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1. Introduction

Nowadays, the increase in the demand for energy is at a substantial rate with the growing economy of the populous developing countries. Currently, this high energy demand mainly depends on fossil fuel resources. Fossil fuels have been depleting day by day, so diversifying fuel resources has been given much more attention. Recently, biofuels (biodiesel or ethanol), biomass, and solar energies have been wide spread. Among them, biodiesel is a renewable and environmentally friendly alternative for the diesel engine. Generally, transesterification, the reaction of vegetable oil or animal fat with an alcohol to form fatty acid methanol esters (FAME) and glycerol, is the most common method for biodiesel preparation under acid or base catalysis.^{1–4}

Preparation of KF-La₂O₂CO₃ solid base catalysts and their excellent catalytic activities for transesterification of tributyrin with methanol[†]

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A series of 25% KF-La₂O₂CO₃ catalysts (25-KF-LOC-x, x = 673, 723 and 773) were prepared at different calcination temperatures, which were tested as basic catalysts for the transesterification of tributyrin with methanol to produce methyl butyrate and characterized by means of XRD, SEM, CO2-TPD, FTIR, XPS and XRF. It was found that the calcination temperature greatly influences the catalytic activity, and its order is 25-KF-LOC-673 < 25-KF-LOC-723 < 25-KF-LOC-773. Especially, the 25-KF-LOC-773 catalyst exhibits a very high activity, and the conversion of tributyrin is nearly 100%, the yield of methyl butyrate reaches 94% at 308 K. The activation energy of the 25-KF-LOC-773 catalyst is as low as 55.03 kJ mol⁻¹. The excellent catalytic activity of the 25-KF-LOC-773 catalyst can be attributed to the largest amount of surface hydroxyl among these 25-KF-LOC-x catalysts. The results indicate that the Brønsted base is the main active site at low reaction temperature. The recycling use and stability have been investigated over the 25-KF-LOC-773 catalyst. The results indicate that the 25-KF-LOC-773 catalyst has a high stability after being stored for 90 days. The deactivation of the used 25-KF-LOC-773 catalyst at 308 K is due to the loss of hydroxyl on the surface. However, the conversion of tributyrin can reach 91%, and the yield of methyl butyrate also can achieve 64% when the transesterification reaction is performed at 338 K over the second used 25-KF-LOC-773 catalyst. It indicates that the second used 25-KF-LOC-773 catalyst still possesses good catalytic activity at the higher reaction temperature due to the unchanged strong Lewis basic sites provided with surface oxygen anions

> Most biodiesels today are produced by transesterification in the presence of homogeneous catalysts such as sulfuric acids, sodium methoxide, sodium or potassium hydroxide, which are more effective and provide much faster reaction rates than heterogeneous catalysts. However, homogenous catalysts have many disadvantages such as separating problems between the catalyst and the products, and sensitivity to water and acid, which directly limits the production of biodiesels.5-7 In this case, heterogeneous catalysts, such as solid base and acid,⁷⁻¹⁸ and immobilized enzyme,^{19,20} have been studied to replace the homogeneous catalyst. In previous publications, many kinds of solid base catalysts have been investigated for the transesterification of triglycerides with methanol, including alkali and alkali earth metal oxides,^{12-15,18} hydrotalcites,^{7,8,21-24} zeolites,²⁵ and anion exchanged resins.²⁶ Among them, the hydrotalcite(-like) compounds have attracted interest as catalysts for vegetable oil transesterification due to their high surface area and the tunable basicity using chemical composition modification.^{7,8,21} Additionally, CaO and CaO supported catalysts have been widely investigated because of their high activities for the transesterification of triglycerides with alcohols.^{18,27} However, a problem for the hydrotalcite(-like) and the CaO catalysts is



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that the active species end up leaching from the solid catalyst and acting as a homogeneous catalyst in the reaction.^{28–30} This drawback considerably limits the utility of such simple, cheap, and environmentally benign catalysts.

In recent years, many researchers have shown much interest in rare earth oxides (REOS) as catalysts for transesterification or as catalyst supports due to the strong basicity and good catalytic activity of REOS as CaO.^{12,31,32} However, some important questions from a fundamental point of view remain unclear and unsolved except the leaching of active species. For example, most of these reported catalysts for the transesterification of triglycerides require high temperatures (>423 K) and long reaction times (from 2 h to 24 h) to get higher than a 90% FAME yield.³³⁻³⁵ In fact, the leaching of active metal species or catalyst deterioration in the liquid-phase reaction is a particular problem for most solid-base catalysts.^{36,37} In addition, how to improve the stability and recycling of solid base catalyst in the atmospheres is also one of the key problems. Hence, much recent effort has been devoted to developing the novel solid base catalysts with high activity and stability.

In our previous work, the prepared KF–La₂O₃ had a good catalytic performance for the transesterification of tributyrin with methyl alcohol.³⁸ However, the KF–La₂O₃ catalyst deactivated rapidly when exposed to air. Thus, in this paper, we report a new solid base 25% KF–La₂O₂CO₃ catalyst, using the transesterification of tributyrin with methyl alcohol as the probe reaction. The relationship between transesterification activity and surface basicity of the catalyst is discussed for the 25% KF–La₂O₂CO₃ catalysts prepared at different calcination temperatures. The recycling and stability are also investigated.

