



# ONE-POT SYNTHESIS OF SULFONATED CARBON/ PALYGORSKITE SOLID-ACID CATALYST FOR THE ESTERIFICATION OF OLEIC ACID WITH METHANOL

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**Abstract**—Sulfonated carbon is a ‘green,’ solid-acid catalyst. For applications purposes, its surface area needs to be improved and its preparation needs to be made environmentally friendly. The objective of the present study was to provide a green and economical method of preparing a sulfonated carbon catalyst by using palygorskite (Plg) fiber as a support for sulfonated carbon. Sulfonated carbon/palygorskite solid-acid catalyst (SC-Plg) was synthesized via one-step carbonization-sulfonation by mixing palygorskite with sucrose as the carbon source and *p*-toluenesulfonic acid as the sulfonating agent. The catalyst was characterized by SEM, EDX, TEM, FTIR, and nitrogen adsorption-desorption isotherms. The results indicated that sucrose-derived carbon was loaded uniformly on the surface of Plg fibers and formed the SC-Plg catalyst. The inexpensive Plg fibers could replace sucrose-derived carbon and increase the surface area of the resulting catalyst. The SC-Plg shows significant catalytic performance and excellent stability when used in the esterification of oleic acid with methanol. The conversion of oleic acid reached 68.09%, even after five cycles. This work paves the way for the development of highly active, carbon-based, solid-acid composite catalysts using a natural Plg nanofiber template.

**Keywords**—Catalyst · Esterification · Palygorskite · Sulfonated carbon

## INTRODUCTION

Homogeneous liquid-acid catalysts, such as sulfuric acid, have been used extensively in acid-catalyzed reactions due to their significant catalytic properties. Use of these liquid-acid catalysts has decreased gradually in the chemical industry due to poor recyclability, significant corrosivity, and subsequent environmental pollution. Compared with liquid acids, solid acids are ‘greener’ catalysts that have attracted attention due to their ease of recycling and good catalytic properties (Okuhara, 2002; Yang et al., 2011; Ngaosuwan et al., 2016). The active groups of most solid-acid catalysts leach out easily during aqueous reactions, however, resulting in the rapid loss of catalytic activity, which limits application (Okuhara, 2002).

Sulfonated carbon catalysts prepared by the sulfonation of incompletely carbonized natural organic products have greater catalytic activities and stability in aqueous solutions (Toda et al., 2005). The raw materials used for sulfonated carbon catalysts are very cheap and can be obtained from natural materials, including sucrose (Toda et al., 2005), starch (Budarin et al., 2006), cellulose (Suganuma et al., 2008), and biomass residue (Ma et al., 2014; Tao et al., 2015; Guo et al., 2017), but these sulfonated carbon catalysts often have smaller surface areas, which limits their catalytic activity (Suganuma et al., 2008; Nakajima and Hara, 2012; Tao et al., 2015). The introduction of a porous structure in sulfonated carbon cata-

lysts during the sulfonation and carbonization process is essential, therefore (Budarin et al., 2006). The loading of amorphous carbon on the surface of porous materials increases the surface area of catalysts and improves their catalytic properties (De Vyver et al., 2010; Nandan et al., 2011; Valle-Vigón et al., 2012), but the sulfonation of carbon after sucrose carbonation typically requires the use of sulfuric acid as the sulfonating agent.

One-step hydrothermal carbonization methods in aqueous solutions at low temperatures have been developed to overcome these problems. To prepare sulfonated carbon catalysts, numerous organic materials, such as furfuraldehyde (Xiao et al., 2010), water hyacinth (Laohapomchaiphon et al., 2017), and glucose (Zhang et al., 2011; Zhan et al., 2014; Yang et al., 2019) have been used as the carbon sources, while *p*-toluenesulfonic acid provided the -SO<sub>3</sub>H group. These carbon-based acid catalysts exhibited strong acidities and significant catalytic performances. The thermal treatment of a mixture of glucose and *p*-toluenesulfonic acid (TsOH) under solvent-free conditions also forms a sulfonated carbon solid-acid catalyst (Zhang et al., 2010a; Wang et al., 2011a; Xu et al., 2016). Compared with hydrothermal carbonization, thermal treatment methods are simpler and more eco-friendly, and the sulfonated carbon, solid-acid catalysts obtained are typically very efficient when used in reactions such as esterification (Zhang et al., 2010a), fructose dehydration (Wang et al., 2011a), and corn cob hydrolysis (Xu et al., 2016).

