



Esterification of oleic acid to produce biodiesel catalyzed by sulfonated activated carbon from bamboo

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ABSTRACT

A series of heterogeneous acid catalysts are synthesized from bamboo activated carbon through arylation using sulfonic acid without reductant. Both the catalyst synthesis conditions and parameters for esterification of oleic acid with ethanol are optimized. The heterogeneous acid catalysts are characterized by XRD, FTIR, N_2 adsorption-desorption, EDX and acid-base neutralization titration. At the molar ratio of benzenesulfonic acid group to bamboo activated carbon of 1, sulfonation temperature of 50 °C and sulfonation duration of 10 min, the heterogeneous acid catalyst presents the mesoporous microstructure with surface area of 225.71 m²g⁻¹ and pore volume of 0.12 cm³g⁻¹, and total acid density of 1.69 mmol g⁻¹. With the catalyst added mass percentage of 12% (relative to the oleic acid mass) and molar ratio of ethanol to oleic acid of 7 at 85 °C for 180 min, esterification efficiency of 96% is achieved, which is higher than 91% of esterification with methanol at 65 °C. Microstructure shrinkage is the main reason for catalyst deactivation, and the regenerated heterogeneous acid supplies the catalytic efficiency of 94%.

1. Introduction

Due to gradual depletion of the traditional fossil residues and increased deterioration of the environmental pollutions, alternative renewable fuels were paid more and more attentions recent years. Biodiesel [1], usually produced through transesterification of triglycerides from vegetable oils or animal fats, emerges with conspicuous features. Biodiesel possess the similar physicochemical properties with fossil diesel, such as cetane value, lubricity, kinematic viscosity and flash point, etc, and could be directly applied in engine without mechanical modification [2,3]. Catalytic capabilities of the homogeneous alkali hydroxides or alcoholates would be crippled if free fatty acids (FFAs) exist in the crude oil due to saponification [4]. Thus, conversion of FFAs into esters through esterification becomes a necessary pre-treatment process for resource with FFAs [5]. For esterification, application of the homogeneous acid catalysts, such as H₂SO₄, HCl or HF, etc, are restricted due to the equipment corrosion and environment pollution, which however can be avoided by the heterogeneous acid catalysts, such as zeolite [6], heteropolyacids [7], cation exchange resin [8] and niobic acid [9]. Unfortunately, they are subjected to more or less drawbacks of low acid sites density, poor mass transfer and expensive preparation cost.

The carbon based heterogeneous acid catalysts were validated to be proper for esterification owing to the advantages of chemical inertness, mechanical stability, structural diversity and surface hydrophobicity. Carbon-containing materials of multiwall carbon nanotube [10], glycerol [11], oilseed cake [12], starch [13] and bagasse [14], etc, have been used as carbon precursors for heterogeneous acid catalyst preparation. Activated carbon is widely used as catalyst support in chemical and environmental application. Besides hydrophobicity of the catalyst surface to guarantee efficient absorption of long chain organic molecule of fatty acids and beneficial elimination of water byproduct to deactivate the catalyst [15,16], microstructure of the carbon material could be regularly adjusted to be of profound significance for the catalytic capability through physical or chemical activation [17,18]. Arylation was used to synthesize the 4-sulfophenyl activated carbon based heterogeneous acid catalyst, where 4-sulfobenzene diazonium supplies active sites and H₃PO₂ presented as reductant. Under low synthesis temperature (< 5 °C), the catalyst gained big surface area and exhibited acceptable catalytic capability [19]. Recently, Malins et al [20] conducted arylation of activated carbon with diazonium salts from 20 °C to 85 °C to synthesize the heterogeneous acid catalyst without H₃PO₂, where the catalyst showed the similar catalytic performance with commercial Amberlyst-15 for biodiesel production. However, reports

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about the promising approach of arylation performed higher than 5 °C for the carbon based heterogeneous acid catalyst were relatively rare till now.

Our previous researches [21,22] synthesized a series of carbon based heterogeneous acids catalysts from bamboo through partial carbonization and sulfonation. However, due to the incorporation of high densities of hydrophilic molecules into the carbon bulk by binding with the flexible carbon sheet, direct carbonization led to the sulfonated catalyst with poor porosity [23]. It could be speculated that application of the bamboo activated carbon for heterogeneous acid catalyst synthesis through arylation could simultaneously manifest advantages of the developed microstructure to strengthen mass transfer and plentiful active sites to accelerate chemical reaction for biodiesel production, which however has not been reported till now.

In this study, a series of heterogeneous acid catalysts are synthesized from bamboo activated carbon through arylation with sulfanilic acid, where the synthesis conditions are optimized from molar ratio of benzenesulfonic acid group (Ph–SO₃H) to bamboo activated carbon, sulfonation temperature and sulfonation duration. To reveal catalytic mechanism, characterizations of XRD, FTIR, N₂ adsorption-desorption, EDX and acid-base neutralization titration are conducted. Meanwhile, influences of catalyst added mass percentage (relative to the oleic acid mass), molar ratio of ethanol to oleic acid, esterification temperature and esterification duration on catalytic capability in esterification of oleic acid with ethanol are investigated. Esterification of oleic acid with methanol is also carried out to validate compatibility of the heterogeneous acid with different alcohols. To acquaint stability of the heterogeneous acid in catalyzing esterification, homogeneous catalytic effect, reusability and regenerability are profoundly estimated under the optimized esterification condition.