2. Experimental

All chemicals used in this work are of an analytical grade, purchased from Tianjin Kermel Chemical Reagents Development Centre, and used as received without further purification.

2.1. Catalysts preparation

The La₂O₂CO₃ (denoted as LOC) was synthesized by the homogeneous precipitation method using lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O) as a lanthanum source and urea to raise the pH of the solution and also as a source of carbon.³⁹ Lanthanum nitrate (0.010 mol, 4.330 g), urea (0.40 mol, 24.024 g) and water (5.56 mol, 100 g) were mixed at a molar ratio of 1:40:556 and the mixed solution was heated at 353 K and then kept at that temperature. At a predetermined time, the resulting mixture was cooled to room temperature, the redundant solution was filtered, and the resulting solid was washed with water three times and then dried at 363 K for 4 h, and calcined at 773 K for 3 h. Then, La₂O₂CO₃ support was obtained.

The KF supported on $La_2O_2CO_3$ catalysts (25% KF-La₂O₂CO₃) were prepared by the impregnation method.

KF·2H₂O (3.186 mmol, 0.300 g) and La₂O₂CO₃ (3.246 mmol, 1.200 g) were added into 120 mL distilled water, and then the mixture was stirred in a water bath at 313 K for 12 h to evaporate the water and obtain the solid product. Then the solid products were dried at 363 K overnight, calcined at different temperaturea (673, 723 and 773 K, respectively) for 3 h based on the TG-DTA measurement (Fig. S1†). Thus, 25% KF-La₂O₂CO₃-*x* catalysts were obtained and denoted as 25-KF-LOC-673, 25-KF-LOC-723 and 25-KF-LOC-773, in which 25 is the KF percentage content in the total catalyst amount and *x* is the calcination temperature.

2.2. Catalyst characterizations

The Thermogravimetric-differential thermal analysis (TG-DTA) profiles were recorded on a HCT-1 thermal analyzer at a heating rate of 10 K min⁻¹ in static atmosphere. X-ray diffraction (XRD) patterns of the catalysts were obtained with a D/MAX-3B X-ray Diffractometer (Rigaku Co.), using Cu Ka radiation combined with a Ni-filter. The morphology was observed by scanning electron microscopy (SEM) on a Hitachi S-4800 field emission electron microscope operating at 20 kV. The surface area was derived from N2 sorption measurement at 77 K with a Micromeritics Tristar 3000 physisorption instrument. In each case, the sample was degassed under vacuum at 423 K for 4 h before the measurement. The FT-IR spectra were carried on a PE Spectrum One FT-IR spectrometer in KBr disks at room temperature. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo ESCALAB 250 spectrometer using a monochromatic AlKa X-ray source (15 KV, 150 W) and analyzer pass energy of 100 eV. Binding energies (BE) are referenced to the C (1s) binding energy of carbon taken to be 284.7 eV. The content of K was analyzed by X-ray fluorescence spectrometer (XRF) using a Bruker S4 Explorer instrument. Carbon dioxide temperature programmed desorption (CO₂-TPD) was carried out in a full automatic instrument (XQ TP-5080, China) and performed in the following procedure. Firstly, 100 mg of the catalyst was mounted in a quartz tube and calcined under a helium stream (30 mL min⁻¹) at 573 K for 1 h. After the catalyst was cooled down to 298 K, pure CO2 was introduced into the system at the rate of 20 mL min⁻¹ for 1 h. Then the catalyst was flushed in He flow (30 mL min⁻¹) to remove physisorbed CO₂ at 298 K. Finally the sample was gradually heated from 298 K to 873 K at a ramp of 10 K min⁻¹. The CO₂ desorption was monitored by a thermal conductivity detector (TCD) and recorded by a computer.

2.3. Catalytic evaluation

All the catalytic experiments were carried out in a 30 mL double layer glass reactor equipped with a reflux condenser, a magnetic stirrer and a superthermostat. The standard condition was as follows: 1.00 mL (3.42 mmol) of tributyrin and 102.4 mmol of methanol were added into the flask. After the mixture was heated to the desired temperature (298–338 K), 30 mg of catalyst was added, and then the reaction was carried out under these conditions for 60 min.

Tributyrin is successively transesterified by methanol to yield dibutyrin, monobutyrin, glycerol and for each step 1 molecule of methyl butyrate (Scheme 1). Tributyrin, dibutyrin, monobutyrin, glycerol and methyl butyrate in the liquid product were identified by GC-MS (Agilent 6890/5973N). The distillate at 64 °C from the reaction products, the azeotrope of methanol and methyl butyrate, is further identified using ¹H NMR spectroscopy (AVANCE III 400, BRUKER) (Fig. S2[†]). The liquid products were analyzed quantitatively by gas chromatography (SP-2100 China, FID detector) with an OV-1 capillary column (30 m \times 0.25 mm \times 0.33 µm) according to the literature.^{22-24,27,40} The quantitative analysis of the mixture was determined by the calibration curves, using cyclohexanone as the internal standard. Methyl butyrate yield is defined as the moles of methyl butyrate produced divided by the moles of tributyrin reacted divided by 3 (since three moles of methyl butyrate are produced per mole of tributyrin at complete conversion).