Clay minerals are relatively inexpensive and widely available porous materials when compared with biomass-derived carbon. Palygorskite (Plg) is a nanofibrous, natural clay mineral often used as a catalyst carrier due to its porous structure and hydrothermal stability (Zhang et al., 2010b). In a previous work, sulfonated carbon/Plg catalyst was prepared by the

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carbonization of sucrose on a Plg support, followed by sulfonation by concentrated sulfuric acid. The resulting composite exhibited good catalytic performance for the synthesis of *n*-butyl acetate (Jiang et al., 2012).

The aim of the current study was to develop a green and economic method of preparing a sulfonated carbon, solid-acid catalyst with a large surface area by combining Plg nanofibrous support with simultaneous calcination and sulfonation of a mixture of sucrose and TsOH at low temperature without water. Three further objectives were: (1) to evaluate the catalytic activity of the sulfonated carbon/Plg solid acid catalyst with regard to the synthesis of methyl oleate; (2) to compare its performance with other solid-acid catalysts; and (3) to investigate the effects of the amounts of sucrose and TsOH on the catalytic performance and stability.

## MATERIALS AND METHODS

### Materials

Plg was acquired from Gaojiawa, Xuyi, China, and pretreated by milling, followed by soaking in HNO<sub>3</sub> solution (5 wt.%) for 24 h under magnetic stirring. Pretreated Plg was centrifuged, washed with distilled water, and then dried in an oven at 80°C. The sucrose and NaCl were purchased from Tianjin Kemio Chemical Reagent Co., Ltd., (Tianjin, China). TsOH and NaOH were supplied by Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). The HNO<sub>3</sub>, oleic acid, and methanol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were of analytical grade and used as received without further purification.

In a typical synthesis, 5 g of sucrose and 1 g of TsOH were dissolved in 15 mL of distilled water, and then pretreated Plg (5 g) was added. After stirring at room temperature for 1 h, the mixture was dried under vacuum at 40°C and then transferred into an alumina combustion boat that was subsequently placed in a horizontal tube furnace. The mixture was heated to 200°C at a heating rate of 5°C/min and held at the target temperature for 3 h under a N<sub>2</sub> atmosphere. The product obtained was referred to as SC-Plg-*n*, where *n* denotes the mass of sucrose added. For comparison, sulfonated carbon (SC) was prepared from a mixture of sucrose and TsOH under the same conditions without Plg. The effect of Plg on the catalytic performance of SC was investigated by changing the amount of sucrose. The final products were denoted as SC-Plg-1, SC-Plg-3, SC-Plg-5, and SC-Plg-7 when the dosages of sucrose were 1, 3, 5, and 7 g, respectively.

### Characterization

The X-ray diffraction (XRD) patterns of samples were collected using a D8 Advance X-ray powder diffractometer (Bruker, Karlsruhe, Germany). The sample morphologies were investigated using scanning electron microscopy (SEM, S-3000N, Hitachi Corporation, Tokyo, Japan). Elemental analysis of the catalysts was performed on an energy-dispersive X-ray spectrometer (EDX, EX-250, Horiba Corporation, Kyoto, Japan). Transmission electron microscopy (TEM) images were obtained using a JEM 2100F transmission electron

