Applied Catalysis A: General 469 (2014) 284–289

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

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

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ARTICLE INFO

Article history:
Received 26 June 2013
Received in revised form
16 September 2013
Accepted 21 September 2013
Available online 29 September 2013

Keywords:
Solid acid
Peanut shell
Acidity
Biodiesel

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_3H 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_2SO_4. The catalytic reaction tests indicate that this solid acid catalyst exhibits high activity and excellent recyclability for biodiesel production.

1. Introduction

Liquid acids such as H_2SO_4, H_3PO_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_2SO_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

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http://dx.doi.org/10.1016/j.apcata.2013.09.038

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 hexamethylbenzene (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.

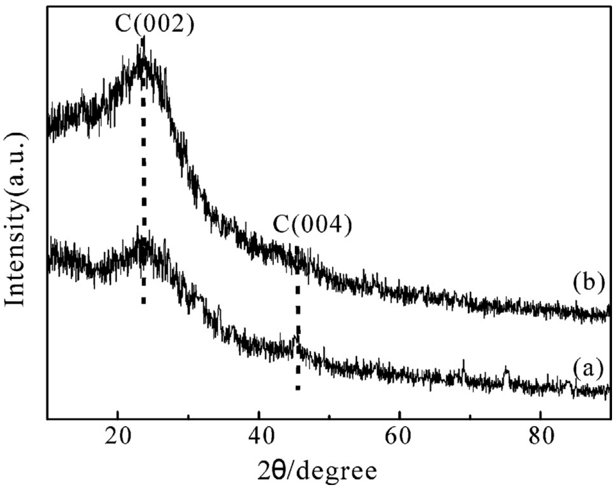


Fig. 1. XRD patterns of (a) peanut shell carbon and (b) the solid acid.

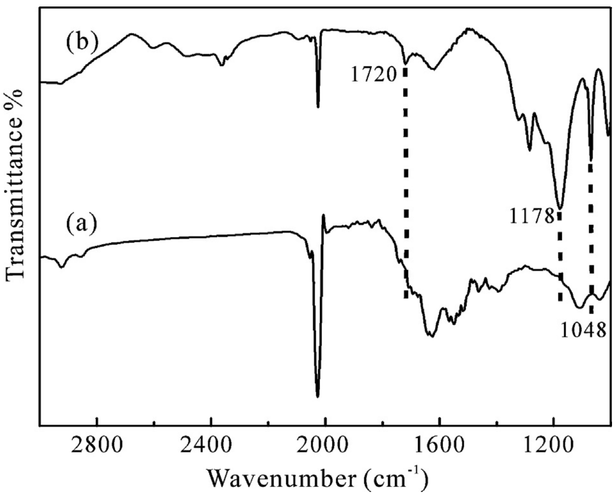


Fig. 2. The FT-IR spectra of (a) peanut shell carbon and (b) the solid acid.

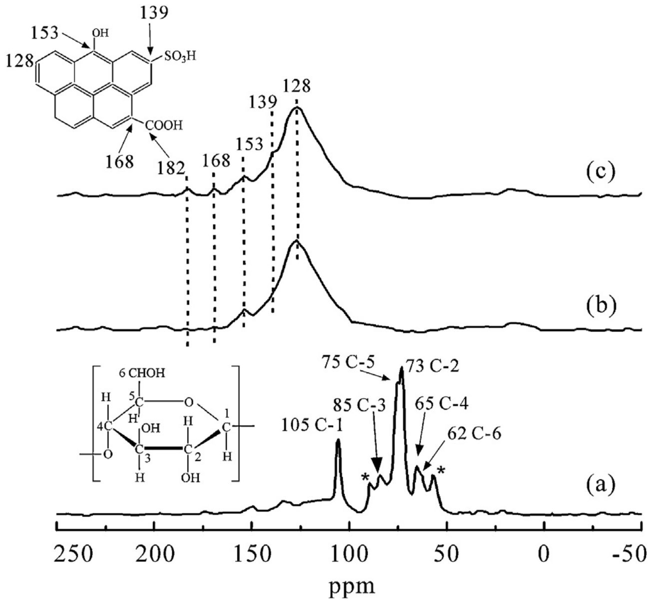
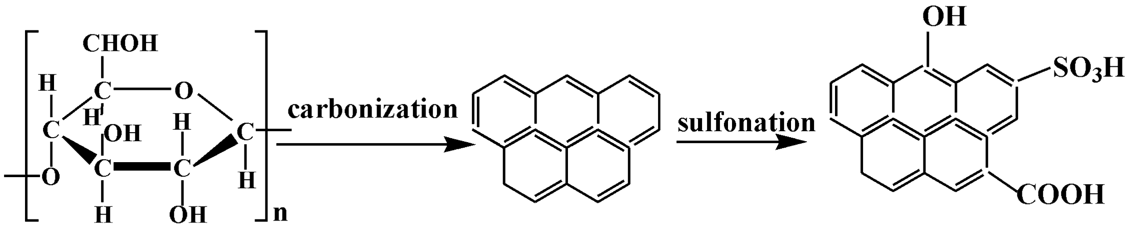


