the lower activity of Ru-La/γ-Al_2O_3(II) than that of Ru-La/γ-Al_2O_3(I)(Table 2) could be attributed to the difficult reduction of ruthenium oxide[16,34] and the bad dispersion of ruthenium (the large size of Ru particles). Especially, the presence of La in 4%Ru-9%La/γ-Al_2O_3(I) not only got the smallest size of Ru particles, but also promoted the full reduction of ruthenium oxide. As a result, it showed the highest activity for the hydrogenation of methyl propionate.

Table 2 Effect of La loading method on the catalytic performance of the catalysts for hydrogenation of methyl propionate[a]

La loading method	La_2O_3/γ-Al_2O_3 mass ratio(%)	Conversion(%)	Selectivity(%)		
			1-PO[b]	PA[c]	TREF[d]
I	5	82.8	96.5	2.8	0.7
II		68.6	97.2	1.8	1.0
I	7	93.9	92.8	4.8	2.4
II		72.5	94.0	3.6	2.4
I	9	98.1	94.8	3.4	1.8
II		66.4	96.6	2.0	1.4
I	11	96.2	89.3	8.3	2.4
II		45.4	95.1	3.7	1.2

a. Reaction conditions: 0.1 mL of methyl propionate; 2.0 mL of H_2O; temperature, 180 °C; hydrogen pressure, 5.0 MPa; 4%Ru-La/γ-Al_2O_3 catalyst, 52.6 mg; reaction time, 10 h; *b*. 1-propanol; *c*. propionic acid; *d*. transesterification.

On the other hand, the promoting effects of La on the catalytic activity could be from an electronic effect as well as the structure effect(the dispersion of Ru). From the viewpoint of chemical adsorption, the adsorption of carboxyl group on Ru center is carried out by the coordination of the lone pair of electrons of oxygen in carboxyl group to *d*-orbit of Ru[35]. According to the reported results[33,36—38], a base metal oxide, such as La_2O_3, could donate electrons to the *d*-orbit of Ru and increase the electronic density of Ru, so the electron-rich Ru center would be generated. If Ru atom is electron-rich, it seems to be unfavorable to the adsorption. Why is the catalytic activity enhanced? We suggest that the adsorption of carboxyl group on active center is not main reason for the activation of substrate, the back-donating of electrons on the active center to π^* of carboxyl group plays a key role in the activation of substrate. The fact that the full reduction of ruthenium oxide can promote the catalyst activity also supports the suggestion. Therefore, the electron-rich center, which is caused by the addition of La, improves the catalytic activity.

3.3 Effect of Reaction Time on the Hydrogenation

Fig.6 shows the effect of reaction time on the hydrogenation of methyl propionate over Ru-La/γ-Al_2O_3 with the different loading of lanthanum. The conversion of methyl propionate and the selectivity to propanol increased with extending reaction time from 2 h to 6 h. But the initial selectivity to propanol decreased with the addition of lanthanum due to the increase of propionic acid content. The results clearly prove that the acid intensity and number of acid sites are not the major reason to lead to the hydrolysis of methyl propionate to propionic acid. Although a high content of propionic acid was formed under the condition of a short reaction time, the formed propionic acid could be effectively hydrogenated into propanol. According to the results in Table 3, with propionic acid as a substrate, catalyst 4%Ru-9%La/γ-Al_2O_3(I) was still highly effective. If 9%La/γ-Al_2O_3 and γ-Al_2O_3 were used as the catalysts, the methyl propionate of 44.6% was converted to propionic acid over γ-Al_2O_3, and the methyl propionate of 69.7% was converted to propionic acid over 9%La/γ-Al_2O_3. Obviously, propionic acid was formed by the hydrolysis of the substrate on the surface of La_2O_3 and γ-Al_2O_3 rather than on the active ruthenium center. In other words, due to the introduction of La, the decreases of the acidic intensity and acidic center numbers are not the real reason to cause the improvement of the catalyst activity.