3. Results and discussion

3.1. XRD characterization

Fig. 1 shows the XRD patterns of 25-KF–LOC-*x* catalysts with different calcination temperatures. It is observed that a new phase of LaOF appears at $2\theta = 26.88$, 31.06, and 52.62 ° (PDF 01-077-0204) for 25-KF–LOC-*x* catalysts. With the increase in calcination temperature from 673 K to 773 K, the intensities of the characteristic peak of LaOF increase significantly, while the peak intensities corresponding to La₂O₂CO₃ phase decline. In addition, the diffraction peaks of KF are not found in the XRD patterns of all 25-KF–LOC-*x* catalysts. It can be inferred that the presence of an interaction between KF and La₂O₂CO₃, results in the formation of the new LaOF phase for 25-KF–LOC-*x* catalysts.

3.2. SEM characterization

Fig. 2 is the SEM of the LOC and 25-KF-LOC-773 catalysts. From Fig. 2a it can be seen that the LOC support shows a slippery rod structure with length varying from 2 to 5 μ m and a diameter of about 0.5-1 μ m. The rod structure remains almost unchanged after loading KF (Fig. 2b), but the surface becomes rough, stacked by a number of nanoparticles. It also indicates that chemical reaction may occur to the formation of LaOF phase between KF and La₂O₂CO₃ support confirmed by the above XRD results. The BET surface area of 25-KF-LOC-*x* catalysts is only 2.3-3.5 m² g⁻¹, which is lower



Scheme 1 Transesterification reaction of tributyrin with methanol.



Fig. 1 XRD pattern of the 25-KF-LOC-*x* catalysts (A: LOC; B: 25-KF-LOC-673; C: 25-KF-LOC-723; D: 25-KF-LOC-773; ● LaOF).

than that of LOC. Moreover, the surface area increases slightly with the calcination temperature, which is in agreement with the SEM results.

3.3. IR characterization

Fourier transform infrared (FTIR) spectroscopy is usually employed as an additional probe to evidence the presence of hydroxyl groups as well as other organic and inorganic species. The FTIR spectra of 25-KF-LOC-x catalysts are shown in Fig. 3. For all of the catalysts, a broad band at 3300–3700 cm⁻¹ is assigned to the stretching and bending vibrations of O-H bond, which indicates the presence of hydroxyl on the catalyst surface.41 A prominent absorption band at around 1461 cm⁻¹ can be observed for these samples. According to the literature,⁴² the band centered at 1461 cm⁻¹ and the narrow band at 859 cm⁻¹ are ascribed to the C-O stretch mode and the bending mode of structural carbonate, respectively. A shoulder band around 1655 cm⁻¹ may be attributed to the vibration of hydrogen bonding between hydroxy and carbonate. The sharp band observed around 1365 cm⁻¹ due to the v_3 vibration of the CO₃. The bands below 800 cm⁻¹ are mostly due to the metaloxygen vibration.43,44 Compared with the intensity of the La-O vibration, the intensity of the hydroxyl groups peak (at 3300–3700 cm⁻¹) gradually enhances with increases in calcination temperature for the 25-KF-LOC-x catalysts. When the calcination temperature is 773 K, there exists a mass of hydroxyl on the surface of the 25-KF-LOC-773 catalyst. The order of the amount of hydroxyl groups for 25-KF-LOC-x catalysts is 25-KF-LOC-773 > 25-KF-LOC-723 > 25-KF-LOC-673. However, there is only a small amount of hydroxyl group on the surface of the LOC support. Thus, the IR results demonstrate that the 25-KF-LOC-773 catalyst possesses the largest amount of hydroxyl groups among the 25-KF-LOC-x catalysts. In order to confirm the role of the hydroxyl group, the 25-KF-LOC-773 catalyst was treated at room temperature using CO_{2} ,



Fig. 2 SEM of the LOC and the 25-KF-LOC-773 catalysts (a: LOC, b: 25-KF-LOC-773, c: the second used 25-KF-LOC-773).



Fig. 3 FT-IR spectra of the LOC and the 25-KF-LOC-x catalysts (A: LOC; B: 25-KF-LOC-673; C: 25-KF-LOC-723; D: 25-KF-LOC-773; E: 25-KF-LOC-773 after CO₂ treatment).

and the FTIR spectra of post-treatment catalysts are shown in Fig. 3E. After the 25-KF–LOC-773 catalyst is treated by CO₂, the band around 3370 and 1655 cm⁻¹ assigned to hydroxyl drops off obviously, while the other peaks almost remain unchanged. It indicates hydroxyl on the surface has intense interactions with CO₂ which then leads to the weakening of the hydroxyl peak. Therefore, the hydroxyl group on the 25-KF–LOC-*x* catalysts plays the role of the basic sites.

