Ph-SO₃H-modified mesoporous carbon as an efficient catalyst for the esterification of oleic acid

Liang Geng, Gang Yu, Yu Wang, Yuexiang Zhu*

Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 10087, China

ABSTRACT

Mesoporous carbon materials with thin pore walls (∼1.7 nm) were synthesized using low-cost γ-Al₂O₃ as a hard template and *in situ* polymerized resorcinol–furfural resin as the carbon precursor. Compared with sugar, resin, a widely used carbon precursor, has higher carbon yield and simplifies the synthetic process. Ph-SO₃H modified mesoporous carbon was synthesized by covalent grafting of Ph-SO₃H groups on mesoporous carbon via the diazonium salt. The resulting materials were characterized by means of nitrogen adsorption analysis, TEM, ^{13}C NMR, XRD, FTIR and sulfur elemental analysis. The modified carbons were shown to possess high surface area (∼1000 m²/g), a bimodal pore size distribution and high strong acid density (1.86 mmol H⁺/g). These sulfonated carbons were used as solid acid catalysts in the esterification of oleic acid and methanol, a key reaction in biodiesel production. Compared with the traditional solid acid Amberlyst-15, the optimized carbon catalyst exhibited much higher activity with a rate constant (1.34 h^{-1}) three times to that of Amberlyt-15 and a turnover frequency (TOF) of 128 h^{-1} eight times that of Amberlyst-15. The efficient catalytic ability was attributed to the high surface area and a proper mesopore texture. This carbon catalyst could then be easily separated from the product by filtration. The catalyst was reused six times, and no distinct activity drop was observed after the initial deactivation.

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1. Introduction

Due to its renewable feedstock and low CO₂ emission, biodiesel produced from vegetable oil is considered a sustainable fuel to replace conventional diesel [1]. The production of biodiesel usually involves the transesterification of triglycerides catalyzed by a homogeneous base, such as NaOH, KOH or NaOCH₃ [1–3]. However, the free fatty acid (FFA) contained in the crude vegetable oil will be saponified by the basic catalysts. Therefore, a pre-esterification process is necessary to convert FFA into the corresponding esters before transesterification. Conventionally, the catalysts for pre-esterification are liquid H₂SO₄, which is toxic, corrosive and costly to neutralize, separate and recycle. Therefore, the development of a green and easily separated acid catalyst has received much attention [4].

Among heterogeneous catalysts, carbon-based solid acid is ideal for many reactions owing to such advantages as chemical inertness, mechanical stability, structural diversity and surface hydrophobicity. For the pre-esterification of FFA, much work has focused on sulfonated carbon as the solid acid [5–16]. Using inexpensive

biomass (sucrose [6], glucose [7,9], starch [10,11] or biochar [12]) as the carbon precursor, the pioneering work in this area synthesized carbon catalysts through direct carbonization of precursors followed by sulfonation in concentrated H₂SO₄ [5–16]. Such catalysts performed well in the esterification of fatty acid, but direct carbonization led to carbon catalysts with low porosity and low surface area, which is unfavorable for reactant accessibility to active sites. Moreover, the carbon yield of sugar is low. For instance, the theoretical carbon yield of sucrose is 40%, while the actual yield is only approximately 20% [17].

A new type of sulfonated ordered mesoporous carbon (OMC) has been developed for FFA pre-esterification [18–21]. In this work, the organic precursors were first impregnated into the pores of an ordered mesoporous silica template (typically SBA-15) and carbonized, and then the template was removed by treatment with HF solution. The remaining carbon materials were sulfonated by concentrated H₂SO₄ [18,19] or 4-benzene-diazoniumsulfonate (4-BDS) [20,21] to yield OMC-based solid acids with high surface area and large pores. This improved texture facilitates the diffusion of fatty acid molecules with long carbon chains to the active site, thereby increasing the catalytic efficiency. In most cases, silica templates must be prepared beforehand through multiple steps, which inevitably increase the cost of this type of catalysts.

* Corresponding author. Tel.: +86 10 62751703; fax: +86 10 62751708.
E-mail address: zhuyx@pku.edu.cn (Y. Zhu).

Our previous work reported the synthesis of carbon-based solid acid with sucrose as the carbon precursor, commercial γ-Al_2O_3 as the template and 4-BDS as the sulfonating agent [22–25]. Owing to delicate control of the sucrose loading on the template surface, such catalysts consist of small and thin carbon sheets. They can readily disperse in methanol to efficiently catalyze the esterification of oleic acid with methanol. The highest turnover frequency (TOF) observed was seven times that of Amberlyst-15. However, due to the low carbon yield of sucrose, repeated impregnation and carbonization was necessary in the synthesis of such catalysts.

Recently, we successfully synthesized mesoporous carbon materials with thin walls and large surface areas using resorcinol–furfural resin, which *in situ* polymerized on an alumina surface, as the carbon precursor [17]. Owing to the carbon yield of resorcinol–furfural resin being as high as 50%, one polymerization–carbonization process was sufficient. Moreover, resorcinol–furfural resin tends to form complete carbon frameworks that are stable enough to support themselves. In this paper, Ph-SO_3H groups were attached on the surface of these carbon materials via 4-BDS. N_2 adsorption analysis showed these modified materials still possessed the mesoporous structure and a large surface area (∼1000 m^2/g), and their strong acid density, determined by sulfur elemental analysis, reached 1.86 mmol H^+/g. The optimal carbon catalyst was identified with a TOF of 128 h^{-1}, eight times that of Amberlysts-15 and even higher than that of previously reported sucrose catalysts (109 h^{-1}) [25]. Due to the complete carbon framework, the catalyst was easy to separate from the liquid reaction system by filtration. The optimal catalyst was reused several times with no significant drop in activity after the initial deactivation.

