



## Effect of calcination temperature on the activity of solid Ca/Al composite oxide-based alkaline catalyst for biodiesel production

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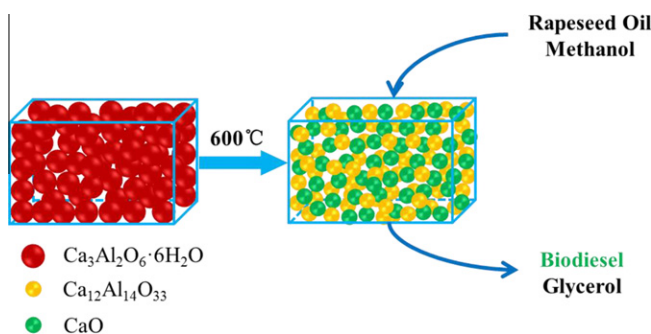
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### HIGHLIGHTS

- ▶ A solid base catalyst based on  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  and CaO was developed.
- ▶ The catalyst showed excellent catalytic activity with biodiesel yields >94%.
- ▶ The effect of calcination temperature on the catalytic activity was investigated and optimal temperature was determined.
- ▶ Structure and properties of the catalyst were studied.
- ▶ The synergistic mechanism between crystalline  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  and CaO of the catalyst was revealed.

### GRAPHICAL ABSTRACT

The Ca/Al composite oxide which contains  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  and CaO was prepared successfully by a simple method and used as an environmentally benign solid catalyst in the transesterification of rapeseed oil with methanol. The effect of the calcination temperature ranging from 120 °C to 1000 °C on the catalytic activity was investigated. The catalyst calcined at 600 °C showed the highest activity with >94% yield of biodiesel. The activity of the catalyst was closely related to its specific surface area and crystalline structure. In particular, the generation of crystalline  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  vastly improved the catalytic activity due to the synergistic effect between  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  and CaO.



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### ABSTRACT

A solid Ca/Al composite oxide-based alkaline catalyst containing  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  and CaO was prepared by chemical synthesis and thermal activation from sodium aluminate solution and calcium hydroxide emulsion. The effect of calcination temperatures ranging from 120 °C to 1000 °C on activity of the catalyst was investigated. The catalyst calcined at 600 °C showed the highest activity with >94% yield of fatty acid methyl esters (i.e. biodiesel) when applied to the transesterification of rapeseed oil at a methanol:oil molar ratio of 15:1 at 65 °C for 3 h. Structure and properties of the catalyst were studied and the characterizations with XRD, TGA, FTIR, BET, and SEM demonstrated that the performance of the catalyst was closely related to its specific surface area and crystalline structure. In particular, the generation of crystalline  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  improved the catalytic activity due its synergistic effect with CaO.

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## 1. Introduction

Biodiesel is commonly produced by the transesterification of triglycerides with methanol using homogeneous alkaline catalysts such as NaOH and KOH (Ma and Hanna, 1999; Pinto et al., 2005; Lotero et al., 2005.); however, production costs are rather high as not only a number of washing and purification steps need to be performed to meet quality requirements but also due to the equipment corrosion caused by acid and alkaline conditions (Canakci, 2007; Granados et al., 2007; Ji et al., 2006; Karmee and Chadha, 2005). Although homogeneous base processes are relatively fast and show high conversions (Semwal et al., 2011), the generation of wastewater is an environmental concern and it is difficult to remove the catalysts from the reaction mixture.

As heterogeneously catalyzed processes generally do not generate large amounts of wastewater and are easy to separate from reaction mixtures, they could prove more environmentally friendly than homogeneous catalysts (Semwal et al., 2011; Martino et al., 2008). Particularly, solid base catalysts can allow the production of high quality glycerol as by-production (Bournay et al., 2005).

Metal oxides (Yan et al., 2010; Furutaa et al., 2006), zeolites (Brito et al., 2007), and hydrotalcites (Cantrella et al., 2005; Trakarnpruk and Porntangjitlikit 2008) have been explored as heterogeneous catalysts for triglyceride transesterification. CaO has also been investigated and was found to exhibit high activity. For example, Kawashima et al. (2008) found that with calcium oxide as catalyst a 90% of biodiesel yield could be achieved in the transesterification of rapeseed oil with refluxing methanol within 3 h. Reddy et al. (2006) reported that nanocrystalline CaO showed high catalytic activity (99% conversion) in the transesterification reaction of poultry fat and soybean oil at room temperature. Some research has shown that soluble substance leached from CaO during transesterification. Gryglewicz (1999) reported that CaO dissolved slightly in methanol and formed a suspension in the reaction mixture. The separation of CaO from biodiesel after the reaction is very difficult due to gel formation in the lower glycerol layer (Guo et al., 2007; Jiang et al., 2006; Yan et al., 2007). Therefore, it is critical to develop a solid catalyst that not only possesses exceptional catalytic activity and high stability, but is also easily separable from the biodiesel product.