Fig. 3. ^{13}C CP/MAS NMR spectra of (a) peanut shell, (b) peanut shell carbon and (c) the solid acid. The asterisk denotes spinning sidebands.

62 ppm can be assigned to C1, C2, C3, C4, C5 and C6 of the D-glucose units in peanut shell, respectively. The peaks at 128 and 153 ppm are due to polycyclic aromatic carbon atoms and aromatic carbon bonded to phenolic OH, respectively [22]. It is noteworthy that the signals at 139 ppm (aromatic carbon bonded to the SO_3H group), 168 ppm (carbon atom bonded to the COOH group) and 182 ppm (carbon atom in the COOH group) can be clearly observed in the solid acid [23]. In addition, the FT-IR results have confirmed the existence of SO_3H groups in Fig. 2. Consequently, it can be concluded that the SO_3H groups and COOH groups are successfully formed on the solid acid (Scheme 1).

The type and strength of acid sites are the fundamental properties of the solid acid. Trimethylphosphine (TMP) is an extensively used probe molecule to discriminate Lewis and Brønsted sites in the solid acids [24]. The ^{31}P single pulse spectrum obtained after adsorbing TMP onto the surface of peanut shell solid acid is shown in Fig. 4a. Two peaks at −3 and −60 ppm are observed in the spectrum. The former can be unambiguously assigned to TMP adsorbed on the Brønsted acid sites and the latter is generally originated from physisorbed TMP. It is obvious that negligible amount of Lewis sites exist in the peanut shell solid acid since no signal appears between −32 and −58 ppm [25]. Therefore, the three resonances at 56, 72 and 82 ppm in the ^{31}P NMR spectrum of TMPO adsorbed on the solid acid can be all attributed to the Brønsted sites in the solid acid (Fig. 4b) [26]. The resonance at 45 ppm is ascribed to the physisorbed TMPO [26], while the other three signals at 56, 72 and 82 ppm can be assigned to TMPO adsorbed on the weakly acidic OH groups, the Brønsted acid sites —COOH and —SO_3H groups, respectively [27]. The large chemical shift of 82 ppm indicates that the acid strength of the solid acid is stronger than that of HZSM-5 with the Si/Al ratio of 75 (having a ^{31}P chemical shift of 75 ppm) [28]. Acetone-2-^{13}C is a reliable NMR probe molecule for determining the relative acid strength of the solid acid [29]. Three peaks at 219, 229 and 243 ppm are observed in the ^{13}C CP/MAS spectrum of acetone-2-^{13}C adsorbed on the solid acid (Fig. 4c). Similarly, the signal at 219 ppm is due to the relatively weaker acidic —OH groups and resonance at 229 is due to the strong Brønsted acid sites (—COOH groups). The 243 ppm signal corresponds to Brønsted sites (SO_3H groups) with an acid strength weaker than that of 100% H_2SO_4 (having a ^{31}C chemical shift of 245 ppm) [30].



Scheme 1. Schematic illustration of the preparation of solid acid.

