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Synthesis of sulfonated porous carbon nanospheres solid acid by a facile chemical activation route

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ABSTRACT

Generally, porous carbon nanospheres materials are usually prepared via a template method, which is a multi-steps and high-cost strategy. Here, we reported a porous carbon nanosphere solid acid with high surface area and superior porosity, as well as uniform nanospheical morphology, which prepared by a facile chemical activation with $ZnCl_2$ using resorcinol-formaldehyde (RF) resins spheres as precursor. The activation of RF resins spheres by $ZnCl_2$ at 400 °C brought high surface area and large volume, and simultaneously retained numerous oxygen-containing and hydrogen-containing groups due to the relatively low processing temperature. The presence of these functional groups is favorable for the modification of $-SO_3H$ groups by a followed sulfonation treating with sulphuric acid and organic sulfonic acid. The results of N_2 adsorption–desorption and electron microscopy clearly showed the preservation of porous structure and nanospherical morphology. Infrared spectra certified the variation of surface functional groups after activation and the successful modification of $-SO_3H$ groups after sulfonation. The acidities of catalysts were estimated by an indirect titration method and the modified amount of $-SO_3H$ groups were examined by energy dispersive spectra. The results suggested sulfonated porous carbon nanospheres catalysts possessed high acidities and $-SO_3H$ densities, which endowed their significantly catalytic activities for biodiesel production. Furthermore, their excellent stability and recycling property were also demonstrated by five consecutive cycles.

1. Introduction

With the depletion of fossil fuel reserves and raising concerns about global warming, the finding and production of sustainable and eco-friendly resources for substituting the fossil fuels are an urgent assignment. Biodiesel is becoming a promising contender for the replacement of petroleum-based fuels due to its renewable, biodegradability and non-toxicity [1–4]. Traditionally, biodiesel is obtained from the transesterification or esterification of vegetable oil and animal fats with short chains alcohols catalyzed by homogeneous base or homogeneous acid. However, homogeneous base catalysts suffer from serious limitation of occurrence of undesirable side reaction such as saponification which brings intricate problem of product separation [5], and homogeneous acids also generate some drawbacks in terms of equipment corrosion in addition to separation and recycling, which severely restrict their commercial industrial application [6]. Consequently, the development and research of novel and efficient catalysts for the preparation of biodiesel are the important industrial challenges.

Solid acid catalysts show the strong potential to take the place of liquid acids because of their advantages of non-corrosion, non-toxicity, water tolerance, and easy separation for reuse. Sulfated solid acid materials, such as SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2, SO_4^{2-}/SnO_2, SO_4^{2-}/Al_2O_3 and so on, were reported and studied extensively their catalytic activities for production of biodiesel [7–10]. Nevertheless, these solid acids possess low surface area, poor porosity, and even worse, sulfate group leaching during the process of biodiesel production. In recent decades, carbon-base solid acids have been focused on much attention due to their inherent chemical inertness, prominent mechanical and thermal stability. Sulfonated carbon material is one of the most promising solid acid catalysts for the preparation of biodiesel [11]. Commonly, sulfonated carbon can be usually prepared by incomplete carbonization of sulfopolycyclic aromatic compounds in sulfuric acid [11] or sulfonation of incompletely carbonized biomass, such as sugar [12] and cellulosic materials [13]. However, these carbon-base solid acids usually possess excellently low surface area and poor porosity, which seriously restrict the improvement of their catalytic properties. To obtain carbon-base solid acids with high surface area and outstanding porosity, sulfonated mesoporous carbon (MC) were

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successfully synthesized, which exhibited connected pore structure, high acid density and excellent catalytic performance in various catalytic applications. For example, Wang et al. obtained sulfonated ordered mesoporous carbon catalysts with a high acid density of 1.93 mmol H^+ g^{-1} and satisfactory catalytic activity [14]. We also reported a sulfonated MC solid acid with an acidity of 1.86 mmol H^+ g^{-1} and improved catalytic performance via the pretreatment of hard-template prepared mesoporous carbon with H_2O_2 [15]. Whereas, the preparation of MC usually needs to use block copolymers, which deeply increase the cost in practical application, furthermore, and the process of preparation is a multi-steps and time-consuming.

Activated carbon with high surface area and developed porosity is generally produced by a simple activation route, which provides an alternative method to prepare sulfonated carbon catalysts with large surface area and well-developed porosity. Activation is divided into physical activation and chemical activation [16]. In physical activation process, the precursors are activated using steam and CO_2 at high heat treatment temperature (>800 °C) [17]. Similarly, the chemical activation with a basic reagent (KOH, NaOH) also requires a relatively high activation temperature (>600 °C) [18]. High activation temperature seriously reduces the amount of active sites, and thus hinders the modification of SO_3H functional groups in the process of sulfonation. Contrary, chemical activation using an acidic reagent ($ZnCl_2$, H_3PO_4, HNO_3 *etc*.) presents several advantages compared with other activation processes, such as the lower activation temperature, larger surface area and higher yield. [19] $ZnCl_2$ uses as a common acidic activation agent, and it has been certified that $ZnCl_2$ activation at temperature less than 600 °C could produce the maximum surface area and optimizing porous structure [20], which favor the grafting of SO_3H functional groups on the surface of carbon materials. Therefore, $ZnCl_2$ activation is a better suited and adopted route for synthesizing porous carbon solid acids with high surface area, superior porosity and high acidity.