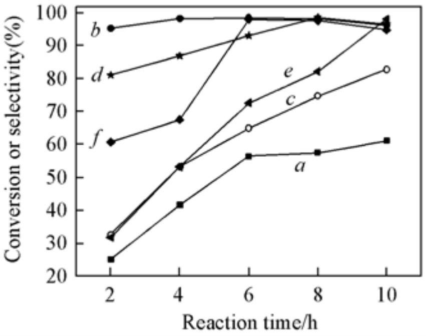

Fig.6 Effect of reaction time on methyl propionate hydrogenation over catalysts with different La contents

Reaction condition: reaction temperature, 180 °C; hydrogen pressure, 5.0 MPa; methyl propionate, 0.1 mL; solvent, 2.0 mL of H_2O; catalyst, 52.6 mg. *a*. Conversion(4%Ru/γ-Al_2O_3); *b*. selectivity (4%Ru/γ-Al_2O_3); *c*. conversion(4%Ru-5%La/γ-Al_2O_3); *d*. selectivity (4%Ru-5%La/γ-Al_2O_3); *e*. conversion(4%Ru-9%La); *f*. selectivity (4%Ru-9%La/γ-Al_2O_3).

Table 3 Hydrogenation performance of 4%Ru-9%La/γ-Al_2O_3(I) for some acid and esters

Substrate	Conversion(%)	Selectivity(%)
Methyl propionate[a]	98.1	94.8
Propionic acid[a]	91.0	94.4
Ethyl acetate[b]	91.2	92.9
Ethyl lactate[c]	98.6	70.6
Methyl laurate[d]	97.8	70.8

a. 180 °C, 5.0 MPa H_2, reaction time 10 h, molar ratio of substrate/catalyst(S/C)=50, selectivity to propanol; *b*. 180 °C, 5.0 MPa H_2, reaction time 10 h, S/C=50, selectivity to ethanol; *c*. 150 °C, 5.0 MPa H_2, reaction time 8 h, S/C=50, selectivity to 1,2-propanediol; *d*. 220 °C, 6.0 MPa H_2, reaction time 6 h, S/C=200, selectivity to lauryl alcohol.

3.4 Effect of Calcination Temperature on the Performance of the Catalysts

Table 4 displays the effect of calcination temperature on activity of the catalysts. From BET measurements, it can be seen that S_{BET} and pore volume of the catalyst firstly increased, and then decreased with the further increase of calcination temperature. At the same time, the conversion of methyl propionate increased with the improvement of the surface structure(the increase of BET surface area and pore volume). When 4%Ru-9%La/γ-Al_2O_3(I) was calcined at 350 °C, it showed a high surface area and a large pore volume, so the catalyst gave the best catalytic activity. According to the TPR profiles in Fig.3 curve *f*, ruthenium oxide in 4%Ru-9%La/γ-Al_2O_3(I), which was calcined at a high temperature of 650 °C, was difficult to reduce under the experimental conditions and the catalyst gave a low activity, so the reduction degree of ruthenium oxide played a key role in its activity. The phenomenon was probably caused by two reasons. One was that the strong interaction between La and Ru or Ru and γ-Al_2O_3 was caused after the catalyst was calcined at a high temperature. It could be similar to Ni-B/SiO_2[33]. After Ni-B/SiO_2 was calcined at a high temperature, its activity decreased since the interaction between Ni^{2+} and the support became too strong to be effectively reduced. The other was that Ru particles were sintered at a high temperature, so the number of Ru active sites decreased.