Wang et al., 2012 synthesized a solid Ca/Al composite oxide-based catalyst for transesterification of rapeseed oil with methanol and showed that the catalyst calcined by 1000 °C reused for at least seven cycles with yields of the FAME maintained above 87%. The catalyst was easily separated from the reaction mixture, as it is insoluble in methanol and methyl esters. The present study focuses on the effect of calcination temperature on the catalytic activity and structure of this catalyst and compares its performance with that of NaOH and CaO.

## 2. Methods

### 2.1. Materials

Rapeseed oil was purchased from Xingwang Oil Corporation (Guanghan, Sichuan, China) and its physical and chemical properties are listed in Table 1. Standard analytical reagents, such as methyl undecanoate, methyl palmitate, methyl oleate, methyl stearate, methyl linoleate, and methyl linolenate were purchased from Sigma Chemical Corporation, USA. Calcium carbonate and aluminum foil were of guarantee reagent grade (GR) and sodium hydroxide and other chemicals were of analytical grade (AR), and were obtained from Kewei Reagent Corporation, Tianjin, China.

**Table 1**

Physical and chemical properties of the rapeseed oil.

Property	Unit	Value
Palmitic acid	wt.%	12
Stearic acid	wt.%	4
Oleic acid	wt.%	16
Linoleic acid	wt.%	20
Linolenic acid	wt.%	5
Erucic acid	wt.%	43
Saponification value	mg KOH/g	190.98
Acid value	mg KOH/g	0.12
Water content	wt.%	0.12

### 2.2. Catalyst preparation

An aqueous solution of sodium aluminate ( $\text{NaAlO}_2$ ) was prepared with 6 g of aluminum foil and 45 mL of 5 mol/mL NaOH. A  $\text{Ca}(\text{OH})_2$  emulsion was prepared by 7 g of calcium oxide (CaO), prepared by calcination of  $\text{CaCO}_3$ , in 50 mL of distilled water. The  $\text{NaAlO}_2$  solution and the  $\text{Ca}(\text{OH})_2$  emulsion were mixed at a Ca:Al molar ratio of 3:2 under 300 r/min stirring rate for 3 h at 80 °C. After the mixture was cooled to room temperature, the solid precipitate was collected through an air pump filtration. The solid material was washed with deionized water until the pH of the washwater was about 7–8. The solid was dried under airflow at 120 °C, followed by calcination in a muffle furnace at temperature ranging from 400 °C to 1000 °C for 8 h.

### 2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns of the samples were recorded on a PANalytical X'Pert diffractometer using  $\text{Cu-K}\alpha$  radiation (40 kV and 100 mA). The diffractograms were recorded in the  $2\theta$  ranges of 10–110° with a 2 h step size of 0.02°. The phases present in the samples were identified according to the Powder Diffraction (PDF) database (JCPDS-International Centre for Diffraction Data (ICDD), 2000).

The specific surface area of Ca/Al composite oxides catalysts was determined by  $\text{N}_2$  adsorption at 77 K using a Micrometrics TriStar 3000 automated system. Prior to analyses, the catalysts samples were degassed at 473 K and  $10^{-6}$  mmHg for 5 h. Specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) model.

Fourier transform infrared (FTIR) spectroscopy was done on a Nicolet 560 spectrophotometer. The FTIR spectroscopy measurements were performed by mixing samples into KBr pellets (32 scans with  $5\text{ cm}^{-1}$  resolution) in the range of 4000–400  $\text{cm}^{-1}$ .

Thermogravimetry differential thermal analysis (TG-DTA) was recorded using a HCT-2 analyzer. The dried samples (prior to calcination) were heated to 1173 K from at a heating rate of 5  $\text{K min}^{-1}$  in an air stream.

Scanning electron microscopy (SEM) was carried out using a XL30 SEM (Philips, Eindhoven, North Brabant, Netherlands). The samples were coated with gold using a sputter coater.

### 2.4. Experimental procedures

Transesterification reactions were carried out in a 150 mL four-neck glass flask equipped with a stirrer, a reflux methanol condenser, and an electric jacket with a thermocouple. Firstly, 45 g of rapeseed oil and 24.5 g of methanol (molar ratio of 15:1) were placed into the reactor, and catalyst at 6 wt.% of the rapeseed oil was added. The reaction was carried out under a stirring rate of 270 r/min at 65 °C for 3 h. The catalyst was removed from the mixture by filtration through an air pump filtration, and washed by

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