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Preparation of a Novel Carbon Based Solid Acid Catalyst for Biodiesel Production via a Sustainable Route

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Abstract A novel carbon-based solid acid catalyst has been synthesized via a sustainable route, by using glycerol, a byproduct in biodiesel production, as a precursor. The newly obtained catalyst is glycerol-derived and amorphous with irregular morphology and mesoporous structure. For both biodiesel production and glycerol utilization, it demonstrates as promising. Compared with amberlyst-15, the commonly used one, the new catalyst has shown highly catalytic activity and recycling performance in esterification of oleic acid and transesterification of triolein. The highly catalytic activity of the catalyst for biodiesel production can be mainly attributed to the high density of acidic $-SO_3H$ groups and hydrophilic groups on its surface.

Keywords Biodiesel · Solid acid · Esterification · Transesterification · Sustainable

1 Introduction

Biodiesel has attracted great attention worldwide as a promising alternative for fossil fuel, owing to its advantages of low emission, biodegradation, non-toxicity and good lubricity. Currently, the production of the biodiesel mainly involves the transesterification of the triglyceride from the high quality oil, such as soybean, sunflower and rape seed oil using alkaline catalysts, such as KOH and NaOH [1–3]. However, for oil with high free fatty acids (FFAs), these catalysts, require that the total FFA content associated with lipid feedstock must not exceed 0.5 wt%, owing to soap formation [4, 5]. Therefore, the critical challenge for biodiesel technology is the handling of oils containing high levels of FFAs in both esterification and transesterification [6]. To tackle the problem, a promising approach using solid acid-catalyst has been proposed and studied for biodiesel production recently [7–11]. Among these solid acid catalysts, even greater attention has been paid to the carbon based solid acid catalysts, because they provide a high number of strong acid sites which can resist catalyst deactivation by water produced during the reaction [12–16]. It is desirable to design a simple protocol to synthesize water-tolerant, yet regenerable and inexpensive carbon based solid acid catalyst with strong acid sites.

With the rapid growth of biodiesel production due to the growing demand of biodiesel, more byproduct, such as glycerol, has been generated and can be obtained at low price. The large amount of glycerol being produced may become a potential waste in the near future [17]. Hence, the utilization of the glycerol has received intensive attention. Great efforts have been devoted to the utilization of waste glycerol [17, 18]. For instance, it can be recycled into energy carriers (hydrogen, syngas and methane), or converted into other chemicals (e.g., acrolein, epichlorohydrin, ethers, esters and alcohols) [19]. Moreover, catalytic steam reforming, aqueous reforming, autothermal reforming, pyrolysis, gasification, photo-conversion and bioconversion of glycerol can be considered to utilize the excess amount of glycerol [17].

Recently, Prabhavathi Devi et al. [20] proposed a new utilization method of glycerol via carbonization of the glycerol to form a carbon solid acid catalyst. Their ideas cast new light both on the utilization of glycerol and the

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development of new carbon based solid acid catalysts for biodiesel production. According to the method, the carbon-based catalyst is prepared in two steps. In the first step, the biomass, such as sugar, starch, is incompletely carbonized to form the polycyclic aromatic carbon sheets [21–24]. Then the sulfonation of the incompletely carbonized materials is taken into action as the second step. However, this two-steps synthesis is complicated, versus one-step synthesis which is more desirable. Furthermore, the sulfonation is carried out with large amount of sulfuric acid at high temperature under inert atmosphere, which is not an environment-friendly process. These challenges call for the development of a facile synthetic route to effectively utilize the excess-supplied glycerol.

In this letter, we report a facile method to synthesize a carbon-based solid acid catalyst with high density of sulfonic acid groups via in situ partial carbonization under hydrothermal reaction conditions. The starting raw material being used is a byproduct in biodiesel production. The catalytic activity and reusability of the new carbon-based solid acid catalyst have been studied in the reactions of esterification of oleic acid and transesterification of triolein with methanol. As a result, an economic and environment-friendly approach has been developed, which may open up a new opportunity for glycerol utilization in biodiesel industry.

