

Application of modified CaO as an efficient heterogeneous catalyst for biodiesel production

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Modified CaO has been prepared and investigated in transesterification of rapeseed oil with methanol to determine its viability as a basic catalyst for use in biodiesel synthesis. It has been found that the fatty acid methyl esters (FAME) yield is greatly enhanced from 66.2 to 96.5% over modified CaO with methanol/oil ratio of 15:1 at 65°C after 4 h. Furthermore, the good catalytic activity, 83.8% yield of FAME, remains even in the 2% water-contained condition over modified CaO. The catalyst has been characterized by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and Fourier transform infrared spectrometry (FT-IR).

Keywords: Ethyl bromoacetate, Surface modification, Calcium oxide, Biodiesel

Biodiesel fuel which is an alternative to classic diesel fuel, belongs to ecological fuels because it consists of methyl esters of fatty acids, derived from vegetable oil or animal fats^{1,2}. Homogeneous catalysts based on NaOH and KOH are mainly used in transesterification reaction with methanol for biodiesel productions^{3,4}. The homogeneous base catalysts can catalyze biodiesel production with the short reaction time under mild reaction conditions, however, it still has several disadvantages which need to be resolved urgently⁵. For example, it is difficult in separating the catalyst and purifying biodiesel products. Moreover, a larger amount of contaminated water is produced by neutralizing and washing the products. In order to solve the aforementioned problems, the development of an eco-friendly and efficient biodiesel production process has been reported.

A large number of solid bases, claimed to be heterogeneous catalysts, such as CaO, MgO, BaO, SrO, La₂O₃, alkali earth oxides, and hydroxides, have been described in literature⁶⁻⁸. Among the reported solid bases, calcium oxide is one of the most promising basic heterogeneous catalyst for its low cost and high catalytic activity⁹, but it is rapidly hydrated and carbonated by contact with room air in few minutes due to chemisorb significant amount of H₂O and CO₂. The activity of poisoning CaO in the transesterification reaction was found to be lower¹⁰.

Some initiatives provide highly activated alkali earth oxides to catalyze transesterification by increasing the number of basic sites or enlarging their surface area. One of the efficient ways for the preparation of highly activated CaO is doping CaO with lithium in a relatively expensive or complicated way¹¹. Nanocrystalline CaO was reported to be a solid catalyst for biodiesel production under room temperature¹². The heterogeneous CaO-La₂O₃ catalyst was prepared for the transesterification of soybean oil and methanol/ethanol and showed better methanolysis activity¹³. However, further studies are required to find more effective ways to stabilize active surface sites for long-term biodiesel production applications.

Kawashima *et al.*¹⁴ developed the activation of CaO by pretreatment with methanol for producing biodiesel. This provides great advantages in improving phase solubility and overcoming mass transfer limitations even in the presence of moisture and free fatty acids. However, its application in large-scale production is limited due to the high temperature and pressure.

In this work, a surface modification technology was developed to prepare the CaO with high catalytic activity and good stability. Subsequently, the efficient solid base catalyst was applied in catalyzing the transesterification reaction of rapeseed oil for biodiesel products. Both the CaO activation

conditions and various reaction conditions for transesterification were investigated.

Experimental Section

Preparation of modified CaO

The surface modification over commercial CaO obtained from Sinopharm Chemical Regents Co., Ltd. (Beijing China) was carried out as follows: 2.8 g commercial CaO particles without elimination of hydroxide and carbonates was added into 37.5 mL methanol solution containing 2.5 mL ethyl bromoacetate (97.0%; TCI Shanghai) under stirring at 65°C under refluxing. After 4 h, the mixture was filtrated and washed with methanol to remove excessive ethyl bromoacetate; then, the modified CaO was obtained after vacuum drying.

