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Sulfonic-Functionalized Carbon Catalyst for Esterification of High Free Fatty Acid

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Abstract

We report synthesis and characteristics of sulfonic-functionalized carbon catalyst in this work. The carbon soild acid was prepared through the sulfonation of the incomplete carbonized mung bean vermicelli and was used as a solid acid catalyst for esterification of high free fatty acid. The catalyst (S_{BET} = 18.1 m^2/g, acid site density of 1.53 mmol H$^+$/g$_{cat}$) could exhibit high esterification activity in the reaction of oleic acid with methanol due to the efficient accessibility of bulky substrate molecule to sulfonic active site during the reaction. This environmentally benign and ecofriendly C-SO$_3$H catalyst could be suited to esterify high FFA feedstocks reducing the production cost of biodiesel.

Keywords: Carbon solid acid; High free fatty acid; Esterification

1. Introduction

Nowadays, the development of efficient solid acids has been increasing interest in various chemical reaction such as hydration and esterification [1]. Especially, the use of solid acid catalysts in the esterification reaction avoids the existing problems - instrument corrosion, waste generation from acid neutralization process, and product separation difficulty associated with the use of homogeneous liquid acid such as sulphuric acid in order to make the process more environmentally friendly and economical [2]. Due to a simple catalyst synthesis, sulfonated solid acid catalysts such as slfonated carbon nanotube,

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sulfontaed mesoporous silica, and sulfonated incompletely carbonized polymers are being used as highly potential novel solid acid catalysts for esterification of Free fatty acid [3, 4, 9]. Recently, sulfonated incompletely carbonized organic compounds gained popularity as solid acids, exhibiting high catalytic performance for various liquid-phase acid-catalysed reactions. The high catalytic activity is related to the formation of flexible materials with small polycyclic aromatic carbon sheets, having high SO_3H active sites during the catalyst synthesis [1, 5-8]. W-Y. Lou et al. reported that the starch-derived catalyst is highly effective, eco-friendly and promising solid acid catalysts compared to other types of the carbohydrate-derived catalysts for esterification of waste oils with high free fatty acid [7]. The esterification of high FFA feedstocks with low molecular weight alcohols can achieve by using sulfonic-functionalized carbon catalysts in one-step process in order to produce the fatty acid alkyl ester products [1, 6, 7]. Of various biomass sources, vermicelli made from mung bean called cellophane noodles that consists of two different kinds of molecules - the unbranched linear and helical amylose consisting of glucose residues in α-1,4 linkage and the branched amylopectin with glucose residues about 1 α-1,6 linkage per 30 α-1,4 linkages, is a common renewable starch source and could be used as a support for making the sulfonic acid immobilized solid acids.

In this study, sulfonated incomplete carbonized biomass-based vermicelli catalysts were synthesized at different carbonization temperatures. The structural properties and acid site densities were characterized by XRD, FT-IR, FE-SEM, BET, and acid-base back titration methods. The catalytic performances of the synthesized solids were conducted through esterification of oleic acid with methanol at different reaction temperature.

2. **Materials and Methods**

2.1. MATERIALS

Commercial branded-vermicelli was purchased from the local markets. Oleic acid ($C_{18}H_{34}O_2$, 99.7 %, Aldrich), methanol (CH_3OH, ACS grade, Aldrich), sulfuric acid (H_2SO_4, 98%, RCI labscan), and all other chemicals used in this work were of analytical reagent grades.
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2.2. METHODS

