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Effects of preparative parameters on the structure and performance of Ca-La metal oxide catalysts for oil transesterification

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Abstract

The effects of preparative parameters on the surface basicity, composition, and transesterification activities of several Ca-La metal oxide catalysts were investigated. Four different preparation methods: ammonia-ethanol-carbon dioxide precipitation, physical mixing, impregnation, and coprecipitation, were studied. It was found that the ammonia-ethanol-carbon dioxide precipitation method resulted in the highest BET specific surface area, base strength and base site concentration. Moreover, catalyst surface composition and basicity are a function of calcination temperature, precipitants, pH, and molar ratio of Ca to La in precursor solution, and storage conditions. XRD, XPS, basicity and BET tests revealed that catalyst structure and dispersion of Ca species strongly influenced the catalyst activity. High surface concentration of Ca species, strong base strength and high concentration of base sites, and high specific surface area are characteristics of an active transesterification catalyst.

Keywords: Biodiesel, Transesterification, Solid base catalyst, Preparation method, Calcination, Precipitant

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1. Introduction

Biodiesel, a renewable fuel with similar combustion properties to fossil diesel, is normally produced by transesterification of highly refined oils with short-chain alcohols. Biodiesel can significantly decrease the exhaust emission of CO₂, SO_x and unburned hydrocarbons from motor vehicles [1, 2]. Biodiesel is environmentally beneficial, and therefore, is a promising alternative to fossil diesel [3].

Conventionally, biodiesel is produced by a transesterification process using a homogeneous strong base catalyst such as sodium hydroxide or potassium hydroxide. The strong base catalysts have many advantages such as high activity (complete conversion within one hour) and mild reaction conditions (65 °C and 1 atm) [4, 5]. However, these homogeneous base catalysts are corrosive and removal of the catalysts from product is not straight forward. In general, a large amount of waste washing water is generated, and a long time is required for phase separation [6, 7]. The use of solid base catalyst can alleviate these problems and thus, recently there is an increased interest in the development of a highly active solid base catalyst for biodiesel production [8, 9].

Some calcium-containing catalysts were reported to be active in oil transesterification with methanol [10-13]. Several traditional methods have been described for the preparation of calcium-containing catalysts. Albuquerque et al. [14] prepared a series of CaO catalysts supported on mesoporous silica using an impregnation method. **Zhu et al. [15] prepared a solid super base by dipping CaO in ammonium carbonate solution.** Kawashima et al. [16] produced CaTiO₃, CaMnO₃, Ca₂Fe₂O₅, CaZrO₃, and Ca-CeO₂ catalysts using a physical mixing method. Ngamcharussrivichai et al. [17] and Wang et al. [18] used precipitation methods to prepare solid base catalysts. However, all these reported calcium-containing catalysts showed much lower activity than a conventional homogeneous NaOH catalyst. Thus, it is desirable to maximize the surface concentration of active catalytic active site [13, 19]. It has been reported that high-loading of active components cannot be easily obtained using an impregnation method [20, 21]. High-loading of active components can be obtained using physical mixing [18, 20]. A major drawback of the physical mixing method is low crystallinity of the catalyst which has a negative effect on catalytic activity [22]. Furthermore, a high-loading catalyst generally result in a low specific surface area, and thus low surface concentration of catalytic sites for transesterification [23, 24]. Precipitation methods

show promise to obtain a high concentration of active catalytic sites [25, 26], however, there are very few reports in relation to the effects of precipitants and preparation process on the structure of Ca-based solid catalysts and their performance in oil transesterification with methanol.

Ngamcharussrivichai et al [17] prepared Ca and Zn mixed oxide catalysts using Na_2CO_3 as precipitant. Wang et al [18] prepared CaO-ZrO₂ catalysts using ammonia solution as precipitant. Since total deposition of metal ions is important [19, 27], it is apparent that a single precipitant cannot effectively precipitate all metal ions in solution. The effects of multiple precipitants on the structure and performance of Ca-base catalyst have not been reported. The objective of this study is to develop a multistep precipitation process to prepare a CaO-La₂O₃ based catalyst with a relatively high base strength, basicity, specific surface area and site concentration. A new precipitation process utilizing ammonia solution (as base precipitant), carbon dioxide (as acid precipitant) and ethanol (as neutral precipitant) was developed. The Ca₃La₁ catalyst prepared by this novel method was compared with those prepared by physical mixing, impregnation, and co-precipitation methods. The effects of catalyst preparative parameters on catalytic activities, such as pH value of precursor metal salt solution, molar ratio of Ca to La and calcination temperature were investigated. For solid base catalyst, proper storage conditions are important for maintaining a high activity [28]. Thus, the effects of adsorbed triglyceride, methanol, CO₂ and H₂O on the activities of CaO-La₂O₃ based catalysts were evaluated.

2. Experimental

2.1 Materials

Soybean oil (0.02% of free fatty acids (FFA) and 0.02 % of water) was purchased from Costco warehouse (Detroit, MI). Methanol (0.03 % water) was obtained from Mallinckrodt Chemicals (Phillipsburg, NJ). Calcium oxide (99.9 %), lanthanum oxide (99.9 %), calcium acetate hydrate (98%), lanthanum nitrate hydrate (98%), ethanol (95 %) and ammonia (99 %) are of analysis grade, and were purchased from Sigma-Aldrich Company (St. Louis, MO).

2.2 Catalyst Preparation

CaO-La₂O₃ series catalysts were prepared by four different methods.