2 Experimental

2.1 Preparation of the Carbon Based Solid Acid Catalyst

For a typical experimental procedure: a mixture of glycerol (10 g) and concentrated sulfuric acid (40 g) was loaded into a 100 mL teflon hydrothermal reactor. The mixed system was gently heated from ambient temperature to 180 °C to facilitate in situ partial carbonization and sulfonation. The reaction mixture was allowed to remain at that temperature for 0.5 h to obtain the polycyclic aromatic carbon compound. The product was cooled to ambient temperature, then was filtered and washed with hot water under agitation until the wash water showed a neutral pH value. The product was collected and dried in a vacuum oven at 120 °C for 12 h until it was moisture-free to obtain the glycerol-based carbon solid acid catalyst.

2.2 Characterization of the Catalyst

The X-ray powder diffraction (XRD) analysis of the products was conducted on a PAnalytical X'pert Pro X-ray Diffractometer equipped with Cu-Kα radiation ($\lambda = 1.54178$ Å), operating at 40 kV and 40 mA. The morphologies of the products were studied by a scanning electron microscope (SEM, Philips XL-30s) with an accelerating voltage at 20 kV. The fourier transform infrared spectroscopy (FT-IR) measurements of samples were characterized via a Nicolet 6700 FT-IR spectrometer. Thermo gravimetric analysis (TGA) of the as-synthesized catalyst was performed in a TA Instrument Q5000 (TA), under flowing nitrogen with a heating rate of 10 °C/min from 25 to 800 °C to determine the stability of the catalyst. X-ray photoelectron spectroscopy (XPS) spectrum was obtained in a Thermo Electron Corporation MultiLab 2000 machine with MgKα radiation (300 W) under 10^{-7} Pa, and calibrated internally by carbon deposit C_{1s} (285.0 eV). The BET specific surface area and pore structure were determined by N_2 adsorption at 77 K using a Micromeritics ASAP 2000 system after the sample was degassed in vacuum at 130 °C overnight. Strong acid density was determined by sulfur elemental analysis (Elementar Vario, EL III, Germany) and total acid density was tested by potentiometric titration with 0.001 M NaOH while the content of –COOH and –SO_3H groups were titrated with 0.05 M $NaHCO_3$ [25].

2.3 Activity Test

Typical procedures for esterification and transesterification: oleic acid (2.56 g) was esterified with methanol (25 mL) in the presence of catalyst (0.25 g) at 65 °C for 4 h. The conversion of oleic acid into biodiesel was estimated by determining the acid value of the product [20]. After the reaction, the catalyst was separated by filtration and washed with acetone. Then the filter cake was dried in a vacuum oven at 120 °C for 2 h for re-use. The reaction time for each cycle is all 10 h. The methanol from the filtrate was removed using a rotary evaporator under reduced pressure to obtain biodiesel in 99 % conversion. The transesterification was performed at 80 °C and under stirring using a methanol/triolein mole ratio of 60:1 with a catalyst concentration of 10 % in a 500 ml three necked round bottomed flask. Aliquots (200 μL) were taken at specified time intervals from the reaction mixture above for GC analysis (Agilent 7890). The GC was fitted with a HP-5HT nonpolar capillary column. The external standard method was adopted as the quantitative method.

3 Results and Discussion

3.1 Catalyst Characterization

As described above, the formation of the carbon based solid acid catalyst was achieved by in situ hydrothermal carbonization of the glycerol with sulfuric acid. The glycerol was the byproduct of the biodiesel production. The process involves the dehydration of the glycerol by sulfuric acid as the first step. Here, the sulfuric acid was used as a functional molecule to simultaneously make the glycerol carbonization and introduce the sulfuric acid groups onto the catalyst. Then after dehydration, the carbon-containing irregularly shaped particles with sulfuric acid groups and hydroxyl groups were formed. The resulted further coalescence of microscopic particles to large particles was caused by subsequent loss of water. The acidity of the catalyst was determined through the neutralization titration, which was about 1.60 mmol/g. The content of the sulfuric acid groups was determined by the elemental analysis. The results showed that the content of the sulfur is about 3.29 %, which is about 1.03 mmol/g.