2.2.1. CATALYST SYNTHESIS

The sulfonic-functionalized carbon catalysts were prepared through a modification of the reported methods [1, 9]. As a typical synthesis, a certain amount of vermicelli made from starch of mung bean was incompletely carbonized at different temperatures (473 K, 573 K and 673 K) for 1 hour under N_2 atmosphere. After grinding the solid materials, 1 g of the resultant powder was heated with 20 cm^3 of concentrated sulfuric acid at 373 K for 10 hours under N_2 atmosphere. The sulfonated mixture was then cooled to room temperature and diluted with distilled water in order to form a black precipitate, followed by filtration and washing repeatedly with hot distilled water (about 353 K) until no sulfate ions was detected. The materials were then dried at 373 K for more than 6 hours. The percentage yields of the synthesized C-SO$_3$H solids (carbonized at 473-673K) are about (25, 29 and 23) wt % based on the mass of raw materials respectively. The synthesized solids were designated as C$_{(carbonization\ temperature)}$- SO$_3$H : C$_{(473)}$ -SO$_3$H , C$_{(573)}$ -SO$_3$H , and C$_{(673)}$ -SO$_3$H respectively.

2.2.2. CATALYST CHARACTERIZATION

The powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE diffractometer with a Cu-Ka$_\alpha$ radiation (λ = 0.15406 nm) operating at 40 kV and 40 mA, over a 2θ range of 10-60°C with a step size of 0.075 at a scanning speed of 7°/min. The FE-SEM images of solids were recorded on a field emission scanning electron microscope (Joel, JSM-6340F, Japan) operating at 15kV. The fourier-transform Infrared (FT-IR) spectra were obtained by using the KBr pellet technique on a FT-IR system 2000 (Perkin-Elmer) spectrometer with 4 cm^{-1} resolution, scanning in the range of 400-4000 cm^{-1}. Samples were dried at 393 K overnight prior to FT-IR measurement. The specific surface areas of the catalysts were calculated using the Branauer-Emmett-Teller (BET) method. The acid-base back titration using HCl and NaOH aqueous solutions was applied for estimation of acid densities of the prepared catalysts.

2.2.3. CATALYTIC ACTIVITY TEST

Liquid-phase esterification reactions of oleic acid which is the main ingredient of crude vegetable oil with high FFA, with methanol were conducted using a 100 cm^3 two-necked flask equipped with a reflux condenser at 333K and 353K for 6h. The molar ratio of methanol to oleic acid (10:1) and 2 wt % of freshly prepared catalyst referred to the weight of oleic acid were used. Once the temperature of the mixture was reached at desired temperatures, the reaction was started after introducing the catalyst, respectively. The percentage yield of methyl oleate was calculated by ^{1}H NMR with a 300 MHz (Bruker DPX 300) spectrometer using TMS as internal standard. The methyl oleate yield was determined by the integration ratio of the signals of methoxy group (3.7 ppm; s, OCH$_3$) of the fatty acid methyl ester to the signal of the α-carbon methylene group (2.3 ppm, t,- αCH$_2$) of for all fatty acid derivatives [9].

3. Results and Discussion

3.1. STRUCTURAL CHARACTERIZATION OF THE SOLID ACID CATALYSTS

The FE-SEM images [Fig. 1 (a) and (b)] show that insignificant aggregation of the irregular particles of the catalysts with micrometer dimensions. The larger surface area (see Table 1) associated with smaller particle sizes of C$_{(573)}$-SO$_3$H catalyst could facilitate the attachement of more - SO$_3$H group to the carbon support, giving the higher acid site density compared to that of C$_{(473)}$ -SO$_3$H . The FE-SEM images revealed the larger SBE of C$_{(573)}$-SO3H than SBET of C$_{(473)}$ -SO$_3$H.