2.2.1 Ammonia-ethanol-carbon dioxide precipitation method:

Appropriate amounts of 2 M La(NO₃)₃ and 1 M Ca(Ac)₂ solutions were mixed, with pH value of the mixture adjusted to 9.0 with a 6 M ammonia solution. Stepwise addition of 100 ml of ethanol was made every 30 minutes (repeated four times) to the boiling mixture solution to promote initial precipitate formation. This was followed by bubbling of 30 mL/min of CO₂ (10 (v) % in air) for 5 minutes at 30 minute intervals to form carbonate precipitate (repeated six times). The pH value of

the precursor solution was maintained at 9.0 by ammonia solution throughout the whole process. The precipitate was filtered and washed with 100 mL of 75 % ethanol solution, dried at 150 °C for 12 hours, calcined at 430 °C for 1 hr, then at 780 °C for 8 hours. This catalyst was labeled as Ca₃La₁. When only Ca(Ac)₂ solution was used, the Ca-containing catalyst was labeled as CaO; and when only La(NO₃)₃ solution was used, the La-containing catalyst was labeled as La₂O₃.

When only ammonia solution was used as precipitant, the prepared catalyst was labeled as Ca₃La₁-NH₃. Analogously, the catalysts were labeled as Ca₃La₁-CH₃CH₂OH and Ca₃La₁-CO₂ when only ethanol or CO₂ was used, respectively.

2.2.2 Physical mixing method

Eighteen grams of CaO and 33g of La₂O₃ were physically mixed with 50g of distilled water and ground in a mortar. This mixture was then dried at 100 °C for 10 hour and, calcined at 780 °C for 8 hours. This catalyst was labeled as CaO-La₂O₃.

2.2.3 Impregnation method

La₂O₃ powder was impregnated with an appropriate amount of 1 M Ca(Ac)₂ solutions, followed by drying at 100 °C for 10 hours, calcined at 780 °C for 8 hours. The process was repeated again to obtain the desired CaO loading. This catalyst was labeled as CaO/La₂O₃.

2.2.4 Co-precipitation method

Appropriate amounts of 1 M Ca(NO₃)₂, 2 M La(NO₃)₃ and 1 M Na₂CO₃ solutions were mixed with vigorous stirring. After the precipitate was formed, it was filtered and washed with distilled water. The solid precipitate were then dried at 100 °C for 10 hours, and calcined at 780 °C for 8 hours. This catalyst was labeled as La₂O₃·CaO.

All catalysts were activated at 780 °C for 1 hour in pure N₂ (30 mL/min) before any kinetic study.

2.3 Catalyst Characterization

The Hammett indicator method was used to determine the basic strength of the catalyst [28, 30]. Basic strength was expressed by an acidity function (H₋) defined by Eq. (1), where [BH⁻] and [B⁻] are the concentrations of the indicator and its conjugated base, respectively, and pK_{BH} is the logarithm of the dissociation constant of the indicator used:

$$H_{-} = pK_{BH} + \log \frac{[B^{-}]}{[BH]}$$

The indicators used were as follows: neutral red (pK_{BH} = 6.8), bromothymol blue (pK_{BH} = 7.2), phenolphthalein (pK_{BH} = 9.8), 2, 4-dinitroaniline (pK_{BH} = 15.0) [31, 32]. Basicity was measured

by the method of Hammett indicator-benzene carboxylic acid (0.02 mol/l anhydrous methanol solution) titration [33].

The specific surface area of the catalysts were determined by a Micromeritics model ASAP 2010 surface area analyzer (North Huntingdon, PA) based on nitrogen adsorption/desorption isotherms acquired at 77.2 K using a 30 s equilibrium interval. The surface area was computed using the BET (Brunauer–Emmett–Teller) model. All catalyst samples were degassed at 200 °C for 5 h prior to analysis to remove any adsorbed molecules from the pores and surfaces.

Thermal decomposition of the catalyst was evaluated by thermogravimetric analysis/differential thermal analysis (TG/DTG) carried out on a Perkin Elmer Pyris-1 (Waltham, MA) operating under a flow of nitrogen (30 mL/min) and at a 10 °C/min heating rate from room temperature to 1273 K.

Powder X-ray diffraction (XRD) patterns were taken with a Rigaku RU2000 rotating anode powder diffractometer (Woodlands, TX) equipped with CuK α radiation (40kV, 200mA), over a 2 θ range of 20°-80°, with a step size of 0.02 ° and a scanning speed of 5°/min.

Energy dispersive spectrometry (EDS) was performed with an Hitachi S-2400 Scanning Electron Microscope (San Jose, CA). Maximum operating voltage used was 25kV.

2.4 Biodiesel Reactions and Product Analysis

Erlenmeyer flasks (25 mL) containing oil, methanol, and catalysts were used as batch reactors. In most studies, 10.0 g of soybean oil, 7.6 g of methanol, and 0.5 g of activated oxide catalyst were put into a flask. Flasks containing the reactant mixture were heated in a shaking bath (Series 25 incubator, New Brunswick Scientific Co.) maintained at 58 °C and shaken with a speed of 450 rpm.

The tube reactor has a dimension of 20 mm i.d. • 355 mm length in which 8 g of Zn₃La₁ catalyst was packed. Reactants were premixed in a beaker and then pumped into the top of the vertically oriented reactor. The flow rate was fixed at 0.2 mL/min (Chrom. Tech. Inc., Apple Valley, MN); reaction temperature was held at 58 °C in a water bath (PolyScience Inc., Warrington, PN); reaction pressure was around 1 atm; resident time was 120 minutes; molar ratio of methanol to oil varied from 15:1.

The concentrations of FAME in the samples were quantified by using a GC-MS (Clarus 500 GC-MS, Perkin-Elmer) with a capillary column (Rtx-WAX Cat. No.12426). Ethyl arachidate (Nu-Chek Prep Inc, Elysian, Minnesota) was used as an internal standard. Water content was analyzed using a Brinkman/Metrohm 831 KF Coulometer (Westbury, NY) according to ASTM D 6304-00. FFA concentration was determined using a Brinkman/Metrohm 809 titrando (Westbury, NY) according to ASTM D 664.

