

Synthesis of porous CaO microsphere and its application in catalyzing transesterification reaction for biodiesel

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Abstract: It is hoped to develop a simple and low cost route for preparing the CaO with a novel morphology which can present high catalytic activity in catalyzing transesterification reaction for biodiesel. The porous CaO microsphere was synthesized by calcining spherical CaCO₃ precursor which was prepared easily by mixing CaCl₂ with Na₂CO₃. The as-prepared CaO microsphere was characterized by scanning electronic microscopy(SEM), powder X-ray diffractometry(XRD) and N₂ adsorption experiment. The results reveal that the synthesized CaO is regular microsphere with many pores in its exterior and interior. The CaO microsphere is applied in catalyzing the transesterification reaction of soybean oil for biodiesel and presents excellent catalytic ability with a transesterification yield of 98.72%. This catalyst could have potential applications in other fields in view of its well-defined morphology, simply synthetic route and low cost.

Key words: porous CaO microsphere; transesterification; catalysis; biodiesel

1 Introduction

Nowadays, world energy crisis has received considerable attention due to an increase demand for energy and limitation of fossil fuels supplement. Alternative renewable fuels are considered feasible route to resolve this serious problem. One of more promising approaches is biodiesel owing to its advantages, such as being non-toxic, bio-degradable, and suitable for agricultural countries[1]. Biodiesel is defined as a methy-ester produced from vegetable or animal oil with diesel quality, which can be used as biofuel.

Homogeneous catalysts based on NaOH and KOH are mostly used in transesterification reaction for biodiesel productions[2-5]. Although the homogeneous base catalysts can catalyze biodiesel production with the fast reaction rate under mild reaction conditions, it still has many disadvantages which need to be resolved urgently. For example, it is difficult in separating the catalyst and purificating biodiesel products. Moreover, a larger amount of industrial waste water is produced by neutralizing and washing the products. On the other hand, heterogeneous catalysts, which were proposed to solve

the aforementioned problems, have aroused great interesting of many researchers.

A number of solid bases, claimed to be heterogeneous catalysts, have been described in literature. A variety of heterogeneous catalysts including metal oxides, hydroxides, alkoxides zeolites, Mg-Al hydrotalcites had been developed to catalyze the transesterification reaction of vegetable oils for biodiesel products[6-9]. Examples also included potassium-loaded alumina[10], solid K₂CO₃-loaded alumina[11], and strontium oxide[12]. There have also been a number of publications devoted to the transesterification activity of calcium oxide and calcium methoxide, which demonstrated generally better performance[13-14]. CaO has attracted many attentions on the transesterification reaction mainly since it possesses relatively high catalytic activity[15]. The activity of commercial CaO in the transesterification reaction was found to be lower[14]. Generally, activated CaO can be obtained by calcining commercial CaO or its precursor[16-17]. Nanocrystalline CaO was reported to be an efficient catalyst for biodiesel production.

In this work, a simple and low cost route was developed to prepare the CaO with a novel morphology.

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Subsequently, the well-defined porous CaO microsphere was applied in catalyzing the transesterification reaction of soybean oil for biodiesel products. To the best of our knowledge, there is less report on catalyzing transesterification reaction for biodiesel using porous CaO microsphere as catalyst.

2 Experimental

2.1 Preparation of CaO

First, 0.33 mol/L Na_2CO_3 solution was rapidly poured into an equal volume of 0.33 mol/L solution of CaCl_2 at room temperature. After intense agitation on a magnetic stirrer for 30 s, the mixture was kept standing for 10 min. Subsequently, the precipitate was centrifugated, washed with pure water and acetone three times respectively, and then dried in air. The procedure resulted in spherical CaCO_3 microparticles[18]. Finally, the synthesized CaCO_3 microparticles were calcined at 1 000 for 2 h to obtain CaO.

2.2 Characterization of CaO

SEM observation was performed on a Hitachi S-3400N scanning electron microscope (Japan). The XRD analysis was recorded with a German Bruker AXS D8 Advance X-ray diffractometer using Cu radiation. The Brunauer-Emmett-Teller (BET) surface area and total pore volume of CaO were measured by using a Quantachrome NovaWin2 instrument. The samples were degassed at 300 for 4 h before the measurements. The total pore volume was calculated by the Barrett-Joyner-Halenda (BJH) method.

2.3 Catalytic tests

Commercial edible-grade soybean oil was purchased from the market and used as the raw material for the production of biodiesel. It is mainly composed of five types of fatty acid triglycerides, including palmitic acid triglyceride (11%), stearic acid triglyceride (4%), oleic acid triglyceride (23%), linoleic acid triglyceride (6%), and linolenic acid triglyceride (5%, mass fraction). The relative molecular mass (891.5) of the soybean oil can be calculated from its saponification value of 188.9 mg/g KOH and acid value of 0.084 52 mg/g KOH.