3.4. CO₂-TPD

The basicity of an oxide surface is closely related to the electrondonating properties of oxygen anions, which increases with the electro-positive character of combined mental ions. The value of electro-negativity of F^- is larger than that of O^{2-} , therefore, the negative charge of lattice oxygen would be drawn toward F^- . Thus, the basicity of the 25-KF-LOC-*x* catalyst should be higher than that of La₂O₂CO₃.¹ CO₂-TPD is widely used for the determination of the surface basicity of the solid base catalyst. Fig. 4 illustrates the CO₂-TPD profiles of LOC and the 25-KF-LOC-*x* catalysts. The CO₂-TPD curve of LOC shows a small CO₂ desorption peak in the range 475-600 K, indicating its low basicity on the surface. All CO₂-TPD profiles of 25-KF-LOC-*x* catalysts



Fig. 4 CO₂-TPD profiles of the LOC and the 25-KF-LOC-*x* catalysts (A: LOC; B: 25-KF-LOC-673; C: 25-KF-LOC-773).

present two desorption bands with desorption temperatures at 300-420 K and 650-850 K, resulting from the interactions between CO₂ and the weak and strong basic sites, respectively. The weak basic sites can be attributed to the Brønsted base, and the strong basic sites can be assigned to the Lewis base. The weak basic sites are caused by the formation of surface hydroxyl during the formation of LaOF.⁴⁴ And the strong basic sites result from the oxygen anions of La2O2CO3 interacting with the highly dispersed KF species, which result in oxygen anions showing Lewis base sites. The TPD curve of the 25-KF-LaOC-773 catalyst without pre-adsorption of CO₂ further confirms the desorption band at 650-850 K is not assigned to the decomposition of La₂O₂CO₃ phase (Fig. S3[†]). The CO₂-TPD data is summarized in Table 1. Based on Fig. 4 and Table 1, the amount of weak basic sites for 25-KF-LOC-673, 25-KF-LOC-723 and 25-KF-LOC-773 is 28, 35 and 77 μ mol g⁻¹, respectively, which increases in the order of 25-KF-LOC-673, 25-KF-LOC-723 and 25-KF-LOC-773, which agrees well with the results of IR. However, the strong basic site shifts to low temperature, and the desorption peak area dramatically decreases when the calcination temperature increases from 673 K to 773 K. In other words, the order of the amount of strong Lewis base sites is 25-KF-LOC-673 (253 μ mol g⁻¹) > 25-KF-LOC-723 (175 μ mol g⁻¹) > 25-KF-LOC-773 (65 μ mol g⁻¹), which is inverse with that of the weak basic sites. Meanwhile,

Table 1 CO₂-TPD data for LOC and the 25-KF-LOC-*x* catalysts

Catalysts	$SA^{a} \left(m^{2} g^{-1}\right)$	$T^{b}(\mathbf{K})$	$WBA^{c} (\mu mol g^{-1})$	$T^{b}(\mathbf{K})$	$SBA^d (\mu mol g^{-1})$	$TBA^{e} (\mu mol g^{-1})$	
LOC	5.4	_	_	542	13	13	
25-KF-LOC-673	2.3	376	28	789	253	281	
25-KF-LOC-723	2.9	369	37	784	175	212	
25-KF-LOC-773	3.5	364	77	753	65	142	
25-KF–LOC-773 ^f	4.7	369	23	742	51	74	

^{*a*} SA: BET surface area. ^{*b*} *T*: temperature of desorption peak. ^{*c*} WBA: weak basic amount. ^{*d*} SBA: strong basic amount. ^{*e*} TBA: total basic amount. ^{*f*} The second used catalyst.

the quantity of weak basic sites increases obviously with the LaOF amount shown in Fig. 5. Nevertheless, the increase in the formation quantity of LaOF leads to the distinct reduction of the amount of strong basic sites, which indicates that the Lewis base sites attributed to oxygen anions obviously decrease with the increase in the calcination temperature. Moreover, this weakening of the strong basic site also would be caused by the gradual loss of surface CO_3^{2-} of $La_2O_2CO_3$ at a high calcination temperature. Combined with the XRD and IR results, it can be found that the more LaOF is produced, the more hydroxyl group on the surface of the 25-KF-LOC-*x* catalyst is formed (Fig. 5 and 6). However, the total basic amount decreases in the order of 25-KF-LOC-673, 25-KF-LOC-723 and 25-KF-LOC-773.

3.5. XPS characterization

The XPS of La 3d for 25-KF–LOC-*x* catalysts are depicted in Fig. 7a and b. The La $3d_{5/2}$ and $3d_{3/2}$ core levels are observed at 833.1–833.8 and 849.8–850.7 eV, respectively, and the corresponding satellite peaks are found to be at 836.6–837.3 and 853.3–854.2 eV. Besides, it has been observed that the splitting energy between the core and satellite peaks is 3.5–4.1 eV, in this work, for both $3d_{5/2}$ and $3d_{3/2}$ components. The binding energies and the multiplet splitting are agreed well with the reported values for La³⁺ compounds.⁴⁵ The trivalent



Fig. 5 Relation plots of LaOF relative amount *versus* hydroxyl relative amount (a) and weak basic amount (b) for the 25-KF–LOC-*x* catalysts.