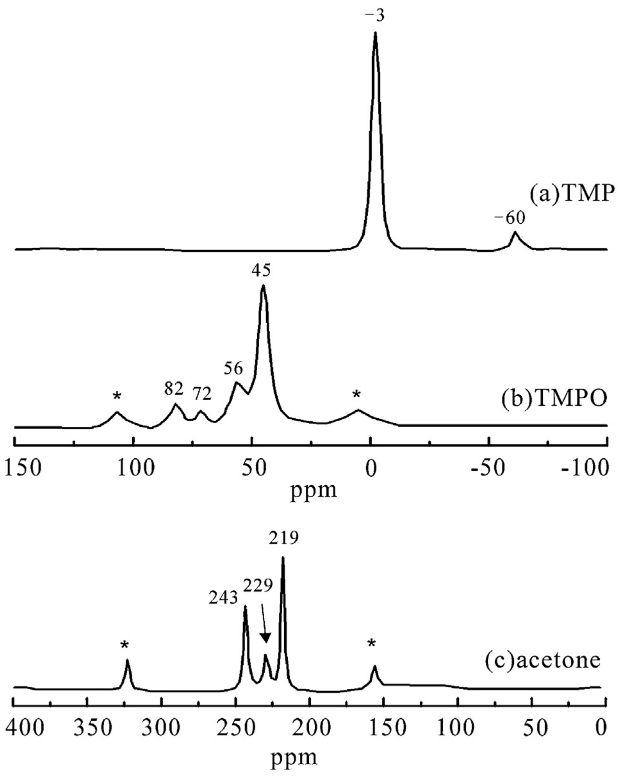


Fig. 4. ^{31}P single pulse with ^{1}H decoupling MAS spectra of (a) TMP and (b) TMPO adsorbed on the solid acid; (c) ^{13}C CP/MAS NMR spectra of 2-^{13}C-acetone (0.2 mmol/g) adsorbed on the solid acid. The asterisk denotes spinning sidebands.

3.2. Catalytic reaction

Fig. 5 shows the influence of methanol/oil molar ratio on the conversion of transesterification reaction. It is known that transesterification reaction is an equilibrium reaction. As an equilibrium reaction, an excess of methanol will increase the conversion by pushing this equilibrium to the right. The conversion rate increases as the methanol/oil molar ratio increases, and the best result of the molar ratio is 9:1 based the experimental data. When the methanol/oil molar ratio is less than 9:1, the reaction is incomplete. While when the methanol/oil molar ratio is more than 9:1, excess methanol will lead to unfavorable glycerolysis reaction of biodiesel and thereby decrease the conversion. Hence, the best result of methanol/oil molar ratio is 9:1.

Fig. 6 shows the influence of catalyst amount on the conversion of transesterification reaction. As the catalyst amount increases from 0.5% to 2.0%, more active sites are available to catalyze the reaction, which will increase the conversion rate. While the conversion rate increase slowly and even decrease when the catalyst amount is higher than 2.0%. From the above results, a catalyst amount of 2 wt% was chosen in the transesterification reaction.

Fig. 7 shows the influence of temperature on the conversion rate. The results showed that the oil conversion increased steadily from 42.3% to 90.2% upon increasing the reaction temperature from 65 to 85 °C. As is known to all, when the reaction temperature increases, the solubility of methanol in oil is enhanced. Consequently, the conversion rate of the reaction of cottonseed oil with methanol increases. Thus, 85 °C is the optimal temperature in the present catalytic system.

The influence of reaction time has also been investigated (Fig. 8). It can be seen that the conversion increases quickly as the reaction time increases from 0.5 h to 2 h. As the temperature further

