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Calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol

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Abstract

In this study, physical and chemical characterizations of calcium methoxide were investigated to assess its performance as an excellent solid base catalyst using some instrumental methods, such as BET surface area measurement, scanning electron micrographs and particle size distribution. Then, it was used to catalyze transesterification of soybean oil to biodiesel with methanol. The effects of various factors such as mass ratio of catalyst to oil, reaction temperature and volume ratio of methanol to oil were studied to optimize the reaction conditions. The results showed that calcium methoxide has strong basicity and high catalytic activity as a heterogeneous solid base catalyst and it was obtained a 98% biodiesel yield within 2 h in this reaction. Besides, the recycling experiment results showed it had a long catalyst lifetime and could maintain activity even after being reused for 20 cycles.

Keywords: Calcium methoxide; Biodiesel; Solid base catalyst

1. Introduction

There is an increasing worldwide concern for environmental protection and for the conservation of non-renewable natural resources. Fatty acid methyl esters (FAME) show great potential as diesel substitutes, and they are known as the sources of biodiesel, which is synthesized by direct transesterification of vegetable oils with a short-chain alcohol in the presence of a catalyst [1–5]. The transesterification reaction can be carried out using both homogeneous (acid or basic) and heterogeneous (acid, basic or enzymatic) catalysts [6,7]. Homogeneous basic catalysts provide much faster reaction rates than heterogeneous catalysts, but it is considerably costly to separate homogeneous catalysts from the reaction mixture [8–11].

Heterogeneous catalysis is an economically and ecologically important field in catalysis research because these catalysts have many advantages: they are noncorrosive, environmentally benign and present fewer disposal problems. They are also much easier to separate from liquid products and they can be designed to give higher activity, selectivity and longer catalyst lifetimes [12–14]. Because of these advantages, research on chemical reaction using solid bases as catalysts has increased over the past decade [15]. Many types of heterogeneous catalysts, such as alkaline earth metal oxides, anion exchange resins, various alkali metal compounds supported on alumina or zeolite can catalyze many types of chemical reactions, such as isomerization, aldol condensation, Knoevenagel condensation, Michael condensation, oxidation and transesterification [16–21]. However, for most anion exchange resins and supported alkali catalysts, the active ingredients are easily corroded by methanol and they exhibit short catalyst lifetimes in the transesterification reaction [22,23]. In contrast, alkaline earth metal compounds are very slightly soluble in organic solvents and they are possibly used to catalyze transesterification reaction as solid base catalysts.

Some researchers found MgO has low activity in transesterification of vegetable oils to biodiesel and CaO provides a slow reaction rate to reach an equilibrium state [24,25].

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Reddy et al. [26] produced biodiesel using nanocrystalline CaO under room temperature. But, the reaction rate was slow and it spent 6–24 h to obtain high conversion with their most active catalyst. They also observed deactivation after eight cycles with soybean oil and after three cycles with poultry fat. Zhu et al. [27] obtained a 93% conversion of jatropha curcas oil using CaO as a catalyst. But, the catalyst must be treated with an ammonium carbonate solution and calcinated at high temperature. Gryglewicz studied alkaline earth metal oxides, hydroxides and alkoxides to catalyze transesterification reaction [12,28]. Most practical catalysts are highly complex materials, and a basic problem is how to relate catalyst behavior with physical and chemical structure. In this study, the authors investigated the physical and chemical characterizations of calcium methoxide solid base catalyst with some instrumental methods. We investigated the effects of various reaction conditions on the biodiesel yields.

2. Experimental

2.1. Materials and catalyst preparation

$Ca(OCH_3)_2$ was synthesized by a directed reaction of calcium with methanol in a slurry reactor at 338 K for 4 h (Eq. (1)). Then, the catalyst was dried at 378 K for 1 h after removal of most of methanol by filtration.

$$Ca + 2CH_3OH \overset{338k}{=} Ca(OH_3)_2 + H_2 \uparrow \tag{1}$$

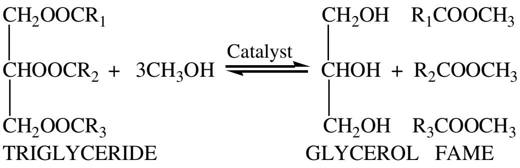
Refined soybean oil was purchased from Tianjin Jiali Oil Plant. The fatty acid composition consists of palmitic acid 12.5%, stearic acid 5.2%, oleic acid 23.5%, linoleic acid 47.8%, linolenic acid 10%, and traces of other acids. Methanol was analytical reagent (AR) and was purchased from Beihua Fine Chemical Co., Beijing. Analytical reagents (e.g. standards for liquid chromatography (HPLC)) were of high grade and were obtained from Sigma Chemical Co. All other chemicals were analytical reagents (AR) and were purchased from Beihua Fine Chemical Co., Beijing.

