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Research article

Blocky shapes Ca-Mg mixed oxides as a water-resistant catalyst for effective synthesis of biodiesel by transesterification

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ABSTRACT

The Ca-Mg mixed oxides were synthetized from a new method using calcium oxalate and magnesium oxalate as the precursors for transesterification of soybean oil. To elucidate their composition, morphology and basic properties, the resulting materials were characterized using: XRD, SEM, TEM, CO_2-TPD and Nitrogen adsorption-desorption. The results showed that the catalyst with neat blocky structure had better water-resistance compared to the pure calcium oxide. And the CaO-MgO exhibited higher amounts of basic site and provided higher catalytic activity in the methanolysis process. The highest biodiesel yield reached 98.4% over CaO-MgO with a Ca-to-Mg molar ratio of 1:3 under the optimal reaction conditions: 1.0 wt% of catalyst adding, 12:1 of methanol/oil and reacting at 70 °C for 2 h. Hopefully, this kind of stable solid base catalyst could confirm the yield of FAME still above 90% after using 5 times which demonstrated the good reusability of mixed oxide CaO-MgO catalyst.

1. Introduction

In the past few decades, biodiesel has taken the place petrol to become one of the most potential renewable energy [1,2]. Particularly, biodiesel is monoalkyl esters of long chain fatty acids and usually derived from renewable feedstock such as non-edible oil, edible oil and even waste cooking oil, which meets the requirements of green chemistry [3,4]. Nowadays, biodiesel has become widely acceptable in the energy market because of its unique features including higher cetane number, reduction of most exhaust emissions, biodegradability, inherent lubricity, lacking of sulphur, higher flash point, positive energy balance, compatibility with the existing fuel distribution infrastructure, domestic origin and renewability in comparison with petrodiesel [5,6]. Transesterification reaction is a widely used method to produce biodiesel [7]. And the key of transesterification reaction is the appropriate and effective catalyst.

In recent years, great attention has been paid to heterogeneous catalysts because of its excellent properties [8,9]. The biggest advantage of heterogeneous catalysts is its easy separating by simple methods compared with homogeneous catalysts [10,11]. Meanwhile conventional alkali, acid, solid or enzyme catalyzed process could drive up the cost of processing (30–40%) [12,13]. The major problems for utilization of these catalysts are expensive and complicated to synthesis in large scale production [14]. Consequently, CaO was considered as one of the most promising catalyst for methanolysis at mild reaction conditions in conventional process [15–17]. However, the resultant CaO catalyst typically provides micron-sized dense particles with low surface area of 1–2 m^2/g. So, many attentions have been devoted to increasing the surface area of CaO catalyst by different kinds of ways, for instance, the gel-combusted CaO catalyst [9], the modified CaO catalyst [18,19] and the supported CaO catalyst [20–23].

In spite of the increased surface area, water and CO_2 can be absorbed by CaO under ambient conditions, which results in a decrease in catalytic activity [24]. In order to solve this problem, some composite catalysts have been synthesized to enhance the stability of CaO, such as CaO-MgO mixed oxides [25,26]. In this report, Ca-Mg mixed oxides were advantageously prepared by the thermal decomposition of Ca-Mg oxalate, and the surface profile of the mixed oxides was changed in order to provide more active sites which led to the increase in catalytic activity.

In the present study, the neat blocky mixed oxide CaO-MgO catalyst was prepared with the simple oxalate precipitation method and pure CaO was also prepared to make a comparison. Soluble starch was added to the reaction solution during the chemical precipitation as a kind of surfactant. The physicochemical properties of the developed catalysts were thoroughly investigated, and the results indicated that the bimetallic CaO-MgO had better surface morphology and surface area. The strong interaction of binary active phases in the composition of bimetallic CaO-MgO with the aim of improves the stability and durability of catalytic activity in order to make it suitable for biodiesel production. Then, the performance of catalyst was evaluated for the synthesis of biodiesel. Finally, the repeatability of mixed oxide CaO-MgO and pure CaO were compared and the results showed that the mixed oxide CaO-MgO

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could effectively extend the catalyst lifetime. The mixed oxide CaO-MgO represented a novel class of heterogeneous catalyst which was particularly attractive in the practice of biodiesel synthesis in an environmentally friendly manner.

2. Experimental section

2.1. Catalyst preparation

Several Ca-Mg bi-metal oxalate precursors with different Ca/Mg ratios were synthesized by the simple strategy according to the report [27] with a slight modification. In a typical procedure, 15 mmol $MgCl_2 \cdot 6H_2O$ and 5 mmol $CaCl_2$ were dissolved in 50 mL deionized water. Then, 0.2 g soluble starch was added into the solution with accompanying ultrasonic dispersion for 30 min. 20 mmol $Na_2C_2O_4$ was dissolved into 50 mL deionized water at 80 °C under stirring for at least 1 h. Then the solution was slowly dropped into the former solution with vigorous stirring. For a while, white precipitate was formed. This reaction mixture was then stirred for 30 min at room temperature. The precipitated products were separated by centrifugation, subsequently washed with deionized water for 3 times, then dried at 90 °C overnight. Mesoporous Ca-Mg bi-metal oxides were obtained after calcining at 700 °C for 3 h.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a D8 X-ray diffractometer (Bruker AXS, German) to identify the composition and phase of the samples. Morphology of the samples were observed by SEM using a Rigaku S-4300 spectrometer (Japan). The voltage was 20 kV and the vacuum degree of the sample room was better than 10^{-4}. Transmission electron microscopy (TEM) image was collected on a JEM-2100 transmission electron microscope (JEOL, Japan) to examine the morphology and size of sample. The specific surface area of the catalysts was measured according to the Brunauer-Emmet-Teller (BET) method with nitrogen adsorption-desorption on a ASAP 2020 instrument (Micromeritics, USA) and the degas condition was 200 °C for 5 h. Basicity of the CaO-MgO was determined using temperature programmed desorption of CO_2 with an AMI-200 instrument.