In order to establish the physical and chemical properties of the carbon based solid acid catalyst, the characterizations of the structure and morphology were conducted. Figure 1 shows the XRD pattern and SEM image of the as obtained carbon based catalyst. As shown in Fig. 1a, the XRD pattern of the catalyst exhibits two weak diffraction peaks with 2θ values between 10–30° and 35–50°, which can be assigned to the (002) and (101) plane of the carbon that were resulted from the stacks of parallel layers and the regular structure within the individual layer plane segment [13]. This type of pattern is known to be characteristic to carbon states described as clusters made of small fragments of graphene planes plus some amount of disorganized carbon [13]. This structure indicated that the catalyst is still amorphous and far from graphitization.

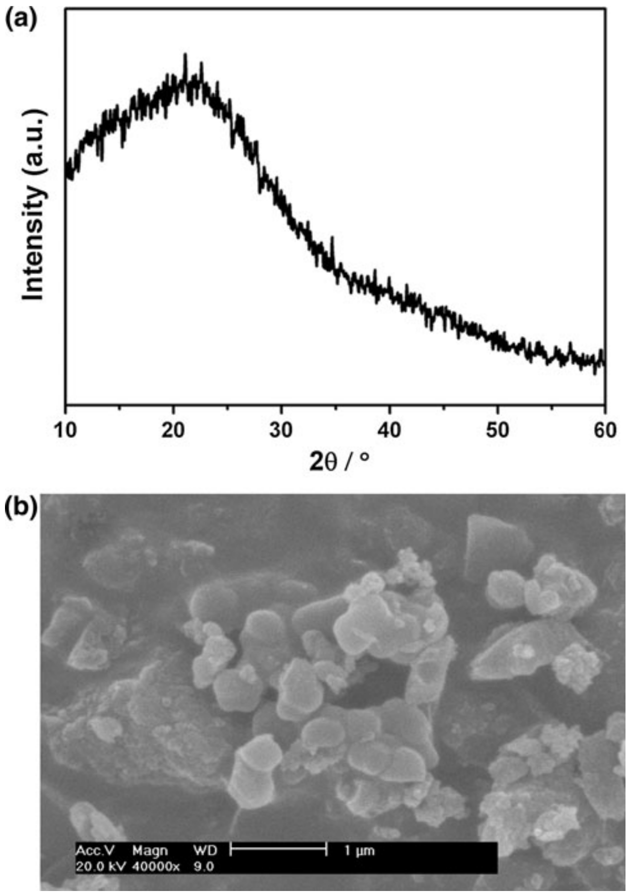

Fig. 1 XRD pattern (**a**) and SEM image (**b**) of the as-obtained carbon based catalyst

For the morphology of catalyst, seeing Fig. 1b, it can be seen that the catalyst were comprised of some irregular particles with a grain size lager than 400 nm. Some of the irregularly shaped particles were aggregated by other small particles. It may be caused by the coalescence of microscopic particles to large particles by the loss of water during the carbonization process. A mesoporous structure was verified by N_2 adsorption isotherm and pore size

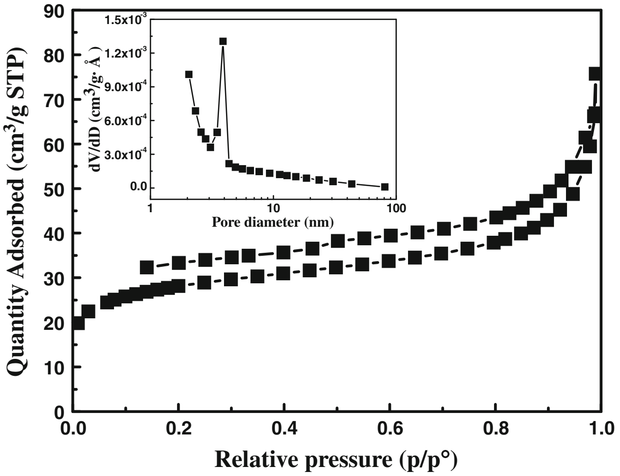

Fig. 2 N_2 adsorption isotherm of the carbon based catalyst. The *inset* is the BJH pore size distribution plot of the carbon based catalyst