Humidity test of the modified CaO

The stability of commercial CaO and modified CaO particles in air was tested by humidity test. The sample particles were kept in a saturated-humidity container at room temperature to allow the absorption of water. After several days, the weight of samples was recorded at regular intervals of 24 h. The moisture absorption ratio (wt%) was evaluated by the following Eq. (1), using the m_1 as increase in weight, and the m_0 as the initial weight.

$$wt\% = \frac{56m_1}{18m_0} \times 100 \quad \dots (1)$$

Transesterification of rapeseed oil

The conversion of rapeseed oil to biodiesel was performed in a 100 mL three-necked, round-bottomed flask with a reflux condenser at 65°C under vigorous stirring. Typical reactions were performed with rapeseed oil and methanol (methanol/ rapeseed oil molar ratio 15:1) using 10 wt% (weight to oil) of catalyst for the specified time.

Reaction products were analyzed using following procedure. The samples were separated from the catalyst and glycerol by decantation¹⁵ and the excess methanol was removed under vacuum. The products were analyzed by the gas chromatography (HP-6890) and a capillary column HP-5 (30 m × 0.32 mm × 0.25 um) using inner standard method. The yield was defined as a ratio of the weight of fatty acid methyl esters determined by gas chromatography to the weight of fatty acid methyl esters given in theory.

Catalyst characterization

A Fourier transform infrared (FT-IR) spectrophotometer was used to identify the functional

group over catalyst surface. TGA experiments were carried out using a TGA/SDTA 851° thermal analysis machine (Mettler-Toledo, Switzerland) under a flow of nitrogen. The sample weight used was about 10 mg with temperature ranged from 25°C to 930°C at a ramping rate of 20°C/min. The XRD analysis was recorded with a German Bruker AXS D8 Advance X-ray diffractometer using Cu radiation ($\lambda = 0.11506$ nm). The nitrogen adsorption and desorption isotherms were measured at -196°C using a Micromeritics ASAP 2010 system. Specific surface areas of the samples were determined by nitrogen adsorption data in the relative pressure range from 0.06 to 0.30 using the BET (Brunauer-Emmett-Teller) equation. Total pore volumes were estimated from the amount of nitrogen adsorbed at a relative pressure of 0.995. Pore volume and pore size distribution curves were obtained from the analysis of the desorption branches of the nitrogen isotherms using the BJH (Barrett-Joyner-Halenda) method.

Results and Discussion

Humidity test of the modified CaO

The moisture erosion of commercial CaO and modified CaO was evaluated by humidity tests with modifier loading in the range from 0.0001 to 0.5 wt%. The moisture absorption over all samples is plotted as a function of absorption time in Fig. 1. All of the tested samples were kept in a vapor-saturated container at room temperature to allow the hydration and carbonation and the weight of each sample were measured at regular intervals of time. From the results, it is shown that the moisture absorption rate continues rising for all samples along with time

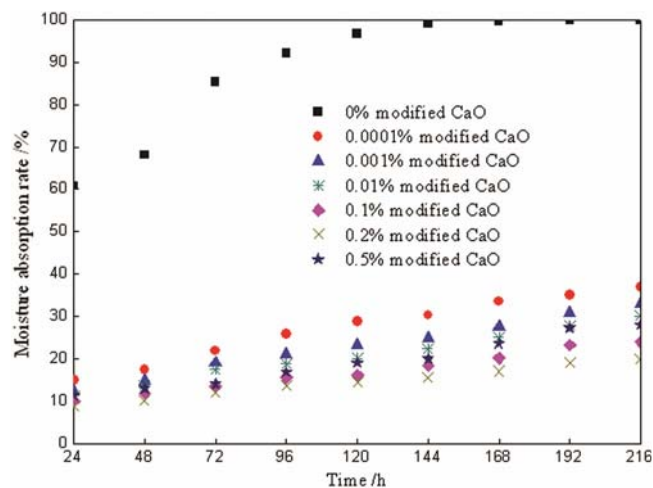


Fig. 1 — Moisture absorption rate over commercial CaO and modified CaO

indicating the unavoidable poison by the atmosphere CO_2 and H_2O . However, the moisture absorption degree of commercial CaO particles increases rapidly and reaches to nearly 100% at 144 h, while very low weight increase over modified CaO at the same time, especially for 0.2% ethyl bromoacetate modified CaO, only 19.9% moisture absorbing rate can be found even after 200 h. It is obviously that low concentration of modifier resulting in a relatively poor water resistance of CaO due to no formation of hydrophobic layer over catalyst surface. On the other hand, too much ethyl bromoacetate gives the large amount of CaBr_2 forming over CaO surface, which is highly water-absorptive and can decrease the resistance to moisture of the modified CaO.

