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Biodiesel production catalyzed by cinder supported CaO/KF particle catalyst

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ABSTRACT

This study aimed to explore base catalysts with high transesterification efficiency to be used for heterogeneous biodiesel production. Cinder, a solid waste from coal burning industry, with 0.9–2.0 mm diameter, served as the support for CaO/KF to prepare base catalyst particle. The catalyst was characterized by base strength, X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), Brunauer–Emmett–Teller (BET) surface area, and the triglyceride (TG) conversions were determined using high performance liquid chromatography (HPLC). The effects of various parameters such as catalyst loading, molar ratio of methanol to oil and reaction time on the activity of catalyst were determined. The reusability and stability of the catalyst were investigated. Results showed that a maximum TG conversion of 99.9% catalyzed by 2.1% catalyst (based on the weight of soybean oil) in 20 min was obtained with methanol/oil molar ratio of 12:1. TG conversions were from 99.9% to 96.6% from the first to the fourth time use of the catalyst particle. The formed $KCaF_3$ and K_2O were the main active components for the catalyst activity. The leakage of K and Ca to the water and methanol and the occupation of the active sites by oleic acid were the main reasons for the decrease of TG conversion during repeated use of the catalyst. Fluoride leached into soybean oil, oleic acid, water, and biodiesel were negligible. However, about 3.0 and 1.5 mg F were dissolved into methanol and glycerol. It should be considered in the processes of recycling methanol and purifying glycerol.

1. Introduction

Among the options explored for alternative energy sources, biodiesel is one of the attractive alternatives [1,2] due to its renewability, biodegradability, and non-toxicity [3]. The most common way to produce biodiesel is through transesterification, especially alkali-catalyzed transesterification [4]. Unlike homogeneous, heterogeneous catalysts are environmentally benign and could be operated in continuous processes. Moreover they can be reused and regenerated [5]. Therefore, heterogeneous catalysts are now being tried extensively for biodiesel synthesis. These catalysts are poised to play an important role in future for biodiesel production at industrial level [6].

Nowadays, a wide variety of solid base catalysts for transesterification reactions have been investigated such as metal oxides [7–11], basic hydrotalcites [12], basic zeolites [13], and ion exchange resins [14]. Moreover, various supported catalysts were prepared using supports such as ZnO [15,16], Al_2O_3 [17,18], MgO [19], CaO [20,21], mesoporous silica [22], alumina/silica [23,24], NaX zeolite [25], flyash [26], and activated carbon [27,28]. It was demonstrated that these solid base catalysts showed various catalytic activities ranging from 48.9% to 99% of conversion in different operation conditions [5,29]. To obtain higher conversion, high temperature or long reaction time, and even high pressure, were needed for the reaction. For example, the transesterification from soybean oil catalyzed by nano-MgO solid base needed 24 MPa and 250 °C to obtain 99% conversion [30], and the one catalyzed by KF/ZnO solid base needed 9 h to obtain 87% conversion [31]. In the present paper, one of our aims was to investigate solid base catalyst which can catalyze transesterification with high conversion rate under moderate temperature and shorter time. Moreover, most studied solid catalysts were powder form which made them difficult to be separated from liquid products with high viscosity. So another aim of this research is to prepare solid catalyst particle at low cost.

The reusability of the solid catalyst is another important concern considering the economic benefit of industries. Among the solid catalysts, KF/CaO nanocatalyst showed not only high catalytic ability but also high reusability [20]. KF/CaO catalyzed biodiesel yield was in excess of 91% after 16 cycles. It was also demonstrated that the formation of $KCaF_3$ was the main reason for the enhancement of catalytic activity [20]. This paper aimed to investigate KF/CaO on natural waste material (cinder) to prepare solid catalyst particle with optimum size and with high catalytic ability and reusability.

Cinder is one of the major wastes produced by burning coal. It has some good properties for the production of solid catalyst. It

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contains high content of metal oxides such as Al_2O_3, K_2O, MgO, CaO, and SiO_2, which make it alkaline to some extent. In addition, cinder is full of pores with different sizes and can be made into particles with controlled diameter. Hence, it is an ideal support of solid base catalyst for biodiesel production.

In the present paper, solid base catalysts were prepared by loading CaO and KF on cinder. The solid catalyst product was characterized by Hammett titration, Brunauer–Emmett–Teller (BET) surface area, powder X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS). Effects of the catalyst loading, molar ratio of methanol to oil, and reaction time on the catalyst activity were investigated to optimize transesterification conditions. The reusability and stability of the solid catalyst were evaluated by batch experiment and the reasons for the deactivation of the catalyst were also discussed.

2. Experimental

2.1. Materials

The raw soybean oil was produced by Wuhan Baifu Oils & Fat Co. Limited (Wuhan, China). Cinder used as the support of synthesized catalyst was obtained from the coal-fired boiler room at the Cancer Hospital of Hubei Province. KF (99%), CaO (99%), methanol (99.5%), oleic acid (99%), glycerol (99%), H_2SO_4 (95–97%) and HNO_3 ($\geqslant$65%) are analytical reagent and were purchased from Aopu Chemical Company (Wuhan, China). Methanol and acetone of HPLC grade were purchased from Tedia Company Inc. (Fairfield, OH, USA) and Mallinckrodt Baker, Inc. (Phillipsburg, New Jersey, USA), respectively.

