



# Preparation and esterification performance of sulfonated coal-based heterogeneous acid catalyst for methyl oleate production



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## ABSTRACT

A series of coal-based heterogeneous acid catalysts are prepared by partial carbonization followed by sulfonation approach and the performances in esterification for methyl oleate production are conducted. Characterization methods of XRD, N<sub>2</sub> adsorption-desorption, SEM, TG, FTIR, EDX, acid density tests and Hammett indicator method are carried out to reveal the physical and chemical characteristics of the prepared catalysts. Catalyst with the highest acid density of 1.09 mmol g<sup>-1</sup> could be prepared under the condition of carbonization temperature at 350 °C for 2 h and sulfonation with concentrated sulfuric acid at 135 °C for 4 h. Acid value reduction of 97.29% on oleic acid through esterification with methanol, which is catalyzed by this coal-based heterogeneous acid, could be achieved under the optimized condition of 10 wt.% catalyst dosage, molar ratio of methanol/oleic acid of 10, reaction temperature at 67 °C and reaction duration of 4 h. Characterization results demonstrate that carbon in the catalyst, which is composed of aromatic carbon sheets with —COOH and —SO<sub>3</sub>H groups, is in amorphous structure and its acid strength is 3.3 < pK<sub>a</sub> < 0.8. Meanwhile, this catalyst could provide favorable thermal stability high to 220 °C and retain satisfactory catalytic activity after five cycles. In addition, catalytic capability could be reactivated with the acid value reduction efficiency of 95.30% after the fifth re-usage.

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## 1. Introduction

Usage of the renewable energy, such as biodiesel, has received extensive attentions worldwide in recent years with depletion of the fossil fuel and deterioration of the environmental conditions. Biodiesel is renewable, biodegradable and environmental benign, which brings about a series of economical, environmental and social advantages [1]. It can be blended with petroleum diesel to arbitrary proportion or used directly for the similar viscosity and solidification point. Biodiesel is mainly composed of less viscous fatty alkyl methyl esters (FAMES) and commonly obtained by transesterification of triglycerides (high-quality oils, such as vegetable oils of soybean oil, and sunflower oil) with short-chain alcohol (methanol or ethanol) catalyzed by NaOH, NaOCH<sub>3</sub> or CaO, etc. [2,3]. However, in the primary stage, the main restricting factor for biodiesel commercialization is raw material cost. Some low-cost and low-quality feedstock, including waste cooking oils (WCOs) and animal fats also can be used, where large amounts of free fatty acids (FFAs) in the low-quality feedstock usually result in base catalysts surface deactivation arising from the saponification reaction

[4]. So, conversion of FFAs into FAMES through esterification is an obligatory pre-treatment process before transesterification [5]. Traditionally, concentrated sulfuric acid used for acid value reduction could perform excellent catalytic activity. Nevertheless, the drawbacks of equipment corrosion, environmental pollution and difficult recyclability caused by this homogeneous acid catalyst are prerequisite to be overcome. Alternatively, a number of prospective heterogeneous acid catalysts, which are easily separated from the reactants and products through suction filtration, get attractive routes for biodiesel production and could eliminate the problems mentioned above [6]. Several types of heterogeneous acid catalysts have been reported, such as heteropolyacids [7], zeolite [8], anion exchange resin [9], and zirconium oxide [10] but they are generally subjected to one or more problems of low acid density, bad operational stability, expensive preparation cost and deactivation under rigorous conditions [11].

Recently, among the heterogeneous acid catalysts, the carbon-based ones have attracted abundant attentions for their low preparation cost, high catalytic activity and pollution-free, etc. These catalysts, which possess polycyclic aromatic carbon sheets in amorphous carbon structure with large amounts of —SO<sub>3</sub>H groups, can be simply prepared by partial carbonization and then sulfonated with concentrated sulfuric acid or fuming SO<sub>3</sub>. Zong et al.

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[12] prepared the carbon-based heterogeneous acid catalyst from D-glucose, which showed strong catalytic activity for biodiesel production from high fatty acids. Rao et al. [13] synthesized a carbon-based acid catalyst by sulfonation of the partially carbonized de-oiled canola meal and this catalyst possessed enough acidic sites of  $-\text{SO}_3\text{H}$  groups to guarantee the excellent catalytic activity in esterification, where conversion of 93.8% was achieved after 24 h at 65 °C using 1:60 molar ratio of FFAs to methanol and 7.5 wt.% catalyst dosage. Further, carbon-based materials, such as glycerol [6], PET-derived activated carbon [14] and bagasse [11] are applied for the heterogeneous acid catalyst preparation.

Basic structure of the carbon-based heterogeneous acid catalyst is polycyclic aromatic carbon sheets consisting of amorphous carbon functionalized with some specific functional groups. Meanwhile, coal mainly consists of aromatic polymer with oxygen existing in the form of phenolic hydroxyl and carbonyl. Theoretically, after carbonization and sulfonation, heterogeneous acid catalyst, which contains abundant oxygenic functional groups, could guarantee the high catalytic activity. Thus, it is of great interest to extend coal application as carbon precursor for the heterogeneous acid catalyst preparation. To date, Liu et al. [15] prepared a new efficient coal based heterogeneous acid to catalyze the synthesis of 3,4-Dihydropyrimidin-2(1H)-Ones using aldehydes,  $\beta$ -ketoesters and urea or thiourea under solvent-free conditions, where the catalyst could be recycled up to 4 consecutive batch runs without losing its catalytic activity. Zhong et al. [16] utilized trichloroacetic acid to modify the coal tar pitch with sulfonation using concentrated sulfuric acid to prepare the heterogeneous acid and studied the activity in catalyzing esterification for ethyl acetate production. Moreover, combustion fly ash from coal combustion could be synthesized as the efficient heterogeneous acid catalyst upon modification of *ortho*-phosphoric acid and was used to catalyze esterification between 4-aminobenzoic acid and methanol [17].