3. Results and Discussion

3.1 Effect of preparation method

The XRD spectrum of Ca-La metal oxide catalysts which were prepared by four different preparation methods were shown in Figure 1. For the Ca₃La₁ catalyst, Ca(OH)₂ and La(OH)₃ phases were identified, indicating that Ca₃La₁ consisted of a mixture of each hydroxide. For CaO/La₂O₃, only the La(OH)₃ phase was identified and no Ca crystalline peaks were detected, even though the EDS results (Table 1) show that this catalyst had a bulk Ca to La ratio of 0.3. The XRD spectrum of the CaO/La₂O₃ also shows that there was a slight shift of the peaks at 27.2° and 28.0° which corresponded to the (1, 1, 0) and (1, 0, 1) planes of La(OH)₃, respectively.

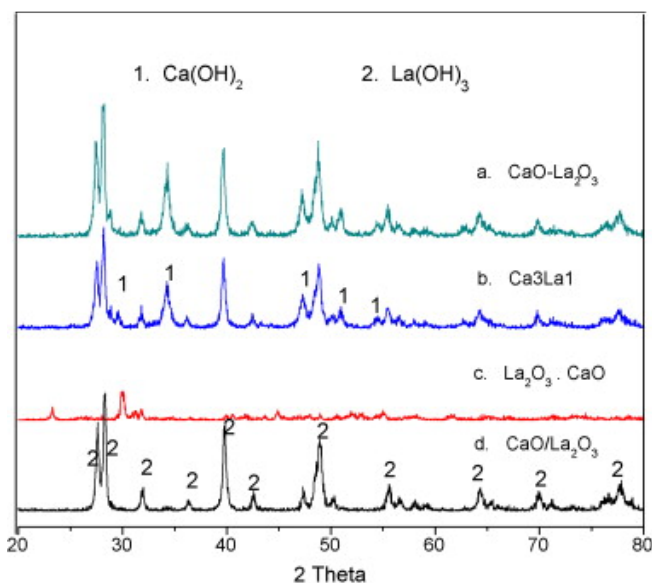


Fig. 1. XRD spectrum of Ca₃La₁, CaO/La₂O₃, La₂O₃·CaO, and CaO-La₂O₃.

These shifts suggest that La³⁺ ions in the host lattice were partially substituted by Ca²⁺ ions [34]. For La₂O₃·CaO, there were no evident diffraction patterns of Ca or La species suggesting a highly amorphous nature of this material [35]. For CaO-La₂O₃, the physically mixed sample, both Ca(OH)₂ and La(OH)₃ phases were found. However, the half-width of peaks of Ca(OH)₂ and La(OH)₃ phases were smaller than those of the Ca₃La₁ catalyst, indicating that the crystal size of CaO-La₂O₃ was bigger than Ca₃La₁. The XRD measurements suggest that calcium can exist as segregated Ca(OH)₂ crystal (as in Ca₃La₁ and CaO-La₂O₃), incorporated into the La species lattice (as in CaO/La₂O₃), or amorphous form (as in La₂O₃·CaO), as a result of different preparation procedures.

It has been reported that the base sites over heterogeneous catalysts are active centers for transesterification [36, 37]. Thus, it is interesting to correlate the effects of base strength and basicity of the catalysts on activity. As indicated in Table 1, Ca₃La₁ shows the highest value in base strength (9.8 < H < 15). Moreover, the total basicity of the catalysts is in the order of: Ca₃La₁ >

CaO/La₂O₃ > CaO-La₂O₃ > La₂O₃/CaO. As discussed before, Ca₃La₁ exhibits the best transesterification activity among these catalysts.

The catalysts prepared by traditional methods have low BET surface areas (< 10 m²/g) as compared to Ca₃La₁ (62.6 m²/g, Table 1). XPS and EDS results show that surface atomic molar ratios of Ca to La for Ca₃La₁, CaO/La₂O₃ and La₂O₃·CaO catalysts are higher than bulk ones.

This suggests that the ammonia-ethanol-carbon dioxide precipitation method, impregnation method and co-precipitation method can promote Ca dispersion on the surface of the catalyst.

Table 1. BET specific surface area, surface atomic ratio of Ca to La, bulk molar ratio of Ca to La, and basicity of Ca₃La₁, CaO/La₂O₃, La₂O₃·CaO, CaO-La₂O₃.

Catalyst	Preparation method	Bulk atomic ratio of Ca to La	Specific surface area (m ² /g)	Surface atomic ratio of Ca to La	Basicity (mmol/g)			
					6.8 < H ₊ < 7.2	7.2 < H ₊ < 9.8	9.8 < H ₊ < 15	Total basicity (mmol/g)
Ca ₃ La ₁	Ammonia-ethanol-carbon dioxide precipitation method	3.5	62.6	4.2	2.0	10.4	1.2	13.6
CaO/La ₂ O ₃	Impregnation method	0.3	5.3	2.7	5.1	3.4	–	8.5
La ₂ O ₃ ·CaO	Co-precipitation method	0.4	9.9	0.7	0.8	–	–	0.8
CaO-La ₂ O ₃	Physical mixing method	3.5	6.2	3.1	3.8	2.1	–	5.9