microscope (JEOL Corporation, Tokyo, Japan). Fourier-transform infrared (FTIR) spectra of catalysts were recorded on a Nicolet 5700 spectrometer (Thermo Fisher Nicolet Corporation, Waltham, Massachusetts, USA) with a resolution of 4 cm<sup>-1</sup> using KBr pellets with 1% sample content. The KBr pellets were compressed under 30 MPa after drying in the infrared oven. The elemental analysis of the catalyst was carried out with an Elementar Vario EL III element analyzer (Elementar Corporation, Hannah, Germany). N<sub>2</sub> adsorption/desorption isotherms of the catalysts were obtained using a Micromeritics TriStar II 3020 instrument (Micromeritics Instruments Corporation, Norcross, Georgia, USA) at -196°C (77 K). Before measurement, the samples were outgassed for 12 h at 150°C in an N<sub>2</sub> atmosphere.

The number of -SO<sub>3</sub>H groups on the surfaces of catalysts was determined by titration (Jiang et al., 2012) in which the catalyst (0.1 g) was dispersed in 20 mL of NaCl solution (2 mol/L) and then stirred magnetically for 24 h. The filtrate was titrated with NaOH solution (6 mmol/L) and phenolphthalein was used as an indicator.

### Catalytic Performance

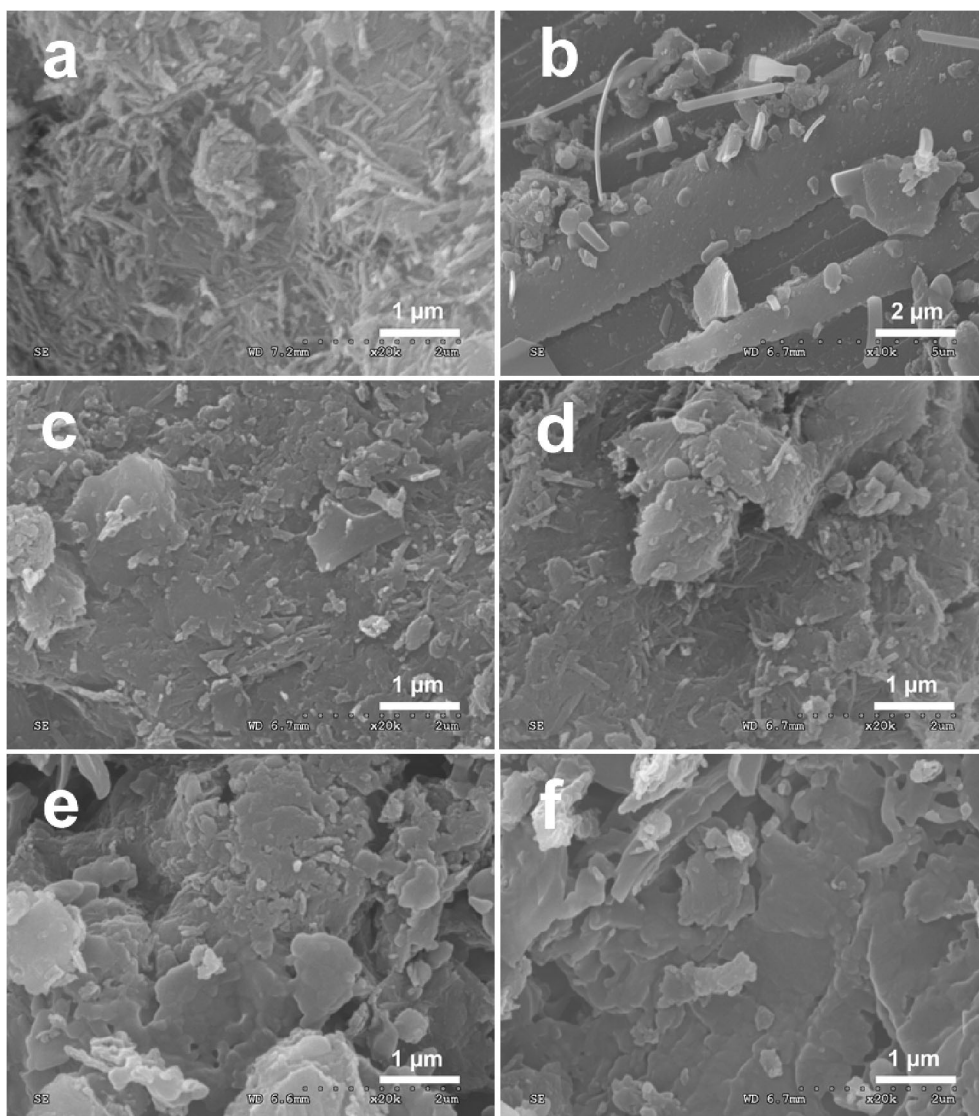
Esterification of oleic acid with methanol was used to investigate the catalytic properties of SC and SC-Plg catalysts. In a typical experiment, 1 g of oleic acid and 8 mL of methanol were added to a 25 mL round-bottom flask equipped with a reflux condenser and mechanical agitator. When the reaction mixture reached 65°C, 0.05 g of catalyst was added, and the mixture was heated at reflux for 4 h under magnetic stirring. After the reaction, the mixture was centrifuged to separate the solution from the catalyst. The supernatant (0.5 mL) was diluted with 10 mL of *n*-hexane and then analyzed using gas chromatography (GC – Agilent 6820 GC with a DB-1 capillary column, Agilent Technologies Inc., Palo Alto, California, USA). Heptadecane was used as an internal standard.

