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Fabrication of $-SO_3H$ functionalized aromatic carbon microspheres directly from waste *Camellia oleifera* shells and their application on heterogeneous acid catalysis

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ABSTRACT

Sulfonic acid groups functionalized aromatic carbon microspheres (Ar-CMSs–SO_3H) were first successfully fabricated directly from waste *Camellia oleifera* shells by simple steps in the assistance of phloroglucinol. As a heterogeneous solid Brønsted acid catalyst, the as-prepared Ar-CMSs–SO_3H showed considerably high activity because of its numerous spherical microstructure and abundant surface sulfonic acid groups (–SO_3H). Subsequently, the as-prepared Ar-CMSs–SO_3H was applied to the synthesis of biofuels 5-ethoxymethylfurfural (EMF) from biological platform compounds 5-hydroxymethylfurfural (HMF). The catalytic results showed that both sulfonation conditions in the course of Ar-CMSs–SO_3H preparation and catalytic reaction conditions in the course of EMF synthesis had a significant effect on the EMF yield and HMF conversion rate.

1. Introduction

Currently, Brønsted acid catalysts have been widely applied in many areas, such as biofuels development, industrially chemicals production, and drug intermediates synthesis [1–6]. Therefore, the fabrication of reusable heterogeneous solid Brønsted acid catalysts with high efficiency and low cost has important implications for human's sustainable development [7–9]. In recent years, many heterogeneous solid Brønsted acid catalysts with complex structures were prepared using expensive raw materials through a tedious step. However, the high production costs severely limit the practical application of these solid acid catalysts [10–12].

In order to reduce the production cost, some researchers prepare $-SO_3H$ modified activated carbon (AC–SO_3H) solid acid catalyst by sulfonation reaction directly using waste biomass as raw materials [13–15]. However, bulk structures and insufficient sulfonation sites severely inhibit the catalytic activity of AC–SO_3H because of the large mass transfer resistance in the course of catalytic reaction and few number of $-SO_3H$ active sites. Hydrothermal carbonization is a promising strategy for the synthesis of carbon materials directly from waste biomass [16–19]. Carbon materials obtained by hydrothermal carbonization process typically exhibit spherical microstructure and aromatic carbon framework, which are suitable for the preparation of heterogeneous solid Brønsted acid catalyst by sulfonation reaction. Specifically, spherical microstructure and aromatic carbon framework facilitates the introduction of $-SO_3H$ by sulfonation reaction. Our previous work has shown that aromatic carbon microspheres can be directly fabricated using waste *Camellia oleifera* shells by carefully controlling the hydrothermal carbonization conditions [20]. However, preparation of aromatic carbon microspheres with wide-range and high-quality directly from waste crude biomass is really a hard technical challenge.

In recent years, the development of renewable biofuels has been widely concerned by many researchers with the growing depletion of non-renewable energy [21–23]. 5-Ethoxymethylfurfural (EMF) is considered an attractive liquid biofuel with an energy density of $8.7\,kW\,h\,L^{-1}$, which is greater than that of ethanol ($6.1\,kW\,h\,L^{-1}$) and similar to that of gasoline ($8.8\,kW\,h\,L^{-1}$) and diesel ($9.7\,kW\,h\,L^{-1}$) [24]. Compare with glucose and fructose raw materials, the synthesis of EMF directly from 5-hydroxymethylfurfural (HMF) can be achieved in a high yield by etherification with homogeneous acid catalysts (e.g., H_2SO_4, HNO_3, and HCl) because the isomerization and intramolecular dehydra-

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tion reaction steps are avoided [25]. However, as is well known, homogeneous acid catalysis suffer from some serious drawbacks, such as difficulty in recovering the catalyst, causing environmental pollution, corroding the equipment [26,27].

In this article, $-SO_3H$ functionalized aromatic carbon microspheres (Ar-CMSs–SO_3H) were first successfully fabricated directly from waste *Camellia oleifera* shells by simple steps in the assistance of phloroglucinol. The as-prepared Ar-CMSs–SO_3H heterogeneous solid Brønsted acid catalyst showed a considerably high activity owing to its numerous spherical microstructure and abundant surface $-SO_3H$. Subsequently, the as-prepared Ar-CMSs–SO_3H solid Brønsted acid catalyst was applied to the synthesis of biofuels EMF from biological platform compounds HMF. The catalytic results showed that both sulfonation conditions in the course of Ar-CMSs–SO_3H preparation and catalytic reaction conditions in the course of EMF synthesis had a significant effect on the EMF yield and HMF conversion rate. The production costs of EMF are expected to be significantly reduced due to the excellent acid catalytic activity and low manufacturing costs of as-prepared Ar-CMSs–SO_3H heterogeneous solid Brønsted acid catalyst.

2. Experimental

2.1. Chemicals and reagents

Waste *Camellia oleifera* shells (abbreviated WCOSs) were collected from Jiangxi Green Sea Oil Co., Ltd, China. Crude WCOSs were dehydrated, crushed, and then passed through a 200-mesh sieve to prepare WCOSs powder. Activated carbon (abbreviated AC) was prepared by calcinations the WCOSs powder at 450 °C for 5 h at a heating rate of 5 °C/min under argon protection. Multi-walled carbon nanotubes (specific surface area >200 $m^2 g^{-1}$, abbreviated MWCNTs) were purchased from Chengdu Organic Chemicals Co., Ltd. 5-Hydroxymethylfurfural ($C_6H_6O_3$, 98%, abbreviated HMF) was purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. 5-Ethoxymethylfurfural ($C_8H_{10}O_3$, 97%, abbreviated EMF) and phloroglucinol ($C_6H_6O_3$, $\geq$99.0%) were purchased from Shanghai Macklin Biochemical Co., Ltd. All chemicals were used without further purification. Ultra-pure water was used in the high-performance liquid chromatography analysis. Deionized water was used in the catalyst preparation.