Table 4 Effect of calcination temperature on textural property and catalytic activity of catalyst 4%Ru-9%La/γ-Al_2O_3(I)[a]

Calcination temperature/°C	S_{BET}/($m^2 \cdot g^{-1}$)	Pore volume/($cm^3 \cdot g^{-1}$)	Conversion(%)	Selectivity(%)		
				1-PO[b]	PA[c]	TREF[d]
200	103.8	0.24	79.1	98.1	1.2	0.7
350	163.8	0.34	92.4	98.5	1.0	0.5
450	159.5	0.33	76.6	99.5	0.3	0.2
550	155.7	0.32	70.3	98.8	0.8	0.4
650	151.9	0.32	61.7	98.1	1.3	0.6

a. Reaction conditions: 0.1 mL of methyl propionate; 2.0 mL of H_2O; temperature, 180 °C; hydrogen pressure, 5.0 MPa; 4%Ru-9%La/γ-Al_2O_3(I) catalyst, 52.6 mg; reaction time, 8 h; *b*. 1-propanol; *c*. propionic acid; *d*. transesterification.

3.5 Test for Other Substrates

The results for the hydrogenation of different substrates over 4%Ru-9%La/γ-Al_2O_3(I) are shown in Table 3. It could be seen that the catalyst can not only catalyze the hydrogenation of short chain carboxylic acid esters, but also be effective for the hydrogenation of long chain and substituted carboxylic esters. Miyake *et al.*[39] found that Rh-Sn/γ-Al_2O_3 was suitable for the hydrogenation of methyl laurate, but it only gave a selectivity of 43.2% to lauryl alcohol at a methyl laurate conversion of 71.7%. In this case, 4%Ru-9%La/γ-Al_2O_3(I) showed a high efficiency in water for the hydrogenation of methyl laurate to lauryl alcohol. Even if the reaction temperature was only 220 °C, the methyl laurate conversion could be up to 97.8% and the selectivity for lauryl alcohol was over 70%, both are much higher than the reported ones.

4 Conclusions

In this work, it has been demonstrated that the hydrogenation of methyl propionate to propanol can be efficiently performed over Ru-La/γ-Al_2O_3. The addition of a suitable amount of lanthanum(La_2O_3/γ-Al_2O_3 mass ratio of 9%) to Ru/γ-Al_2O_3 catalyst results in the improvement of Ru dispersion and the full reduction of ruthenium oxide. On the other hand, that the introduction of La_2O_3 causes the acidity change of the catalyst is not the major reason to lead to the catalyst activity improvement. So the effects of lanthanum involve both structure effect and electronic effect.

References

[1] Fang C., Chen Y. J., Mao H., Zhao J., Jiang Y. F., Zhao S. L., Ma J., *Chem. J. Chinese Universities*, **2015**, *36*(1), 124

[2] Yang J., Zhao W. B., Yang C. F., Sun X. D., Wang Q., Zhu Y. Q., Chen H., *Chem. J. Chinese Universities*, **2013**, *34*(7), 1679

[3] Costa C. M. M., Jordão E., Mendes M. J., Santos O. A. A., Verduraz F. B., *React Kinet Catal. Lett.*, **1999**, *66*, 155

[4] Deshpande R. M., Buwa V. V., Rode C. V., Chaudhari R. V., Mills P., *Catal. Commun.* **2003**, *3*, 269

[5] Santos S. M., Silva A. M., Jordão E., Fraga M. A., *Catal. Commun.*, **2004**, *5*, 377

[6] Zhou Y. F., Wei J., Fan G. Y., Fu H. Y., Li R. X., Chen H. , Li X. J., *Chem. Lett.*, **2009**, *38*, 1304

[7] Yang Q., Zhang J., Zhang L., Fu H. Y., Zheng X. L., Yuan M. L., Chen H., Li R. X., *Catal. Commun.*, **2013**, *40*, 37

[8] Fan G. Y., Zhang Y., Zhou Y. F., Li R. X., Chen H., Li X. J., *Chem. Lett.*, **2008**, *37*, 852

[9] Jiang H. B., Jiang H. J., Su K., Zhu D. M., Zheng X. L., Fu H. Y., Chen H., Li R. X., *Appl. Catal. A*, **2012**, *447/448*, 164

[10] McAlee A. J., *J. Chem. Soc. C*, **1969**, 2454

[11] Rieke R. D., Thakur D. S., Roberts B. D., White G. T., *J. Am. Oil. Chem. Soc.*, **1997**, *74*, 333