The catalytic performance of Ca-La based catalysts prepared by different preparation methods is presented in Figure 2. The FAME yields after one hour for these catalysts were between that achieved by homogeneous NaOH or H₂SO₄ catalysts. Ca₃La₁ needed about 60 minutes to get to the highest FAME yield (95.3 %), which shows a similar catalytic activity to NaOH and is higher than CaO/La₂O₃, CaO-La₂O₃ and La₂O₃·CaO. The catalytic activity trend of Ca₃La₁, CaO/La₂O₃, CaO-La₂O₃ and La₂O₃·CaO parallels the variability of total basicity in Table 1; i.e. the higher the

basicity, the higher the activity of catalyst, which is in good agreement with early studies [13, 38, 39]. The effect of catalyst components was also studied. Using an ammonia-ethanol-carbon dioxide precipitation method, binary metal oxides catalyst, Ca₃La₁, single CaO-containing, and single La₂O₃-containing catalysts were prepared. Figure 2 shows that binary metal oxides catalyst has a higher activity than pure metal oxides. Our previous study shows that there was a strong interaction between Ca and La species in the binary catalyst prepared by the ammonia-ethanol-carbon dioxide precipitation method, which resulted in high basicity, high BET surface area and high catalytic activity in oil transesterification [39].

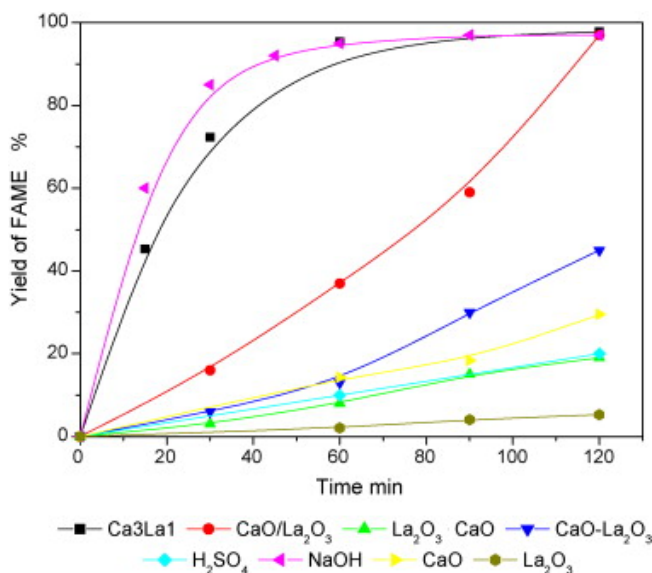


Fig. 2. Transesterification activities of Ca₃La₁⁽¹⁾, CaO/La₂O₃⁽¹⁾, La₂O₃-CaO⁽¹⁾, CaO-La₂O₃⁽¹⁾, CaO⁽¹⁾, La₂O₃⁽¹⁾, H₂SO₄⁽²⁾ and NaOH⁽³⁾. Reaction conditions: (1) 10 g of soybean oil, 7.6 g of methanol, 0.5 g of catalyst and 65 °C; (2) 20 g of soybean oil, 7.3 g of methanol, 0.6 g of H₂SO₄ and 65 °C; and (3) 20 g of soybean oil, 4.5 g of methanol, 0.2 g of NaOH and 65 °C.

3.2 Effect of calcination temperature

Since the catalyst prepared by the ammonia-ethanol-carbon dioxide precipitation method showed promising activity in oil transesterification, the effects of preparative parameters, such calcination temperature, calcium loading, pH value, ammonia, CO₂ and alcohol addition, and storage conditions, were investigated to optimize the catalyst structure and activities.

Figure 3 is a TG curve of uncalcined Ca₃La₁. The total weight loss from 50 °C to 920 °C was about 87 %. The weight loss before 200 °C was about 10 % which corresponded to the desorption of physically adsorbed molecules (H₂O and CO₂) [40]. The weight loss from 300 ~ 430 °C was about 70 % which can be attributed to the decomposition of Ca(OH)₂, La(OH)₃ and Ca(OCH₂CH₃)₂ [41, 42].

Lastly, the weight loss at 700 ~ 780 °C was considered to be the decomposition of carbonate salts such as CaCO₃ and La₂CO₃ [43, 44].

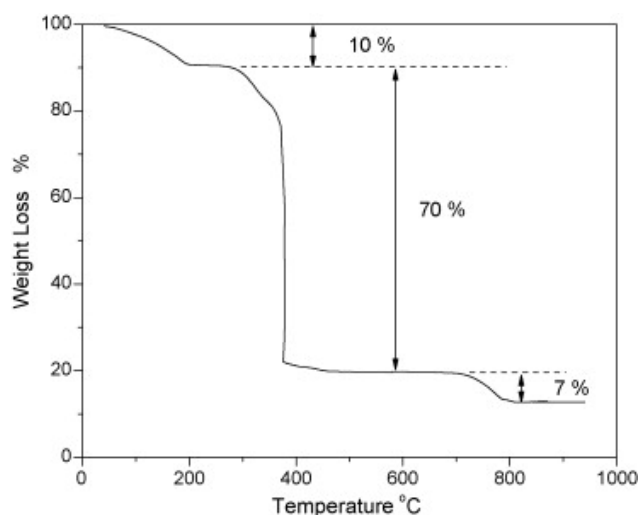


Fig. 3. Weight losses as a function of temperature of uncalcined Ca₃La₁. Note the three weight loss stages.

Based on the TG curve, the Ca₃La₁ catalyst was calcined at 300 °C, 450 °C, 780 °C and 950 °C respectively, and the total basicities were measured (Figure 4). It can be observed that the basicity of the catalysts initially increased with the calcination temperature and reached a maximum at 780 °C; but decreased when the calcination temperature exceeded 780 °C. BET surface area in Table 2 shows a similar trend. 780 °C was considered to be the optimal calcination temperature to obtain a maximum value in both basicity and BET surface area.

