Full Length Article

Alcohothermal carbonization of biomass to prepare novel solid catalysts for oleic acid esterification

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GRAPHICAL ABSTRACT

Novel solid acids were synthesized *via* biomass carbonization with supercritical ethanol and subsequent sulfonation of alcohothermal chars. Sulfonic alcohothermal chars exhibited better stability than sulfonated hydrothermal and pyrolytic chars in oleic acid esterification.
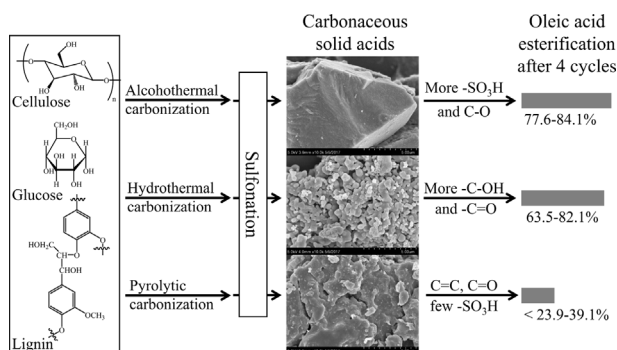
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ABSTRACT

Novel solid acids with improved stability were the first time synthesized through biomass carbonization with supercritical ethanol and subsequent sulfonation of alcohothermal chars. Sulfonic groups and other oxygenated functional groups were easier to be loaded on alcohothermal chars than hydrothermal and pyrolytic chars during sulfonation, and exhibited better stability. For the esterification of oleic acid at 80 °C, sulfonated alcohothermal chars lost 9.0–18.9% of their activity after four reaction cycles, while it was 13.0–30.8% for sulfonated hydrothermal chars and more than 58.4–71.3% for sulfonated pyrolytic chars. As a result, C(HY, E)-S and C(Glu, E)-S still gave esterification yield of > 83% after four reaction cycles. Sulfonated pyrolytic chars exhibited oxygenated functional structure bonded with mainly C=O linkage, which possibly contributed to their worse performance in esterification than sulfonated solvothermal chars.

1. Introduction

Nowadays, biodiesel has drawn more and more attentions as one kind of green renewable fuel, as it provides similar physicochemical properties and combustion performance like conventional petroleum diesel but contains low sulfur and less particulate matter emissions [1].

More importantly, it is easy to be biodegraded. The research of biodiesel production through esterification and transesterification over acid or base catalysts using spent lipids or inedible plant oils is the most welcomed [1], while these waste lipids or oils normally contain high concentration of free fatty acids (FFAs). FFAs seriously hamper base-catalyzed reactions because of saponification, and therefore an additional deacidification step using acid catalyst is necessary before base-catalyzed transesterification [2,3].

Sulfonated carbon-based materials are known as good acid catalysts for deacidification reactions, as they are easy to be synthesized and exhibited excellent activity under mild conditions. However, due to the leaching or deactivation of functional groups, the life of carbon-based solid acid is usually limited, and can be used for less than five runs. Li et al. [4] prepared solid acid catalyst from the sulfonation of rice husk char, which cycled for seven times in the esterification of oleic acid, with biodiesel yield of > 95%. The sulfur content of catalysts after cycle experiments decreased by 22.7%. Wei et al. [5] compared the activity of classical mineral acid H_2SO_4 and sulfonated graphene oxide catalyst. They found that the activity over graphene oxide catalyst was more exceptional than H_2SO_4 in the hydrolysis of cellobiose and Fischer esterification because of hydrophobic cavities with oxygen-containing groups on its surface, which benefited the catalyst to anchor with reactants and promoted the attack of protons. $C-SO_3H$ bond was more stable than $C-O-S$ bond on the graphene sheets. Malins et al. [6] carbonized cellulose by concentrated H_2SO_4 for the catalyst in the esterification of rapeseed oil fatty acids. The conversion over the prepared catalyst decreased to less than 75% in the fifth cycle, and further decreased to 16.3% after nine cycles. This quick decline was ascribed to the products and other impurities adhered on the catalyst surface, while the activity of catalyst could be partly recovered by intensive and sequential washing with ethanol/ethyl acetate and aqueous HCl.

For sulfonated carbonaceous solid acid catalysts, the performance of solid catalysts might have a strong connection to the physical texture and chemical structure of carbonaceous precursors before sulfonation. Here, the sulfonation precursors could be activated carbon [7], starbons [8], graphene oxide [5] and other purchased carbonaceous materials, or were prepared through the carbonization of lignocellulosic biomass or man-made polymerization materials. The physicochemical properties of different biomass materials and carbonization methods surely influenced the physicochemical properties of obtained biochars, and then affected the performance of sulfonated catalysts. For example, hydrothermal carbonization with subcritical water accelerated the carbonization at lower reaction temperature than pyrolysis [9]. The obtained hydrothermal chars showed abundant surface oxygen-containing groups but lower condensation and less porosity than pyrolytic chars [10–12]. As a result, the hydrothermal chars could be sulfonated to carbonaceous solid acids, and achieved excellent results than other sulfonated catalysts in biomass reactions [13–15]. Alcohothermal carbonization under supercritical conditions was another feasible method to produce functional carbonaceous materials [16,17]. However, until now, only one literature by Huang et al. [18] in our group was found to produce more stable solid acid through the reaction of lignin material with supercritical ethanol. Biodiesel yield of > 81% was achieved from oleic acid esterification after 5 cycles. However, it was not sure that the alcohothermal carbonization method could be also used for other biomass materials such as cellulose and glucose, which showed quite different physicochemical properties from lignin.

