Carbon-based acid catalyst from waste seed shells: preparation and characterization

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A carbon-based solid acid catalyst was prepared by the sulfonation of carbonized seed shells of *Jatropha curcas* (*J. curcas* L). The structure of amorphous carbon consisting of polycyclic aromatic carbon sheets attached a high density of acidic SO_3H groups (2.0 mmol $\cdot$ g^{-1}) was identified with scanning electron microscopy (SEM), fourier transform infrared (FTIR) spectroscopy, powder X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The performance of the solid acid catalyst was evaluated for biodiesel production in the esterification of oleic acid with methanol. 95.7% yield of biodiesel was obtained after 2 h reaction and the conversions with re-used catalyst varied in the range of 95.7% to 95.1%, showing better activity and stability than commercial catalyst amberlyst-46. It was also observed that the prepared catalyst showed enhanced activity in the transesterification of triolein with methanol when compared with other solid acid catalysts. A synergistic effect results from the high density of SO_3H groups and the good access of reactants to the acidic sites can be used to explain the excellent catalytic activity, as well as the strong affinity between the hydrophilic reactants and the neutral OH groups bonded to the polycyclic aromatic carbon rings.

Keywords: carbon-based solid acid, waste seed shells, esterification, transesterification, biodiesel.

INTRODUCTION

Biodiesel is an environmentally safe and alternative fuel source, which produced from plant oils, recycled cooking greases or oils, and animal fats[1, 2]. Usually, both esterification and transesterification occur in the preparation of biodiesel from raw oils that contain high levels of free fatty acids (FFAs), such as jatropha oil, karanja oil, and animal fats[3, 4]. The esterification of FFAs by liquid acid catalysts (H_2SO_4) is a process commonly used for biodiesel production, but it requires energy intensive separation operations which lead to waste and environmental pollution[5]. Heterogeneous solid acid catalysts have unique advantages in esterification and transesterification reactions. Thus, the use of heterogeneous solid acid catalysts to replace homogeneous ones could eliminate the problems associated with homogeneous catalysts and could enhance the use of high acid value oil to be used as feedstock for synthesis of biodiesel[6, 7]. In the last decades, various solid acids (resins, zeolite, sulfated zirconia, polyaniline sulfate, heteropolyacid, metal complexes, sulfated tin oxide, and acidic ionic liquid) have been explored as potential heterogeneous catalysts in the production of biodiesel[8, 9]. Some common problems, such as low acid site concentrations, hydrophilic character of catalyst surfaces, and active site leaching, have hampered their practical applications. High cost is another obstacle for the commercialization of the above acid catalysts[10].

Recently, a new class of catalysts derived from incomplete carbonization of simple natural products such as sugar, starch or cellulose, has been reported to have better catalytic performance for esterification of FFAs, and higher stability than other solid acid catalysts. Such environmentally benign alternative catalysts have found applications in various acid-catalysed reactions including esterification, transesterification, and hydrolysis[11, 12].

The rapid growth of biodiesel industry has resulted in an oversupply of byproducts, such as seed shells, oilseed cakes and glycerol. Glycerol and oil asphalt -based heterogeneous catalysts have been reported[13, 14]. Activated carbon was also prepared by using various low-cost coconut shell and nut shells[15, 16]. However, to the best of our knowledge, there has been no report on carbon-based catalyst prepared from seed shells.

In order to realize the efficient utilization of the by-product (seed shells), a carbon-based solid acid catalyst derived from waste seed shells was prepared in this study. The catalyst was characterized by SEM, FTIR, XRD and XPS. For the preparation of biodiesel, the catalytic activities of the catalyst in esterification and transesterification were also investigated.

EXPERIMENTAL

Material

The seed shells of *J. curcas* L were collected from local market. The oil of *J. curcas* L (average molecular weight was 862.07) was obtained from the Ruifeng Plantation Company, Guizhou Province, China. Amberlyst 46 was purchased from the Dow Chemical Company. Methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, methyl linolenate, methyl heptadecanoate, oleic acid and methanol were purchased from Sigma-Aldrich (USA). All other chemicals and reagents were analytical grade and obtained commercially.