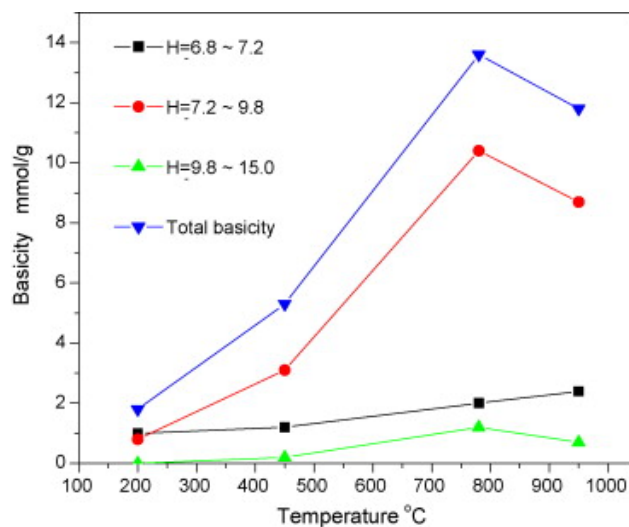


Fig. 4. Basicity of Ca₃La₁ calcined at different temperature. Note the basicity at 780 °C.

Table 2.

BET specific surface area, surface atom ratio of Ca to La, binding energy and surface percentages of La, Ca and lattice oxygen.

Catalyst calcinations temperature (°C)	Binding energy (eV)				Surface percentage (at.%)			Surface atom ratio of Ca:La	Specific surface area (m ² /g)
	La _{3d}	Ca _{2p 1}	Ca _{2p 2}	O _{lat}	O _{lat}	Ca ²⁺	La ³⁺		
300	833.4	347.9	346.7	528.7	60.6	3.2	0.6	5.3	5.0
450	833.7	347.6	346.3	529.0	62.2	5.6	2.1	2.7	41.5
780	833.6	348.2	346.7	528.9	70.8	12.5	3.0	4.2	62.6
950	833.8	348.0	346.5	528.9	60.3	11.3	4.6	2.4	20.2

The chemical state and surface composition of the catalysts as determined by XPS are shown in Table 2. The binding energy (BE) of La 3d_{5/2} remained constant at 833.4 ~ 833.8 eV as calcination temperature increased. The BE of the two Ca 2P_{3/2} components were at 347.6 ~ 348.2 eV for CaCO₃ and 346.3 ~ 346.7 eV for Ca(OH)₂ species, respectively [45]. Therefore, it appears that the outermost surface layers of the catalyst was carbonated and hydrated. The presence of CaO can be neglected since the BE of Ca in CaO is below that of Ca(OH)₂ [46] and it is not observable in the XPS spectra. The difference between the TG curve, XPS and XRD can be attributed to contact with ambient environment when preparing XPS and XRD samples. CaO in fresh catalysts could react with H₂O and CO₂ in the air, forming hydroxide and carbonate salts [13]. Thus, there is no characteristic BE line for CaO. Two photoemission lines can be seen for O_{1s}, which correspond to two distinct oxygen species. The line with low BE (528.7 ~ 529.1 eV) was attributed to oxygen ions in the crystal lattice (O_{latt}); the line (530.8 ~ 531.2 eV) was to the adsorbed oxygen [46, 47]. Crystal lattice oxygen has a strong Lewis base site and it is generally considered as the active center for oil transesterification [48-50]. Table 2 shows that the surface concentration of O_{latt} and Ca²⁺ initially increased with calcination temperature, reached the highest value at 780 °C, and then decreased with further increase in temperature. On the other hand, surface La³⁺ kept increasing with calcination temperature.

The effect of calcination temperature on the catalytic activity of Ca₃La₁ is shown in Figure 5. The catalyst calcined at 780 °C shows the highest activity and a FAME yield of 95.3 % can be obtained in

90 minutes. The catalysts calcined at 300 °C and 450 °C show low conversions even with an extended reaction time (180 minutes). The catalyst calcined at 950 °C shows a relatively high activity and a yield of 87.8 % was reached after 180 minutes. Catalyst activity increased with calcination temperature until 780 °C and then slightly decreased with further temperature increase. The catalyst activities also displayed a similar pattern as basicity (Figure 4), BET surface area and surface Ca^{2+} and O_{latt} concentration (Table 2) as a function of calcination temperature.

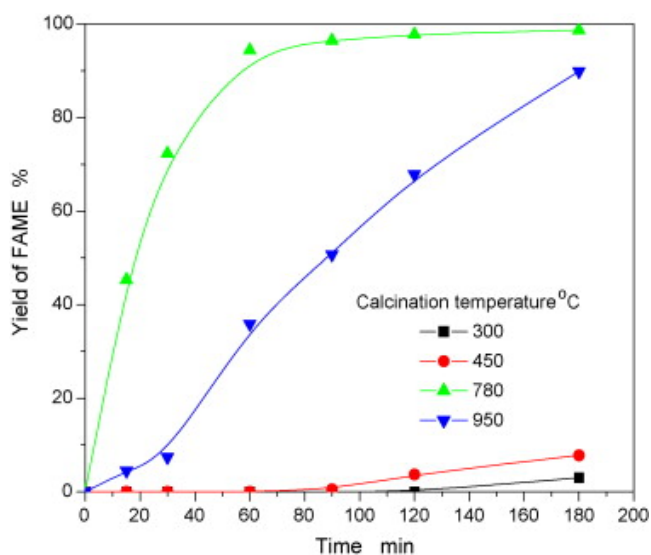


Fig. 5. Yield of FAME based on the catalysts calcined at 300 °C, 450 °C, 780 °C and 950 °C. Reaction conditions: 10 g of soybean oil, 7.6 g of methanol, 0.5 g of catalyst and 65 °C.