Characterization of catalyst

The Fourier transform infrared (FT-IR) spectra of the commercial CaO and modified CaO was studied. For the two samples, the spectra bands at 1260 cm^{-1} and 1477 cm^{-1} correspond to vibration modes of mono and bidentate carbonates, which provided the poisoning of CO_2 over their surface. The infrared spectra demonstrated the characteristic absorb of C=O between 1600 and 1400 cm^{-1} indicates the presence of calcium carbonate formed in both of the catalysts, which is greatly intensified over the modified CaO due to the carboxyl group in ethyl bromoacetate. The important feature of the modified CaO appears in the C-H (carboxyl group) stretching (2800 - 3200 cm^{-1}) and in the C-O (acetate) stretching (1220 cm^{-1}). As a result, a hydrophilic CaO was obtained which can be confirmed by the dispersion experimental presented in Fig. 2 showing that the CaO particles moves from methanol phase (lower) to the interface of methanol-rapeseed oil phase. The hydrophilic surface of CaO plays an important role to the efficiency of heterogeneous transesterification because of the diffusion of grease to CaO surface become easier over modified CaO.

The TG/DTG thermogram of the commercial CaO and modified CaO revealed that for the two samples, there are two steps in the TG curve in the temperature range from 400°C to 700°C corresponding to the decomposition of $\text{Ca}(\text{OH})_2$ and CaCO_3 formed by the hydration and carbonation of CaO in the storage and preparation process¹⁶. The CaCO_3 decomposition peak of modified CaO moves to the higher temperature range (714°C) compared with commercial CaO (684°C), which indicates that the thermal stability of modified CaO is enhanced due to

the deposition of organic modified over CaO surface as suggested in the previous report¹⁷. Furthermore, the weight loss for decomposition of CaCO_3 over modified CaO is much higher than commercial CaO due to more CaCO_3 formed during modifying process as suggested by the result of XRD in Fig. 3.

The XRD patterns of the commercial and modified CaO are shown in Fig. 3. The calcium oxide characteristic diffraction peaks appeared at 32.1° , 37.3° , 53.9° , 64.6° , 67.5° and 80.1° , and the modification process improve the dispersion of CaO particles with decrease the intensity of CaO diffraction peak. The calcium hydroxide characteristic diffraction peaks appeared at 17.9° , 28.6° , 34.1° , 46.9° and 50.7° , and the modified calcium oxide on the diffraction intensity is significantly higher than that of unmodified calcium oxide. In addition, calcium carbonate peak located at 29.2° and 38.9° can be observed over the modified CaO. Thus, the modification process is inevitable erosion of water and carbon dioxide in the air, which is in great agreement with the result of Infrared spectroscopy and TG analysis.



Fig. 2 — Dispersion of CaO particles in the methanol phase (lower) and rapeseed oil phase (upper) before and after modifying

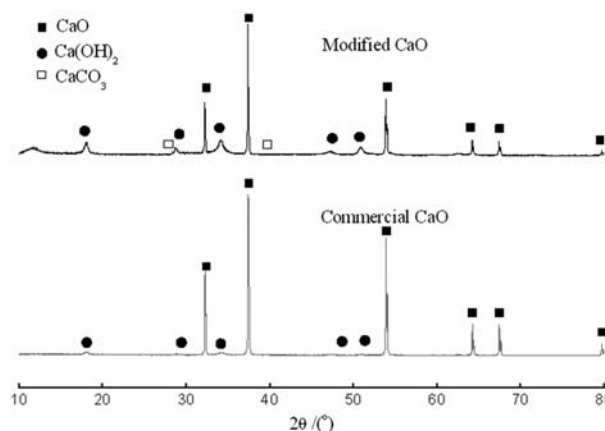


Fig. 3 — XRD patterns of the commercial and modified CaO

The specific surface areas, pore volume and average pore diameter of both of samples are shown in Table 1. From the results, it can be seen that the modifying gives large surface area of CaO from 2.54 to 28.22 m²/g, which is contributed to the high dispersive of CaO particle size as supported by XRD results.

