



Synthesis porous carbon-based solid acid from rice husk for esterification of fatty acids



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ABSTRACT

A porous carbon solid acid was synthesized from biomass rice husk by incompletely carbonization, sodium hydroxide leaching and concentrated H₂SO₄ sulfonation. The solid acid was characterized by XRD, FT-IR, N₂ adsorption-desorption and solid-state NMR spectroscopy. The characterization results reveal that the carbon solid acid shows ultra high surface area of 1233 m²/g and stronger acid strength than that of HZSM-5(Si/Al = 38) zeolite. The catalytic performance was tested by the esterification of oleic acid with methanol. The results indicate that this solid acid catalyst is an excellent catalyst compared with other conventional solid acid.

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1. Introduction

Currently industrial esterification processes are carried out by the catalysis of homogeneous Brønsted acids such as sulfuric acid. However, these homogeneous acid catalysts are difficult to be separated, and also cause serious environmental and corrosion problems. Recently, the application of solid catalysts instead of homogeneous liquid catalysts has been paid much attention in view of their convenience of separation and lack of corrosion or toxicity problems [1–5].

Due to the low densities of effective acid sites, inorganic-oxide solid acids such as zeolite or composite oxide cannot satisfy adequate requirement in esterification reactions [6,7]. Although strong acidic ion-exchange resins such as Nafion contain abundant sulfonic acid groups (–SO₃H), that function as strong acid sites, their catalytic activities are generally much lower for their very low surface area [8]. These limitations have restricted the practical utility of acidic cation-exchangeable resins. Recently, a new type of sulfonated carbons derived from incomplete carbonization of simple natural product such as sugar, starch or cellulose, has been reported to show better catalytic performance for esterification of fatty acids, and higher stability than sulfonated mesoporous silica

[5,9,10]. However, such materials were nonporous and exhibited low surface area, which may limit the accessibility to the active sites. The carbon solid acid with unique porous properties is synthesized here as an ideal candidate for the development of the high active catalyst.

Every year three million tons of rice husk (RH) are produced in China. So far, such a resource is mainly considered as a waste, and consequently burnt without any profit, except in a few cases of domestic uses for cooking and heating [11]. The main objective of the present work was to prepare carbon based solid acid from rice husk by incomplete carbonization, leaching and sulfonation. The solid acid catalyst was also characterized by X-ray diffraction (XRD), Fourier-transform infrared spectra (FT-IR), scan electron microscope (SEM) and solid state nuclear magnetic resonance (NMR) spectroscopy. The research results will be helpful to obtain the fundamental information of the roles of surface functional groups in the solid acid, which is crucial in the design of a novel carbon-based solid acid for industrial application.

2. Experimental

2.1. Sample preparation

Rice husk from a grain depot in Wuhan was used as raw material. Rice husk was calcined at 450 °C for 15 h under a N₂ flow, and then followed by grinding and leaching with 1 M NaOH at 100 °C K

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for 5 h at the ratio of solid to liquid of 1 g: 10 ml to remove silica in the rice husk. After carefully washing with deionized water, the dried rice husk carbon was sulfonated with concentrated H_2SO_4 (98wt%), at 150 °C under a N_2 flow for 8 h at the ratio of solid to liquid of 1 g: 10 ml. At last, the mixture was diluted with deionized water, filtered, washed thoroughly, and dried at 120 °C for 12 h to obtain the carbon solid acid catalyst.

The elemental analysis of the rice husk is listed in Table 1.

Recycling experiments were performed to determine the catalytic stability of the solid acid catalysts. At the end of each esterification cycle, the catalyst was centrifuged, washed with ethanol and dried at 105 °C for 2 h before reusing.

2.2. Sample characterization

The concentration of acid sites on the catalysts was determined by titration method in aqueous solution. One gram of the sample was placed in 50 ml of 0.05 M NaOH solution. The vials were sealed and shaken for 24 h and then 5 ml of the filtrate was pipetted and the excess of base was titrated with HCl. The numbers of acidic sites were calculated from the amount of NaOH that reacted with the catalyst.

Surface area and porosity properties of samples were evaluated by N_2 adsorption/desorption isotherms carried out on a Micromeritics ASAP 2020 sorption analyzer. Prior to the adsorption–desorption measurements, all the samples were degassed at 150 °C in N_2 flow for 12 h.

X-ray diffraction (XRD) was performed with a Philips X'PERT-Pro-MPD diffractometer, operating with $\text{Cu K}\alpha$ radiation (40 kV, 30 mA) and Ni filter.

All the NMR experiments were carried out at 9.4 T on a Varian Infinityplus-400 spectrometer with resonance frequencies of 400.12, 100.4 MHz for ^1H , ^{13}C , respectively. The 90° pulse widths for ^1H , ^{13}C were measured to be 3.7, 4.4 μs , respectively. The chemical shifts were referenced to tetramethylsilane (TMS) for ^1H , to hexamethylbenzene (HMB) for ^{13}C , respectively. The magic angle spinning rate was 5 kHz.

For the adsorption of probe molecules 2- ^{13}C -acetone, the samples were kept at 400 °C under the vacuum less than 1×10^{-3} Pa for at least 8 h. The adsorption of 2- ^{13}C -acetone was performed at room temperature with a loading of ca. 0.1 mmol per gram catalyst.

