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Fuel

journal homepage: www.elsevier.com/locate/fuel

A new solid base catalyst for the transesterification of rapeseed oil to biodiesel with methanol

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HIGHLIGHTS

▶ A new solid catalyst containing $Ca_{12}Al_{14}O_{33}$ and CaO was synthetically prepared.
▶ The catalyst has good activity with ME (methyl ester) content reached 90%.
▶ The catalyst can be used for at least 7 cycles with the ME content over 87%.
▶ The catalyst can be separated from reaction system effectively and easily.
▶ This study may provide benefits for developing a continuous biodiesel process.

ARTICLE INFO

ABSTRACT

A new solid base catalyst containing $Ca_{12}Al_{14}O_{33}$ and CaO was prepared by chemical synthesis method and was used in the transesterification of rapeseed oil with methanol to produce biodiesel. The catalyst was characterized by Hammett indicators, X-ray diffraction (XRD), infrared spectroscopy (IR), Brunauer–Emmett–Teller (BET) and scanning electron microscopy (SEM), separately. The effect of various factors was investigated to optimize the reaction conditions. The results showed that the ME (methyl ester) content reached 90% after reacting for 3 h at 65 °C, with a methanol/oil molar ratio of 15:1, the amount of catalyst of 6 wt.% and the stirring rate of 270 rpm. Moreover, the catalyst could be used repeatedly for at least 7 cycles with the ME content over 87%, due to its high stability. In particular, this solid base catalyst can be separated from reaction system effectively and easily, as it is insoluble in both methanol and methyl esters, which may provide significant benefits for developing an environmentally benign and continuous process for synthesizing biodiesel.

1. Introduction

The research on application of alternative renewable fuels has attracted tremendous attention in recent years due to the fear for the imbalance between diminishing fossil fuel reserves and soaring global energy demands. Many strategies and methods have been developed, in which the transesterification of vegetable oils or animal fats with short carbon-chain alcohols (methanol or ethanol) to produce a mixture of fatty acids esters (known as biodiesel) has great importance because biodiesel possesses many advantages over conventional fossil fuels, including proper lubricity, good biodegradability, excellent combustion efficiency and low toxicity [1–5]. Therefore, biodiesel can be employed for a clean substitute for fossil fuel without any modification to diesel engines, boilers or other combustion equipments [6–8].

Two kinds of catalysts, homogeneous and heterogeneous catalysts, have been used in the transesterification reaction [9,10]. The conventional process of biodiesel is the transesterification of oils with methanol or ethanol in the presence of homogeneous catalysts, such as NaOH and KOH, which are the catalyst precursors. The real catalysts may be Na or K ethoxydes. However, homogeneous base catalytic systems have some basic technological problems, such as the production of wastewater to a serious threat for environment and the difficulty for removal of the base catalysts after reaction [11–14], although homogeneous base processes are relatively fast and show high conversions.

Recently, solid base catalysts have been increasing attention as substitutes for the highly pollutant liquid homogeneous catalysts to produce biodiesel, as they generally do not generate large amount of wastewater. For example, $KF/\gamma\text{-}Al_2O_3$ and $Na/NaOH/\gamma\text{-}Al_2O_3$ are highly active in the transesterification of vegetable oils [14,15]. However, the active ingredients of most of these supported alkali catalysts are sensitive to moisture and easily corroded by short carbon-chain alcohols, resulting in reducing lifetime of the

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catalysts and therefore limiting their industrial applications [16,17]. Another solid base catalyst of CaO has also been investigated and found that it has high activity and relative long lifetime [18–21]. However, the separation of CaO catalyst from biodiesel product after the reaction is very difficult attributed to gel phenomenon in the lower glycerol layer [22–24]. Therefore, it is critical to develop a novel solid catalyst that not only possesses exceptional catalytic activity and high stability, but also is easily separable from the transesterification product of biodiesel.

In this study, a novel solid base catalyst was prepared. The physical and chemical characterizations of the catalyst with some instrumental methods were investigated. It was used to catalyze transesterification of rapeseed oil with methanol for the synthesis of biodiesel, and the effects of various factors were studied to optimize the reaction conditions.

## 2. Experimental

2.1. Materials

Rapeseed oil was purchased from Xingwang Oil Corporation (Guanghan, Sichuan, China). Analytical reagents using as standards for gas chromatograph (GC) were purchased from Sigma Chemical Corporation, USA. Other chemicals were analytical reagents (AR) and purchased from Kewei Reagent Corporation, Tianjin, China.

2.2. Preparation of catalyst

The solid base catalyst was prepared by chemical synthesis methods as follows.

(1) Preparation of hydrated tricalcium aluminate ($Ca_3Al_2O_6\cdot6H_2O$).

