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High activity ordered mesoporous carbon-based solid acid catalyst for the esterification of free fatty acids

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Sulfonated mesoporous carbon catalysts were synthesized using a carbonization–sulfonation method and employed to the pre-esterification of free fatty acids contained in high acid value oil. Various synthesis parameters, such as composition of carbon precursor, carbonization and sulfonation temperature, were systematically investigated. The catalysts were characterized by N_2 adsorption, small angle XRD, HRTEM, FT-IR and strong acid density analysis. The results indicated that they have a high surface area, uniform pore size, large mesopore volume, high acid density and good catalytic activity. Among them, MC600-S160 exhibited a highest activity and good stability for the esterification of FFA with methanol, the FFA conversion reached 94.6% after reaction for 3 h.

1. Introduction

With the ever-increasing price of petroleum and environmental pollution caused by the combustion of fossil fuels, the search for new renewable and ecologically friendly resources as alternatives for traditional fuels is an increasingly urgent topic [1–5]. Among them, biodiesel (fatty acids methyl esters, FAME), which mainly produced by transesterification of triglycerides with methanol has gained much attention [6]. However, the feedstock such as vegetable oils and animal fats usually contain large amount of free fatty acids (FFAs), which may form unwanted soap by-products during the alkali-catalyzed transesterification reactions, decreasing the biodiesel yield substantially and creating serious problem of biodiesel separation [7]. Generally, it is necessary to reduce the acid value of the feedstock to less than 2 mg KOH/g (FFA content of about 1%) before transesterification [2,8]. Therefore, a two-step process was proposed by researchers [6,8–13]. That is converting FFA into esters by an acid-catalyzed pre-esterification process followed by alkali-catalyzed transesterification process. Conventionally, the acid catalyst is sulfuric acid (H_2SO_4) [14–16], which is relatively cheap and also shows a good catalytic performance. But it involves some potential drawbacks such as non-recyclable, equipment corrosion, costly to neutralize, difficult to separate the product from the homogeneous reaction mixtures and high consumption of energy in purification. Hence, enormous efforts have been made on the development of new acid catalysts which can avoid the drawbacks mentioned above and also show a good catalytic performance.

As a replacement for liquid acids, carbon-based solid acids were considered as promising catalysts since the discovery of sugar catalyst [17]. Among them, sulfonated carbon materials [17–24] have been researched most for the pre-esterification of FFA. These catalysts were usually prepared through a carbonization–sulfonation method with biomass such as sucrose, glucose, starch, cellulose or corn straw as carbon precursor and concentrated or fuming sulfuric acid as sulfonation reagent. Such catalysts incorporated high amounts of $-SO_3H$ and showed good catalytic performance in esterification, despite of the low porosity and low surface area which may hinder the diffusion of reactant to active sites. Meanwhile, catalysts prepared by sulfonation of carbon nanotube [25,26] for esterification had been reported, but the sulfonation temperature was high.

Recently, sulfonated ordered mesoporous carbons (OMCs), synthesized by either nanocasting method with SBA-15 as template [27–33] or self-assembly of F127 and phenolic resol under acidic condition [34] have emerged as promising solid acids for the pre-esterification of FFA due to their high BET area, uniform porosity, large pore size and good hydrophobicity. These characteristics make the catalytic active sites easily accessible for long-chain FFA molecules, and then the catalytic activity is very high.

Within the scope of this paper, we demonstrate the synthesis of sulfonated mesoporous carbon catalysts with SBA-15 as template, glucose glycerol solution as carbon precursor and concentrated

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H_2SO_4 (98%) as sulfonation reagent. The resultant catalysts were employed to investigate the pre-esterification of FFA for reducing the acid value of oil to less than 2 mg KOH/g. And the effects of carbon precursor composition, carbonization and sulfonation temperature on textual parameters, strong acid density and catalytic performance were systematically investigated.

2. Experimental

2.1. Catalysts preparation

SBA-15 template was prepared according to the procedure reported in literatures [35–37]. For a typical synthesis, 1 g of triblock copolymer P123 was dissolved in 35 mL 2 M HCl at 38 °C with stirring, subsequently, 2.1 g TEOS was added and stirred at 60 °C for 24 h. Then the mixture was aging at 120 °C for 24 h in a hydrothermal reactor. The solid product was filtered, washed with distilled water, dried and calcined in air for 5 h at 550 °C. Mesoporous carbon was synthesized as follow, 3 g SBA-15 was impregnated with glucose glycerol solution at a mass ratio of 5:1 (SBA-15/glucose), and the mixture was kept in a tubular furnace at 150 °C for 3 h in air. Subsequently, the temperature was raised to 500–800 °C in N_2 atmosphere and maintained for 3 h. The resultant C/SBA-15 composite was washed with 30% HF solution to remove the silica framework. The mesoporous carbon MC-Tc (Tc represents the carbonization temperature) was obtained after filtration, washing and drying. Then MC-Tc was sulfonated using concentrated H_2SO_4 (1 g MC of 20 mL 98% H_2SO_4) at 120–200 °C for 10 h. The mixture was filtered, washed with deionized water until the pH of wash water was about 7–8 and dried at 120 °C for 4 h. The sulfonated sample was denoted as MC-Tc-Ts (Ts represents the sulfonation temperature).