Recycling experiments were carried out to determine the catalyst stability. At the end of each reaction cycle, the catalyst was recycled by centrifugation, washed with acetone, and dried at 80°C.

## RESULTS AND DISCUSSION

### Preparation and Characterization of Catalyst

The SEM images of Plg, SC, and SC-Plg catalysts (Fig. 1) indicated that rod-shaped Plg crystals aggregated to form fibrous bundles, while SC produced larger solid particles with smoother surfaces. Carbon was produced mainly by the carbonization of sucrose, and the amount increased as the amount of sucrose increased. Rod-shaped Plg crystals firstly adsorbed the liquid mixture composed of sucrose and TsOH and then were enveloped by the thick liquid formed during the process of drying. Finally, carbon materials were formed on the surface of Plg fibers after sucrose carbonization, and dispersed Plg fibers were embedded in the black carbon solid particles and disappeared gradually with increasing sucrose content. No Plg fibers were observed in the catalyst when the sucrose dosage was 7 g, indicating that the



**Fig. 1** SEM images of **a** Plg, **b** SC, **c** SC-Plg-1, **d** SC-Plg-3, **e** SC-Plg-5, and **f** SC-Plg-7

coatings on the Plg fibers were too thick to encase the Plg crystals completely and thus form smooth, compact solids.

