



Study on preparation of Ca/Al/Fe₃O₄ magnetic composite solid catalyst and its application in biodiesel transesterification

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ABSTRACT

A magnetic composite solid catalyst was prepared by loading calcium aluminate onto Fe₃O₄ nanoparticles via a chemical synthesis method. The optimum conditions for the catalyst preparation were investigated. The influences of the molar ratio of Ca to Fe, calcining temperature, calcining time on the catalytic performance were studied. The catalyst with the highest activity was obtained when the molar ratio of Ca to Fe was 5:1; calcining temperature was 600 °C and calcining time was 6 h. The catalyst was characterized by thermogravimetric analyses (TGA), X-ray diffraction (XRD), scanning electronic microscope (SEM), Brunauer–Emmett–Teller method (BET) and vibrating sample magnetometer (VSM). Furthermore, the magnetic composite solid catalyst showed high catalytic activity for transesterification reaction for preparing biodiesel and the biodiesel yield reached 98.71% under the optimum conditions. The activity and recovery rate of this magnetic composite catalyst can be well maintained after 5 cycles of catalysis. This catalyst showed magnetism and can be easily separated magnetically. Both the catalytic activity and the recovery rate of the magnetic composite solid catalyst were much higher than those of pure calcium aluminate catalyst.

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1. Introduction

Biodiesel has attracted attention in recent years as a renewable biofuel with less pollutant emissions compared to mineral diesel on its combustion [1,2]. Transesterification is the most common method for biodiesel preparation. Most biodiesel today is produced in the presence of homogeneous catalysts such as sodium methoxide, sodium or potassium hydroxide [3]. Freedman et al. [4] reported that NaOH can transform vegetable oil to biodiesel completely in an hour. But their disadvantages are the complicated processes of post treatments and pollution.

In this case, researches have focused on finding a suitable heterogeneous catalyst that can be easily separated and give a high yield and conversion without compromise [5]. Since the catalytic activity of basic catalysts is higher than that of acid solids, they have been preferably studied. Heterogeneous solid base catalysts have been presently reported such as metal oxides CaO [6–9], SrO [10] and so on; alkali-doped metal oxides KF/MgO [11], CaO/Al₂O₃ [12], MgO/Al₂O₃ [12], Li/CaO [13], CaO/ZnO [14] and so on; supported ones, such as Na/NaOH/γ-Al₂O₃ [15] and KF/γ-Al₂O₃ [16]; hydrotalcites Mg–Al [17–19], KF/hydrotalcite [20], KF/Ca–Mg–Al hydrotalcite [21] and so on; sodium aluminate [22], SnCl₂ [23], calcium ethoxide [24] and mayenite [25]. Although these heterogeneous catalysts have

advantages in catalyst separation and pollution reduction, most of them have some limitations in catalytic activity and stability.

The heterogeneous base catalyst for biodiesel preparation has been developed in our group. Heterogeneous base catalyst K/KOH/γ-Al₂O₃ was prepared and used in the transesterification of rapeseed oil with methanol to produce biodiesel [26]. The result showed that the catalyst K/KOH/γ-Al₂O₃ had high catalytic activity and the yield of biodiesel could reach as high as 84.52% after 1 h reaction at 60 °C, with a 9:1 molar ratio of methanol to oil, a catalyst amount of 4 wt.%. However, after two-times use, it was found that the biodiesel yield decreased to 37.6%, and the catalyst lost weight of 10.8%, which meant the relatively low stability and recovery rate of the catalyst. Therefore, the development of a heterogeneous catalyst with high activity and stability is still in high demand.