Effect of reaction variables

Effect of modifier loading

The loading of modifier has great effect on the reactivity of modified CaO. In our work, the activity of modified CaO with different amount of ethyl bromoacetate was tested at reaction temperature of refluxing (65°C) with molar ratio of methanol to oil at 15:1 using 10 wt% loading of modified CaO as catalyst and shown in Fig. 4. From the result, the conversion of rapeseed oil increases with the amount of ethyl bromoacetate and reaches the optimal value at 0.02%, giving FAME yield as high as 96.5% which is greatly higher than 66.2% yield of FAME in the presence of commercial CaO. This is probably because of the modifier over CaO surface that accelerates the diffusion of reactants to CaO surface resulting high reaction rate in the heterogeneous reaction. Further increasing the amount of modifier causes the decrease of FAME yield due to the occupation of activity site by excessive modifier.

Effect of molar ratio of methanol to oil

Commonly, the stoichiometric ratio for transesterification of rapeseed oil and methanol requires 3:1 (methanol/oil). However, in practice, the molar ratio of methanol to oil should be higher than that of the theoretic ratio due to drive the completion of the reaction to achieve more products, FAME. Fig. 5 indicates that the yield increased when molar ratio of methanol to oil increased from 5:1 to 15:1, the yield of fatty acid methyl ester increases from 80.1% to 96.5%. Further increase in methanol results in a decrease in fatty acid methyl ester yield due to a dilution effect by too much alcohol. Therefore, the highest yield was obtained when the molar ratio was very close to 15:1.

Table 1 — Nitrogen physisorption data of the commercial and modified CaO

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore Diameter (nm)
Modified CaO	28.22	0.1677	23.775
Commercial CaO	2.54	0.0121	19.195

Effect of catalyst dosage

The effect of catalyst dosage on transesterification efficiency was investigated over 0.2% modified CaO with a reaction time of 6 h, a methanol/oil molar ratio of 15:1 under a reaction temperature of 65°C. As indicated from Fig. 6, the yield of FAME markedly increased at the beginning with the increase of catalyst dosage from 3% to 10% (weight to oil). The yield attained the maximum value when using 10% catalyst. However, with further increase of the catalyst content, the FAME yield decrease due to the formation of soap in the presence of a high amount of catalysts, which increase the viscosity of the reactant and cause the diffusion of reactant to the catalyst surface difficult. Therefore, 10% modified CaO was optimal in the reactions of this study.