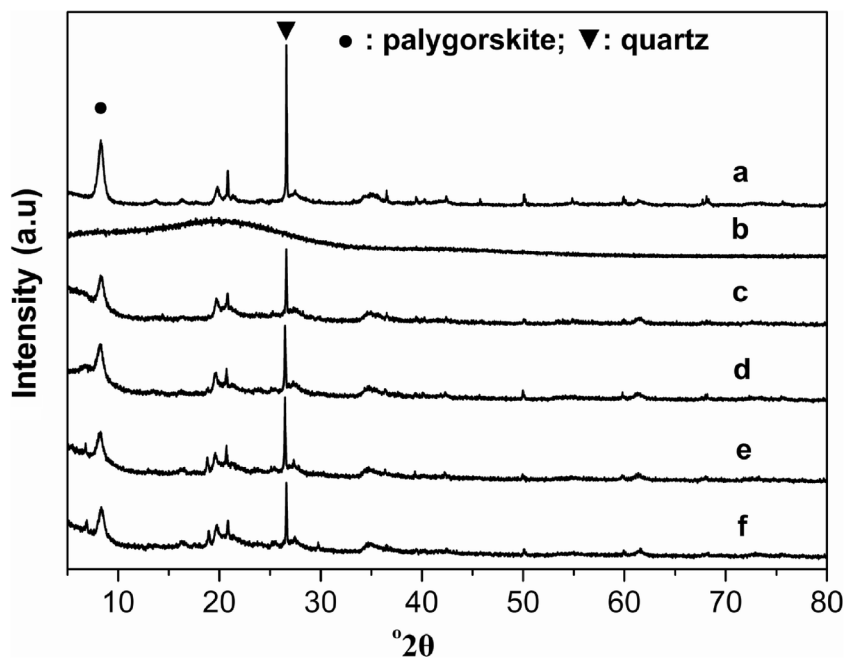
The XRD patterns of Plg, SC, and SC-Plg catalysts (Fig. 2) revealed that Plg contained two diffraction peaks at  $8.3$  and  $26.55^{\circ}2\theta$ , which were ascribed to Plg and quartz, respectively (Jiang et al., 2012). A weak and broad diffraction peak from  $15$  to  $30^{\circ}2\theta$  was observed in the SC patterns due to the presence of an amorphous carbon material (Tang and Niu, 2019). The intensity of the characteristic diffraction peaks of Plg and quartz decreased significantly after loading the carbon material, but their intensity did not change as the sucrose dosage increased. This suggested that carbon derived from sucrose carbonization was loaded uniformly on the Plg surface.

The TEM images of Plg and SC-Plg-5 (Fig. 3) exposed rod-shaped Plg fibers 10–30 nm long, and nanosized spherical

particles were also observed, which may be of quartz or another impurity. The TEM images of SC-Plg-5 (Fig. 3b) further revealed that the rod-shaped Plg fibers and spherical nanoparticles were coated with a carbon nanolayer after sucrose carbonization.

The  $N_2$  adsorption-desorption isotherms of Plg and SC-Plg catalysts showed type IV isotherms with H3 hysteresis loops (Fig. 4) (Jiang et al., 2012), indicating the presence of mesopores. Plg exhibited the largest amount of  $N_2$  adsorbed. The amount of  $N_2$  adsorbed by SC-Plg and the hysteresis loop volume decreased gradually upon increase of the sucrose dosage due to the formation of a carbonaceous coating.

The textural properties of Plg, SC, and Plg-SC catalysts (Table 1) included a BET surface area and pore volume of  $169 \text{ m}^2/\text{g}$  and  $0.324 \text{ cm}^3/\text{g}$ , respectively, for Plg. Due to the nonporous structure of SC, no BET surface area or



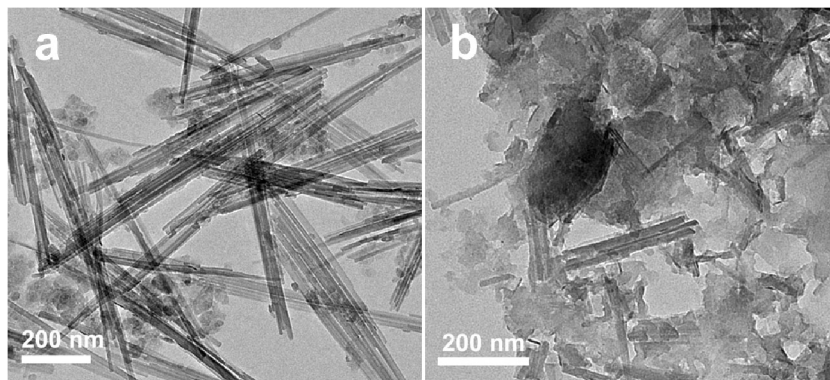
**Fig. 2** XRD patterns of **a** Plg, **b** SC, **c** SC-Plg-1, **d** SC-Plg-3, **e** SC-Plg-5, and **f** SC-Plg-7

pore volume was recorded. The introduction of Plg increased efficiently the surface area and pore volume of the resultant catalyst. The BET surface area and pore volume of SC-Plg catalysts decreased as the carbon content increased. The results indicated that carbon was deposited successfully in the mesopores and on the external surface of Plg, which decreased the BET surface area and pore volume.