2.2. Preparation

In a typical synthesis, 1.6 g of WCOSs powder and 0.4 g phloroglucinol were uniformly dispersed in 60 mL of deionized water by using a 500 W ultrasonic crasher for 1 h. The resulting suspension was stirred for 6 h at room temperature and then subjected to hydrothermal treatment at 230 °C for 24 h at a heating rate of 1 °C/min. The byproducts of the hydrothermal carbonization reaction were removed through extraction by using water as solvent. After drying at 60 °C for 24 h, the final aromatic carbon microspheres products were obtained and denoted as Ar-CMSs. Subsequently, 0.2 g of Ar-CMSs was placed in a 50 mL round bottom flask and then 11.04 g of concentrated H_2SO_4 was added. After sulfonation at 110 °C for 6 h, the resulting suspension was diluted with 1000 mL deionized water and then filtration. After washing with water to neutral and drying, the final $-SO_3H$ functionalized Ar-CMSs heterogeneous solid Brønsted acid catalyst was obtained and denoted as Ar-CMSs–SO_3H. The above Ar-CMSs–SO_3H catalyst was prepared under the optimum sulfonation conditions. For comparison, Ar-CMSs–SO_3H was also prepared under different sulfonation temperature (90, 110, 130, and 150 °C), sulfonation time (3, 6, 9, and 12 h), and adding amount of concentrated H_2SO_4 (5.52, 11.04, 16.56, and 22.08 g). In addition, AC–SO_3H and MWCNTs–SO_3H were prepared by the same method but use AC and MWCNTs as supports.

2.3. Characterizations

Field emission scanning electron microscopy (FESEM) images were recorded using a Nova NanoSEM450 field emission scanning electron microscope. The chemical compositions and elemental mappings of the samples were determined by energy-dispersive X-ray (EDX) spectrometer equipped on FESEM. Nitrogen gas porosimetry measurements were performed on a Quantachrome NOVA 2000e surface area and porosity analyzer after the samples were outgassed under a vacuum at 70 °C for 20 min and 150 °C for 6 h, respectively. X-ray diffraction (XRD) patterns were obtained using a D8ADVANCE diffractometer via Cu-$K\alpha$ radiation. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iS5 FTIR apparatus. Raman scattering spectra were recorded on a Jobin-Yvon HR 800 instrument with an Ar+ laser source of 488 nm wavelength in a macroscopic configuration. X-ray photoelectron spectra (XPS) was performed using an Axis Ultra DLD instrument with a monochromated Al-*Ka* source at a residual gas pressure of less than 10^{-8} Pa. All the binding energies were referenced to the C 1s peak at 285 eV of the surface adventitious carbon. Thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses were conducted under N_2 flow by using a TGAQ 5000 instrument. A sample was placed in a sample pan and heated from room temperature to 1150 °C at a heating rate of 10 °C/min. Loadings of $-SO_3H$ in the as-prepared catalysts were determined on a Flash EA-1112 elemental analyzer.

2.4. Catalytic test

The etherification of HMF with EtOH to produce EMF was carried out in a 50 mL round bottom flask at 80–140 °C for 4–28 h under nitrogen protection. A typical experiment included a mixture of 63 mg of HMF, 25 mL of EtOH, and 50 mg of catalyst. After catalytic reaction, 0.1 mL of suspension was extracted and diluted tenfold with acetonitrile. After centrifugation, 0.1 mL upper reaction solution was taken out and then further diluted tenfold with acetonitrile. The EMF yield and HMF conversion rate were analyzed using an Agilent 1100 series high-performance liquid chromatography (HPLC): C_{18} column, DAD detector ($\lambda = 280$ nm), and acetonitrile/water (30/70 v/v) was used as a mobile phase at a flow rate of 1.0 mL/min. The byproducts in the synthesis of EMF from HMF were identified by Agilent 1100 series high-performance liquid chromatography/mass spectrometry detector (HPLC/MSD Trap/VL).

3. Results and discussion

3.1. Characterization

3.1.1. Morphology

The morphology of as-prepared Ar-CMSs, Ar-CMSs$-SO_3H$, and AC–SO_3H was characterized by FESEM observation and the elemental analysis of as-prepared Ar-CMSs$-SO_3H$ was performed through EDX spectrometer equipped on FESEM. From Fig. 1a we can clear observe that carbon microspheres with numerous spherical microstructures were successfully fabricated through hydrothermal carbonization of WCOSs in the assistance of phloroglucinol. Our previous work has proved that the successful fabrication of aromatic carbon microspheres directly from WCOSs could be attributed to the synergistic effect between the components in WCOSs through nucleation growth and direct condensation mechanisms [20]. Ryu et al. think that the dehydrated products of mono-saccharides can immediately react with phloroglucinol,