2.2. Catalyst preparation

The cinder-based catalyst was prepared by wet impregnation method. Available cinder with diameter grade of 0.9–2.0 mm was obtained after drying and sieving. Five grams of CaO powder and 10 g cinder were immersed in 10 mL distilled water, and were stirred and dried by a constant temperature magnetic stirrer. After the water evaporated, the solid CaO-cinder was immersed in 10 mL of 1 g mL^{-1} KF solution for 1 h, and then stirred and baked by a constant temperature magnetic stirrer followed by calcination in muffle furnace at 500 °C for 5 h. The prepared catalyst was sealed by plastic membrane for further use.

2.3. Catalyst characterization

The basic strength of the sample ($H\_$) was determined using Hammett indicator. About 100 mg of the sample was shaken with 5 mL cyclohexane and three drops of Hammett indicators-benzene solution (0.1%, w/w) and then left to equilibrate for 2 h when no further color changes were observed. The Hammett indicators used and the corresponding $H\_$ values are as follows: 4-nitroaniline ($H\_ = 18.4$), 2, 4-dinitroaniline ($H\_ = 15.0$), phenolphthalein ($H\_ = 9.8$) [32,33]. The basic strength is defined as being stronger than the weakest indicator, which exhibits a color change, and weaker than the strongest indicator that produces no color change.

BET surface areas of the synthesized catalysts were carried out according to the multipoint N_2 adsorption–desorption method using an instrument of SSA-4200 Surface Area and Pore Size analyzer (Beijing Builder Electronic Technology Co., Ltd., China). Prior to measurements, all samples were out-gassed overnight under vacuum at 573 K.

The sample morphology and elemental chemical analysis were also characterized at room temperature by a Quanta 200 SEM system equipped with EDS detector (FEI company, The Netherlands). The accelerating voltage was 20 KV.

XRD was performed on a D/MAX-RB powder X-ray diffractometer (Rigaku Corporation, Japan) at room temperature. Cu Kα radiation ($\lambda = 0.15418$ nm), with a step size of 0.02° in the 2θ range from 5° to 65°, was used in all samples. The data were processed with the Jade 5.0 software. The peaks were identified using the Powder Diffraction File (PDF) database created by International Centre for Diffraction Data (ICDD).

2.4. Batch experiment of transesterification reaction

The transesterification of raw soybean oil was carried out using a 250-mL 3-necked flask equipped with a water cooled condenser, a thermometer, and a magnetic stirrer, in a water bath at a temperature of 338 K. Appropriate amounts of methanol, raw oil, and catalyst were added to the reaction flask and stirred at 600 rpm. Samples were manually withdrawn at different times during the run. The reaction mixture was cooled and settled down for 2 min, and 40 μL upper solution was extracted and diluted with 1960 μL acetone. The diluted solution was filtered through 0.45 μm membrane and used for HPLC analysis. All experiments were performed under atmospheric pressure and duplicated.

For the reusability experiment, the supernatant biodiesel and glycerol layer were discharged and the solid catalyst was left in the flask after the first transesterification reaction. Same amount of fresh soybean oil and methanol were added into the flask and performed the same procedure as above again.

2.5. Analysis of biodiesel yield

Ester conversions were determined according to Ref. [34]. The biodiesel products were analyzed using HPLC system equipped with a variable wavelength detector (SPD-10A/10AV, SHIMADZU corporation, KYOTO, Japan). A personal computer equipped with a Chemstation program and a Kromasil C18 column (particle size 5 μm, 4.6 mm id × 200 mm L, Akzo Nobel/Eka Chemicals, Sweden) was used. The mobile phase was HPLC grade methanol. The flow rate of the mobile phase was 1.0 mL min^{-1}. The detection wavelength was 205 nm. The column temperature was 40 °C. Soybean oil and biodiesel samples were diluted with HPLC grade acetone and then filtered through a 0.45 μm micro-pore membrane prior to analysis. The percentage of triglyceride (TG) conversion was calculated using:

$$\text{TG conversion}(\%) = (\text{TG}_{\text{oil}} - \text{TG}_{\text{sample}})/\text{TG}_{\text{oil}} \times 100\%$$

where TG_{oil} was referred to the total HPLC peak area of triglycerides in the soybean oil diluted solution, and TG_{sample} was referred to the total HPLC peak area of triglycerides in the diluted biodiesel samples.

2.6. The stability of catalyst

The stability of catalyst in oleic acid, water, methanol, biodiesel, glycerol and crude oil were investigated. One gram of catalyst was immersed in 10 g oleic acid, biodiesel, glycerol, crude oil, and 10 mL water, and methanol, respectively, and was shaken for 1 h with the speed of 100 rpm. Then the resultants were transferred and centrifuged for 30 min with the speed of 4500 r/h, and the supernatant were used for the analysis of K and Ca contents. All the recovered solid catalyst (about 0.99 g) was used to catalyze the transesterification reaction under the following conditions: soybean oil = 50 g; reaction temperature = 65 °C; methanol/oil molar ratio = 12:1; reaction time = 20 min.