The energy-dispersive X-ray (EDX) spectrum of SC-Plg-5 (Fig. 5) showed that Si, Mg, Al, Fe, O, and K were derived from Plg (Jiang et al., 2012). S and C derived from sucrose and TsOH also appeared in Fig. 5, indicating that a S-containing carbon material was loaded onto the surface of the Plg fibers.

The FTIR spectra were used to reveal the identity of the S-containing organic functional groups in Plg and SC-Plg-3 (Fig. 6). The two adsorption bands at 465 and 1083  $\text{cm}^{-1}$  were attributed to the Si–O–Si bands in Plg (Araújo Melo

et al., 2002), which disappeared after a carbon layer formed on the surface of Plg fibers. The bands at 3409 and 1620  $\text{cm}^{-1}$  were ascribed to the O–H stretching vibrations and C=C skeletal vibrations (Xiao et al., 2010; Laohapornchaiphon et al., 2017). The results further illustrated that Plg fibers were covered by a carbon layer (Wang et al., 2011b), corresponding to the analysis results of the TEM images of SC-Plg. Five weak bands at 1008, 1040, 1125, 1220, and 1379  $\text{cm}^{-1}$  were clearly visible in the FTIR spectrum of the SC-Plg catalyst. The vibrational bands at 1008 and 1040  $\text{cm}^{-1}$  were assigned to the S=O asymmetric stretching of  $\text{SO}_3\text{H}$  groups (Geng et al., 2011), while the vibrational bands at 1125, 1220, and 1397  $\text{cm}^{-1}$  were assigned to the asymmetric  $\text{SO}_2$  stretching of  $\text{SO}_3\text{H}$  groups (Peng et al., 2010; Geng et al., 2011). These results show that  $-\text{SO}_3\text{H}$  groups were introduced into the carbonaceous material by adding TsOH to the synthesis mixture.



**Fig. 3** TEM images of **a** Plg and **b** SC-Plg-5

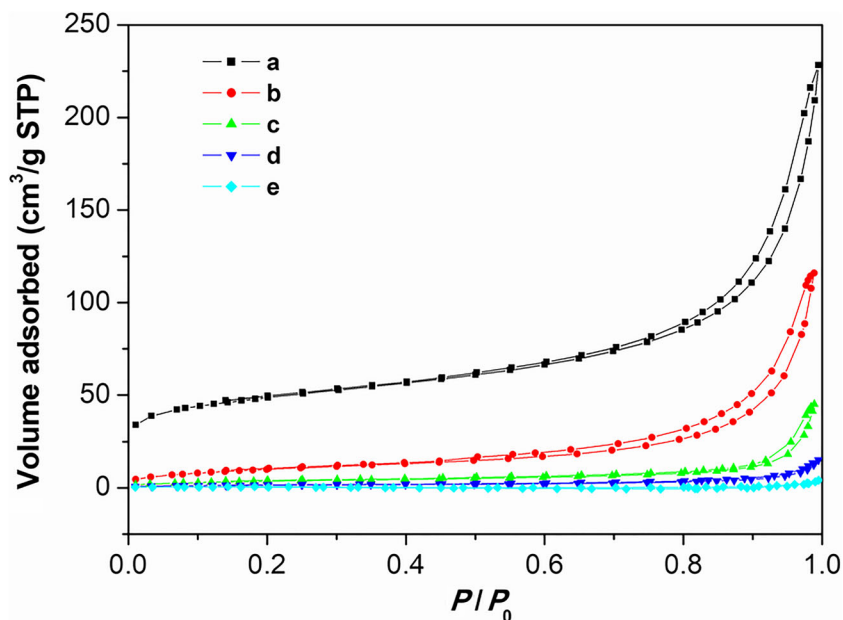


Fig. 4  $N_2$  adsorption isotherms of a Plg, b SC-Plg-1, c SC-Plg-3, d SC-Plg-5, and e SC-Plg-7