2. Experiments

2.1. Catalysts synthesis

Synthesis of heterogeneous acid catalyst from the bamboo activated carbon is familiar with the procedure in the reported literatures, but some adjustments are conducted [20,24]. After dried at 105 °C in vacuum oven overnight, the bamboo activated carbon is mixed with sulfanilic acid (analytical grade, Kermel Chemical Reagent Co., Ltd, Tianjin, China) under vigorous stirring to load active sites of Ph–SO₃H group and pH value of the mixture emulsion is controlled to be 7–8 by NaOH throughout the sulfonation process. At termination, NaNO₂ (Kermel Chemical Reagent Co., Ltd, Tianjin, China) is added to the reaction mixture and completely dissolved through de-ionized water addition. Then, 25% of aqueous HCl (Laiyang Fine Chemical Plant, Shandong, China) is dropwise added to avoid spontaneous rise of the reaction temperature. After filtrated under vacuum and washed by de-ionized water to be pH neutral, the slurry is purified by acetone to purge the impurities and then dried in oven for use. For the best synthesis of the heterogeneous acid catalyst, influence factors of the molar ratio of Ph–SO₃H to bamboo activated carbon (from 0.1 to 1.5), sulfonation temperature (from 30 °C to 80 °C) and sulfonation duration (from 2 min to 60 min) are primarily investigated, where values of the other two factors are fixed if one of the three factors is varied in the above range for investigation.

2.2. Catalysts characterizations

Crystalline phase of the catalyst is analyzed by X-ray diffraction (XRD) on a Bruker Advanced D8 X-ray diffraction analyzer, Germany, which uses Cu K α radiation source with the voltage of 40 kV, electricity of 100 mA, scanning range from 10 to 90°, scanning speed of 4° min⁻¹ and scanning step of 0.02°. Functional group of the catalyst is detected by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) on a Bruker Vertex 70 FTIR spectrometer, Germany. The

scanning range is from 600 to 4500 cm⁻¹ with resolution of 4 cm⁻¹ and 16 scans per spectrum. Microstructures parameters of the catalyst are tested through N₂ adsorption-desorption instrument, Micromeritics ASAP 2020, USA. After desorbed under vacuum at 200 °C, catalyst microstructure parameters are isothermally measured at –196 °C using nitrogen as the adsorbed substance. Then, surface area is calculated by Brunauer-Emmett-Teller (BET) equation and pore volume is estimated by Barrett-Joyner-Halenda (BJH) model. Elemental analysis is carried out through the energy dispersive X-ray spectroscopy (EDX) on the Vario EL CUBE apparatus, Elementar, AR, Germany, with the accuracy of 0.3%. Contents of carbon, hydrogen, nitrogen and sulfur are directly determined and oxygen content is calculated by difference. Total acid density of the catalyst is determined by the acid-base neutralization titration method. About 0.05 g catalyst is mixed with 30 mL NaOH solution (0.02 mol L⁻¹) under ultrasonication effect at ambient temperature for 1 h to replace hydron with sodion. The mixture is then filtered and washed with de-ionized water several times, where the filtrate is titrated by HCl solution (0.01 mol L⁻¹) to be erythroid with phenolphthalein as indicator. For every catalyst, triple experiments are conducted and the consumed NaOH solution and HCl solution volume on average is used to calculate the total acid density.

2.3. Esterification experiments

Esterification of oleic acid with ethanol is catalyzed by the heterogeneous acid derived from bamboo activated carbon on a batch-type experimental system, where a 250 mL three-necked glass flask reactor is fitted with a coiled condenser for ethanol reflux, a mechanical stirrer to reduce mass transfer resistance among the reagents and a water bath to guarantee the reaction temperature [25]. Oleic acid (Kermel Chemical Reagent Co., Ltd, Tianjin, China), ethanol (Fuyu Chemical Co., Ltd, Tianjin, China) and catalyst are sequentially poured into the reactor at the set temperature and the slurry mixture is then vigorously agitated throughout esterification. Upon accomplishment, the heterogeneous acid is mechanically separated from the liquids products through vacuum filtration and the excess ethanol and by-produced water are removed through vacuum distillation. Then, catalytic capability of the heterogeneous acid is labeled as acid value reduction efficiency (η) shown in Eq. (1).

$$\eta = \frac{AV_{in} - AV_{out}}{AV_{in}} \times 100\% \quad (1)$$

where AV_{in} and AV_{out} are acid values (AV) of the original and the esterified oleic acid, respectively, mgKOH g⁻¹, and measured according to GB 5009.229-2016.

Esterification parameters are optimized from the heterogeneous acid catalyst added mass percentage (from 1% to 14%), molar ratio of ethanol to oleic acid (from 0.5 to 13), esterification temperature (from 45 °C to 95 °C) and esterification duration (from 3 min to 300 min). Repeated experiments are conducted under the optimized condition to validate creditability of esterification results.

2.4. Stability of the heterogeneous acid

Homogeneous catalytic effect is unavoidable for the heterogeneous acid due to active sites leaching. To determine this negative effect, the fresh heterogeneous acid is mixed with ethanol and stirred under the optimized esterification condition but at the absence of oleic acid. After separated through filtration, the ethanol is used for oleic acid esterification under the optimized condition, but no more heterogeneous acid is added, where homogeneous catalytic effect generated from active sites leaching into ethanol is determined. The other parallel experiment to reveal the homogeneous catalytic effect for active sites leaching into oleic acid is also conducted, which follows the similar route expect for the replacement of ethanol by oleic acid.

To investigate reusability of the heterogeneous acid derived from

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