

Ordered mesoporous carbon supported ferric sulfate: A novel catalyst for the esterification of free fatty acids in waste cooking oil



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ABSTRACT

Ordered mesoporous carbon (OMC) supported ferric sulfate (FS) catalysts were prepared by impregnation, and their catalytic activity for the esterification of the free fatty acids (FFAs) in waste cooking oil (WCO) with methanol was evaluated. The FS/OMC catalysts were characterized by N₂ adsorption–desorption, powder X-ray diffraction and transmission electron microscopy. The results indicated that catalysts retained the ordered mesoporous structure, and the FS was well dispersed on the surface of the OMC. The FT-IR spectrum of pyridine adsorbed on the FS/OMC catalysts showed the presence of strong Lewis acid sites on the surface of the catalysts. The FS/OMC catalysts exhibited excellent catalytic performances for FFA esterification. In addition, the process variables that influence the esterification of FFAs, such as the FS loading, the amount of catalyst, the molar ratio of methanol to FFAs, the reaction temperature and the reaction time, were investigated and optimized. The FS/OMC catalysts are reusable and maintained their original catalytic activities after six uses.

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1. Introduction

Biodiesel consists of fatty acid methyl esters (FAMES) which are obtained from the transesterification of vegetable oil and animal fats with low molecular weight alcohols. Biodiesel is considered a promising alternative fuel to replace petroleum-based fuels because of its biodegradability, non-toxicity and favorable combustion emission profile. The expenses of the raw materials are the major contributor to the cost of biodiesel production [1–3]. Therefore, low-cost waste cooking oils (WCOs) from restaurants and food industries are economical raw materials for biodiesel production [4–6]. However, WCOs contain large amounts of free fatty acids (FFAs), which lead to the formation of soaps in the presence of an alkaline catalyst. Thus they cannot be converted to biodiesel using a one-step transesterification process. In order to utilize WCOs effectively, two-step methods for the production of biodiesel from WCOs with high FFA content have been proposed and widely studied [7–9]. In these processes, the FFAs in the WCO are converted to FAMES through an acid-catalyzed esterification with methanol in the first step, and then an alkali-catalyzed transesterification reaction converts the triglycerides to FAMES in the second step [10–12].

Although sulfuric acid has high catalytic activity for FFA esterification, it is difficult to recycle and gives rise to equipment corrosion and environmental pollution. Compared with homogenous acid catalysts, heterogeneous solid acid catalysts are ease of separation, low corrosive

and environmentally friendly. A variety of solid acid catalysts, such as cation-exchange resins [13,14], solid superacids [15,16], zeolites [17] and carbon based solid acids [18–25] have been applied to the heterogeneous catalytic esterification of FFAs from WCO. Recently, ferric sulfate (FS) was reported as a homogeneous acid catalyst with good activity for the esterification of FFAs in WCO, and a higher FFA conversion (97.22%) was obtained than that for a liquid sulfuric acid catalyst [11, 12]. Gan et al. [26] proposed a mechanism involving the release of a proton during the hydrolysis of the [Fe(H₂O)₆]³⁺ metal complex which formed from the FS dissolved in the water. Patil et al. [27,28] reported that ferric sulfate showed good catalytic activity for the methanolysis of FFAs in WCO.

Despite the fact that ferric sulfate is insoluble in oil and sparingly soluble in methanol [11], the small ferric sulfate particles tended to adhere to the oil, making it difficult to separate from the oil after the reaction for reuse [29]. In order to overcome this problem, ferric sulfate supported catalyst has been widely investigated. Đokić et al. [30] showed that the esterification of oleic acid with a ferric sulfate catalyst supported on silica gel and conformed to a pseudo-homogeneous third order kinetic model. Gan et al. [29] reported a good catalytic performance for esterification using ferric sulfate support on active carbon.

In recent years, ordered mesoporous carbon (OMC) has drawn widespread attention due to its well-defined pore structures, high specific surface area and regular structure [31]. The ordered mesoporous structure provides more active sites for the reaction of large molecules. In addition, the hydrophobic surface of the carbon-based solid acid inhibits the adsorption of water, and thus effectively protects the catalytic active sites for esterification.

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In this work, FS catalysts supported on OMC were prepared and characterized and their catalytic performances for the esterification of WCO with methanol were investigated. The effects of the pore structures and the surface acidity on the catalytic activity were investigated and the experimental conditions, such as the FS loading, the amount of catalyst, the molar ratio of methanol to FFAs, the reaction temperature and the reaction time, were optimized. In addition, the reusability and leaching of the catalysts were investigated.

2. Experimental

2.1. Materials

Triblock poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) copolymer Pluronic F127 ($M_w = 12,600$, PEO₁₀₆PPG₇₀PEO₁₀₆) was purchased from Aldrich Corporation, USA. Other chemical reagents were purchased from Guangfu Chemical Corporation, China. All chemicals were analytical grade and were used as received without any further purification.

WCO was collected from a local restaurant. The WCO sample was filtered to remove the suspended waste residue, and then heated to evaporate the residual water. The WCO was stored in a sealed bottle at room temperature, and its acid value and FFA content were measured daily for 30 consecutive days until a stable equilibrium was achieved. The acid value and FFA content of the WCO were 28.05 mg KOH/g and 20 wt.%, respectively. The free fatty acid profile indicated that the WCO contained palmitic, stearic, oleic and linoleic fatty acids.