Preparation of carbon-based catalyst

Firstly, the seed shells were pre-treated to remove water and residual esters. 10 g of seed shells were carbonized for 5 h at 350°C under N_2 flow to produce a brown--black solid. Secondly, the solid was ground to powders and heated in 200 ml of concentrated H_2SO_4 (>96%) at 100°C under an N_2 atmosphere. Thirdly, after heating for 8 h and then cooling to room temperature, 1000 ml of distilled water was added to the mixture to form a black precipitate. The precipitate was cooled to ambient

temperature and washed with hot water under agitation until the wash water showed a neutral pH value.

Characterization of carbon-based catalyst

SEM images of the carbon-based catalyst were recorded by using a Philips XL30 ESEM instrument at 10 kV. XRD pattern of the catalyst was obtained on a Philips X'Pertpro diffractometer using Co Ka radiation with an accelerating voltage of 40 kV and current of 40 mA. FTIR spectra of the catalyst were obtained on a Nicolet-560 spectrometer. Thirty two scans were accumulated with a resolution of 4 cm^{-1} for each spectrum. The surface properties of the catalyst were characterized by XPS in a Perkin–Elmer PHI 1600 ESCA system with a monochromatic Mg Ka source and a charge neutralizer.

### Esterification of free higher fatty acids and transesterification of triolein

The esterification and transesterification reactions were carried out in a three-neck round bottom flask immersed in a silicon oil bath at 80°C. For esterification reactions, 0.1 mol of methanol, 0.1 mol of oleic acid and 0.14 g of catalyst were added to the flask. For transesterification of triolein, 0.3 mol of methanol, 0.01 mol of *J. curcas* L. seed oil and 0.2 g of catalyst were added to the flask. After reaction, the catalyst was separated by filtration and washed with methanol for re-use. The contents of biodiesel in the reaction mixture were quantitatively

The SEM image of the prepared solid acid was shown in Figure 2. As can be seen from Figure 2, the solid acid powders were irregular particles. Additionally, the Brunauer-Emmett-Teller (BET) surface area of the catalyst after dehydration was about 6.54 m^2 g^{-1}, which was higher than the cellulose-derived material[17].

Evidence for the successful preparation of solid acid was also obtained by FTIR experiments (Fig. 3). The vibration bands at 1037 cm^{-1} and 1367 cm^{-1} in the FTIR spectrum indicated that the resulting material possesses SO$_3$H groups[19]. The peaks at 1727 cm^{-1} and 1594 cm^{-1} were assigned to C=O and O-H vibrations in the catalysts[17].

Figure 4 showed XRD patterns for the carbonized shells before (Figure 4a) and after (Fig. 4b) sulfonation. The XRD patterns exhibited two broad but weak diffraction peaks at 2θ angles of 20°–30° and 40°–50°, which could attribute to amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion[20].