Fig. 6 Relation plots of hydroxyl relative amount *versus* weak basic amount for the 25-KF-LOC-*x* catalysts.

nature of La atoms in 25-KF–LOC-x is confirmed by the characteristic satellites found at higher BE for each of the 3d_{5/2} and 3d_{3/2} core-level peaks. The splitting of these lines is believed to occur due to the transfer of the electron from oxygen ligands to the La 4f (initially empty).⁴⁶ In Table 2 and Fig. 5a and b, the splitting of the La 3d core-level peaks becomes more and more obvious from 25-KF-LOC-673, 25-KF-LOC-723 to 25-KF-LOC-773, which should be related to the formation of LaOF resulting in the transfer of the electron from oxygen ligands to the La 4f. It also explains the formation of base sites on the 25-KF-LOC-x catalysts. In addition, compared with La₂O₂CO₃, the La 3d peaks shift to low binding energy for all the 25-KF-LOC-x samples, which indicates the increase in electron density of La. Thus, the presence of an interaction between KF and La₂O₂CO₃ can be inferred, which is consistent with the formation of the new LaOF phase in the XRD results.

The O 1s core level spectra of the 25-KF-LOC-*x* catalysts are presented in Fig. 7c. Two peaks can be well fitted in the O 1s spectra with binding energy of 530.1 and 531.4 eV for LOC. The peak in the lower binding energy side is assigned to the oxygen of the La–O bond, while the one appearing at the higher binding energy side can be fitted with the oxygen of the La–O-C and C–O bonds.⁴⁵ The O 1s peaks of 25-KF-LOC-*x* catalysts became broaden, which is attributed to the formation of the new phase that leads to

Catalysis Science & Technology



Fig. 7 XPS of La 3d and O 1s for the LOC and the 25-KF-LOC-*x* catalysts (a: La 3d_{3/2}; b: La 3d_{5/2}, c: O 1s. A: LOC; B: 25-KF-LOC-673; C: 25-KF-LOC-723; D: 25-KF-LOC-773).

Table 2 XPS data of the 2	25-KF–LOC-x catalysts
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Catalysts	La 3d _{3/2}	Area	$\mathrm{RA}^{a}\left(\% ight)$	La 3d _{5/2}	Area	$\mathrm{RA}^{a}(\%)$	O 1s	Area	\mathbf{RA}^{a} (%)	O/La ^b
25-KF-LOC-673	854.2	19938	58.5	837.3	33 745	74.8	532.9	17 214	50.1	17.35
	850.7	14165	41.5	833.8	11 388	25.2	530.9	15 121	44.0	
							528.3	2040	5.9	
25-KF-LOC-723	854.0	23 3 56	51.0	837.3	35 992	55.3	532.4	14877	39.3	14.33
	850.4	22440	49.0	833.6	29 112	44.7	530.6	17 555	46.5	
							528.3	5349	14.2	
25-KF-LOC-773	853.8	16234	41.1	837.0	26824	47.0	532.4	11 429	35.2	11.92
	850.0	23 299	58.9	833.3	30 184	53.0	530.6	15 865	48.9	
							528.3	5145	15.9	

^a RA: relative area of each fitted peak in all the peaks for the every La 3d_{3/2}, La 3d_{3/2} and O 1s peaks. ^b The surface atom ratio of O to La.



Fig. 8 Relation plots of total basic amount versus atom ratio of O to La.

the presence of a new environment of the surface oxygen. For the 25-KF–LOC-*x* catalysts, a peak is observed at 528.3 eV except the two peaks around 530.1 and 531.4 eV similar to the LOC sample, which can be ascribed to the oxygen of the surface OH.

In Fig. 7 and Table 2, the relative peak intensity in the lower binding energy side of La $3d_{3/2}$ and La $3d_{5/2}$ significantly increases, which illustrates the increase in the amount of La coordinated with O. And, the oxygen quantity of surface hydroxyl obviously increases with the calcination temperature varying from 673 K to 773 K for the 25-KF-LOC-*x* catalysts, which is consistent with the number of weak basic sites.

Fig. 8 presents a plot of the total base amount in Table 1 *versus* the surface atom ratio of O to La in Table 2, from which there exists the linearity between the total base

amount and the quantity of O on the catalyst surface. Thus, it can be inferred that the surface O provides the basicity of the 25-KF-LOC-*x* catalysts, meanwhile, with the increase in calcination temperature, the content of surface O declines, and the total base amount also decreases.

3.6. Catalytic activities

No product can be detected using the LOC as catalyst in our experimental conditions. The catalytic activities over the 25-KF–LOC-*x* catalysts are shown in Fig. 9. Apparently, the yield of methyl butyrate was very low (10%) for the 25-KF–LOC-673 catalyst prepared at 673 K. Subsequently, the calcination temperature rose to 723 K, the conversion of tributyrin increased significantly to 90% over the 25-KF–LOC-723 catalyst, but the yield of methyl butyrate was only 62%. Then, the conversion of tributyrin was nearly 100% and the yield of methyl butyrate reached 94% over the 25-KF–LOC-773 catalyst. Thus, the 25-KF–LOC-773 catalyst shows an excellent catalytic performance for the transesterification of tributyrin. 773 K was thought to be the ideal calcination temperature in the preparation process of the KF–LOC catalyst.