Sodium aluminate ($NaAlO_2$) aqueous solution and calcium hydroxide ($Ca(OH)_2$) solution were mixed in a 1000 ml beaker. The mixture was stirred vigorously at 80 °C for 3 h. After the mixture was cooled to room temperature, the solid precipitate was collected by filtration. The solid was washed with deionized water until the pH of the washing solution maintained between 7 and 8 to give product hydrated tricalcium aluminate ($Ca_3Al_2O_6\cdot6H_2O$), in which the reaction is as the following equation:

$$3Ca(OH)_2 + 2NaAlO_2 + 4H_2O \rightarrow Ca_3Al_2O_6 \cdot 6H_2O + 2NaOH \qquad (1)$$
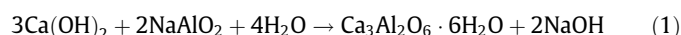
(2) Generation of the solid base catalyst.

The hydrated tricalcium aluminate was then calcined at 1000 °C for 8 h in a muffle furnace. The catalyst was cooled down to 400 °C, then it was extracted from the muffle furnace and kept in a desiccator for future use.

2.3. Catalyst characterization

Hammett indicators, XRD, IR, BET, and SEM techniques were separately used to characterize the prepared catalyst.

Base strength of catalysts ($H\_$) and base total amount of catalysts were measured by using Hammett indicators [25,26], including bromthymol ($H\_$ = 7.2), phenolphthalein ($H\_$ = 9.8), 2, 4-dinitroaniline ($H\_$ = 15.0) and 4-nitroaniline ($H\_$ = 18.4).

X-ray diffraction (XRD) measurements were performed with a PANAlytical X'Pert diffractomer using Co Kα radiation (λ = 0.179 nm) at 40 kV and 40 mA. Data were collected over a 2θ range of 10–110° with a step size of 0.02° at a scanning speed of 5 min^{-1}.

IR measurements were performed with a Nicolet 560 spectrometer (Nicolet, Madison, Wisconsin, USA). The infrared spectra were recorded at room temperature in the range of 400–3500 cm^{-1}, with 300 scans and 4 cm^{-1} resolution. The KBr pellet technique was applied for determining IR spectra of the samples.

The BET surface area of the catalysts was measured by the nitrogen adsorption method at −196 °C using a Tristar 3000 instrument (Micromeritics, Norcross, GA, USA).

The surface morphology of the catalyst was investigated by a XL30 SEM (Philips, Eindhoven, North Brabant, Netherlands). SEM was operated at 20.0 kV of an accelerating voltage.

2.4. Reaction procedures

The transesterification reactions were carried out in a 150 ml four-neck glass flask equipped with a stirrer, a water cooling condenser and an electric jacket with thermocouple. Firstly, 45 g of rapeseed oil was poured into the reactor with an amount of methanol according to desired molar ratio of methanol to rapeseed oil. The molar ratio of methanol to rapeseed oil ($N_{methanol:oil}$) and average relative molar mass of rapeseed oil ($\overline{M}_{oil}$) were calculated [27] as follows:

$$N_{methanol:oil} = \frac{m_{methanol}\overline{M}_{oil}}{m_{oil}M_{methanol}} \qquad (2)$$

$$\overline{M}_{oil} = \frac{M_{KOH} \times 1000 \times 3}{SV - AV} \qquad (3)$$

where $m_{methanol}$ is the mass of methanol, g; m_{oil} is the mass of rapeseed oil, g; $M_{methanol}$ is molar mass of methanol, g mol^{-1}; SV is saponification value of rapeseed oil, mg KOH g^{-1}; AV is acid value of rapeseed oil, mg KOH g^{-1}; M_{KOH} is molar mass of KOH, g mol^{-1}.

After the mixture was stirred and heated to setting temperature (30–65 °C), the catalyst (2–8 wt.% relative to rapeseed oil) was added to the reaction system. The reaction was carried out under a stirring rate of 60–360 rpm. Very small amount of samples (0.5 ml) were collected by drip tube each time from the reaction mixture at the interval of 1 h for analysis to calculate the ME content. After the reaction was completed, the catalyst was removed from the mixture by filtration, and then it was washed by methanol. The catalyst was dried and then was kept in a desiccator for future reuse. The filtrated solution was further separated by a batch distillation to steaming out the excessive methanol. Next, a standard layering process for the residual liquid was required to obtain product of biodiesel and by-production of glycerol.

2.5. Analysis

As the products in the methyl ester phase consist of methyl esters, monoglycerides, diglycerides and unreacted triglycerides, the amount of methyl esters (i.e. biodiesel) produced was calculated based on an internal standard using methyl salicylate as a reference standard. The methyl ester (ME) content then is calculated by the following expression which is similar to Ref. [28]:

$$\begin{aligned} \text{ME content (wt.\%)} &= \frac{\text{Calculated weight of methyl esters}}{\text{Weight of methyl ester phase}} \\ &\quad \times 100\% \\ &\approx \frac{\sum f_{ester}A_{ester}}{A_{reference}} \times \frac{m_{reference}}{m_{esters}} \times 100\% \end{aligned} \qquad (4)$$

where $m_{reference}$ is the mass of internal standard, g; m_{esters} is the mass of methyl esters, g; $A_{reference}$ is the area of internal standard; A_{ester} is the area of methyl ester; f_{ester} is correction factor of methyl ester.

The methyl esters samples were analyzed in an Sp-2100 gas chromatograph equipped with a flame ionization detector and a capillary column H.J. PEG-20 M (30 m × 0.32 mm × 0.5 μm).