



Calcium oxide functionalized with strontium as heterogeneous transesterification catalyst for biodiesel production



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HIGHLIGHTS

- Four different preparation methods were compared to functionalize CaO with Sr.
- Preparation methods significantly affected the catalyst stability.
- The basicity was found to parallel catalytic activity in transesterification.
- High catalytic activity of 0.5Sr/Ca-ICP900 was attributed to the Sr_xCa_{1-x}O and SrO₂.

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ABSTRACT

The application of calcium oxide (CaO) as transesterification catalyst for biodiesel production is restricted due to the requirement of long reaction time and high molar ratio of methanol to oil. To solve this problem, CaO was functionalized with strontium (Sr/Ca catalyst) through the solid mixing method, wet impregnation method, co-precipitation method and improved co-precipitation method, respectively. Stability of the prepared catalyst, including the homogeneous contribution of leached active sites and the catalyst reusability, was investigated to screen the optimal preparation method, and the improved co-precipitation method was proved to be the most ideal method for the strongest interaction between Sr and Ca. The Sr/Ca catalysts were then characterized by X-ray diffraction (XRD), thermogravimetric analysis–derivative thermogravimetric (TGA–DTG), Hammett indicator (basic strength and basicity) and Fourier transform infrared spectroscopy (FTIR). Moreover, effects of the activation temperature and Sr/Ca molar ratio on catalytic activity were concerned. At activation temperature of 900 °C and Sr/Ca molar ratio of 0.5, the maximum conversion 98.31% of palm oil to fatty acid methyl esters could be achieved under the mild transesterification condition of 5 wt.% catalyst amount (based on oil weight) and 9 molar ratio of methanol to oil at 65 °C for 30 min.

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1. Introduction

Associated with the diminishing fossil fuel supplies and increasing environmental concerns, broad researches have been focused on the renewable energy resources [1,2]. Biodiesel, a promising and renewable green fuel, is normally produced through transesterification of vegetable oils or animal fats with methanol using alkalis, acids, enzymes and even under supercritical condition [1,3]. In commercial biodiesel production, alkali homogeneous catalysts (KOH or NaOH) are preferred for the high catalytic activity and short reaction time [4]. However, they are difficult to be

separated from the production mixture and lead to plenty of waste water [5].

Therefore, substantial attentions are fixed on the heterogeneous catalysts, which could offer simple isolation from the production mixtures and be recycled requiring no cleansing with water [3,6–8]. Among these heterogeneous catalysts, calcium oxide (CaO) is a representative for its broad resource, environmental friendly and low cost. However, owing to that the heterogeneously catalyzed transesterification consists of three phases (oil–catalyst–methanol), the reaction rate is quite slow for the mass transfer among the phases. The application of CaO in transesterification is thus restricted for requirement of the long reaction time and high molar ratio of methanol to oil [8,9]. The development of CaO-based catalyst is to make the transesterification accomplished efficiently

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under mild reaction conditions in short reaction time that remains an intriguing challenge.

To improve the catalytic activity and increase the reaction rate of CaO, it was generally functionalized with metal oxides or alkali metal salts, such as ZrO [10], KF [11], and K₂CO₃ [12]. But these reported CaO-based catalysts were not stable and suffered from the leaching of active sites into methanol. It was also found that CaO was partially soluble in the methanol [13,14], for which, it is concerned to cause a homogeneous contribution and lose the advantages of its heterogeneous nature. As a consequence, stability of the CaO-based catalyst would be greatly reduced. According to the report, strontium oxide (SrO) possesses high basic strength and is dissolved in neither methanol nor fatty acid methyl ester (FAME) [8].

To enhance the catalytic activity and guarantee the catalytic stability, this study aimed to functionalize CaO with SrO (Sr/Ca catalyst) through four different preparation methods, namely, the solid mixing method, wet impregnation method, co-precipitation method and improved co-precipitation method. First of all, to obtain the optimal preparation method, the homogeneous contribution of leached active sites and the catalyst reusability were evaluated and compared, where effects of the activation temperature and Sr/Ca molar ratio on catalytic activity were also concerned. Meanwhile, the Sr/Ca catalysts were characterized by X-ray diffraction (XRD), thermogravimetric analysis–derivative thermogravimetric (TGA–DTG), Hammett indicator (basic strength and basicity) and Fourier transform infrared spectroscopy (FTIR). Finally, catalytic activity of the Sr/Ca catalyst was assessed via the transesterification of palm oil with methanol from parameters of the catalyst amount (ξ), molar ratio of methanol to oil (γ), reaction time (τ) and reaction temperature (T_r).

2. Experimental

2.1. Materials

Commercial palm oil was purchased from local market and the fatty acid compositions, listed in Table 1, were determined by gas chromatograph (Shimadzu Co., Ltd., Japan) equipped with a flame ionization detector (GC–FID). Acid value (A.V.) and saponification value (S.V.) of the palm oil were 0.27 mg KOH/g and 181.55 mg KOH/g, respectively, based on which the average molecular weight was calculated to be 928.39 g/mol.