During the first stage of carbonization process, dehydration and –C-O-C- bond cleavage of the starting materials had been occurred, resulting in the formation of amorphous materials containing polycyclic aromatic carbon sheets [5]. The XRD profiles of the incomplete carbonized vermicelli at different temperatures before and after sulfonation are shown in Figure 2(a) and (b). The broad C (002) diffraction peaks (2θ = 10°- 30°) of all XRD patterns are assigned to amorphous carbon [1, 8]. After sulfonation, the peak intensities became weaker due to the immobilization of the sulfonic group on the carbon support and it was obviously weaker in the sulfonated samples carbonized at 473 K and 573 K. Furthermore, the mentioned C(002) diffraction peaks for both sulfonnic-modified materials were shifted to the larger 2θ values (see Fig.2(b)), indicating that the carbonization process was still being occurred during the sulfonation of carbon solid in concentrated sulphuric acid resulted in smaller polycyclic carbon rings. In the case of material carbonized at 673 K, a weak C(101) diffraction peak (2θ = 35-50°) of graphite structure could be found. This can due probably to the more carbonized material, composing of larger and harder carbon materials as a result of plane growth and stacking of carbon sheets than those carbonized less than 673 K. The presence of hard carbon material also affects the catalytic activity of the synthesized solids. Of different types of catalysts, the catalyst prepared from the material carbonized at 573 K shows

the highest acid site (Table 1) since more sulfonic groups could be incorporated to the amorphous flexible soft carbon sheets giving higher acid site density which was consistent with the reported literature [5].
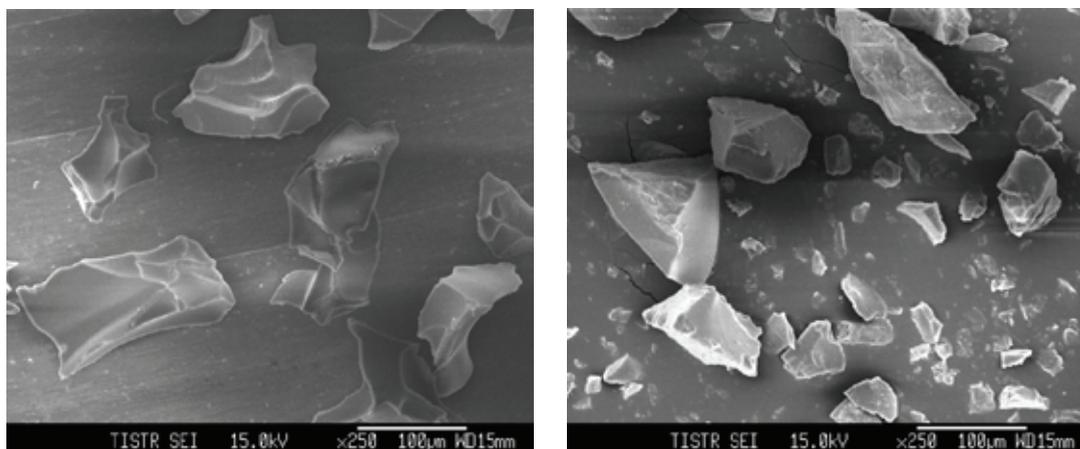

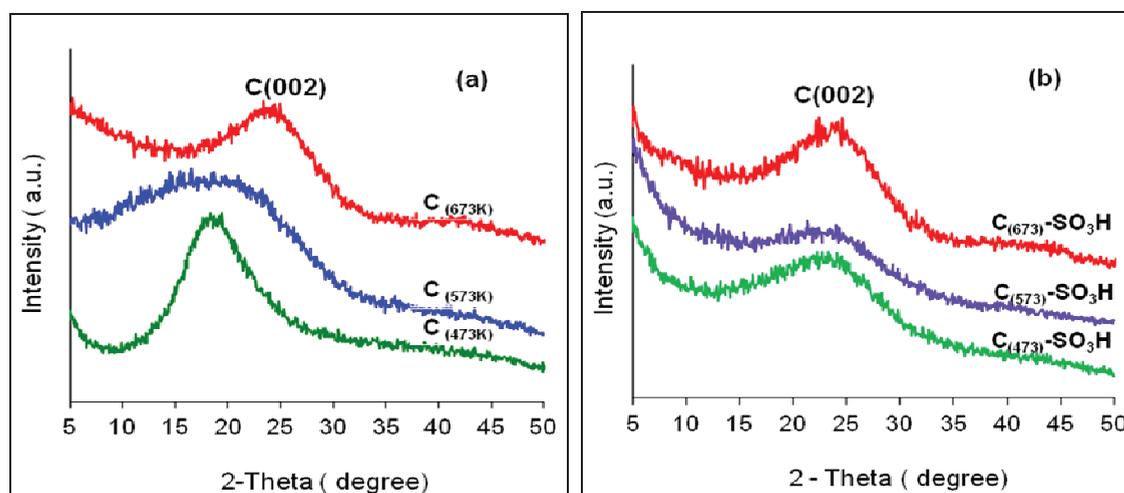Fig. 1. FE-SEM images of prepared catalysts; (a) $C_{(473)}$ -SO$_3$H (b) C $_{(573)}$-SO$_3$H