2.3. Catalytic performance

Dehydrated soybean oil (0.01 mol), methanol (0.12 mol), and CaO-MgO catalyst (1 wt% soybean oil) were mixed in 50 mL stand-up flask and heated to 70 °C for 2 h under stirring with a constant speed. After the reaction, the catalysts were separated by centrifugal filtration and layers (methyl ester, glycerol, and methanol) were separated by decantation. The desired biodiesel was mainly contained in the upper phase.

The samples were analyzed by an FULI GC9790 gas chromatograph, equipped with a flame ionization detector (FID) and SE-54 capillary column. Nitrogen was used as carrier gas. The oven program was set to an initial temperature of 150 °C (held for 1 min), increasing to 215 °C at a rate of 5 °C min^{-1}, where the temperature was held for 6 min. The temperatures of injector and interface were both held constant at 300 °C. The internal standard method was used with methyl salicylate as internal standard to determinate the yield of biodiesel.

The conversation of soybean oil was calculated by the GC and the yield of biodiesel was calculated by the following equation:

$$\begin{aligned}\mathrm{Yield} &= \frac{m_{actual}}{m_{theoretical}} \approx \frac{C_{esters} \times n \times V_{esters}}{m_{oil}} \\ &\approx \frac{C_{esters} \times n \times V_{oil}}{m_{oil}} \\ &\approx \frac{C_{esters} \times n}{\rho_{oil}}\end{aligned} .$$

Where m_{actual} (g) and $m_{theoretical}$ (g) presented the actual mass and theoretical mass of biodiesel respectively; m_{oil} (g) was the mass of soybean oil; n indicated the diluted multiple of biodiesel; C_{esters} (g/mL) showed the mass concentration of biodiesel; ρ_{oil} (g/mL) remarked the density of soybean oil; V_{esters} (mL) and V_{oil} (mL) expressed the volumes of biodiesel and soybean oil, respectively [28–30].

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. Powder XRD

The XRD pattern (Fig. 1) with Mg/Ca molar ratio 1–4 displayed the featured diffraction peak. At first, in mixed oxide CaO-MgO catalyst, peaks at 32.2°, 37.3°, 53.8°, 64.2° and 67.4° proved the major phase were CaO (JCPDS File no. 37–1497). The XRD pattern (Fig. 1) revealed the MgO (JCPDS File no. 65–0476) phase of the massive catalyst with well-defined diffraction peaks at 2θ values of 43.0°, 62.4° and 78.8°. The diffraction lines at 53.8° and 62.4° 2θ were ascribed to the (220) reflection of CaO and MgO, respectively. Simultaneously, these diffractograms also showed two intense lines (43.0° and 62.4°), which were typical to MgO-like phase [31] of mixed oxide CaO-MgO catalyst. As expected, by increasing the Mg/Ca molar ratio, the X-ray signals associated with MgO became more intense, and concomitantly those of CaO decreased. Moreover, the crystalline phases presented in the mixed oxides were consistent with those of pure oxides. This kind of structure could increase the interaction between the Ca and Mg due to the vacancies created by the substitution of Ca ions by Mg ions [32,33]. The strong interaction of active phases with the aim of improves the stability, durability, acid-resistance and water resistence of catalytic activity in order to make it suitable for biodiesel production.

3.1.2. SEM and TEM

The surface morphology of the mixed oxide CaO-MgO catalyst was investigated by SEM and TEM. Fig. 2 presented the SEM micrograph with Mg/Ca molar ratio 1–4, and the TEM micrograph with Mg/Ca molar ratio 3. These images illustrated morphology of the mixed oxide CaO-MgO catalyst appeared as dense massive particles which was composed of small particles. Meanwhile, the higher content of MgO presence in the catalyst could form more structured blocks according to Fig. 2a–d, which also showed the mixed oxide CaO-MgO structure with length varying from 0.5 to 2 μm. From SEM results, the mixed oxide CaO-MgO showed the neat blocky structure which may be one of the reasons that CaO-MgO had better water-resistance compared to

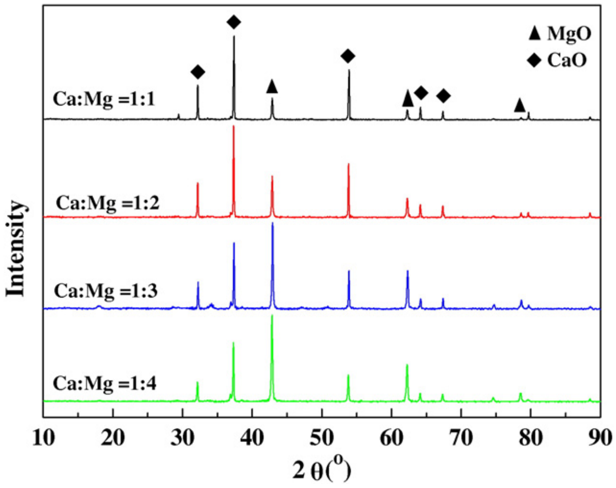

Fig. 1. XRD characteritize patterns of different molar ratio of Ca/Mg catalysts.