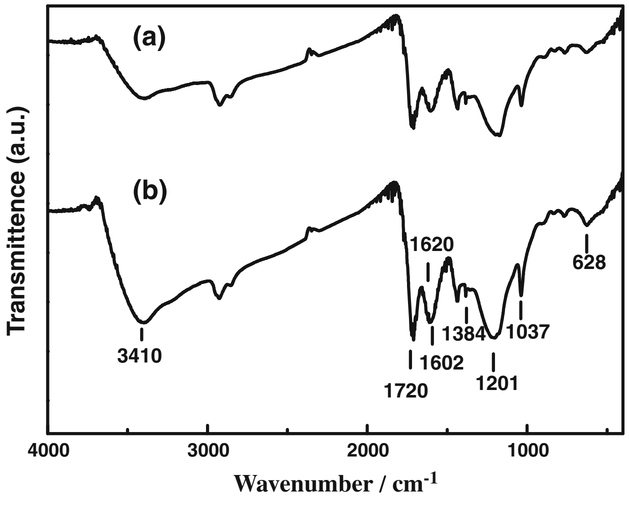

Fig. 3 FT-IR spectra of the fresh carbon based catalyst (**a**) and the recycled catalyst after five runs (**b**)

distribution, as shown in Fig. 2, leading to a high BET surface area of about 87 m^2/g, which is higher than other carbon based catalyst reported [12, 20, 24]. These mesoporous structure and morphology should favor the catalytic activity for production of biodiesel.

Figure 3 shows the corresponding FT-IR spectra of the fresh carbon catalyst (a) and the recycled catalyst (b) after five runs. The bands at 1,620 and 1,384 cm^{-1} appeared in Fig. 3a were assigned to C=C stretching mode in carbon catalyst matrix. The adsorption band at 1,037 and 1,157 cm^{-1} can be assigned to $–SO_3H$ groups and the peaks at 1,037 cm^{-1} are ascribed to the S=O vibration [12, 20, 24], indicating the presence of $–SO_3H$ groups on the carbon based catalyst. This also imply that the $–SO_3H$ groups can be facilely incorporated into the frameworks of the carbon by our facile hydrothermal method. Moreover, the strong peaks at 3,401 cm^{-1} were assigned to the O–H stretching modes of the phenolic –OH groups, providing the presence of –OH groups. The bands at 1,202 and 1,720 cm^{-1} were assigned to the C–O stretching modes and the C=O stretching modes of the carboxyl groups, confirming the presence –COOH functional groups. The titration results revealed that the content of the –OH and –COOH functional groups was about 0.6 mmol/g.

The XPS analysis further confirmed the $–SO_3H$ functional groups presented on the surface of the carbon based catalyst. From Fig. 4a, we can see that only C, S and O elements were detected, indicating that no other impurities existed in the catalyst. Figure 4b presents the narrow scan for S_{2p} region of the catalyst. The peak occurred at 186.0 eV corresponds to the bonded $–SO_3H$ groups [20, 21]. These results also suggested that only $–SO_3H$ groups existed on the surface of the carbon catalyst without any other sulphur state.