Analytical grade CH₃OH, SrCO₃, CaO, Ca(NO₃)₂·4H₂O, Sr(NO₃)₂, Na₂CO₃ and (NH₄)₂CO₃ were obtained from Kermel Chemical Co., Ltd. (Tianjin, China).

2.2. Catalyst preparation

The Sr/Ca catalysts were prepared by the solid mixing method (SM), wet impregnation method (WI), co-precipitation method (CP) and improved co-precipitation method (ICP), where the Sr/Ca molar ratios were set to be 0.5 for SM, WI and CP.

Table 1
Fatty acids compositions of the palm oil.

Fatty acids	Composition (%)
Myristic acid C14:0	0.90
Palmitic acid C16:0	38.85
Daturic acid C17:0	0.24
Stearic acid C18:0	4.44
Arachidic acid C20:0	0.38
Palmitoleic acid C16:1	0.15
Oleic acid C18:1	43.00
Arachidonic acid C20:1	0.14
Linoleic acid C18:2	11.61
Linolenic acid C18:3	0.29

For SM, SrCO₃ was calcined at 1000 °C for 3 h to obtain SrO and then grounded with CaO, after which the mixture was activated at 900 °C for 3 h. The prepared catalyst was labeled as Sr/Ca–SM. For WI, CaO was mixed with Sr(NO₃)₂ aqueous solution (0.1 mol/L). After stirred at room temperature for 1 h, the mixture was desiccated at 120 °C. Then, the powder was activated at 600 °C for 3 h [15] and denoted as Sr/Ca–WI. For CP, 0.1 mol/L Na₂CO₃ was dropwise added into the Ca(NO₃)₂·4H₂O and Sr(NO₃)₂ solution with vigorously stirring. Then, the generated precipitate was filtered and washed with deionized water till to pH = 7 to form the precursor. After desiccation at 120 °C, the precursor was activated at 900 °C for 3 h, and the achieved catalyst was defined as Sr/Ca–CP.

For ICP, 0.1 mol/L (NH₄)₂CO₃, which replaced for Na₂CO₃ in CP, was dropwise placed into the Ca(NO₃)₂·4H₂O and Sr(NO₃)₂ solution. Then, the generated precipitate was filtered and washed with deionized water till to pH = 7 to form the precursor. After desiccation at 120 °C, the precursor was activated at 900 °C for 3 h, and the achieved catalyst was defined as Sr/Ca–ICP. Different from SM, WI and CP, the Sr/Ca molar ratio varied from 0.1 to 1.

2.3. Transesterification procedure

For transesterification, palm oil and methanol were placed into a three-necked round bottom flask, which was equipped with a water-cooled condenser, a thermometer and a motor stirrer, and the freshly activated catalyst was added into the reactor when the liquid mixture was heated to the pre-set temperature. Reaction was vigorously stirred throughout transesterification. At termination, catalyst was filtered from the liquid products and the excess methanol was then evaporated under vacuum. After these pre-treatments, the liquids were transferred into a separating funnel and layered as biodiesel at top and glycerol at bottom under gravity.

The conversion (η) of palm oil to fatty acid methyl ester (FAME) was used to assess the catalytic activity, and was determined by Vertex70 FTIR analyzer (Bruker, Co., Ltd., Germany) with a single reflection horizontal ATR accessory (Pike Technologies, Co., Ltd, USA). The unique band at 1436.7 cm⁻¹, which was attributed to the CH₃ asymmetric deformation in O–CH₃, was detected in FAME but not in the feedstock oil [3]. Each ATR spectrum was collected at 25 ± 1 °C in the spectrum scope of 4500–600 cm⁻¹ with 4 cm⁻¹ spectral resolution. The absorbance at 1436.7 cm⁻¹ was analyzed through the OPUS 7.2 and then η was calculated through Eq. (1).

$$\eta(\%) = \frac{\text{Calculated weight of FAME (g)}}{\text{Weight of palm oil (g)}} \times 100\% \quad (1)$$

2.4. Catalyst stability evaluation

For homogeneous contribution of the leached active sites, catalyst was firstly stirred in methanol at 65 °C without palm oil. After 30 min, catalyst was quickly filtered under vacuum and the remaining methanol was then mixed with palm oil for transesterification under vigorous stirring at 65 °C for 30 min. If catalyst was lixiviated, conversion would be observed due to the homogeneous contribution. In parallel, reusability of the catalyst was assessed through the consecutive transesterifications. After one transesterification, filtered catalyst from the liquid products was directly reused for the next cycle without any treatment.

2.5. Catalyst characterizations

The activation temperature for catalyst preparation was analyzed through thermogravimetric analysis–derivative thermogravimetric (TGA–DTG) on a TGA/SDTA 851e

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