To show the efficacy and advantages of the 25-KF–LOC-773 catalyst, a comparison with literature-reported similar transesterification reaction of tributyrin with methanol has been made. Different catalysts show different catalytic activities for this reaction when the molar ratio methanol to tributyrin is 30:1. Mg–Al hydrotalcite is an important kind of solid base catalyst for the transesterification reaction of tributyrin with methanol.^{22–24} Among these catalysts, the decomposed-rehydrated Mg–Al hydrotalcite catalyst could reach over 80% tributyrin conversion and nearly 80% yield to methyl butyrate within 400 min at 333 K.²² 84% tributyrin conversion and nearly 52% yield to methyl



Fig. 9 Catalytic activities of the 25-KF-LOC-*x* catalysts ($\$ conversion of tributyrin, $\$ yield of methyl butyrate, A: 25-KF-LOC-673; B: 25-KF-LOC-723; C: 25-KF-LOC-773. Reaction conditions: 30 mg of catalyst, the ratio of catalyst to tributyrin is 30 (mg g⁻¹), molar ratio of methanol to tributyrin = 30:1, 308 K for 60 min).

butyrate were obtained over the MgZr mixed oxide with a 11:1 molar ratio of Mg to Zr prepared by precipitation at 333 K and a reaction time of 22 h.⁴⁷ Moreover, the conversion of tributyrin and yield of methyl butyrate decrease to 61% and 25% for the third run, respectively.

Fig. 10 is a plot of the tributyrin conversion versus the surface oxygen of the hydroxyl in Table 2, which displays linearity between the conversion of tributyrin and the oxygen amount of the surface hydroxyl. According to the order from 25-KF-LOC-673, 25-KF-LOC-723 to 25-KF-LOC-773 catalyst, the oxygen amount of the surface hydroxyl increases, and the catalytic activity is also markedly enhanced. These results can prove that the surface hydroxyl is one of the active base sites of the 25-KF-LOC-773 catalyst at the low reaction temperature of 308 K. Thus, it can be inferred that the hydroxyl provides active sites. When the XRD, IR, CO₂-TPD and XPS results are taken into consideration, it can be inferred that a new phase LaOF is generated after KF loading, meanwhile, increasing the calcination temperature, the amount of LaOF increases significantly. Although the content of surface O declines, the amount of the surface hydroxyl as the active sites increases. In conclusion, the total base amount on the catalyst surface decreases, but the conversion of tributyrin and yield of methyl butyrate still increase. It suggests that the surface hydroxyl is the main active basic species at low reaction temperatures.

3.7. Kinetic studies

The kinetics tests of the transesterification of tributyrin were carried out for the 25-KF–LOC-773 catalyst due to its excellent catalytic performance. According to the references about the transesterification reaction of triglyceride with methanol,^{48,49} the transesterification reaction of the tributyrin (T) with methanol should also be to proceed in 3 steps to produce dibutyrin (D), which further reacts with methanol to yield monobutyrin (M) that finally reacts with methanol to produce



Fig. 10 Relation plots of conversion of tributyrin *versus* the surface hydroxyl amount.

methyl butyrate (MB) and glycerol (G). The three steps are described in the following eqn (1)-(3), respectively.

$$T + Methanol \xleftarrow{K_1}{K_2} D + MB$$
(1)

$$D + Methanol \xleftarrow{K_3}{K_4} M + MB$$
(2)

$$M + Methanol \xleftarrow{K_5}{K_6} G + MB$$
(3)

Since one mole of methyl butyrate is generated per mole of methanol reacted at each step, in all, six rate constants are reported in the literature for the whole reaction from tributyrin to methyl butyrate as shown by eqn (4) given below:

$$\Gamma + 3$$
Methanol $\xleftarrow{K}{K'}$ G + 3MB (4)

According to the above equation, transesterification results ultimately in the production of methyl butyrate and therefore, all the intermediate reaction products (*e.g.* D and M) can be ignored. In addition, although the transesterification reaction is reversible, Diasakov *et al.* proposed that the reverse reaction in excess methanol wase not important and could be ignored.^{49–51} Thus, a simple mathematical model expressing the whole conversion as one step has been developed.^{18,48} In this study, all the reactions were carried out with a methanol: tributyrin molar ratio of 30:1. With such a large excess of methanol, several studies suggested that the overall transesterification reaction is in accord with the pseudo first order kinetic. Thus, based on the references results,^{18,48,52–57} the pseudo first order kinetic model should be given as eqn (5)

$$-\ln(1-\text{yield}_{\text{methyl butyrate}}) = kt \tag{5}$$

where yield_{methyl} butyate is the yield of methyl butyrate at time t (min). A plot of $-\ln(1-yield_{methyl})$ as a function of

time will be linear, with a slope equal to the reaction rate constant *k*.

The kinetics of the 25-KF–LOC-773 catalyzed transesterification of tributyrin has been studied at a 30:1 methanol:tributyrin molar ratio in the temperature range of 273–291 K, and plotting a graph between $-\ln(1-\text{yield}_{\text{methyl}})$ butyrate) *vs. t* as given in Fig. 11a. The plots are represented by straight lines, validating the first-order reaction model. The rate constants were calculated from these plots and found to be 0.0024, 0.0071 and 0.0105 min⁻¹ at 273, 285 and 291 K, respectively.

