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Waste carbide slag as a solid base catalyst for effective synthesis of biodiesel via transesterification of soybean oil with methanol

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ABSTRACT

A highly efficient solid base catalyst was prepared from waste carbide slag and tested for biodiesel production from soybean oil with methanol. The effect of calcination temperature for carbide slag and various reaction parameters on the catalytic performances was systematically investigated. The carbide slag waste calcined at 650 °C (CS-650) exhibited 91.3% yield of fatty acid methyl esters (FAME) at reaction temperature of 65 °C, methanol/oil molar ratio of 9, catalyst/oil mass ratio of 1.0 wt.% within a short reaction time of 30 min, which was much higher than that of commercial CaO. Furthermore, the relationship between the surface basicity and activity indicated that stronger basicity was responsible for the higher catalytic activity. The merits of high catalytic activity, low cost, and abundant storage make the waste carbide slag a promising catalyst in the production of biodiesel.

1. Introduction

Biodiesel is a mixture of fatty acid alkyl esters produced by transesterification of vegetable oil or animal fats with mono-alkyl alcohols. Compared to conventional fossil fuels, biodiesel has attracted considerable interest as an alternative and sustainable fuel because of its high flash point, higher cetane value, low viscosity, high lubricity, biodegradability, and environmental-friendliness [1]. Homogeneous or heterogeneous catalysts can be used for biodiesel production. Nowadays, biodiesel is commercially produced using homogeneous base catalysts, such as NaOH, KOH, CH_3ONa and CH_3OK [2,3]. However, homogeneous base catalysts possess major drawbacks such as difficulties in disposing the products via neutralization, and washing with a large volume of water.

One of the main attempts to overcome the above-mentioned drawbacks of homogeneous catalysts is to utilize heterogeneous catalysts [4–7]. Solid base catalysts have attracted much attention due to the advantages of eco-friendly and easily separable property. Various solid base catalysts such as metal oxides CaO [8], and SrO [9]; mixed oxides Ca/La [10], Ca/Zn [11], and Ca/Al/Fe_3O_4 [12]; alkali-doped metal oxides Li/ZnO [13]; hydrotalcites [14,15] and zeolites [16–18] have been explored for the transesterification of triglycerides with alcohols. Among the solid base catalysts, a number of CaO-containing catalysts were reported in recent years, which are well documented in literatures [19, 20]. As an important solid base catalyst, CaO has the advantages of abundance in nature, high catalytic activity, noncorrosive and environmentally benign properties [6,21–25].

Recently, the utilization of CaO-based catalysts derived from various waste resources has drawn growing attention with respect to the views of the economic efficiency and environmental protection [20]. For instance, CaO-based catalysts derived from oyster shell [26], crab shell [27], mussel shell [28,29], eggshell [30,31], short necked clam shell [32], cockle shell [33] and blast furnace slag (BFS) [34] have been reported for biodiesel production. However, these catalysts suffer from the disadvantages to some extent, e.g. low catalytic activity, large catalyst amount involved, or complicated procedure for catalyst preparation. Thus, the development of catalyst with higher catalytic activity and low cost is still highly desirable to improve the production efficiency and to reduce the investment.

Carbide slag, also known as calcium carbide residue (CCR), is commonly generated as a solid waste from the hydrolysis reaction of calcium carbide in the industrial production of ethyne gas, which is the raw material of polyvinyl chloride (PVC) and some other products. Millions of tons of carbide slag are generated and mainly disposed as land filler every year, resulting in severe waste management and environmental problems. The carbide slag waste consists primarily of $Ca(OH)_2$ [35], indicating that carbide slag waste can be employed as a promising feedstock to prepare CaO-based catalyst. Unfortunately, few studies were previously reported concerning the utilization of carbide slag waste as catalyst [36]. Therefore, the development of carbide slag in biodiesel synthesis is an interesting topic in views of the effective

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utilization of waste resource and its application in the production of energy chemicals.

In this work, the solid base catalysts from waste carbide slag were prepared by a facile calcination activation procedure and tested in the transesterification of soybean oil with methanol. The effect of calcination temperature on the catalytic activity of carbide slag-based catalysts was investigated. The compositions and structures of catalysts were characterized by X-ray fluorescence spectroscopy (XRF), thermogravimetric analysis (TGA), X-ray diffraction (XRD), N_2 sorption, Fourier transform infrared (FTIR) spectroscopy, Field-emission scanning electron microscope (FE-SEM), and temperature programmed desorption of CO_2 (CO_2-TPD). In addition, the parameters for the transesterification reaction, including the reaction temperature, methanol/oil molar ratio, catalyst dosage, and reaction time were investigated to optimize the process in details. Moreover, the stability of the solid catalyst was evaluated.

2. Experimental

2.1. Materials

Fresh commercial edible grade soybean oil was obtained from a local market and used without any pretreatment. The acid value of the soybean oil was measured to be less than 0.1 mgKOH/g by titration method, and the average molecule weight was 894.5 g/mol, calculated from the saponification index (Sv = 188.2 mgKOH/g). The moisture content of the soybean oil was determined as 0.03%. Carbide slag waste was obtained from Inner Mongolia Yili Energy Co., Ltd. in Erdos, China. Methanol (99.9% purity) was obtained from Xilong Chemical Industry Incorporated Co., Ltd., China. Hexane (96% purity) was obtained from Sinopharm Chemical Reagent Co., Ltd., China. Methyl undecanoate (99% purity) used as the internal standard was purchased from Alfa Aesar. The reference standards which are methyl myristate (99% purity), methyl palmitate (≥99% purity), methyl oleate (99% purity), methyl stearate (99% purity), methyl linoleate (99% purity), eicosanoic acid methyl ester (98% purity) and methyl docosanoate (99% purity) were purchased from Sigma-Aldrich for gas chromatography (GC) analysis. All other chemicals were of analytic grade and were used as received without further purification.