The various solid acids were employed as catalysts for the esterification of oleic acid with methanol. The $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst in this case was prepared using the classic two-step method [12]. The HZSM-5 zeolite ($\text{Si}/\text{Al} = 38$) and Nafion NR 50 were pursued from Shanghai Guoyao Corporation. Prior to the reaction, all the catalysts were dried at 120 °C for 5 h. The experiments were carried out by mixing oleic acid with methanol in a flask equipped with a reflux condenser, an oil bath and a magnetic stirrer. Once the mixture had reached the reaction temperature, the catalyst was added. The mixtures were withdrawn and centrifuged to separate the solution from the catalyst. Analysis of the reaction mixtures was carried out in an HP 6890 series gas chromatograph equipped with a flame ionization detector (FID).

3. Results and discussion

Fig. 1 illustrates the XRD patterns of rice husk, rice husk carbon and the carbon solid acid. The diffraction peak arising at around

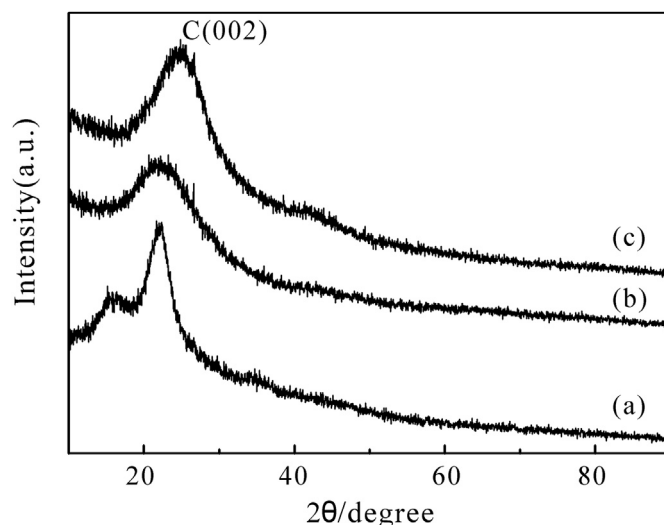


Fig. 1. XRD patterns of (a) rice husk; (b) rice husk carbon and (c) the carbon solid acid.

$2\theta = 25^\circ$ is corresponded to the diffraction of C (002) [13]. Compared with that of rice husk, the peak of the impurities ($2\theta = 18^\circ$, silica) was disappeared in the spectrum of rice husk carbon and the solid acid. According to Dahn's conclusion [14], it indicates that the solid acid and rice husk carbon consist of a single layer of polyhexagonal carbon atoms after leaching, implying that the BET surface area of the solid acid may be dramatically high.

FT-IR spectroscopy was employed to explore the changes in functional groups induced by preparation process. It shows that the difference of the spectroscopy is mainly the bands of oxygen functionalities in the samples (Fig. 2). Two bands at 1039 and 1182 cm^{-1} in the solid acid can be assigned to the SO_2 asymmetric and symmetric stretching modes, respectively [5]. It indicates that sulfonic acid group was found on the surface of the sulfonated solid acid. The band at 1700 cm^{-1} can be attributed to the C=O stretching mode of the $-\text{COOH}$ groups, while the broad band centered at 3429 cm^{-1} was assigned to the $-\text{OH}$ stretching mode [5]. The band at 1647 cm^{-1} can be attributed to the C=C stretching mode of the samples. Therefore, $-\text{COOH}$, $-\text{SO}_3\text{H}$ and $-\text{OH}$ were found as the functional groups on the solid acid.

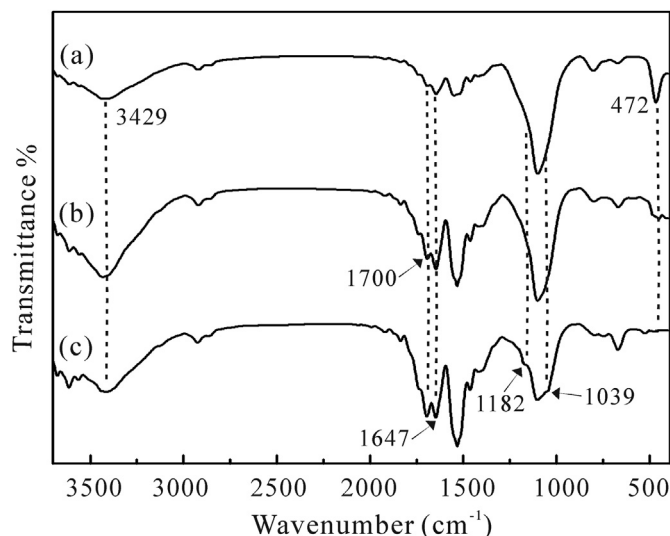


Fig. 2. FT-IR spectra of (a) rice husk, (b) rice husk carbon and (c) the carbon solid acid.

Table 1
Element analysis of rice husk (wt%).

| Sample | C | H | O | N | S |
|-----------|-------|------|------|------|------|
| Rice husk | 88.15 | 5.20 | 3.55 | 1.84 | 1.26 |

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