The activation energy (E_a) and pre-exponential factor (A) for the same reaction were determined by following the Arrhenius mode as given in eqn (6).

$$\ln k = -E_{\rm a}/RT + \ln A \tag{6}$$

where *R* is the gas constant and *T* is the reaction temperature in Kelvins. A plot between $\ln k vs. 1/T$ is shown in Fig. 11b. The slopes of the lines provide the activation energy (*E*_a) using the Arrhenius equation. In Fig. 11b, the activation energy calculated from the slope of the Arrhenius plot is 55.03 kJ mol⁻¹, and the corresponding pre-exponential factor is $8.35 \times 10^7 \text{ min}^{-1}$. The activation energy for 25-KF–LOC-773 catalyst is much lower than that of KF–La₂O₃ catalyst (128.9 kJ mol⁻¹) in our previous study.³⁸

3.8. Recycling and stability

The catalytic activities of 25-KF–LOC-773 catalyst were also monitored over the used 25-KF–LOC-773 catalyst for the transesterification reaction of tributyrin. After being used as the fresh 25-KF–LOC-773 catalyst, the used catalyst was dried at 353 K and calcined at 773 K. For the second reused 25-KF–LOC-773 catalyst, the conversion of tributyrin rapidly decreased from 98.5% to 5.5%, while the yield of methyl butyrate only got to 0.76% at 308 K shown in Fig. 12 (run 1 and run 2-1). It illustrates that there is an obvious downward trend in the catalytic performance of the reused the 25-KF–LOC-773 catalyst in regard to its reusability. It is inferred that the decrease in the



Fig. 11 (a) Plots of $-\ln(1-yield_{methyl, butyate})$ versus time at different temperatures. (b) Arrhenius plot of $\ln k$ versus $10^3/T$ for the reaction of tributyrin with methanol (reaction conditions: 15 mg of 25-KF-LOC-773 catalyst, the ratio of catalyst to tributyrin is 15 (mg g⁻¹), molar ratio of methanol to tributyrin = 30 : 1).



Fig. 12 Catalytic activities of the fresh and the used 25-KF-LaOC-773 catalysts at different conditions ($\$ conversion of tributyrin, $\$ yield of methyl butyrate, reaction conditions: 30 mg of KF-La₂O₂CO₃ catalyst, the ratio of catalyst to tributyrin is 30 (mg g⁻¹), molar ratio of methanol to tributyrin = 30 : 1, reaction time for 60 min, reaction temperature at 308 K (run 1: fresh catalyst, run 1-1: fresh catalyst delayed for 90 days, run 1-2: fresh catalyst after absorption of CO₂, run 2-1: the second used catalyst).

catalytic activity has something to do with the loss of active species on the catalyst surface when the fresh catalyst is used. However, when the transesterification reaction was performed at 338 K over the second used 25-KF-LOC-773 catalyst, the conversion of tributyrin can reach 91%, and the yield of methyl butyrate also can achieve 64%, as shown in Fig. 12 (run 2-2). It indicates the second used 25-KF-LOC-773 catalyst still possesses good catalytic activity in the high reaction temperature. Based on the CO2-TPD results, it can be suggested that the catalytic activity at 338 K is provided by the strong Lewis basic sites. It is interesting that 97.2% of the conversion to tributyrin and 87.0% of the yield to methyl butyrate can be obtained at 308 K after the fresh 25-KF-LOC-773 catalyst was placed into the silica gel desiccator in the atmosphere for 90 days. Moreover, the catalytic activity was tested at the same reaction conditions using the fresh 25-KF-LOC-773 catalyst previously absorbed CO2 at the room temperature. The results show that the conversion of tributyrin and the yield of methyl butyrate get to 96.8% and 76% (Fig. 12 (run 1-2)), respectively, which indicates that the 25-KF-LOC-773 catalyst remains the high activity and the resistance for CO_2 in the atmosphere. Thus, these results indicate that the 25-KF-LOC-773 catalyst has high stability.

In addition, the third and the forth recycling experiments were carried out over the 25-KF–LaOC-773 catalyst, and their results are shown in Fig. S4† (run 3-1 and run 4-1). The conversion of tributyrin and yield of methyl butyrate decrease to 34% and 66% for the third run (run 3-1), respectively. However, when the forth recycling experiment was performed, the catalyst exhibited an almost complete deactivation, whith the conversion of tributyrin rapidly decreasing from 34% to 4%, while the yield of methyl butyrate only got to 0.57%, as shown in Fig. S4† (run 4-1). The results indicate a gradual loss of the basic sites with the increase in the recycling experiment.

A series of experiments were performed in order to analyze the deactivation reason and improve the recyclability of the 25-KF-LOC-773 catalyst. The second used 25-KF-LOC-773 catalysts were characterized by XRD, SEM, FTIR, CO2-TPD and XRF. The XRD patterns of the fresh and the second used 25-KF-LOC-773 catalysts are shown in Fig. 13. It is found that there is almost no difference in the characteristic diffraction peaks between the fresh and the second used 25-KF-LOC-773 catalyst. However, the morphology of the second used of 25-KF-LOC-773 catalysts is totally changed, the rod structure disappears and turns into an aggregate which is made up by spheres with a diameter between 200 and 400 nm (Fig. 2c). The BET surface area of the second used 25-KF-LOC-773 catalysts increases from 3.5 m² g⁻¹ to 4.9 m² g⁻¹ due to the formation of sphere structures (Table 1). Additionally, the FTIR spectra of the fresh and the second used 25-KF-LOC-773 catalysts are also quite different, as shown in Fig. 14. For the second used 25-KF-LOC-773 catalyst, the intensity of the peak at 3370 cm⁻¹ assigned to hydroxyl drops off obviously, while the other peaks almost remain unchanged. It indicates that hydroxyl groups on the surface have leaching, which leads to the weakening of the hydroxyl peak. It also shows the obvious difference between the fresh and the second used 25-KF-LOC-773 catalyst in the CO₂-TPD curves (Fig. 15). The peak which is attributed to hydroxyl basic sites at 300-420 K becomes weak for the second used 25-KF-LOC-773 catalyst, which indicates the decrease in the amount of the weak basic sites resulting from hydroxyl on the surface of the second used 25-KF-LOC-773 catalyst. But the peak intensity of the strong basic sites slightly decreases, and the strong basic amount still gets to 51 μ mol g⁻¹ (Table 2). Thus, it suggests that the loss of hydroxyl on the surface of the second used 25-KF-LOC-773 catalyst leads to the decrease of catalytic activity at the reaction temperature of 308 K.