3.3 Effect of precipitants

Table 3 shows the catalyst structure and performance of precipitates of ammonia solution, ethanol and CO_2 . Using NH_3 solution, major precipitates formed were hydroxides such as $\text{La}(\text{OH})_3$ and $\text{Ca}(\text{OH})_2$ [51]. EDS results show that for $\text{Ca}_3\text{La}_1\text{-NH}_3$ catalyst, the bulk molar ratio of Ca to La is only 0.4, which is much lower than that of the original precursor solution (3:1 of Ca to La). This suggests that Ca ions present in the original solution were not totally precipitated. BET results show that it has a low specific surface area as compared to Ca_3La_1 . The Hammett indicator results show that it had a low base strength and small amount of basicity. Correspondingly, the FAME yield using $\text{Ca}_3\text{La}_1\text{-NH}_3$ was only 5.6 % at 90 minutes. Using CO_2 as precipitant, carbonates such as CaCO_3 and La_2CO_5 were formed [51, 52]. Similar to $\text{Ca}_3\text{La}_1\text{-NH}_3$, $\text{Ca}_3\text{La}_1\text{-CO}_2$ has a low bulk ratio of Ca to La, low BET surface area, and poor basicity resulting in a poor transesterification activity. When ethanol was used as a precipitant, the major precipitate formed is ethylate [51, 52]. $\text{Ca}_3\text{La}_1\text{-CH}_3\text{CH}_2\text{OH}$ exhibited a high specific surface area and a wide distribution of base strength (Table 3). However, it still had a low bulk ratio of Ca^{2+} to La^{3+} , and low FAME yield (32.1 % after 90 minutes).

However, as discussed earlier, Ca3La1 catalyst, in which ammonia, ethanol and CO₂ were sequentially used as precipitants, had the highest bulk ratio of Ca to La, highest total basicity and highest FAME yield.

Table 3. Bulk molar ratio of Ca to La, BET specific surface area, basicity and yield of FAME of Ca3La1–NH₃, Ca3La1–CO₂, Ca3La1–CH₃CH₂OH and Ca3La1. Reaction conditions: (1) 10 g of soybean oil, 7.6 g of methanol, 0.5 g of catalyst and 65 °C.

Catalyst	Bulk atomic ratio of Ca to La	Specific surface area (m ² /g)	Basicity (mmol/g)				Yield of FAME (%) ⁽¹⁾
			6.8 < H ₊ < 7.2	7.2 < H ₊ < 9.8	9.8 < H ₊ < 15	Total basicity (mmol/g)	
Ca3La1–NH ₃	0.4	7.1	0.2	–	–	0.2	5.6
Ca3La1–CO ₂	1.6	17.4	1.1	0.7	–	1.8	27.9
Ca3La1–CH ₃ CH ₂ OH	1.2	66.9	1.3	7.2	1.0	9.5	32.1
Ca3La1	3.5	62.6	2.0	10.4	1.2	13.6	95.3

In this sequential precipitation approach, the addition of NH₃ solution (base precipitant) could quickly increase pH value of the precursor solution. Bubbling in CO₂ (acid precipitant) led to the formation of carbonate and slightly decreased the pH value. Thus, by adjusting the NH₃ and CO₂ addition, and maintaining the pH value, Ca and La can be precipitated in the desired ratio from the precursor solution. There are two possible functions of ethanol. Firstly, during the calcination process the ethylate decomposes and generates a large amount of CO₂ and H₂O. These gases may expand the volume of catalyst precursor and lead to the formation of micropores which yields a high specific surface area [27]. Secondly, base strength of CaO prepared from CaOCH₂CH₃ is much higher than that prepared from CaCO₃ and Ca(OH)₂ [53]. Thus, ethanol may enhance the catalyst basicity. The cooperative effect of the three precipitants leads to a more complete and uniform precipitation and a high specific surface area, base strength and basicity, resulting in a high transesterification activity.

3.4 Effect of precursor solutions

Table 4 shows that if the pH value was kept at 6.0 or 7.5, the final catalyst had a relatively low bulk molar ratio of Ca to La, which suggests that Ca^{2+} in precursor solution was not fully precipitated. XPS results show that the surface percentage of lattice oxygen, and the Ca^{2+} and La^{3+} increased with pH value of precursor solution, and led to a higher catalytic activity (Figure 6). These findings are consistent with previous studies that pH value and molar ratio of Ca to La in the precursor solution have an impact on the precipitation process [52, 54].

Table 4. Effects of pH value of the precursor solution on the bulk molar ratio of Ca to La and surface percentages of La, Ca and lattice oxygen.

pH value of precursor solution	Bulk atomic ratio of Ca to La	Surface percentage (at.%)		
		O_{lat}	Ca^{2+}	La^{3+}
pH 6.0	2.7	48.2	3.1	0.5
pH 7.5	2.8	54.1	8.2	0.8
pH 9.0	3.1	70.8	12.5	3.0

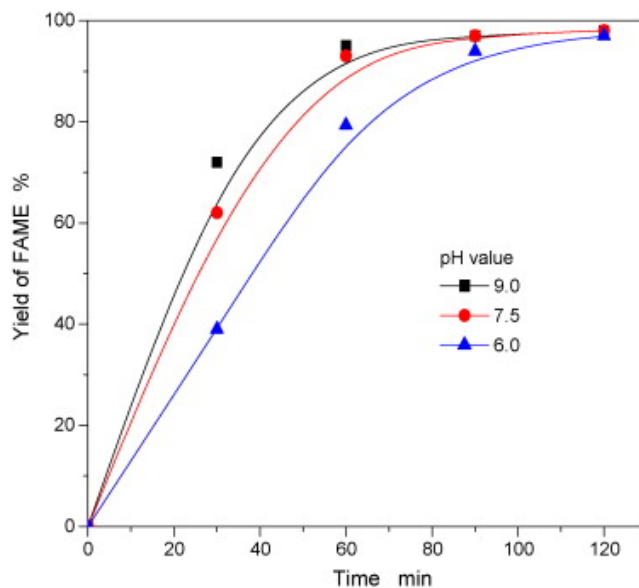


Fig. 6. Yield of FAME based on the catalysts prepared from the precursor solution with 6.0, 7.5 and 9.0 of pH. Reaction conditions: 10 g of soybean oil, 7.6 g of methanol, 0.5 g of catalyst and 65 °C.