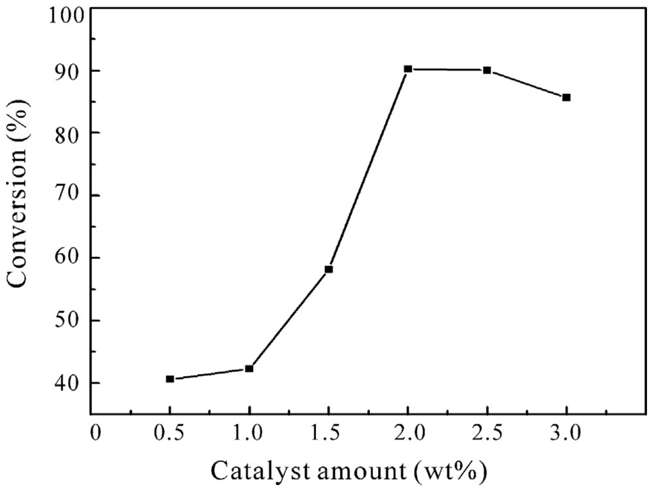


Fig. 6. Influence of catalyst amount on the conversion of transesterification reaction. Reaction conditions: temperature = 85 °C; methanol/oil molar ratio = 9:1; reaction time = 2 h.

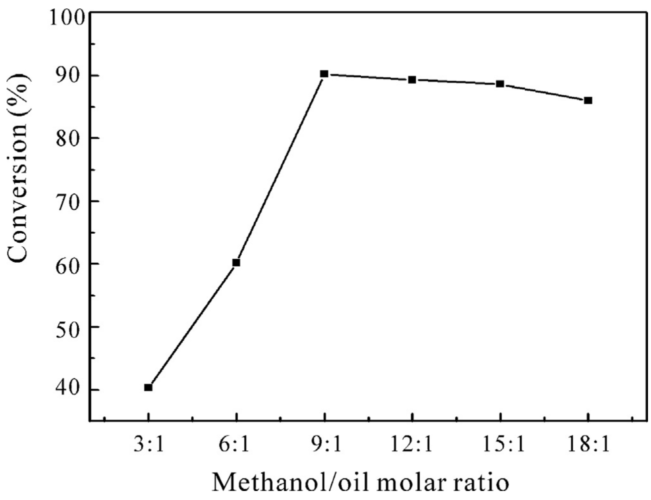


Fig. 5. Influence of methanol/oil molar ratio on the conversion of transesterification reaction. Reaction conditions: temperature = 85 °C; catalyst amount = 2%; reaction time = 2 h.

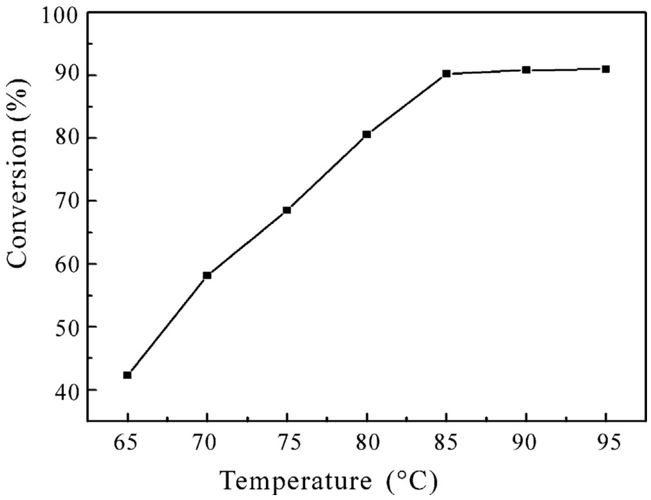


Fig. 7. Influence of reaction temperature on the conversion of transesterification reaction. Reaction conditions: catalyst amount = 2%; methanol/oil molar ratio = 9:1; reaction time = 2 h.

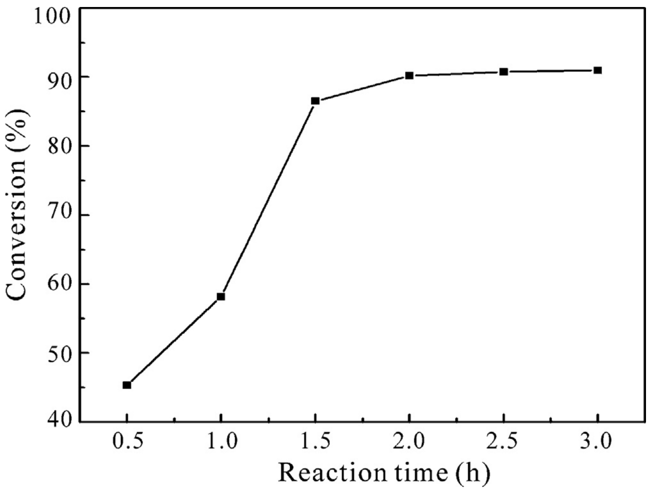


Fig. 8. Influence of reaction time on the conversion of transesterification reaction. Reaction conditions: temperature = 85 °C; catalyst amount = 2%; methanol/oil molar ratio = 9:1.

increases, the conversion rates increase very slowly. Therefore, 2 h is the best reaction time for this catalytic system.