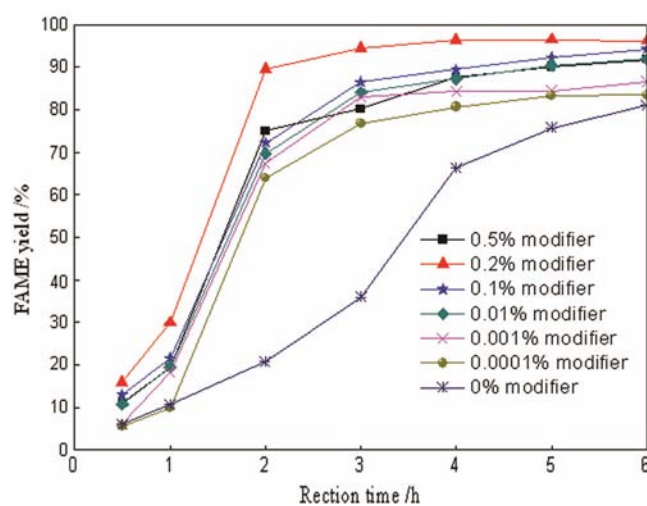


Fig. 4 — Effect of loading of modifier on the yield of FAME

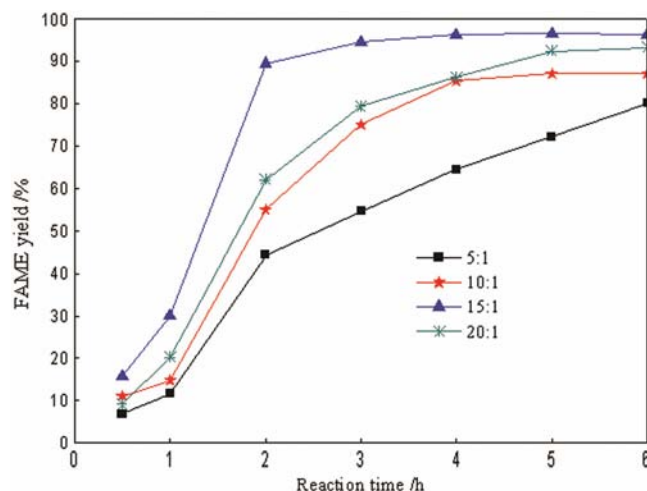


Fig. 5 — Effect of molar ratio of methanol to oil on the yield of FAME

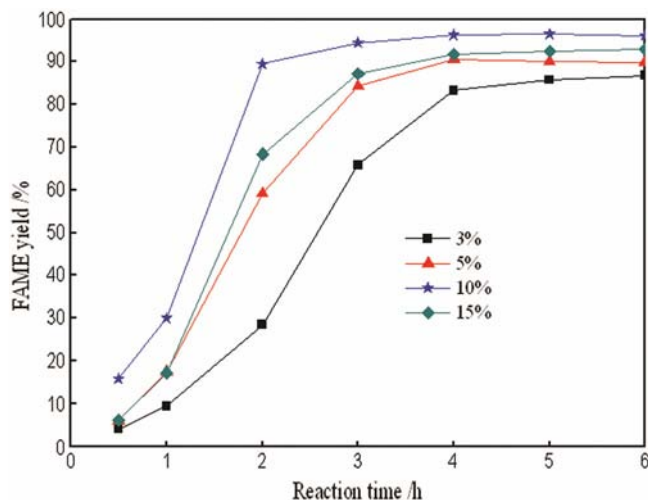


Fig. 6 — Effect of catalyst dosage on the yield of FAME

Effect of reaction time

In order to investigate the relationship between yield and time, the reaction was carried out at 15:1 molar ratio of methanol to oil using 10% modified CaO as a catalyst under the reaction temperature of 65°C for different reaction time from 0.5 to 6 h. The results showed that there was a great increase of FAME yield in the initial time from 0.5 to 2 h which indicated that the reaction was very rapid in the beginning, reaching the maximum value after 4 h. From 5 to 6 h the yield of FAME decreases slightly attributed to the hydrolysis of esters to form soap as suggested by Tamilmani *et al.*¹⁸.

Water resistance test

As illustrated from the moisture absorption rate test that modified CaO showed good water resistance, then the comparative study on water resistance of the modified CaO and commercial CaO (Table 2) was carried out under the optimum reaction condition: 65°C, 15:1 molar ratios of methanol/oil, and 10 wt% catalyst (weight to oil) loading. From Table 2, it can be seen that the reaction maintains 83.8% yield of FAME even 2.0% water contained in the reaction system, while for commercial CaO, the yield of FAME decreased to 50.1%. The former is due to the hydrophobic surface protective layer over CaO surface after modifying which can effectively resist the diffusion of water to the surface of CaO by its low polarity.

Conclusion

A simple and low cost route to prepare high efficiency heterogeneous catalyst has been established by modifying commercial CaO with ethyl bromoacetate.

Table 2 — Water resistance test over commercial CaO and modified CaO

Water content (%)	Yield of FAME (%)	
	Commercial CaO	Modified CaO
0.5	87.9	92.7
1.0	74.4	89.4
2.0	50.1	83.8
5.0	27.0	57.9
10.0	19.7	39.3

It was shown that the obtained catalyst has a high activity under mild reaction conditions. The yield of FAME over modified CaO is greatly enhanced to 96.5% after 4 h compared with 66.2% over commercial CaO. Furthermore, the modified CaO showed good stability in high water containing reaction system. The possible reason should be contributed to the great enhancement of grease diffusion to catalyst surface which has been changed to be hydrophilic by the modifier. From this view, this novel efficient solid base catalyst has great potential for practical biodiesel production and other base-catalyzed heterogeneous reactions.

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