The amount of acidic- $SO_3H$  groups on the surface of SC and SC-Plg determined by neutralization titration with NaOH are listed in Table 1. The acid content of SC was 0.345 mmol/g. The acid amount of SC-Plg decreased sharply after the introduction of Plg, but increased as the amount of sucrose increased. The acidity ranged from 0.019 to 0.051 mmol/g, less than that of sulfonated mesoporous carbon (2.3 mmol/g) (Peng et al., 2010). As shown in Table 1, the S and C contents in SC and SC-Plg measured by elemental analysis also increased with the amount of sucrose. The results suggest that TsOH reacted with the carbon derived from sucrose, causing the sulfur content to increase with the amount of sucrose. The S content in the catalysts was significantly greater than that determined by

neutralization titration. This illustrates that sulfur atoms in the carbon material increased with the amount of sucrose, but some sulfur atoms were encapsulated in the carbonaceous material, and were not released in the subsequent reaction.

#### Catalytic Performance of Catalyst

Esterification of oleic acid with methanol was used to evaluate the catalytic activity of the SC-Plg catalyst (Table 1). The conversion of oleic acid was 50.37% without a catalyst, which increased to 65.07% after adding Plg, due to the acidity of Plg. Obviously, the limited improvement in oleic acid conversion was attributed to the small number of acid sites on Plg (Araújo Melo et al., 2002). The  $-SO_3H$  groups in SC

Table 1 Textural properties, composition analysis, acid density, and catalytic properties of catalysts

Catalysts	BET surface area ( $m^2/g$ )	Pore volume ( $cm^3/g$ )	C content (wt.%)	S content (mmol/g)	Acid amount of $-SO_3H$ (mmol/g)	Conversion <sup>a</sup> (%)
—	—	—	—	—	—	50.37
Plg	169	0.324	—	—	—	65.07
SC	—	—	65.64	1.070	0.345	88.87
SC-Plg-1	38	0.166	9.21	0.439	0.019	79.63
SC-Plg-3	14	0.064	16.86	0.518	0.023	82.79
SC-Plg-5	5	0.019	22.56	0.547	0.048	84.68
SC-Plg-7	1	0.005	26.59	0.641	0.051	81.45

<sup>a</sup> Conversion of oleic acid

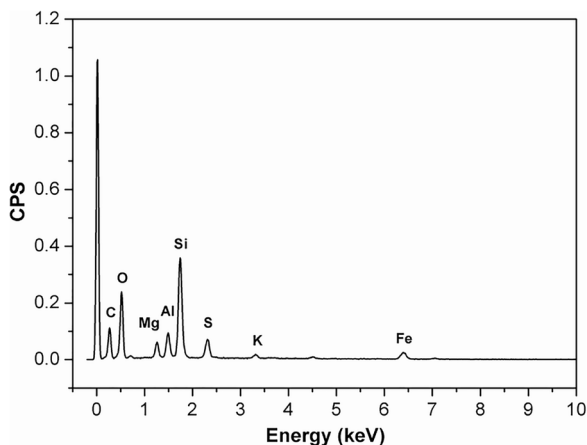


Fig. 5 Energy-dispersive X-ray spectrum of SC-Plg-5

released  $H^+$  ions which reacted with ketonic oxygen of oleic acid and increased the electropositivity of the carbonyl carbon atom. Nucleophile methanol subsequently attacked the carbonyl carbon atom. Methyl oleate was formed after the removal of the  $H_2O$  molecule and  $H^+$  ion. Due to its abundant  $-SO_3H$  groups, the introduction of SC greatly enhanced the conversion of oleic acid to 88.87%. In contrast, Plg (50 wt.%) was added to SC by mechanical mixing and then the physical mixture of SC and Plg was used as the catalyst. The conversion of oleic acid was reduced to 77.38%. These results indicated that SC possessed greater acidity than Plg, resulting in greater catalytic activity. The conversion of oleic acid over SC-Plg decreased slightly when Plg nanofibers were added to SC by simultaneous calcination and sulfonation of a mixture of sucrose,