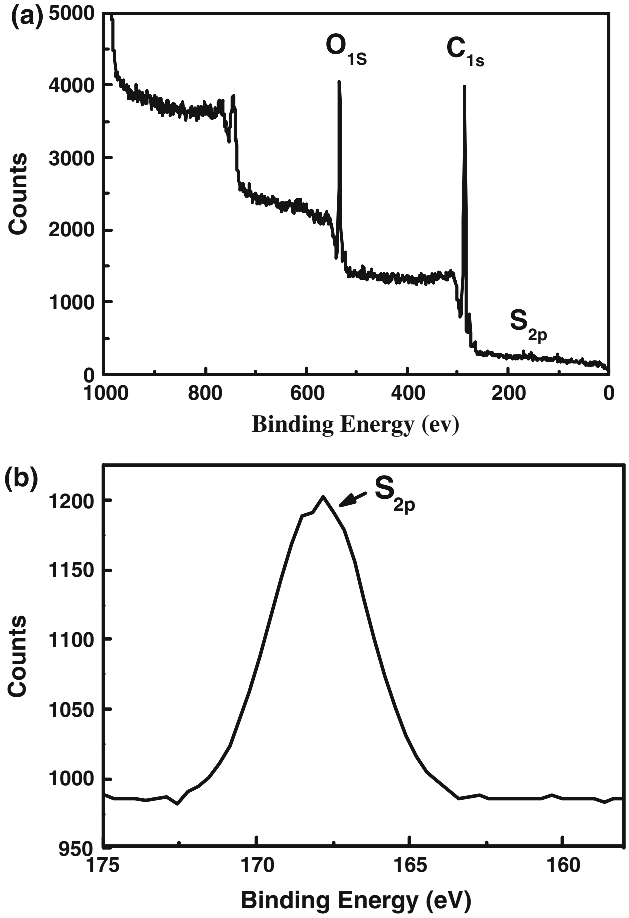

Fig. 4 Overall (**a**) and S_{2p} XPS spectra of the carbon based catalyst

3.2 Catalyst Evaluation

The catalytic activity of the obtained catalyst was firstly evaluated in the esterification of oleic acid with methanol for the production of biodiesel at 65 °C in the presence of 10 % catalyst. Figure 5a shows the catalytic results of the

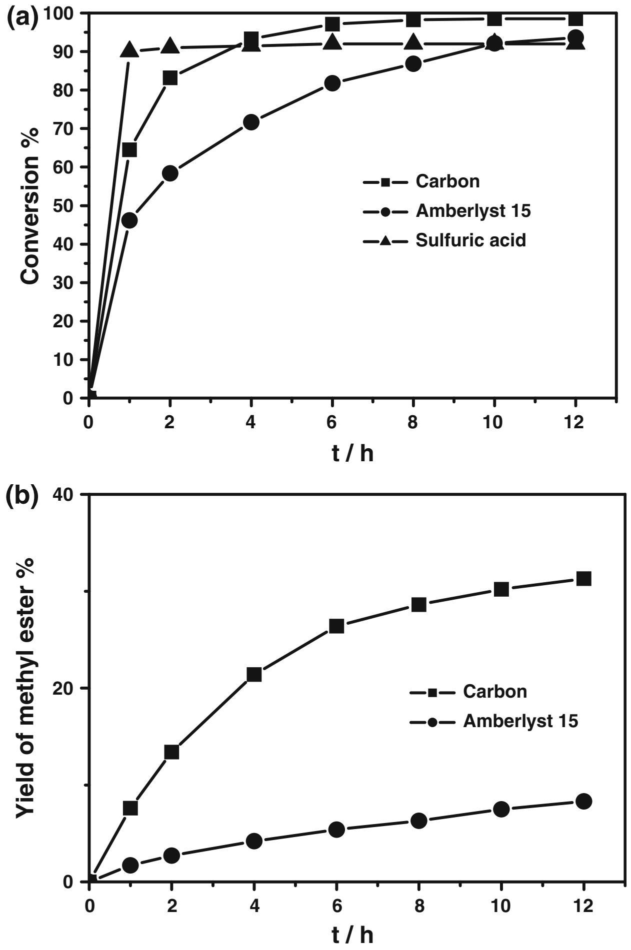

Fig. 5 Esterification of oleic acid with methanol by the carbon based catalyst, the amberlyst-15 catalyst and sulfuric acid (**a**) and transesterification of triolein with methanol by the carbon based catalyst and the amberlyst-15 catalyst (**b**)

carbon based catalyst in comparison to a typical solid acid catalyst, amberlyst-15. The carbon based catalyst showed a much higher esterification activity, especially in the initial stage. Compared with sulfuric acid, the catalytic activity of carbon catalyst is about 80 % of the sulfuric acid under the same reaction conditions. Moreover, the carbon catalyst also showed higher catalytic performance for transesterification of triolein. As shown in Fig. 5b, the carbon catalyst showed higher yield of methyl oleate, confirming the high catalytic activity of the carbon catalyst. It is well known that the amberlyst-15 was an ion exchange resin bearing macropores. Although it has high acid density (about 5.3 mmol/g), most of acid sites resided in a poorly swelling network can only be penetrated by small ions (H^+, Na^+) instead of large molecules such as oleic acid. With respect to the carbon solid acid catalyst, the high catalytic activity cannot be explained simply by the high density of strongly acidic –SO_3H groups and good access of reactants to the –SO_3H groups in the carbon material. It is reported that in addition to the high density of acidic –SO_3H groups, the hydrophilic –COOH and –OH groups in the carbon catalyst also played an important role in promoting the activity of the catalyst [26]. One possible explanation for the high catalytic activity of the solid acid carbon catalyst bearing –SO_3H, –COOH and phenolic –OH groups may be the strong affinity between the hydrophilic parts of the reactants and the almost neutral –OH groups bonded to carbon catalyst matrix [27]. Thus, the strong affinity favored the dispersion of the catalyst in methanol, resulting in the high catalytic activity.