Table 5 shows that molar ratios of Ca to La in the precursor solution were different with those on the catalyst surface. When the molar ratio is 3.0: 1.0 in the precursor solution, the surface percentage of lattice oxygen and total amount of lattice oxygen, and the concentration of Ca²⁺ and La³⁺ were highest, and led to the highest catalytic activity (Figure 7). Thus, a basic precursor solution (pH 9.0) and 3.0: 1.0 molar ratio of Ca to La in solution were identified as the optimal conditions for the ammonia-ethanol-carbon dioxide precipitation method.

Table 5. Effects of molar ratio of Ca to La of the precursor solution on the surface molar ratio of Ca to La and surface percentages of La, Ca and lattice oxygen.

Molar ratio of Ca to La in precursor solution	Surface atomic ratio of Ca ²⁺ to La ³⁺	Surface percentage (at.%)			
		O _{lat}	Ca ²⁺	La ³⁺	Total amount of O _{lat} , Ca ²⁺ and La ³⁺
1.0:0	—	37.4	15.3	—	52.7
9.0:1.0	7.0:1.0	53.1	15.5	2.2	70.8
3.0:1.0	4.2:1.0	70.8	12.5	3.0	86.3
1.0:1.0	1.7:1.0	69.3	8.0	4.5	81.8
1.0:3.0	1.0:1.2	58.5	6.0	7.2	81.8
1.0:9.0	1.0:2.0	64.6	3.4	7.1	75.1
0:1.0	—	51.9	—	5.6	57.5

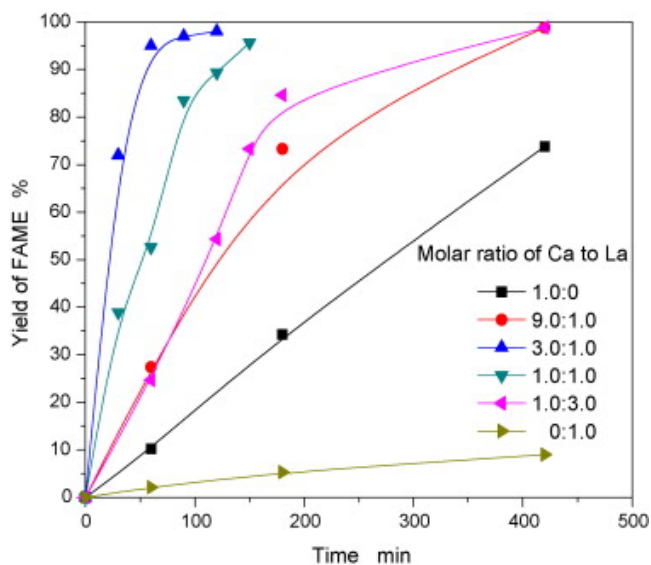


Fig. 7. Yield of FAME based on the catalysts with different molar ratio of Ca to La. Reaction conditions: 10 g of soybean oil, 7.6 g of methanol, 0.5 g of catalyst and 65 °C.

3.5 Effect of storage conditions

Solid base catalysts are often vulnerable because they have a tendency to adsorb acid molecules from the ambient environment and lose activity [19]. As discussed in previous reports [38, 39], CO₂ and H₂O in air can easily poison basic sites on a catalyst surface and change the bulk crystal structure of the catalyst. However, information on the proper storage conditions for these types of the catalyst has not been reported. The effects of exposing the fresh catalysts in air, soybean oil and methanol on the activity of were investigated. The catalyst exposed to soybean oil showed a reaction rate very similar to that of freshly activated Ca₃La₁ catalyst (Figure 8). The catalysts exposed to methanol and air showed a significant decrease in catalytic activity. These findings suggest that active base sites on Ca₃La₁ can be effectively protected from acidic gas in air since soybean oil is non-polar and has a relatively low pK_a value (3.55). On the other hand, methanol has a high pK_a value (15.54) with dissolved acidic gases. Thus, these soluble acidic gases may poison the basic sites and lead to a gradual loss in catalyst activity.