2.2. Characterization methods

N_2 adsorption–desorption isotherms were measured at 77 K using Micromeritics Tristar 3000. All samples were degassed at 473 K for 12 h prior to the measurement. The specific surface area was calculated by Brunauer–Emmett–Teller (BET) method. The total pore volume was estimated from the desorption branch of the isotherm at $P/P_0 = 0.99$ assuming complete pore saturation. Pore size distribution was determined from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) model. Small angle X-ray diffraction (XRD) patterns were collected on D/max-2500 diffractometer produced by Rigaku International Corp. of Japan with Cu Kα radiation (40 kV and 150 mA). Transmission electron microscope (TEM) experiments were conducted on Tecnai G2 F20 field emission microscope (Holland, corporation of FEI) operating at 200 kV with a dot resolution of 0.24 nm. Fourier transform infrared (FT-IR) absorption spectrum were recorded on a Nicolet 6700 FT-IR Microscope (64 scans with 4 cm^{-1} resolution) in the range of 4000–400 cm^{-1} by mixing samples into KBr pellets for the analysis of functional groups in the catalysts.

2.3. Catalytic reaction procedure

The esterification reactions were carried out in a three-neck glass flask equipped with a magnetic stirrer and a reflux condenser. A certain amount of oil and methanol were heated to the scheduled reaction temperature with continuous stirring. Catalyst samples were dried at 100 °C for 1 h before used. In this work, a preliminary optimized reaction conditions as follow were used, the methanol/oil molar ratio was 18:1, reaction temperature was 66 °C, and catalyst/mixed oil mass ratio was 0.5%. The samples of oil phase product were drawn out for acid value analysis at selected reaction time to monitor the progress of esterification reaction.

2.4. Acid density analysis

The strong acid ($-SO_3H$) density of the sulfonated catalysts was determined as follow. 0.1 g sulfonated carbon catalyst was placed in a conical flask, and mixed with 30 mL 0.6 M NaCl solution. The H^+ existed in the form of $-SO_3H$ was exchanged with Na^+ by magnetic stirring for 2 h. Afterwards, the mixture was filtered. With methyl red as an indicator, the filtrate was titrated with 0.1001 mol/L NaOH standard solution. The end point of the titration was reached when the color of filtrate turned from slightly red to bright yellow, and kept at this color for 30 s. And a blank test was done at the same time. The accurate strong acid density was calculated as follow:

$$D_{-SO_3H} = \frac{c_{OH^-} \times (V_1 - V_0)}{m_{cat.}}$$

where D_{-SO_3H} represents the strong acid ($-SO_3H$) density of the catalyst (mmol/g); c_{OH^-} represents the concentration of the NaOH standard solution; V_1 and V_0 represent the volume of the NaOH standard solution consumed in the titration of catalyst and blank test, respectively; and $m_{cat.}$ represents the mass of catalyst.

2.5. Acid value analysis

The acid value of oil was determined using titration analysis according to BS EN ISO 660 (National Standard of the People's Republic of China. GB/T5330-2005). And the conversion of FFA was calculated from acid value using the following equation:

$$\text{FFA conversion } (\%) = \left(1 - \frac{AV_f}{AV_i}\right) \times 100\%$$

where AV_i and AV_f are the acid value of initial oil (18.36 mg KOH/g) and final products, respectively.

3. Results and discussion

3.1. Study on preparation conditions of mesoporous carbon

3.1.1. Characterization of SBA-15 template

Fig. 1 shows the low temperature N_2 adsorption–desorption isotherms of SBA-15 template. The isotherm is typical type-IV curve with two obvious H_1-type hysteresis loops caused by sharp capillary condensation at relative pressures of 0.6–0.85 and 0.85–0.99, corresponding to two kinds of cylindrical connecting mesopores with narrow pore size distribution centered at 6.4 and 18.9 nm. The existence of partial bigger mesopores in SBA-15 template could enhance the stability of OMC framework. The calculated results show a slightly lower BET surface area (651 m^2/g) and larger pore volume (1.41 cm^3/g) compared to literature [37], suggesting the presence of large mesopores.

Fig. 2 shows the small angle XRD pattern and TEM image of SBA-15 template. Fig. 2A displays three well-resolved XRD peaks at 2θ values of 0.85°, 1.47°and 1.70°, d value calculated from Bragg equations are 10.4, 6.0 and 5.2 nm, the d-value ratios of these peaks are exactly $1:1/3^{1/2}:1/2$, which can be indexed as 1 0 0, 1 1 0 and 2 0 0 reflections of the ordered 2-D hexagonal mesostructures (p6 mm). The lattice parameter a calculated by the following equation: $1/d^2 = 4\,(h^2 + k^2 + hk)/(3a^2) + l^2/c^2$ is 12.0 nm. The TEM image of SBA-15, presented in Fig. 2B, indeed confirms the presence of a wide range of typical stripe-like hexagonal arrangement of mesopores, which is consistent with the results of XRD and N_2 adsorption discussed above.