Based on the results above, the highest conversion of 90.2% can be achieved under optimized transesterification conditions giving as follows: the methanol/cottonseed oil molar ratio is 9:1, the catalyst amount is 2.0 wt%, the reaction temperature is 85 °C and the reaction time is 2 h. However, the conversions achieved in this work are still relatively low for commercial application. Thus, the activity of the solid acid catalyst needs to be further improved. More research work such as how to increase surface area and amount of functional groups on the catalyst is in progress. In fact, the solid catalyst can be also used for another stage of transesterification reaction after separation to obtain high conversion during the industrial application.

The reusability of peanut shell solid acid was investigated by carrying out subsequent reaction cycles. At the end of each cycle, the catalyst was centrifuged, washed with acetone, and dried before reusing. The results for consecutive reaction cycles are shown in Table 2. As shown in Table 2, the conversion rate decreases from 90.2% to 50.3% in five cycles. After five cycles, the spent solid acid was washed with ether, dried at 120 °C under the vacuum, impregnated in 1 M H_2SO_4 solution for 5 h, washed with deionized water, and dried at 120 °C to regenerate it. The regenerated solid acid was used again and its original activity was mostly recovered. In fact, the total acid density of the spent solid acid decrease from 6.85 mmol/g to 3.42 mmol/g (Table 1), while the total acid density of the regenerated solid acid increases to 6.12 mmol/g, indicating that most of the acid sites have been recovered by the regeneration process. Thus, the catalytic activity loss is probably due to some active acid sites of the catalyst being covered by adsorbed intermediates or product species. These covered acid sites can be reactivated by simple regeneration process.

Table 3 lists the biodiesel parameters obtained from the biodiesel of cycle 1 to cycle 4. As can be seen, all the quality parameters we tested completely meet the requirements of EN 14214 Standard [31]. In addition, the cetane number is higher than that of the standard and the sulfur content of is very low in the produced biediesel, indicative of almost zero contamination emission during biodiesel consumption.

Table 2
Effect of repeated use of peanut shell solid acid on the conversion of transesterification.

	Recycle time				
	1	2	3	4	5
Conversion rate (%)	90.2	86.1	74.3	65.2	50.3

Catalyst amount, 2.0 wt%; methanol/oil molar ratio, 9:1; reaction temperature, 85 °C; and reaction time, 2 h.

Table 3
Quality parameters of the produced biodiesel and the respective requirements according to EN 14214.

Parameter	This work	EN14214
Water content (mg kg^{-1})	400	≤500
Acid value (mg KOH g^{-1})	0.40	≤0.50
Kinematic viscosity at 40 °C ($mm^2\ s^{-1}$)	4.35	3.5–5.0
Cetane number	52	≥51
Free glycerin (wt%)	0.018	≤0.02
Total glycerin (wt%)	0.18	≤0.25
Sulfur content (mg kg^{-1})	1.20	≤10.0

4. Conclusions

In summary, the nature of the acid sites in the peanut shell derived solid acid has been studied by XRD, FT-IR and solid state NMR spectroscopy. The 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_3H 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_2SO_4. The catalytic reaction tests indicate that this solid acid catalyst exhibits high activity in biodiesel production reaction (90.2% conversion rate). In addition, the spent solid acid can be recovered by simple treatment. The results in this work can help us to understand the formation of acid sites on the sulfated carbon-based solid acids.

Acknowledgements

We are very grateful to the financial supports from the School Foundation of WUST (2010XZ012) and the Open Research Fund of Key Laboratory for Ferrous Metallurgy and Resources Utilization of Ministry of Education (FMRU201209).

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