2.2. Catalyst preparation

Carbide slag-based catalysts were prepared by calcining the raw carbide slag waste in the temperature range of 400–1100 °C. In brief, the raw carbide slag (denoted as Raw CS) was ground, sieved to obtain a particle size of 100 meshes and dried at 105 °C. The obtained fine powder was then calcined using a muffle furnace at the desired temperature for 4 h (denoted as CS-T, where T represented the calcination temperature of the raw carbide slag). Additionally, commercial CaO was treated at 800 °C for 4 h for comparison.

2.3. Catalyst characterization

The bulk element compositions of the samples were analyzed by X-ray fluorescence (XRF, AXIOS) with normalizing sample composition to 100%. The measurements were taken onto pressed pellets using boric acid as a binder.

TGA was carried out using a METTLER TOLEDO TGA/DSC 1 from room temperature up to 850 °C at a ramping rate of 10 °C min^{-1} in a N_2 flow of 40 mL min^{-1} using α-Al_2O_3 as standard.

The crystal structure was identified by powder X-ray diffraction (XRD) using a PANalytical Empyrean diffractometer at 40 kV, 40 mA with Cu Kα radiation. Scans were performed at a step size of 0.0070°(2θ) over the 2θ range of 10°–90° with LaB_6 as the reference sample to calculate the crystallite sizes of CS-T (T > 400 °C) samples according to the Williamson–Hall method [37]. For other samples, scans were performed at a step size of 0.0130° (2θ) over the 2θ range of 5°–90°.

N_2 sorption measurement was performed using a Quantachrome Autosorb-1 at 77 K and the samples were degassed under vacuum at 573 K for 3 h before measurement. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method using N_2 adsorption data ranging from $P/P_0 = 0.05$ to 0.30. The total pore volumes were determined from the amounts adsorbed at relative pressures of 0.99. Pore size distributions were calculated from desorption branches by the Barrett–Joyner–Halenda (BJH) method.

The FTIR spectroscopy experiments were recorded on a Tensor 27 Fourier-transform infrared spectrometer applying KBr pellet technique from 4000 to 400 cm^{-1}. The spectra reported here were the accumulation of 16 scans at 4 cm^{-1} resolution and plotted in the transmittance mode.

FE-SEM was conducted on a FEI SEM Quanta 250 microscope.

CO_2-TPD was carried out to determine the basicity of samples using an AutoChem II 2920 equipped with a thermal conductivity detector (TCD). About 50 mg of sample was heated in situ in 25 mL min^{-1} of helium gas at 120 °C for 0.5 h in order to remove adsorbed impurities. After that, the sample was cooled to 50 °C and saturated with 25 mL min^{-1} of 10% vol.% CO_2/He for 1 h. Weakly adsorbed CO_2 was eliminated by flushing with a 25 mL min^{-1} of helium gas at 50 °C for 0.5 h, and increased to 800 °C with a ramping rate of 10 °C min^{-1}.

2.4. Transesterification procedure

The catalytic performances were evaluated in the transesterification of soybean oil with methanol. Typically, soybean oil, methanol, and catalyst were added into a 100-mL three-neck round bottom flask equipped with a thermocouple, a water-cooled condenser and a mechanical stirrer. The reaction mixture was vigorously stirred at 500 rpm for the required reaction time at a certain temperature. After the reaction, the reaction mixture was decanted and placed in a centrifuge to separate the solid catalyst. Methanol was vaporized to separate from the biodiesel prior to analysis. The mixture was then agitated and separated by centrifugation. Then a sample was taken from the upper layer and prepared for gas chromatographic analysis. The gas chromatography was carried out in a GC-2010 Plus (Shimadzu, Japan) equipment with an Rtx-WAX capillary column (30 m × 0.25 mm × 0.25 μm), an autosampler and a flame ionization detector. Methyl undecanoate was used as the internal standard, hexane as the solvent, and nitrogen as the gas carrier. The fatty acid methyl esters (FAME) yield was calculated by the following formula:

$$\text{FAME yield} = \frac{\text{Total weight of FAME}}{\text{Total weight of oil}}$$

2.5. Catalyst reusability

The reusability of the solid catalyst which represents its capacity to perform the same catalytic activity was evaluated by conducting several experimental runs after the first batch under the conditions obtained for the highest FAME yield. The solid catalyst was recovered from the reaction mixture after the first run by centrifugation. The liquid mixture (methanol, methyl esters and glycerol) was centrifuged and the remaining solid with adhered oil particles were thoroughly washed with hexane and methanol. The solid catalyst was dried at 100 °C overnight. The recovered catalyst was then used for the next run.

3. Results and discussion

3.1. Characterization of the catalyst

The composition of the raw carbide slag is determined by XRF. As shown in Table 1, CaO (expressed as wt.% of metal oxides) is the