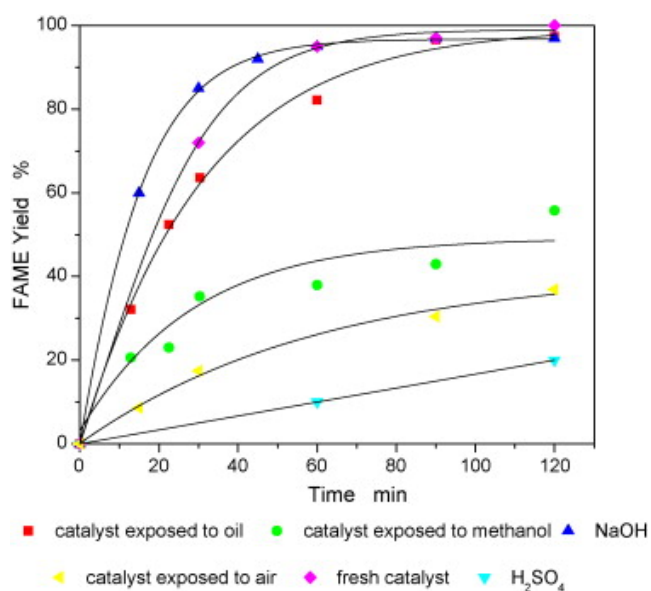


Fig. 8. Yield of FAME based on H₂SO₄⁽¹⁾, NaOH⁽²⁾ and the catalysts stored in soybean oil, methanol and air⁽³⁾. Reaction conditions: (1) 20 g of soybean oil, 7.3 g of methanol, 0.6 g of H₂SO₄ and 65 °C; (2) 20 g of soybean oil, 4.5 g of methanol, 0.2 g of NaOH and 65 °C; and (3) 10g of soybean oil, 7.6 g of methanol, 0.5 g of catalyst and 65 °C.

3.6 Catalyst durability

Ca3La1 catalyst was successfully recycled three times in a batch stir reactor (see Figure 9a), but its activity dropped in the fourth cycle. And in a continuous fix bed reactor the yield of FAME maintained higher than 92 % for 14 days, but from the 15th day catalyst deactivation can be observed (see Figure 9b). The deactivation of Ca3La1 catalyst was supposed to be related with the active site blockage by adsorbed intermediates or product species, such as diglyceride, monoglyceride, and glycerin and the contamination by O₂, H₂O, and CO₂ in air as stated in 3.5 section [13, 33]. Some researchers also suggested that the deactivation was caused by leaching of catalyst components especially for the calcium containing species [55, 56]. Further study about prolonging catalyst life should be done.

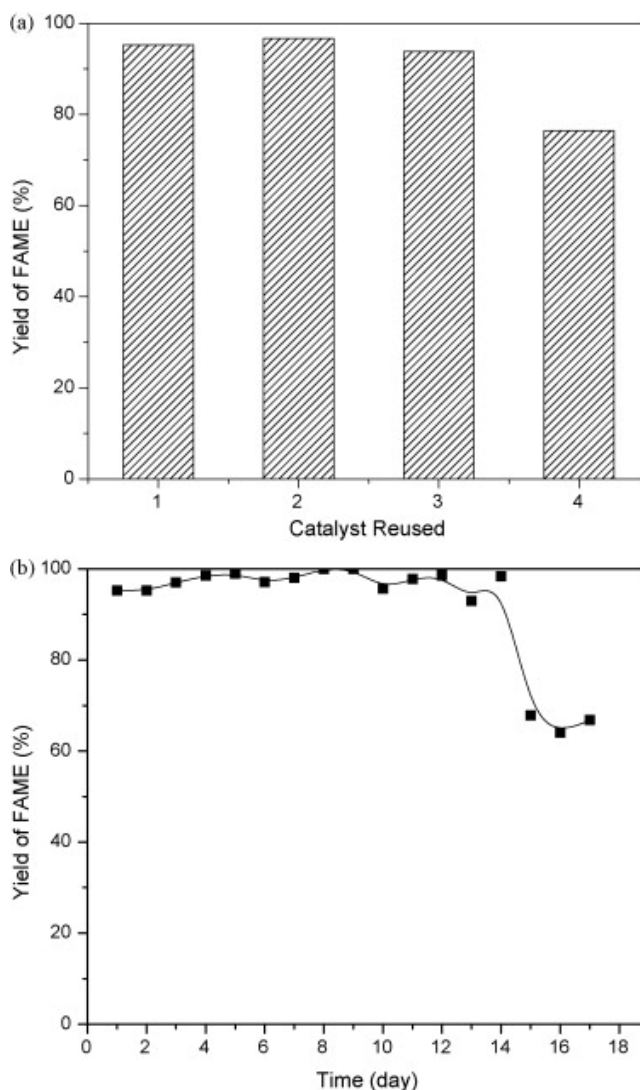


Fig. 9. Reusability of Ca3La1 catalyst. (a) In a batch stir reactor. Reaction conditions: 10 g of soybean oil, 7.6 g of methanol, 0.5 g of catalyst and 65 °C and (b) in a fix bed continuous reactor. Reaction conditions: molar ratio of methanol to oil is 15:1, flow rate 0.2 mL/min, 8 g of Ca3La1 catalyst, resident time 120 min, 58 °C.

4. Conclusion

A sequential precipitation method with ammonia solution, ethanol and carbon dioxide as precipitants for solid base catalyst preparation has been developed. A cooperative effect among the precipitants allows a more complete and uniform precipitation process, a higher specific BET surface area, higher concentration of strong base sites, and a high catalytic activity in the oil transesterification reaction for biodiesel production.

The structure of Ca and La metal oxides depends on the precipitation methods. Three types of Ca structures were observed: 1. Ca species segregated on the surface in the samples prepared by the ammonia-ethanol-carbon dioxide precipitation method and the physical mixing method. Crystal size of Ca species for Ca₃La₁ was smaller than of the CaO-La₂O₃. 2. Ca incorporated into the La(OH)₃ lattice prepared by the impregnation method, 3. Ca stayed as a non-crystal structure prepared by the co-precipitation method. Segregated and highly dispersed Ca species were obtained by the ammonia-ethanol-carbon dioxide precipitation method.

The calcination temperature, nature of precipitants, pH value, and molar ratio of Ca to La have a significant effect on catalyst structure and activity. The Ca₃La₁ catalyst should be stored in non-polar oil to prevent contamination and deactivation from ambient environment. Using this class of catalysts, which is relatively inexpensive because of low raw materials and manufacturing costs, significantly simplifies the product purification process, and greatly decreases the production cost of biodiesel.

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