The characterizations of XRF can also support our inference. The K:La mole ratio is 38.7% in fresh 25-KF–LOC-773 catalyst, the mole ratio of K:La decreases to 7.1% after being



Fig. 13 XRD patterns of the fresh and the second used 25-KF-LOC-773 (A: fresh, B: the second used).



Fig. 14 FT-IR of the fresh and the second used 25-KF-LOC-773 (A: fresh, B: the second used).



Fig. 15 CO_2 -TPD profiles of the fresh and the second used 25-KF-LOC-773 (A: fresh, B: the second used).

second used. The results suggest that the decrease in activity had a striking correlation with the loss of hydroxys on the surface. When K was leached, in order to keep the balance of charge, the amount of hydroxyl on the surface would also decrease. Therefore, the loss of active sites gives rise to the deactivation of the catalyst during the recycle reaction.⁵⁸ However, the strong Lewis base sites attributed to the surface oxygen anions is unchanged. For the forth used 25-KF–LaOC-773 catalyst, the CO₂-TPD result (Fig. S5C†) displays that the peak at about 750 K attributed to the strong basic sites disappeared. Therefore, it suggests that the loss of Lewis basic sites on the surface of the forth used 25-KF–LOC-773 catalyst leads to the deactivation of the forth used 25-KF– LaOC-773 catalyst. It also confirms that the Lewis basic sites are the active sites in the recycling experiments.

It is well known that the methoxyl anion is the key species in the transesterification of triglyceride with methanol using solid base as the catalyst.² It is beneficial to form methoxyl anion by methanol adsorbed on the Lewis base sites at the high temperature. Therefore, we suggest that the Lewis base sites play a key role in the catalytic activity at high reaction temperature (338 K).

4. Conclusions

The 25% KF supported on La₂O₂CO₃ catalysts (25-KF-LOC-x, x = 673, 723 and 773 K) were prepared by the impregnation method. The 25-KF-LOC-x catalysts obtained at different calcination temperatures varying from 673 K to 773 K show different physical and chemical properties, especially the surface basicity. A LaOF phase was observed in the 25-KF-LOC-x catalysts, furthermore, the amount of LaOF increases with the calcination temperature. The results of XRD, IR and CO2-TPD indicate that the formation of LaOF leads to the generation of the basic sites. Two kinds of basic sites, Brønsted base and Lewis base, are ascribed to the hydroxyl groups and the oxygen anions of La₂O₂CO₃ interacting with KF, respectively. Moreover, the amount of basic sites is different from that of these two kind of basic sites. The order of the amount of the weak base sites is 25-KF-LOC-673 < 25-KF-LOC-723 < 25-KF-LOC-773. On the contrary, the amount of the strong basic sites of the 25-KF-LOC-673 catalyst is the largest, followed by the 25-KF-LOC-723 catalyst and the 25-KF-LOC-773 in the ascending order. However, the total basic amount decreases with the order of 25-KF-LOC-673, 25-KF-LOC-723 and 25-KF-LOC-773. The more LaOF is produced, the more surface hydroxyl groups of the 25-KF-LOC-x catalyst are formed. There exists a linearity relation between the conversion of tributyrin and the amount of surface hydroxyl oxygen. According to the order from 25-KF-LOC-673, 25-KF-LOC-723 to 25-KF-LOC-773 catalyst, the catalytic activity is markedly enhanced. The 25-KF-LOC-773 catalyst exhibits such an excellent catalytic activity that the conversion of tributyrin is nearly 100% and the yield of methyl butyrate reaches 94% at 308 K, which can prove that hydroxyl is one of the active basic sites at low reaction temperature. Furthermore, the 25-KF-LOC-773 catalyst has such a high stability that the high activity is still kept after 90 days. It suggests that the loss of hydroxyl on the surface of the used 25-KF-LOC-773 catalyst leads to the decrease in catalytic activity at a low reaction temperature (308 K). However, the conversion of tributyrin can reach 91%, and the yield of methyl butyrate also can achieve 64% when the transesterification reaction is performed at 338 K over the second used 25-KF-LOC-773 catalyst. It indicates that the second used 25-KF-LOC-773 catalyst still possesses good catalytic activity at the higher reaction temperature due to the unchanged strong basic sites given by surface oxygen anions.

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