2. Experimental

2.1. Catalyst preparation

2.1.1. Source of alumina template

Three types of alumina were used as template: (a) commercial alumina SBA150 (Engelhard Corp., USA), denoted AI; (b) alumina prepared by calcination of pseudoboehmite (Shandong Aluminum Corp., China) at 550 °C for 4 h, denoted AII; and c) alumina prepared by calcination of aluminum hydroxide dried gel (Sinopec Corp., China) at 550 °C for 4 h, denoted AIII. All alumina templates were calcined at 800 °C for 4 h before use.

2.1.2. Preparation of mesoporous carbon materials

Mesoporous carbon materials were prepared according to a previously reported procedure [17]. The alumina templates (AI, AII or AIII) were mixed and thoroughly ground with resorcinol. The weight ratio of alumina to resorcinol, m_c, was calculated according to the empirical formula below.

$$m_c = 1.05 \times 1.5 \times \frac{S_{BET,A} \times 2 \times 12.0}{3 \times (\sqrt{3}/2) \times (1.42 \times 10^{-10})^2 \times 6.02 \times 10^{23}} \quad (1)$$

where $S_{BET,A}$ is the Brunauer–Emmett–Teller (BET) surface area of the alumina template. Typically, 7 g of alumina AI was ground with 1.12 g of resorcinol for at least 20 min. Then, the mixture was transferred to a round bottom flask containing 30 ml of mesitylene, 2.5 ml of furfural and 3 drops of 1,2-ethylenediamine. After stirring at 90 °C for 4 h, the alumina/resorcinol–furfural resin composite was filtered, washed with ethanol three times and dried in an oven at 130 °C.

To obtain the mesoporous carbon, the composite was carbonized under N_2 for 3 h at 500 °C, 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C, respectively, and then immersed in a 24% hydrofluoric acid (HF) solution at room temperature for 3 h to dissolve the alumina.

The remaining carbon materials, denoted C-Ax-*T* (Ax denotes the alumina template, *T* denotes the carbonization temperature), were washed repeatedly with water and dried at 110 °C.

2.1.3. Sulfonation

The sulfonation of C-Ax-*T*s was carried out using a previously reported method [25]. In a typical procedure, 0.22 g of 4-aminobenzene sulfonic acid was dissolved in a 0.05 M HCl aqueous solution and cooled to 5 °C. Then, 90 mg of $NaNO_2$ was added to 4-aminobenzene sulfonic acid to produce 4-BDS. The sulfonation was achieved by mixing the 4-BDS solution prepared above with 0.4 g of C-Ax-*T* and holding the suspension at 5 °C for 3 h. After filtration and thorough washing with water, dimethylformamide (DMF) and acetone, the sulfonated mesoporous carbon catalysts were obtained and denoted SC-Ax-*T*.

Amberlyst-15 (Acros Organics) was ground into a powder for use as a control catalyst and was degassed at 100 °C for 7 h before catalytic tests.

2.2. Characterization

Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2100 high-resolution microscope (Japan) at an acceleration voltage of 200 kV. The N_2 sorption analysis was performed on a Micromeritics ASAP 2010 volumetric adsorption system (US) at 77 K. All samples were degassed at 150 °C prior to measurements. The specific surface area was determined using the BET method based on the adsorption data in the relative pressure (P/P_0) range 0.05–0.20. Pore size distribution (PSD) was evaluated by the Barrett–Joyner–Halenda method from the desorption branch of the isotherm (additional note will be present when evaluated from the adsorption branch). The total pore volume was estimated from the amount of N_2 adsorbed at a relative pressure of 0.99.

Fourier transform infrared (FT-IR) absorbance spectra in the range of 600–4000 cm^{-1} were recorded on a Nicolet iN10 FT-IR Microscope (USA) using pure samples. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX0200 powder diffractometer (Japan) using Ni-filtered Cu K_α radiation at 40 kV and 100 mA. ^{13}C solid state NMR spectra were recorded on a Bruker AVANCE III WB Solid-State NMR Spectrometer with a WVT 4 mm CP/MAS double resonance probe head. The spin rate was 8.0 kHz. Sulfur and carbon elemental analyses were carried out on an Elementar Vario Micro Cube (Germany).

2.3. Catalytic tests

The esterification of oleic acid and methanol was performed in a stirred 20-ml autoclave at 65 °C. Typically, 20 mg of solid acid catalyst or 1.82 mg of H_2SO_4 (contain identical H^+ amount to SC-AI-900) was added to 1 g of oleic acid (99%, TCI) and 8 ml of methanol. At selected reaction times, the autoclave was rapidly cooled in a room-temperature water bath. The catalyst was then removed by filtration, and the product was extracted and diluted with *n*-hexane to 100 ml. The yield of methyl oleate was analyzed by gas chromatography equipped with a FID detector and a BD-5 capillary column, where methyl heptadecanoate (AccuStandard, 10.0 mg/l in hexane) was used as the internal standard.

The stability of SC-AI-900 was investigated by performing the esterification reaction six times with 20 mg of SC-AI-900, 1 g of oleic acid and 8 ml of methanol at 65 °C for 1 h. After each use, the catalyst was recycled by filtration and washed with methanol. After recovery, the catalysts were activated in 0.1 M H_2SO_4 at room temperature, washed with deionized water and dried at 110 °C.