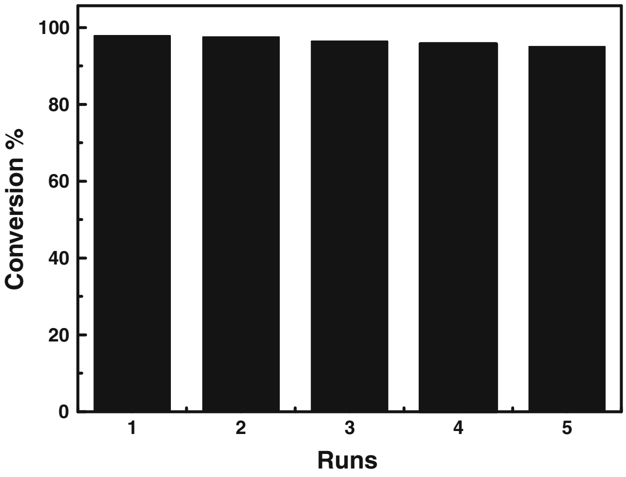

Fig. 6 Recycling performance of the carbon based catalyst in methyl oleate formation by esterification of oleic acid with methanol

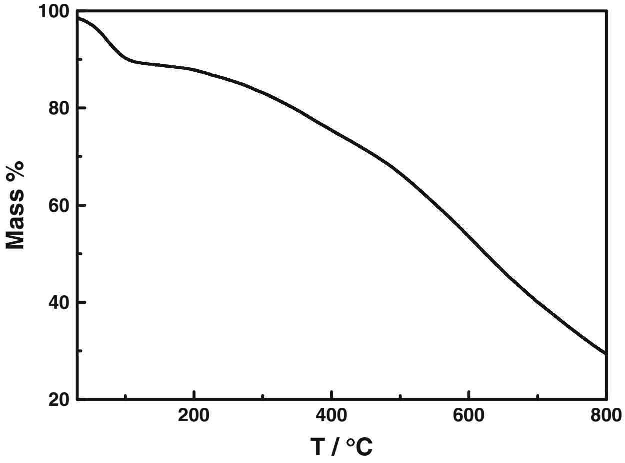

Fig. 7 TGA of the carbon based catalyst

In order to investigate the reusability of the carbon based catalyst, the used catalyst was collected and washed with hot water and acetone. The regenerated catalyst was subjected to esterification again. It was found that the catalytic activity can be still maintained with over 95 % conversion after five runs, as shown in Fig. 6, indicating the high stability of the catalyst. Furthermore, TGA results (Fig. 7) shows that the catalyst can maintain the structure below 450 °C (<18 % weight loss), demonstrating the high thermal stability of the catalyst. The high stability can also be supported by FI-IR characterization and element analysis. In the FI-IR spectrum of the spent catalyst after 5 runs, seeing Fig 2b, no decrease in intensity was observed at the band of 1,037 cm^{-1} due to the stretching modes of S=O, suggesting that –SO_3H groups are still strongly anchored on the surface of the catalyst. Element analysis showed that the sulfur did not leach into the reaction system, leading to the high stability of the catalyst.

4 Conclusions

In conclusion, a sustainable route of synthesis for carbon-based solid acid catalyst for the utilization of glycerol has been successfully developed via an in situ hydrothermal method using glycerol as precursor. The obtained carbon based solid acid catalyst has shown highly catalytic activity and recycling performance in esterification of oleic acid and transesterification of triolein with methanol. This result indicates that the new route of synthesis has provided an effective way for the utilization of glycerol, and may have great potential in biodiesel production.

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