Zhundong coalfield, which is located in northwest China, is one of the largest integrated basin newly found coalfields with an estimated reserve of up to 390 Gt and could meet the requirement of China coal consumption for nearly 100 years [18]. Zhundong coal (ZDC) gains the typical characteristics of high moisture, low ash, low nitrogen and sulfur contents and high calorific value. And Lv [19] reported an investigation on the ZDC structural features through ruthenium ion-catalyzed oxidation and found that condensed aromatic rings linked by short polymethylene bridged linkages, long side chains and oxygen-containing groups were predominant in ZDC. In conclusion, ZDC can be potentially used to provide electricity powder, coal-based chemical raw materials or other applications with advantages of low pollutant emission. Currently, studies on ZDC are concentrated on combustion characteristics [20], hydrolysis characteristics [21] and ZDC gasification [22], etc. Nevertheless, researches on carbon-based heterogeneous acid catalyst prepared from ZDC via partial carbonization followed by sulfonation approach for biodiesel production have been rarely reported.

Herein, in this study, a series of environmentally friendly and high activity of coal-based heterogeneous acid catalysts are prepared to catalyze the esterification of oleic acid with methanol. Two significant catalyst preparation conditions, namely, carbonization temperature ( $T_c$ ) and sulfonation temperature ( $T_s$ ), are explored for their effects on the catalytic activity. Further, characterization approaches of XRD, EDX,  $\text{N}_2$  adsorption-desorption, SEM, TG, FTIR, acid density tests and Hammett indicator method are conducted to explain the influence of preparation conditions on catalyst performance. Meanwhile, optimal parameters of the catalyst dosage ( $\zeta$ ), molar ratio of methanol to oleic acid ( $\gamma$ ), reaction

temperature ( $T_e$ ) and reaction duration ( $\tau_e$ ) in esterification are determined. Besides, cycle usage test of the catalyst is also conducted. Finally, the esterification product is purified and characterized by FTIR for functional groups analysis.

## 2. Materials and methods

### 2.1. Materials

The ultimate and proximate analyses of ZDC are listed in Table 1, where the proximate analysis is performed according to GB/T 212-2008 and ultimate analysis is determined by an elemental analyzer (Vario EL CUBE). For heterogeneous acid preparation, ZDC is milled and sieved to particle size less than 74  $\mu\text{m}$  via a filtrate machine in advance.

### 2.2. Catalyst preparation

ZDC is dried in an oven at 105 °C to remove the moisture under air atmosphere. Then, the dried coal is partially carbonized in muffle furnace for 2 h under nitrogen atmosphere at different temperatures, which are distributed from 300 °C to 550 °C. After the partial carbonization, samples are treated with sulfonation, where the partially carbonized coal and the concentrated sulfuric acid (analytical grade) are heated at the designed temperatures, which are distributed from 105 °C to 165 °C in the oil-bath pan under the magnetic stirring effect for 4 h. Afterwards, the black solid product is cooled to the room temperature and washed repeatedly by the hot de-ionized water (higher than 80 °C) to be neutral. Finally, the resulting product is dried at 105 °C to remove moisture and subsequently estimated for the catalytic activity in methyl oleate described below. The prepared catalyst is denoted as C $_x$  and C $_x$ -S $_y$ , where C and S indicate carbonization and sulfonation, and  $x$  and  $y$  represent the carbonization and sulfonation temperature, respectively.

### 2.3. Catalyst characterizations

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) spectra are performed on a Vertex 70 FTIR analyzer to detect function groups in the coal-based heterogeneous acid catalyst. The FTIR spectrum scope is 4500–600  $\text{cm}^{-1}$  with resolution of 4  $\text{cm}^{-1}$  and 16 scans per spectrum.

Thermogravimetric (TG) measurement is investigated on a Mettler-Toledo TGA/SDTA 851e Thermogravimetric analyzer, where the initial sample is kept at (10  $\pm$  0.1) mg in an aluminum oxide ceramic crucible and heated from 25 °C to 1000 °C at the heated rate of 10 °C/min.

Energy dispersive X-ray spectroscopy (EDX) for ultimate analysis is conducted using an elemental analyzer via Vario ELCUBE apparatus, ELEMENTAR, AR, Germany, with the accuracy of 0.3% and the undetermined oxygen mass fraction is calculated by difference.

$\text{N}_2$  adsorption isotherm is obtained at  $-196$  °C using a Micromeritics ASAP2020 instrument, where the surface area is determined from the linear portion of Brunauer-Emmett-Teller (BET) plot and the pore volume and pore size distribution are

**Table 1**  
Proximate and ultimate analyses of ZDC.

Proximate analysis $w_{\text{ad}}$ (%)				Ultimate analysis $w_{\text{d}}$ (%)				
M	A	V	FC	C	H	O	N	S
13.77	3.18	27.31	55.74	71.60	3.66	19.94	0.51	0.49

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