X-ray photoelectron spectroscopy (XPS) was conducted to investigate the surface element composition of solid acid. As shown in Figure 5a, there were C, O, N, and S element in their XPS survey spectrum. The single peak at 168 eV was assigned to the SO$_3$H groups, indicating that sulfonation of amorphous carbon was successfully achieved and all sulfur in the carbon catalyst was contained in the SO$_3$H groups[21] (Fig. 5b). The binding energy
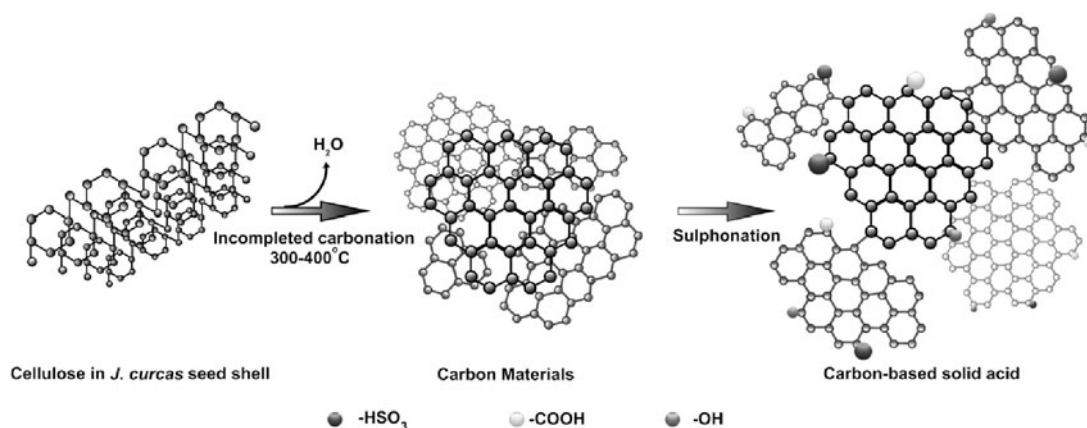

Figure 1. Schematic illustration of the carbon-based solid acid preparation from the *J. curcas* L. seed shell

analyzed by using a gas chromatograph (Beifen Ruili Analytical Instrument Co., Beijing, China) equipped with an SE-30 capillary column (30 m × 0.25 mm; ZKAT Analytical Technology Co., Lanzhou, China).
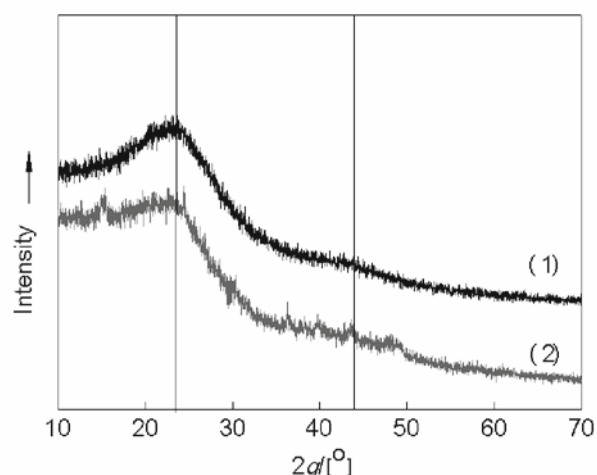
RESULTS AND DISCUSSION