2.2. Catalyst preparation

Phenol and an aqueous solution of formaldehyde (37 wt.%) were used to synthesize a resol precursor solution according to the procedure reported in the literature [32]. The ordered mesoporous carbon material was prepared by the soft template method in the literature [32,33]. In a typical synthesis, 1.00 g of F127 was dissolved in 20.0 g of ethanol and then 1.96 g of resol precursor solution was added to the mixture and the solution was stirred for 10 min to form a homogeneous solution. Then, the solution was transferred to a dish and the ethanol was allowed to evaporate at room temperature for 8 h. The product was heated in a thermostatic oven at 100 °C for 24 h to thermopolymerize the phenolic resins, and then the product was heated at a rate of 1 °C/min to 350 °C and calcined under a nitrogen atmosphere for 5 h to remove the template. Finally, OMC was obtained after the product was calcinated at 500 °C in a nitrogen atmosphere for 5 h. Moreover, the porous carbon (PC) was prepared from resol without adding F127 under the above carbonization condition.

Next 1.0 g of OMC was dispersed into 20 mL of aqueous FS solutions with different concentrations. The solution was sonicated for 1 h, and then stirred overnight. The resulting suspension was dried in a vacuum drying chamber at 100 °C for 6 h. A series of supported catalyst samples were prepared and are denoted by the weight percent of FS. For example, 10-FS/OMC indicates that the catalyst contains 10 wt.% FS.

2.3. Catalyst characterization

N₂ adsorption–desorption isotherms were measured at 77 K using a Micromeritics Tristar 3000 instrument. Prior to the measurement, all samples were degassed at 200 °C for 12 h. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The total pore volume was estimated from the amount of N₂ adsorbed at $P/P_0 = 0.99$. The average pore diameter was determined from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) model. X-ray diffraction (XRD) analysis was carried out using a Rigaku D/Max 2500 type X-ray powder diffractometer, with Cu K α radiation at 40 kV and 40 mA. The morphologies of the catalysts were characterized by high-resolution transmission electron microscopy

(HRTEM, FEI Tecnai G²F20). The S and Fe elemental compositions in the liquid product were determined by inductively coupled plasma with optical emission spectroscopy (ICP-OES, Varian VISTA-MPX).

The pyridine adsorption FT-IR spectra were collected on a Thermo Scientific Nicolet 560 FTIR spectrometer with 64 scans at 4 cm⁻¹ resolution. The samples were in a quartz IR cell, and treated at 200 °C for 2 h in vacuum. When the samples were cooled to room temperature, IR background spectra were recorded. After being exposed to pyridine vapor at ambient temperature for 30 min, the sample was flushed with nitrogen for another 30 min to remove physisorbed pyridine. Then IR spectra were collected at room temperature. All spectra were differences between the spectra of samples with adsorbed pyridine and the backgrounds.

2.4. Catalytic activity measurement for the esterification

The esterification reactions were carried out in a three-neck glass flask equipped with a reflux condenser. A mixture of a known amount of WCO and methanol was continuously stirred and heated to the desired reaction temperature with a heating accuracy of ± 1 °C. Catalyst samples were dried at 100 °C for 1 h before utilization in a reaction. The oil phase products were sampled during the reaction at defined time intervals.

After the esterification was complete, the used solid catalyst samples were separated from the reaction mixture by filtration and were collected for reusability tests. Before reusing they were dried at 100 °C for 1 h. The acid values of oils were measured by titration with a 0.1 M KOH standard solution [34]. The conversion of FFA was determined from the ratio of the acid value after and before esterification using the following formula:

$$\text{FFA conversion} = (AV_i - AV_f) / AV_i \quad (1)$$

where AV_i is the initial acid value of WCO, and AV_f is the final acid value of WCO after the esterification reaction.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Pore structure of the OMC and FS/OMC catalysts

As Fig. 1 shows, all the N₂ adsorption–desorption isotherms exhibited type IV isotherms with an H1 hysteresis loop as defined by IUPAC. This

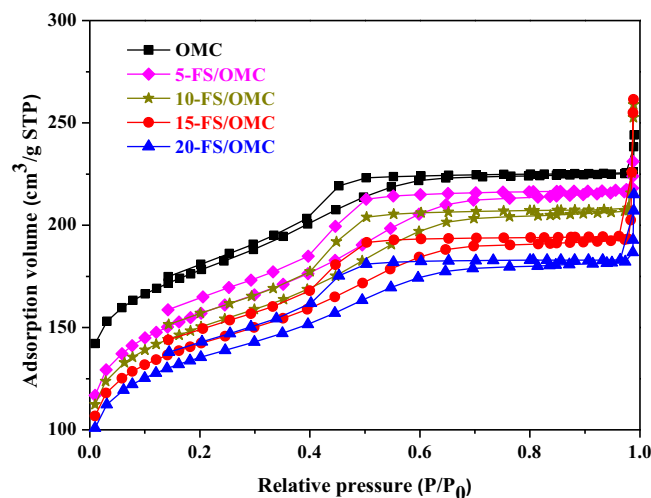


Fig. 1. N₂ adsorption–desorption isotherms of the OMC and FS/OMC catalyst samples.

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