Transesterification reactions were carried out in a 250 mL three-neck glass flask equipped with a condenser and two flat-blade paddle agitators. Typical reactions were performed with 30 mL soybean oil and 12 mL of methanol (methanol-to-oil molar ratio is 1:9) using 3% of CaO at 65 for 3 h[19]. After reaction, the excess methanol was distilled under vacuum and the CaO was separated by centrifugation. The biodiesel was collected for gas chromatographic analysis (Agilent 6820 series

Gas Chromatographs, USA) after removal of the glycerol layer.

3 Results and discussion

3.1 Characterization of synthesized CaO

In order to prove that whether the component of the calcined product is CaO or not, the XRD analysis was performed on a German Bruker AXS D8 Advance X-ray diffractometer using Cu radiation. The obtained XRD pattern of the product is shown in Fig. 1, which displays merely the XRD peaks that can be indexed to CaO (JCPDS card No. 00-037-1497). No remnant of CaCO_3 could be detected in the resultant products by XRD analysis. The results prove that the calcined product is pure CaO powder.

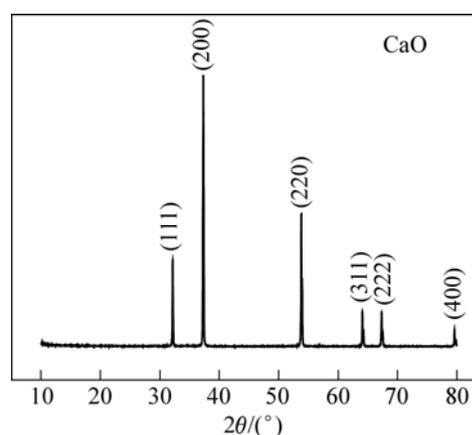


Fig.1 XRD pattern of calcined product

Typical SEM images of as-synthesized CaO are shown in Figs.2(a) and (b). The lower magnification image (Fig.2(a)) indicates that the products consist of mostly regular CaO spheres with diameter in the range of 4–8 μm . The high magnification image (Fig.2(b)) indicates that many pores exist in the exterior and interior of CaO microsphere. Moreover, many irregular nanocrystals in several hundred nanometers connect each other to form specific porous CaO microsphere. The pores can be ascribed to the release of CO_2 from CaCO_3 intermediate. SEM image of the CaCO_3 intermediate is illustrated in Fig.3. Fig.3 shows that CaCO_3 intermediate presents spherical morphology. The surface is very rough and consists of a great number of small CaCO_3 nanoparticles[18]. After the spherical CaCO_3 is calcined at 1 000, CaCO_3 nanoparticles are decomposed into CaO nanoparticles. The CaO nanoparticles combine together in the process of calcination. Thus, large and irregular CaO nanocrystals can be observed in the end product of CaO. Due to the release of CO_2 gas, the pores are formed in the exterior and interior of the CaO microsphere.

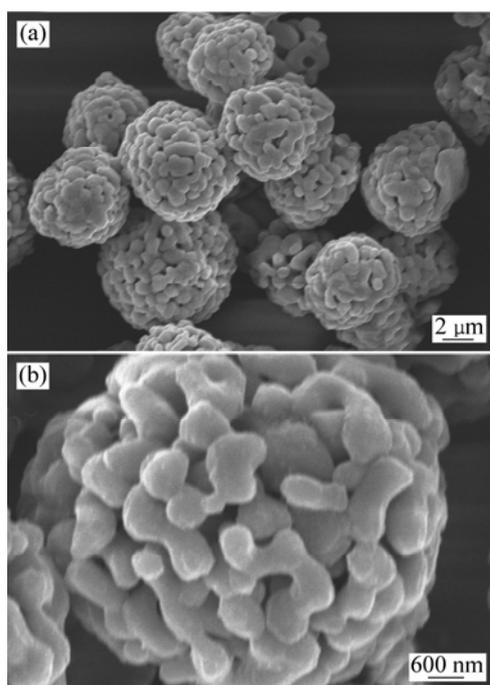


Fig.2 Lower magnification (a) and high magnification (b) SEM images of resulting CaO

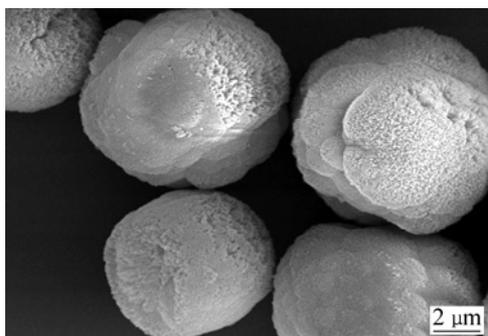


Fig.3 SEM image of resulting CaCO_3 intermediate

The nitrogen adsorption-desorption analysis was conducted and BJH pore-size distributions of the synthesized CaO are presented in Fig.4. Results show that the pores in the CaO microsphere comprise of small pores with size in the range of 15–100 nm and other large pores. In addition, the analysis results also prove that the synthesized CaO possesses a high surface area of $5.3 \text{ m}^2/\text{g}$ and a total pore volume of $0.0249 \text{ cm}^3/\text{g}$.