The solid acid catalysts were prepared by carbonization of the seed shells followed by sulfonation, as shown in Figure 1. Firstly, the seed shells were pyrolyzed at 350°C (the stage of carbonization), accompanied by dehydration and dissociation of -C-O-C-, leading to the formation of polycyclic aromatic carbon rings and the amorphous carbon structure[17, 18]. Secondly, SO$_3$H was introduced into the aromatic carbon rings by sulfonation, leading to the formation of solid acid.
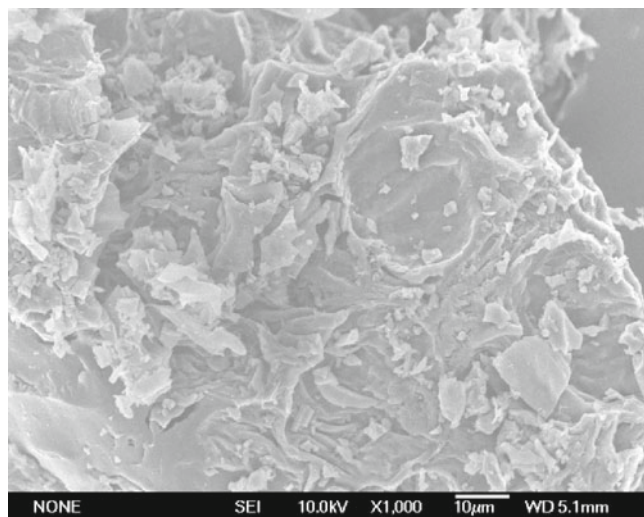
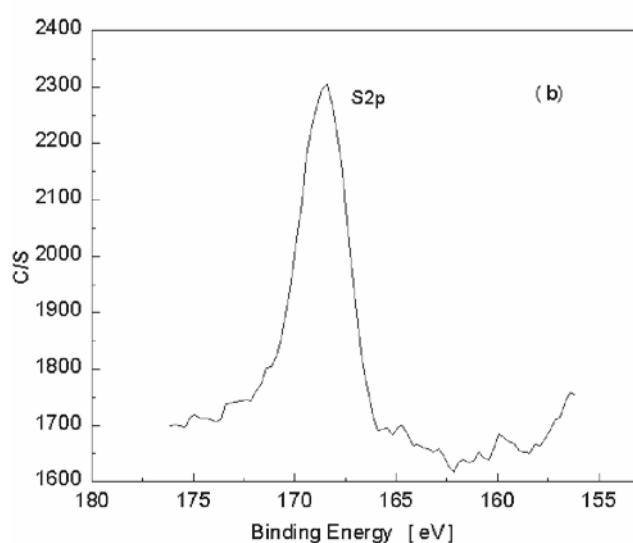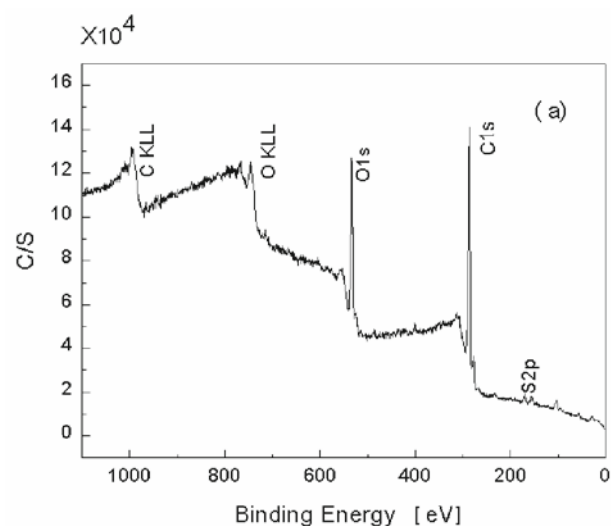**Figure 2.** SEM image of *J. curcas* L. seed shell-derived solid acid
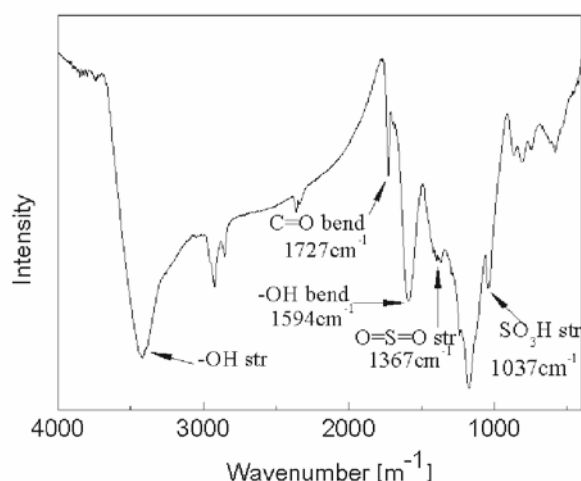
Figure 3. FT-IR spectrum of *J. curcas* L. seed shell-derived solid acid

Figure 4. XRD patterns for carbonized shells. (1) before sulfonation; (2) after sulfonation

Figure 5. (a) XPS survey spectrum of the seed shell-derived solid acid; (b) high-resolution spectrum of S2p of the seed shell-derived solid acid

of O(1s) is deconvoluted on the two components from O-I (S=O and C=O) and O-II (S-O and C-O) shifts up as the SO_3H impregnation, indicating that the acidity increases together with the degree of impregnation[22]. The SO_3H attached to the aromatic carbon atoms was up to 2.0 mmol · g^{-1} and gave the two forms S=O and S-O in 2:1 ratio. All these results indicate that this solid acid catalyst is amorphous carbon consisting of polycyclic aromatic carbon sheets attached a high density of acid sites functioned as catalytic center[9]. Consistent with the high density of acid sites and binding energy of O(1s), the solid acid's catalytic activity also proportionally increases[9].