Nanometer magnetic solid base catalyst can be separated easily from the reagents by an external magnetic field, which can effectively prevent catalyst loss and improve its recovery rate during separation process. Furthermore, magnetic nanoparticles-supported solid catalyst show high dispersion so as to contact reactants more sufficiently based on the high surface area of the supported magnetic nanoparticles. Nanometer magnetic catalyst has been attracting more and more increasing attention in recent years. Fe₃O₄ magnetic particles were used to immobilize lipase as catalyst for biodiesel production. The results showed not only high catalytic activity but also the advantages of easy separation and reuse [27,28]. Hu et al. [29] developed a nanomagnetic solid base catalyst KF/CaO–Fe₃O₄ based on Fe₃O₄ magnetic core by impregnation method. The catalyst recovery was more than 90%. When the reaction was carried out at 65 °C with a methanol/oil

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molar ratio of 12:1 and a catalyst concentration of 4 wt.%, the biodiesel yield exceeded 95% at 3 h of reaction time. Liu et al. [30] prepared nanometer magnetic solid base catalysts for transesterification reaction by loading CaO on Fe₃O₄ with Na₂CO₃ and NaOH as precipitator, respectively. The conversion rate of transesterification reaction catalyzed by nanometer magnetic solid base catalysts under optimum conditions could reach 95% in 80 min, and to 99% in 4 h. Fatty acid methyl esters (FAME) yield was more than 90% after 5-times use and still more than 70% after 10-times use. The recovery rate of the Ca(OH)₂-Fe₃O₄ catalyst after reaction reached up to 91.45%. According to Scherer formula $D = 0.89\lambda / \beta \cos\theta$, the average particle diameter was calculated to be 49.76 nm. But the BET specific surface area of this catalyst was only 3.72 m²/g and the saturation magnetization of magnetic catalysts was smaller than 1 eum/g.

In our work, calcium aluminate catalyst has been developed via a chemical synthesis method for transesterification reaction of biodiesel production. Furthermore, the magnetic composite solid catalyst has been prepared by loading calcium aluminate onto the nanometer Fe₃O₄ to improve the catalytic performance including the catalytic activity and recovery in application to biodiesel preparation.

2. Experimental section

2.1. Materials

Rapeseed oil was purchased from Ningbo zhengda grain and oil Company. Sodium hydroxide, methanol, Al, CaCO₃, absolute alcohol and isopropanol were analytical grade, obtained from Tianjin Jiangtian Chemical Reagent Company, China. Fe₃O₄ (99.5%, 20 nm spherical particles) was purchased from Shanghai Yutian Chemical Company.

2.2. Preparation of Ca/Al/Fe₃O₄ magnetic composite catalysts

NaOH was solved into distilled water, and then aluminum sheet was added into NaOH solution. After reaction, sodium meta-aluminate solution was obtained. CaO obtained by calcining of CaCO₃ at 1000 °C for 10 h, and CaO was added into distilled water, then calcium hydroxide suspensions formed. The molar ratio of NaOH, Al and CaO was 2:2:3. A certain amount of Fe₃O₄ nanoparticles was added into the mixed solution of NaOH and Ca(OH)₂ with vigorous stirring at 80 °C for 5 h. The as-prepared powders were thoroughly washed with deionized water, dehydrated using alcohol, and then dried under vacuum for 12 h. At last, the dried powder was calcined to produce magnetic composite solid catalysts.

The influences of the molar ratio of Ca to Fe, calcining temperature and calcining time on FAME yield were investigated in this work. Besides, in order to compare the catalytic activity of the magnetic composite solid catalyst with that of pure calcium aluminate catalysts, the calcium aluminate catalysts were prepared in the same way.

2.3. Transesterification for biodiesel

The transesterification of 67.5 g rapeseed oil was carried out in a 250 ml round-bottom flask, provided with a thermostatic and magnetic stirring system. In our previous study, the optimum transesterification conditions catalyzed by calcium aluminate were obtained as follows: methanol/oil molar ratio 15:1, catalyst dosage 6 wt.% of rapeseed oil, reaction temperature 65 °C, the stirring rate of 270 rpm and reaction time of 3 h.