3.2 Application of CaO sphere in transesterification reaction for biodiesel

The controllable shape and size become increasingly important in regard to specific applications in material science[20]. The porous CaO microsphere would present efficient catalytic activity in transesterification reaction of vegetable oil for producing biodiesel due to such advantages as high surface area, uniformity, porosity and large size which result in its

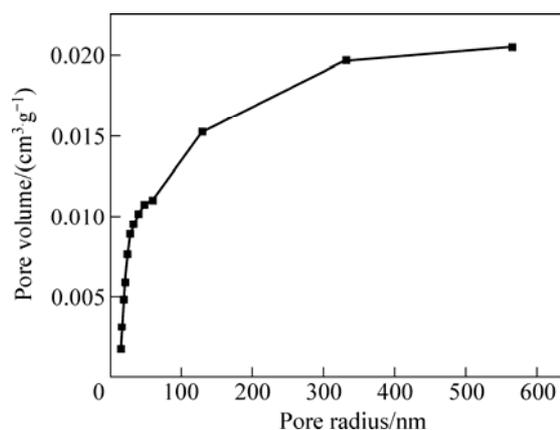


Fig.4 Pore size distributions of CaO microsphere

easy separation from the biodiesel products.

In order to investigate the catalytic activity of the porous CaO microsphere, the CaO was applied in catalyzing transesterification reaction of soyben oil for biodiesel. The yield of biodiesel could be affected by some factors, such as catalyst amount, methanol-to-oil ratio and reaction time. When the CaO microsphere catalyzed the transesterification reaction of soybean oil with methanol for biodiesel, the selected conditions were: methanol-to-oil molar ratio of 9:1, the addition of 3% CaO catalyst, reaction temperature of 65°C , and reaction time of 3 h. After the reaction was over, the excess methanol was distilled under vacuum. Subsequently, the biodiesel products were separated with glycerol and solid CaO by centrifugating.

The obtained biodiesel samples were determined by an Agilent 6820 gas chromatograph equipped with flame ionization detector and a capillary column HP-INNOWAX ($25 \text{ m} \times 0.200 \text{ mm} \times 0.2 \mu\text{m}$). Except the oven temperature, the other conditions for gas chromatographic analysis were same as those in Ref.[21]. After an isothermal period of 9 min, the gas chromatographic oven was heated at $40^\circ\text{C}/\text{min}$ to 220°C and kept at this temperature for 11 min. Under these conditions, the fatty acid methyl esters in the biodiesel products were separated and determined by the gas chromatographic method. Fig.5 shows the gas chromatograms corresponding to the standards and biodiesel products. In Figs.5(a) and (b), the chromatographic peaks 1, 2, 3, 4 and 5 are related to the fatty acid methyl esters of methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl linolenate, respectively. The average biodiesel yield for 5 parallel determinations of the biodiesel products is 98.72%.

The result on the biodiesel yield of 98.72% demonstrates that the porous CaO microsphere shows high catalytic activity in catalyzing transesterification

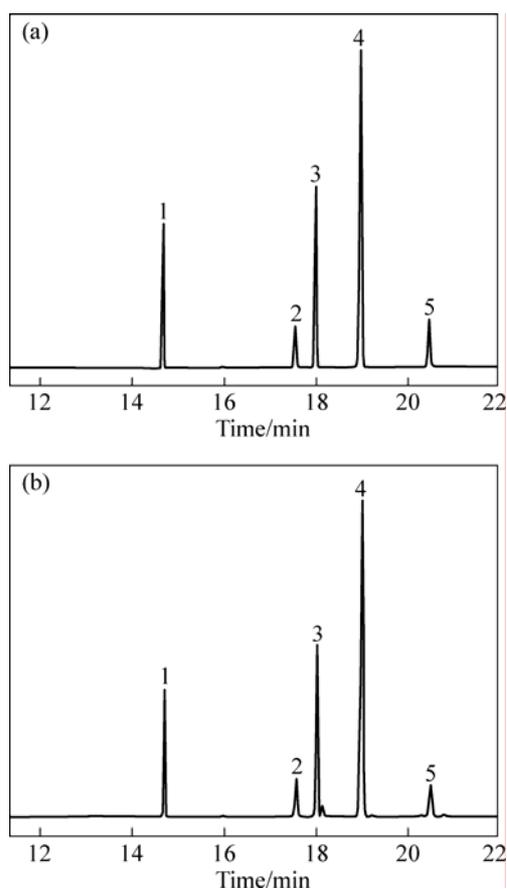


Fig.5 Gas chromatograms of standards (a) and products (b)

reaction for biodiesel.

4 Conclusions

1) A simple and low cost route was developed to fabricate a porous CaO microsphere with a high surface area, large size, uniformity and porosity.

2) The porous CaO microsphere presents excellent catalytic ability as a heterogeneous base catalyst in transesterification reaction of vegetable oil for biodiesel products.

3) This catalyst could also be applied in other fields in view of its well-defined morphology.

4) Simply synthetic route, low cost and great potential of industrialization production are the highlight attractiveness of the porous CaO microsphere.

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