[12] Pouilloux Y., Autin F., Guimon C., Barrault J., *J. Catal.*, **1998**, *176*, 215

[13] Satos S. M., Silva A. M., Jordão E., Fraga M. A., *Catal. Today*, **2005**, *107/108*, 250

[14] Louessard P., Candy J. P., Bournonville J. P., Basset J. M., *Structure and Reactivity of Surface*, Elsevier, Amsterdam, **1989**, 591

[15] Desphande V. M., Ramnarayan K., Narasimhan C. S., *J. Catal.*, **1990**, *121*, 174

[16] Narasimhan C. S., Desphande V. M., Ramnarayan K., *Appl. Catal.*, **1989**, *48*, L1

[17] Cheah K. Y., Tang T. S., Mizukami F., Niwa S., Toba M., Choo Y. M., *J. Am. Oil Chem. Soc.*, **1992**, *69*, 410

[18] Luo G., Yan S. R., Qiao M. H., Fan K. N., *J. Mol. Catal. A*, **2005**, *230*, 69

[19] Hara Y., Endou K., *Appl. Catal. A*, **2003**, *239*, 181

[20] He D. H., Wakasa N., Fuchikami T., *Tetrohedron Lett.*, **1995**, *36*, 1059

[21] Irusta S., Cornaglia L. M., Lombardo E. A., *J. Catal.*, **2002**, *210*, 7

[22] Wang H. Y., Ruckenstein E., *Appl. Catal. A*, **2000**, *204*, 143

[23] Vazquez A., Lopez T., Gomez R., Bokhimi X., *J. Mol. Catal. A*, **2001**, *167*, 91

[24] Rodríguez-González L., Hermes F., Bertmer M., Rodríguez-Castellón E., Jiménezópez A., Simon U., *Appl. Catal. A*, **2007**, *328*, 174

[25] Xie H. F., Liu Y. Q., Liu C. G., *229th ACS National Meeting*, March 13—17, San Diego, **2005**

[26] Hu S. C., Chen Y. W., *J. Chem. Technol. Biotechnol.*, **2001**, *76*, 954

[27] Koopman P. G. J., Kieboom A. P. G., Bekkum H., *J. Catal.*, **1981**, *69*, 172

[28] Mazzieri V., Pascual F. C., Arcoya A., Largentiere P. C., Figoli N. S., *Appl. Surf. Sci.*, **2003**, *210*(1/2), 222

[29] Wouters B. H., Chen T. H., Grobet P. J., *J. Am. Chem. Soc.*, **1998**, *120*(440), 11419

[30] Subramanian S., Chattha M. S. , Peteres C. R., *J. Mol. Catal.*, **1991**, *69*(2), 235

[31] Church J. S., Cant N. W., Trimm D. L., *Appl. Catal. A*, **1993**, *101*(1), 105

[32] Wang J. Q., Wang Y. Z., Xie S. H., Qiao M. H., Li H. X., Fan K. N., *Appl. Catal. A*, **2004**, *272*(1), 29

[33] Song R. J., Zhang L. Q., Guo S. D., *Nat. Gas. Chem. Ind.*, **1997**, *17*, 7

[34] Luo G., Yan S., Qiao M., Zhuang J., Fan K. N., *Appl. Catal. A*, **2004**, *275*(1/2), 95

[35] Fleisch T. H., Hicks R. F., Bell A. T., *J. Catal.*, **1984**, *87*(2), 398

[36] Betacourt P., Rives A., Hubaut R., Scott C. E., Goldwasser J., *Appl. Catal. A*, **1998**, *170*(2), 307

[37] Li H., Li H. X., Deng J. F., *Catal. Today*, **2002**, *74*(1/2), 53

[38] Chen J. X., Zhang J. X., Zhang J. Y., *React. Kinet. Catal. Lett.*, **2008**, *93*, 359

[39] Miyake T., Makino T., Taniguchi S., Watanuki H., Niki T., *Appl. Catal. A*, **2009**, *364*(1/2), 108