In this paper, we successfully prepared monodisperse sulfonated porous carbon nanospheres solid acid by $ZnCl_2$ activation using resorcinol-formaldehyde (RF) resins spheres as precursor. This catalyst not only possesses uniform spherical morphology, high surface area and large volume, but also exhibits high density of $-SO_3H$ groups, high acidity and excellent catalytic activity. The influence of different sulfonation agents on structure and performance of sulfonated porous carbon nanospheres was investigated. Meanwhile, the relation between various reaction parameters and catalytic property of catalyst were also tested.

2. Experimental

2.1. Preparation of materials

2.1.1. Synthesis RF resins spheres

Monodisperse RF resins spheres were synthesized via the Stöber method using resorcinol and formaldehyde solution as precursors [21]. In a typical synthesis, 0.1 mL of ammonia aqueous solution, 8 mL of absolute ethanol and 20 mL of deionized water were mixed and stirred for more than 1 h. Then, 0.2 g of resorcinol was added and continually stirred for 30 min. Subsequently, 0.28 mL of formaldehyde solution was added to the reaction solution and stirred for 24 h at 30 °C, and then the solution was placed in a Teflon-sealed autoclave and heated for 24 h at 100 °C. The products were obtained by centrifugation and then washed repeatedly with distilled water and oven-dried at 100 °C for more than 10 h. The products were carbonized in a N_2 atmosphere at 400 °C for 2 h to get carbon nanospheres material, which was denoted as C sphere.

2.1.2. Synthesis of sulfonated porous carbon nanospheres

Typically, 1.0 g of the obtained RF resins spheres was dispersed into 20 mL of aqueous sulotion containing 4 g of $ZnCl_2$ and then stirred for 3 h. Subsequently, the solution was put into an oven at 110 °C for 10 h to evaporate the solvent completely to obtain $ZnCl_2$-impregnated RF resins spheres material, and then the material was activated in a N_2 atmosphere at 400 °C for 2 h. After cooling down, the activated samples were thoroughly washed with HCl solution (0.5 M) and distilled water. Finally, the material was dried under vacuum at 80 °C for 10 h to obtain porous carbon nanospheres material, which was denoted as PCS.

Subsequently, the obtained PCS materials were sulfonated using concentrated sulfuric acid and *p*-toluenesulfonic acid, respectively. In a typical synthesis, 1 g of PCS sample and 10 mL of concentrated sulfuric acid were mixed in a Teflon–sealed autoclave and maintained at 150 °C for 8 h. Similarly, 1 g of PCS sample and 1 g of *p*-toluenesulfonic acid were mixed in a 20 mL of Teflon-sealed autoclave and maintained at 150 °C for 8 h. Then, these sulfonated materials were washed repeatedly with hot distilled water (>80 °C) until the sulfate ions were no longer detected in the wash water ($BaCl_2$ precipitation test) and were dried at 80 °C for 6 h. The resulting materials were designated as PCS–SO_3H and PCS–Ph-SO_3H, respectively.

For comparison, other traditional solid acid catalysts were prepared, such as sulfonated ion-exchange resins (Amberlyst-15), sulfonated mesoporous silica (SBA-15–SO_3H and SBA-15–Ph-SO_3H); sulfonated ordered mesoporous carbon (CMK-3–SO_3H) and sulfated zirconia/mesoporous silica composite (SZ/MS).

2.2. Characterizations

X-ray diffraction (XRD) patterns were monitored by a DX-2700 diffractometer (Dandong Haoyuan Instrument Co. Ltd., China) using Cu $K\alpha$ radiation ($\lambda=0.15418$ nm) as an X-ray source. Nitrogen adsorption–desorption isotherms were carried out at -196 °C using a micromeritics ASAP 2020 analyzer. Before adsorption, the samples were out-gassed at 200 °C for 6 h. The specific surface area (S_{BET}) was evaluated using the Brunauer–Emmett–Teller (BET) method, and the pore size distributions were calculated according to the Density–Functional–Theory (DFT) method. Fourier transform infrared spectroscopy (FTIR) spectra of a sample in KBr pellet were recorded on a Nicolet Avatar 370 spectrometer. The morphology and pore structure were observed from a JEOL JEM-2100 transmission electron microscope (TEM) with an accelerating voltage of 200 kV and a scanning electron microscope (SEM, Hitachi S-4800). The energy dispersive spectra were obtained using a Hitachi S-4800 field emission scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (EDS).

The number of acid sites was calculated by using an indirect titration method [22,23], which involves an aqueous ion-exchange step of the catalyst H^+ ions with base of $NaHCO_3$, followed by titration of the resulting solution with HCl aqueous solution (0.1 M). In a typical experiment, 30 mg of the catalyst was dispersed in 50 mL of 5×10^{-3} mol L^{-1} $NaHCO_3$ solution, which was stirred for 24 h and separated by filtration. Then 5 mL of filtrate was taken out for titration with 0.1 M of HCl aqueous solution. Titration was performed three times and the average number was reported. The amount of acid groups in the solid acid catalysts was estimated by the $NaHCO_3$ consumed.

2.3. Catalytic testing

Catalytic reactions were performed in a round bottomed flask equipped with a reflux condenser, magnetic stirrer and an oil bath maintained at a specified temperature. In a typical experiment, 0.01 mol of oleic acid (OA) was mixed in anhydrous methanol