All the transesterification reactions in this paper were performed under the obtained optimum conditions to determine the catalytic activity of the catalysts. After reaction, the magnetic composite solid catalysts were recycled by magnetic separation. A small amount of the product mixtures was taken and washed with deionized water

at 70 °C, centrifuged for 30 min. Then the sample taken from the oil phase was analyzed by gas chromatography.

2.4. GC and GC-MS analysis of FAME

The sample was taken from the oil phase and determined by GC (SP-2100) with capillary column of H.J.PEG-20M (30 m × Φ0.32 mm × 0.5 μm). To detect the yield of biodiesel, methyl salicylate was used as internal standard, ethyl acetate as solvent. The column temperature was 130 °C, the temperatures of the injector and detector were respectively 180 °C and 280 °C. Programmed temperature was that initial temperature was 130 °C remaining 3 min, the temperature was elevated by 30 °C/min to 190 °C, then elevated by 5 °C/min to 230 °C remaining 5 min.

The components of fatty acid methyl esters after transesterification reaction were determined by GC-MS (6890-5973N, Agilent). The ion source of MS was electron ionization at 230 °C with capillary column of HP-INNOWax (30 m × Φ0.25 mm × 0.25 μm). The interface and quadrupole temperatures were 250 °C and 150 °C respectively. The initial column temperature was 160 °C remaining 2 min, and then was programmed elevated by 5 °C/min to 240 °C remaining 10 min. There were mainly seven components including methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, methyl linolenate, methyl cis-11-eicosenoate and methyl erucate respectively.

The FAME yield was calculated by internal standard method using the following equation:

$$\text{Yield}_{\text{FAME}} = \frac{\sum f_{\text{ester}} A_{\text{ester}}}{A_{\text{internal}}} \times \frac{m_{\text{internal}}}{m_{\text{esters}}} \times 100\% \quad (1)$$

In formula (1), A_{ester} is the peak area of fatty acid methyl esters, A_{internal} is the peak area of internal standard (methyl salicylate), m_{internal} is the mass of internal standard (methyl salicylate), m_{esters} is the mass of fatty acid methyl esters and f_{ester} is the correction factor of fatty acid methyl esters. The correction factors of methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, methyl linolenate, methyl cis-11-eicosenoate and methyl erucate were determined as 0.8250, 1.1789, 0.8121, 0.8154, 0.9556, 1.9434, 3.0437 respectively.

2.5. Characterization of the solid catalysts

The morphologies of the as-prepared calcium aluminate catalysts and magnetic composite solid catalysts were observed by scanning electronic microscopy (SEM, Nanosem 430, FEI, USA). The thermal stability of catalyst was examined using thermogravimetric analyzer (TGA, TA-50, Shimadzu, Japan) from room temperature to 750 °C under an inert nitrogen atmosphere and a heating rate of 10 °C min⁻¹. The magnetic hysteresis loops of the Fe₃O₄ particles were measured with a vibrating sample magnetometer (VSM, LDJ 9600, LDJ Electronics, USA) at room temperature under applied magnetic field of 1T. X-ray diffraction analysis was carried out by using an X'Pert PRD X-ray diffraction system (Philips X'pert, Cu Kα radiation $k = 1.54056 \text{ \AA}$, USA). The specific surface areas of the catalysts were detected by the BET nitrogen adsorption method at -196 °C (Tristar3000, Micromeritics, USA).

3. Results and discussion

3.1. Catalytic activities of magnetic composite solid catalysts

To explore the optimal conditions for catalyst preparation, different molar ratios (10:1, 9:1, 8:1, 7:1, 6:1, 5:1, 4:1, 3:1 and 2:1) of Ca to Fe, calcining temperature (450 °C, 500 °C, 550 °C, 600 °C, 650 °C, 700 °C, 750 °C and 800 °C), calcining time (2 h, 3 h, 4 h, 5 h, 6 h, 7 h, 8 h and 9 h) were studied.

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