In this study, cellulose, glucose and two kinds of lignins were used as the materials in alcohothermal carbonization and were subsequently sulfonated to prepare solid acids. The prepared acid catalysts were characterized by various techniques and tested in the esterification of oleic acid with methanol. The performance of sulfonated catalysts derived from supercritical ethanol reactions was also compared with that of traditional hydrothermal and pyrolytic chars. To the best knowledge of the authors, this was the first report that used supercritical alcohothermal methods to produce biochars and sulfonated catalysts from cellulose, glucose and different kinds of lignin materials. The study might offer a reference for the follow-up researches about the application of supercritical solvents (not only water) to influence and change the surface properties of the biomass-derived biochars and the carbonaceous catalysts.

2. Experimental

2.1. Materials

Cellulose (50 μm, CAS 9004-34-6, Product number 251755) was purchased from J&K scientific Ltd. Glucose (AR, CAS 5996-10-1) was bought from Xilong Chemical Co., Ltd. Alkali lignin (named as HY lignin) was from Huayan Chemical Industrial Company (Qidong, Jiangsu, China), while ethanol soluble portion was extracted and used as the material for carbonization [17]. The elemental composition of HY lignin was C 65.55 wt%, H 5.80 wt%, N 0.58 wt%, S 0.59 wt%, while ash content was 0.53%. HY lignin contained more syringyl (S) units. Dealkaline lignin (CAS 9005-53-2, named as TCI lignin) was directly purchased from Tokyo Chemical Industry Co., LTD [17], and characterized as guaiacyl-type, with elemental composition of C 59.93%, H 4.92%, N 0.12%, S 2.15% and ash content of 3.42%. All carbonization materials were dried in an oven at > 80 °C overnight before use.

Concentrated sulfuric acid H_2SO_4 (95–98%) was purchased from Shandian Medicine Co., Ltd (Kunming, Yunnan). Dehydrated ethanol (≥ 99.7%), dehydrated methanol (> 99.5%) and oleic acid (purity of 80%) were bought from Xilong Chemical Factory Co., Ltd. (Shantou, Guangdong). Methyl esters of [palmitate ($C_{16:0}$), linolenate ($C_{16:1}$), stearate ($C_{18:0}$), oleate ($C_{18:1}$), linoleate ($C_{18:2}$), linolenate ($C_{18:3}$) and heptadecanoic acid ($C_{17:0}$)] with purity of ≥ 99% were obtained from Sigma-Aldrich (Shanghai) as the chromatography standards.

2.2. Synthesis of carbon-based solid acid catalysts

For the solvothermal carbonization of biomass [18], 1.5 g material and 15 mL ethanol/deionized water were loaded in Hastelloy (HC-276) autoclave (4596-HPHT, Parr Instrument Co., Moline, IL, 25 mL rated volume and 33.8 mL dead volume), and then reacted at 260 ± 2 °C for 20 h under magnetic stirring (200 rpm) and initial N_2 pressure of 730 ± 10 psi, with heating rate of about 6 °C/min. The pyrolysis of cellulose, HY lignin and TCI lignin was performed in a tubular furnace (SGL-1100, Shanghai Daheng Optics and Fine Mechanics Co., Ltd.) [18]. Solid biomass of 2.5 g was laid in a crucible, heated to 450 °C at rate of 5 °C/min under N_2 flow (30 mL/min) in a tubular furnace (SGL-1100, Shanghai optical precision machinery co., LTD), and reacted for another 5 h. After reactions, the obtained black solids were fully collected, repeatedly washed with ethanol and acetone, grounded and finally dried at 35 °C for at least 24 h. The chars were named as "C-(material, solvent/pyrolysis)". Cel, Glu, TCI and HY referred to cellulose, glucose, TCI lignin and HY lignin, respectively, while E, W and P were the abbreviation of ethanol, water and pyrolysis, respectively.

For the sulfonation of biochars, 1 g char was mixed with 20 mL 98% H_2SO_4, and treated in a Pyrex vial in oil bath at 150 °C for 10 h, with magnetic stirring (500 rpm) [19,20]. After treatment, the obtained sulfonated chars were washed by hot distilled water (≥ 80 °C) repeatedly until the *pH* of filtrate reached about 7. Sulfonated chars were dried at 80 °C for 24 h, grounded, and named as "C-(material, solvent/pyrolysis)-S". For example, C(Cel, E)-S meant that biochar prepared by the carbonization of cellulose in supercritical ethanol at 260 °C for 20 h was sulfonated and used as catalyst.

2.3. Catalyst characterization

Elemental compositions (C, H, N and S) of biochars and sulfonated catalysts were determined by an elemental analyzer (Elementar Vario