Fig. 2. XRD patterns of incomplete carbonized vermicelli at different temperatures
(a) before sulfonation   (b) after sulfonation

It has been reported that the sulfonated carbon catalysts are composed of polycyclic aromatic carbon with –COOH, -OH, and –SO3H functional groups [1, 5, 10]. The FT-IR spectra (Fig. 3) of the vermicelli carbonized at 573K before and after sulfonation showed that the broad band at around 3414-3422 cm^{-1} is due to the stretching mode of O-H of –COOH and Phenolic OH [10]. The weak small peaks around 1702-1708 cm^{-1} could be assigned to $\square_{C=O}$ of –COOH group, and the absorption peaks at 1619 and 1384 cm^{-1} are due to $\square_{C=C}$ of poly aromatic rings [10] respectively. The peaks at 1035 cm^{-1} for $\square_{O=S=O}$ (sym), as

well as 1171 cm^{-1} for $\square_{O=S=O}$ (unsym) [10] correspond to the SO$_3$H stretching modes which were appeared after the sulfonation. There were no significant differences between the FT-IR spectra of catalysts prepared at different conditions.
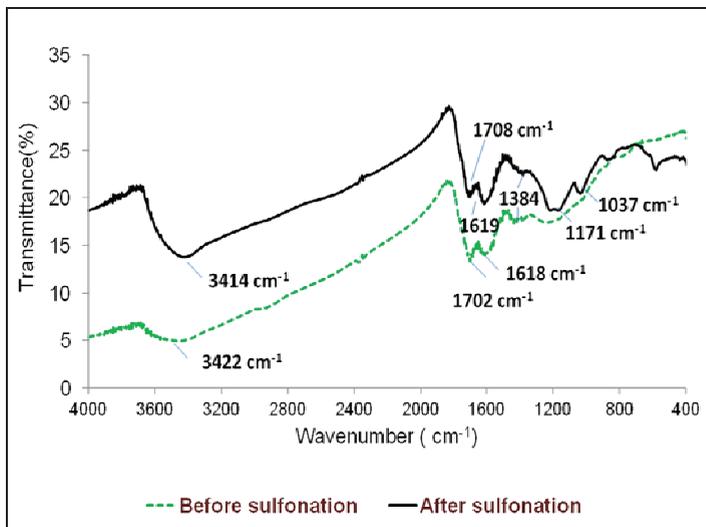

Fig. 3. FT-IR spectra of incomplete carbonized vermicelli at different temperatures
------: before sulfonation ---- : after sulfonation

   Table 1 showed that the larger surface area of the C$_{(573)}$-SO$_3$H catalyst with higher acid site density, suggesting the attachement of more –SO$_3$H groups to the carbon support and showing the important factor of incomplete carbonization temperature on the catalyst preparation. The acid site densities of materials (0.58-1.53 mmol H$^+$g^{-1}) could be considered as total acidities due to the contribution of –SO$_3$H group, as well as the phenolic –OH and –COOH group generated during the incomplete carbonization process. In addition, these acid densities are too high to be attributed to – SO$_3$H groups attached to the small carbon surface areas (<1-18 m^2/g), suggesting that – SO$_3$Hgroups in the amorphous carbon bulk takes part in the acid catalyzed reactions.