The catalyst was evaluated in the esterification of oleic acid and methanol for the production of biodiesel at 80°C. As can be seen in Table 1, the yield of methyl oleate reached ca. 80% within 30 min and increased to more than 90% within 2 h in the presence of the seed shell carbon-based solid acids. The commercial catalyst amberlyst-46 was also tested in this reaction and the yields of methyl oleate were 21.7% within 30 min and 77.5% within 2 h. Additionally, the recycle of the catalyst was tried for 4 times to study its activity and stability. After the first reaction run, the catalyst was separated from the reaction mixture and then washed with methanol. After drying, the catalysts were used for the next run at identical conditions. Table 1 also showed that both the catalysts were still active in each recycle run and

Table 1. Esterification catalyzed by *J. curcas* L. seed shell-derived solid acid and Amberlyst 46

Methyl Oleate yield [%] Reuse batches	*J. curcas* L. seed shell-derived solid acids*		Amberlyst 46*	
	30 min	2 h	30 min	2 h
1	82.8	95.7	21.7	77.5
2	80.5	92.9	22.0	78.1
3	83.7	94.3	21.9	77.9
4	82.4	95.1	21.5	77.2

*Catalyst: 0.14 g, oleic acid: 0.1 mol, methanol: 0.1 mol, reaction temperature: 80 °C, reaction time: 2 h.

Table 2. Transesterification catalyzed by solid acids

Catalyst	SO$_3$H density [mmol · g^{-1}]	FAMEs yield [%]	Turnover Frequency [h^{-1}]
J. curcas L. seed shell-derived solid acid	2.0	31.5	1.31
Cellulose derived carbon-based solid acid*	1.2	24.1	1.67
Amberlyst-46*	1.3	17.2	1.10
Amberlyst-15*	4.9	5.0	0.085
Nafion NR50*	0.9	1.5	0.139
Nafion/SiO$_2$*	0.1	1.1	0.917

*Catalyst: 0.2 g, triolein: 0.01 mol, methanol: 0.3 mol, reaction temperature: 80°C, reaction time: 6 h [17].

no obvious activity decrease was observed after 4 times reuses. The maximum turnover frequency (TOF) of seed shell-derived solid acid (597.9 h^{-1}) was much higher than that of amberlyst-46 (241.8 h^{-1}), which can be attributed to the difference of density of acid active sites. In all cases, the selectivities to methyl oleate catalyzed by seed shell-derived solid acid were observed to be >98%.

The solid acid also showed high catalytic performance for the transesterification of triolein (such as *J. curcas* L. seed oil), as compared with other tested solid Brønsted acid catalysts (Table 2). The conversion of triolein catalyzed by the solid acid was 85% and the selectivity of methyl oleate was 37.1%. This high catalytic performance cannot be adequately explained simply by the high density of SO$_3$H groups and good access of reactants to the SO$_3$H groups. The transesterification reaction involves alcohols which are hydrophilic molecules. The strong affinity between the hydrophilic parts of the reactants and the almost neutral OH groups bonded to the polycyclic aromatic carbon rings may contribute to the high catalytic performance of the solid acid. These results were similar with previous reports[17]. Additionally, the high density of strongly acidic SO$_3$H groups and good access of reactants to the SO$_3$H groups are also beneficial for the high catalytic performance.

CONCLUSIONS

In conclusion, an effective, inexpensive and reusable carbon-based catalyst derived from waste seed shells was prepared in this study. The results indicated that this catalyst showed higher catalytic activity than other solid acid as catalyst for efficient production of biodiesel. In addition to biodiesel production, such catalyst would find applications in a wide range of other acid-catalyzed reactions.

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