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Synthesis, characterization and acid catalysis of solid acid from peanut shell

Danlin Zeng*, Shenglan Liu, Wanjun Gong, Guanghui Wang, Jianghua Qiu, Hongxiang Chen

College of Chemical Engineering and Technology, Hubei Key Laboratory of Coal Conversion and New Carbon Material, Wuhan University of Science and Technology, Wuhan 430081, China

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ABSTRACT

A strong Brønsted solid acid was synthesized by sulfonation of the partially carbonized agricultural biowaste peanut shell. The acidity of the Brønsted solid acid was characterized by X-ray diffraction (XRD), Fourier-transform infrared spectra (FT-IR) and solid-state nuclear magnetic resonance (NMR) spectroscopy. The characterization results show that sulfonation on the peanut shell carbon produces a carbon based solid acid containing three functional Brønsted acid sites: weak acidic —OH groups, strong acidic —COOH and —SO$_3$H groups. The acid strength of the solid acid is stronger than that of HZSM-5(Si/Al = 75), but still weaker than that of 100% H$_2$SO$_4$. The catalytic reaction tests indicate that this solid acid catalyst exhibits high activity and excellent recyclability for biodiesel production.

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1. Introduction

Liquid acids such as H$_2$SO$_4$, H$_3$PO$_4$ and HF are the most widely used acid catalysts in chemical industry over the past decades. However, the usage of these homogeneous acids cause lots of serious problems such as hazards in transportation, difficulties in separation, waste acid pollution and equipment corruption [1–4]. The development of environmentally friendly chemical processes has boosted the use of solid acid catalyst due to its convenience in separation and recyclability. Up to now, significant attention has been given to the solid acids such as silica-alumina [5], zeolites [6] and sulfated metal oxides [7]. But the catalytic activity and acidic strength of these acids are still lower than those of homogeneous acids [8]. These disadvantages greatly limited their application in industrial process.

Recently, some carbon-based solid acids prepared from naphthalene or natural products such as sugar were studied by many researchers [9–13]. As environmentally benign catalysts, the carbon-based solid acids show excellent efficiency on the biodiesel production and other esterification reactions [14–17]. But unfortunately, the structure, acid type and strength of the acid sites

on the carbon-based solid acids are still poorly understood. Thus, the acid properties of the solid acid are necessary to be investigated in detail for further industrial application. As an agricultural byproduct with low cost and sufficient supply, peanut shell is an excellent source for preparing solid acid catalyst of high quality. Solid-state nuclear magnetic resonance (NMR) spectroscopy combined with probe molecule technique is a powerful tool to measure the acidity of solid acids [18,19]. Herein, we used agricultural biowaste peanut shell as the raw material to prepare a strong solid Brønsted acid catalyst. We also studied the acid properties of the solid acid by using trimethylphosphine (TMP), trimethylphosphine oxide (TMPO) and 2-^{13}C-acetone as probe molecules as well as ^{13}C cross-polarization (CP)/magic angle spinning (MAS) NMR and FT-IR spectroscopy.

2. Experimental

2.1. Sample preparation

The peanut shell derived solid acid was prepared by sulfonation of the partially carbonized peanut shell. At first, the dried peanut shell was calcined at 723 K for 15 h under a N$_2$ flow to obtain the peanut shell carbon, and then followed by grinding and sulfonation with concentrated H$_2$SO$_4$ at 473 K under a N$_2$ flow for 10 h at a ratio of solid to liquid of 1 g:100 ml. At last, the mixture was diluted with

* Corresponding author. Tel.: +86 27 6886 2181; fax: +86 27 6886 2181.
 E-mail address: zdanly@163.com (D. Zeng).

deionized water, filtered, washed, and then dried at 393 K for 10 h to obtain the solid acid.

Refined cottonseed oil was used as the raw material for the production of biodiesel. According to GC (HP6890) analysis, it is composed of four types of fatty acid triglycerides: palmitic acid triglyceride (29.33 wt%), stearic acid triglyceride (0.88 wt%), oleic acid triglyceride (13.35 wt%) and linoleic acid triglyceride (56.35 wt%). Its average molecular weight is 848.

2.2. Sample characterization

X-ray diffraction (XRD) was performed with a Philips X'PERT-Pro-MPD diffractometer, operating with Cu Kα radiation (40 kV, 30 mA) and Ni filter.

The FT-IR spectra were recorded on Impact 410, Nicoletspectrometer with a resolution of $2 \, cm^{-1}$. 12 mg of each sample was pressed (at $2 \, ton/cm^2$ pressures for 15 min) into a self-supported wafer 16 mm in diameter. The wafers were heated at 200 °C in an IR cell under vacuum ($<10^{-3}$ Pa) for 4 h before the IR spectra of the samples were measured.