Table 1. Textural and chemical properties of solid acid catalysts

Catalyst	S$_{BET}$[a] (m^2/g)	Acid density[b] (mmol H$^+$/g)
C$_{(473)}$-SO$_3$H	1	0.71
C$_{(573)}$-SO$_3$H	18.1	1.53
C$_{(673)}$-SO$_3$H	<1	0.58

[a]S$_{BET}$: BET surface area
[b]Determined by acid-base back titration.

3.2. DETERMINATION OF CATALYTIC ACTIVITY OF THE SOLID ACID CATALYSTS

Although oleic acid with its proton can autocatalyze the esterification reaction, the rate reaction is slow without additional catalyst. Therefore, a proper catalyst needs to be used to accelerate the rate of reaction. Taking into account the acid site density of the synthesized materials, the catalytic performance of $C_{(573)}$-SO_3H catalyst was evaluated   in esterification of oleic acid. Figure 4.depicted the increase in yield percentage of methyl oleate with increasing the reaction temperature. The high esterification activity could be suggested due to the efficient accessibility of bulky substrate molecules to sulfonic active site in the flexible soft carbon sheet during the reaction. The methyl oleate yield of approximate 80 % at 353K was somewhat close to those reported by W-Y. Lou et al [7].
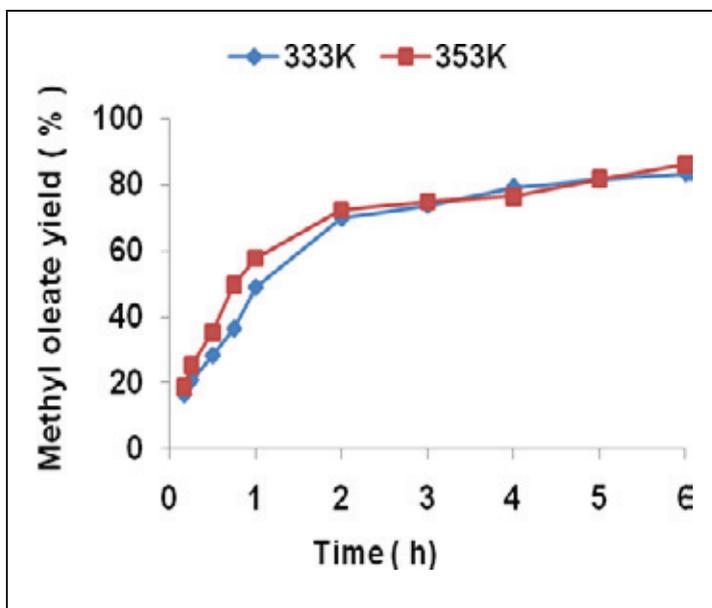

Fig. 4. The yield percentage of methyl oleate : Reaction condition; (10:1) molar of methanol to oleic acid, 2 wt % $C_{(573)}$ –SO_3H, 333K and 353K, 6h

4. Conclusion

The biomass–based sulfonic-functionalized solid material could be synthesized by sulfonation of incomplet carbonized vermicelli and was used as a solid acid catalyst in esterification oleic acid with methanol. Notably,the flexible soft carbon sheets bearing –SO_3H groups could facilitate the accessibility of bulky high fatty acid substrate molecule, yielding the high methyl oleate percentage under mild reaction conditions as well. In addition, The functional –COOH group generated during the proper incomplete carbonization and sulfonation temperature could probably contribute to the catalytic activity of the synthesized solid despite of its weak acidity. The effect of carbonization temperature played an important role in the catalyst preparation as well. The reasonable esterification activity, easier separation and simple praparation of this entitled catalyst could reduce the processing cost of biodiesel production from high free fatty acid feedstocks making the process more economical and environmentally friendly.

Acknowledgements

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