2.2. Apparatus and procedure

The BET surface area, total pore volume, pore diameter and pore size distribution of $Ca(OCH_3)_2$ were measured with a Quantachrome Autosorb-1-C chemisorption–physisorption analyzer. A weighed sample of the catalyst was prepared by outgassing for 1.5 h at 423 K on the degas port. Adsorption isotherms were generated by dosing nitrogen onto the catalyst in a bath of liquid nitrogen at approximately 77 K. The BET surface area was calculated from the adsorption branches in the relative pressure range of 0.05–0.25 bar, and the total pore volume was evaluated at a relative pressure of about 0.99 bar. The pore diameter and the pore size distribution were calculated from the desorption branches using the Barrett–Joyner–Halenda (BJH) method. The particle size distribution was measured using a Malvern Mastersizer MICRO-PLUS laser particle size analyzer and evaluated by a volume concentration. A FTIR-8201 (PC) infrared spectrophotometer was used to identify the surface group of the catalyst. Scanning electron microscopy (SEM) observations were performed on a Hitachi JEOL JSM 7401F microscope operating at 1.0 kV. Thermogravimetry (TG) was performed with a Netzsch TA-449C thermogravimetric analyzer from 25 °C to 800 °C at a heating rate of 10 °C/min under room atmosphere.

2.3. Reaction procedures

The transesterification reactions (Eq. (2)) were carried out in a 100 mL glass reactor with a condenser. Magnetic stirring rate was about 900 rpm by adjusting the speed knob to a graduation of 900 rpm. The reaction procedure was as follows: first, the catalyst was dispersed in methanol under magnetic stirring. Then, the soybean oil was added into the mixture and heated by water circulation. The amount of soybean oil was 28 mL every time. After the reaction, the excess methanol was distilled off under vacuum and $Ca(OCH_3)_2$ catalyst was separated by centrifugation. After removal of the glycerol layer, the biodiesel was collected for chromatographic analysis.



$$\begin{array}{llll} CH_2OOCR_1 & & CH_2OH & R_1COOCH_3 \\ | & & | & \\ CHOOCR_2 + 3CH_3OH & \overset{\text{Catalyst}}{\rightleftharpoons} & CHOH + & R_2COOCH_3 \\ | & & | & \\ CH_2OOCR_3 & & CH_2OH & R_3COOCH_3 \\ \text{TRIGLYCERIDE} & & \text{GLYCEROL} & \text{FAME} \end{array} \tag{2}$$

2.4. Analysis

The biodiesel samples were analyzed in a HP 5890 gas chromatograph equipped with a flame ionization detector and a capillary column HP-INNOWAX (30 m × 0.15 mm × 0.2 μm). 4 μL of the upper oil layer were dissolved in 300 μL of *n*-hexane and 100 μL internal standard solutions (heptadecanoic acid methyl ester – *n*-hexane solution) for GC analysis. Samples (1 μL) were injected by a sampler at an oven temperature of 220 °C. After an isothermal period of 4 min, the GC oven was heated at 10 °C/min to 230 °C, and held for 7.5 min. Nitrogen was used as carrier gas at a flow rate of 2 mL/min measured at 20 °C and as detector make up gas at a flow rate of 30 mL/min. The inlet pressure was 96.4 kPa. The split ratio was 10:1. The injector temperature and detector temperatures were 300 °C and 320 °C, respectively.

The biodiesel yield in each experiment was calculated by the following expression:

$$\text{yield} = \frac{m_{\text{actual}}}{m_{\text{theoretical}}} \times 100\% \approx \frac{C_{\text{esters}} \times n \times V_{\text{esters}}}{m_{\text{oil}}} \times 100\%$$
$$\approx \frac{C_{\text{esters}} \times n \times V_{\text{oil}}}{m_{\text{oil}}} \times 100\% \approx \frac{C_{\text{esters}} \times n}{\rho_{\text{oil}}} \times 100\%$$