For the adsorption of probe molecules trimethylphosphine (TMP), the samples were kept at 673 K in the vacuum of less than 1×10^{-3} Pa for at least 8 h. The adsorption of TMP was performed at room temperature with a loading of *ca.* 0.1 mmol per gram catalyst. The adsorption procedure of trimethylphosphine oxide (TMPO) was different from that of TMP. About 0.5 g of dehydrated sample was mixed with 3 ml CH_2Cl_2 solution containing 0.1 M TMPO in a glove box before the mixture was stirred for 3 h by an ultrasonic shaker, equilibrated for 5 h, and then evacuated under vacuum to remove CH_2Cl_2 and physorbed TMPO before NMR measurements. To minimize the possible chemical exchange and polymerization, the adsorption of 2-^{13}C-acetone was performed at room temperature with a loading of *ca.* 0.1 mmol per gram catalyst.

All the solid state NMR experiments were carried out at 9.4 T on a Varian Infinityplus-400 spectrometer with resonance frequencies of 400.12, 100.4, 161.9 MHz for ^{1}H, ^{13}C, ^{31}P, respectively. The 90° pulse widths for ^{1}H, ^{13}C, ^{31}P were measured to be 3.7, 4.4, 3.6 μs, respectively. The chemical shifts were referenced to tetramethylsilane (TMS) for ^{1}H, to hexamethylbenzene (HMB) for ^{13}C, and to 85% H_3PO_4 solution for ^{31}P, respectively. Repetition times of 6 s for ^{1}H, 60 s for ^{31}P single-pulse experiments were used. The magic angle spinning rate was 5 kHz. For the cross-polarization (CP)/magic-angle spinning (MAS) NMR experiments, the Hartmann-Hahn condition was achieved by using hexamethyl-benzene (HMB), with a contact time of 2.0 ms and a repetition time of 2.0 s.

The concentration of acid sites on the solid acid 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 used NaOH solution.

Surface area and porosity properties of samples were evaluated by N_2 adsorption/desorption isotherms carried out at 77 K 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.

2.3. Catalytic reaction procedure

Transesterification reaction of cottonseed oil and methanol was carried out in an autoclave. An electronic temperature controller was used to maintain the reaction temperature. The reaction mixture consisted of cottonseed oil, methanol and the catalyst. For a typical cycle, the cottonseed oil and methanol were added into the reactor at first. When the designated temperature was reached, the catalyst was added into the reactor. The reaction was started by stirring with a magnetic stirrer. When the reaction was over, the mixture was placed in a separation funnel and allowed for phase separate for 5 h. Then the mixture was separated into two layers. The oil phase consisted of fatty acids methyl (biodiesel). The biodiesel product was quantitatively analyzed with methyl salicylate as internal standard by HP6890 GC, equipped with a flame ionization detector (FID).

Recycling experiments of cottonseed oil transesterification with methanol were performed to determine the catalytic stability of the solid acid. At the end of each transesterification cycle, the catalyst was centrifuged, washed with ether and dried before reuse. The spent solid acid was obtained after 5 recycle times. Then the spent solid acid was washed with ether, dried at 120 °C under the vacuum, impregnated in 1 M H_2SO_4 for 5 h, washed with deionized water and dried at 120 °C to obtain the regenerated solid acid. Pore structure, total acid density of peanut shell carbon and the solid acid (fresh, spent and regenerated) are listed in Table 1.

The following properties of the biodiesel product from cycle 1 to cycle 4 were determined: water content, kinematic viscosity, acid value, cetane number, free glycerin, total glycerin and sulfur content. The determined method is according to EN 14214.

3. Results and discussion

3.1. Catalyst characterization

The powder XRD patterns of the samples are shown in Fig. 1. The XRD pattern exhibits one broad ($2\theta = 20$–$30°$) and another relatively weak ($2\theta = 40$–$50°$) diffraction peak, corresponding to the diffraction of C (0 0 2) and C (0 0 4), respectively. It is indicated that the prepared carbon materials are composed of aromatic carbon sheets [20]. Consequently, we can infer that the solid acid is an amorphous carbon catalyst with relatively high BET surface area.

FT-IR spectra were employed to characterize the functional groups on the peanut shell carbon and the solid acid. As shown in Fig. 2, two bands at 1048 and $1178 \, cm^{-1}$ in the spectra of peanut shell solid acid can be assigned to the SO_2 asymmetric and symmetric stretching modes, respectively [21]. FT-IR results illustrate that the sulfonic acid group is formed on the surface of the solid acid. The band at $1720 \, cm^{-1}$ can be attributed to the C=O stretching mode of the —COOH groups [21]. Obviously, —COOH and —SO_3H are present as functional groups on the surface of the solid acid. Fig. 3 shows the ^{13}C CP/MAS NMR spectra of peanut shell, peanut shell carbon and the solid acid. The signals at 105, 73, 85, 65, 75 and

Table 1
Textural properties, S content and total acid density of the samples.

Sample	$S_{BET}(m^2/g)$	V_{tot} (cm^3/g)	D (nm)	S content (mmol/g)	Total acid density (mmol/g)
Peanut shell carbon	10.23	0.356	30.33	0.20	0.22
Solid acid (fresh)	12.35	0.342	39.25	3.25	6.85
Solid acid (spent)	4.26	0.309	42.35	3.18	3.42
Solid acid (regenerated)	10.25	0.323	36.23	3.20	6.12

S_{BET}, specific surface area from BET method; V_{tot}, total pore volume; D, average pore diameter. S content, elemental (S) content in the sample, measured by elemental analysis.