TsOH, and Plg. The conversion of oleic acid over SC-Plg increased gradually upon increasing sucrose, but the conversion of oleic acid decreased to 81.45% when 7 g of sucrose was used. The greatest conversion (84.68%) was achieved when SC-Plg-5 was used as the catalyst because of the smaller surface area and pore volume of SC-Plg-7, despite its larger  $-SO_3H$  content. This indicated that Plg could replace the expensive sucrose-derived carbon without affecting negatively the catalytic activity. The major role played by Plg was that of support of the SC catalyst and increase of the surface area of the SC catalyst. The conversion of oleic acid was determined by the releasable  $-SO_3H$  groups and pore structure of the catalysts.

To investigate the effect of TsOH on the catalytic activity of SC-Plg, the dosage of TsOH was adjusted from 1 g to 1.5 and 2 g. The C content increased to 25.04% and 26.08%, and the corresponding S contents were 0.778 and 0.916 mmol/g, respectively. The results indicate that carbon materials on the surface of Plg fibers increased with TsOH. The conversion of oleic acid of SC-Plg was reduced to 82.79% in spite of the greater S content when the dosage of TsOH increased to 1.5 g. Subsequently, the conversion of oleic acid of SC-Plg increased to 85.61% when the dosage of TsOH was 2 g. The reduction of catalytic activity of SC-Plg might be caused by the increase in carbon materials despite the larger S content. The  $-SO_3H$  groups existed mainly in the inner part of carbon materials, and the number of  $-SO_3H$  groups released did not increase with TsOH. Excess TsOH did not improve significantly the catalytic activity of SC-Plg.

Comparison of the catalytic activities of various catalysts for the esterification of oleic acid with methanol (Table 2) revealed that the conversion of oleic acid over SC-Plg-5 catalyst was

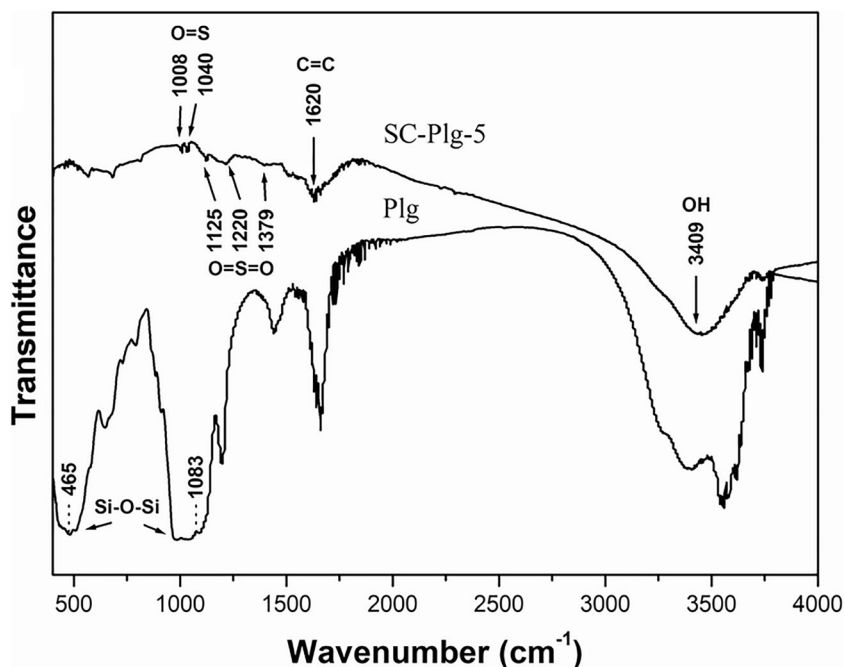


Fig. 6 FTIR spectra of Plg and SC-Plg-5

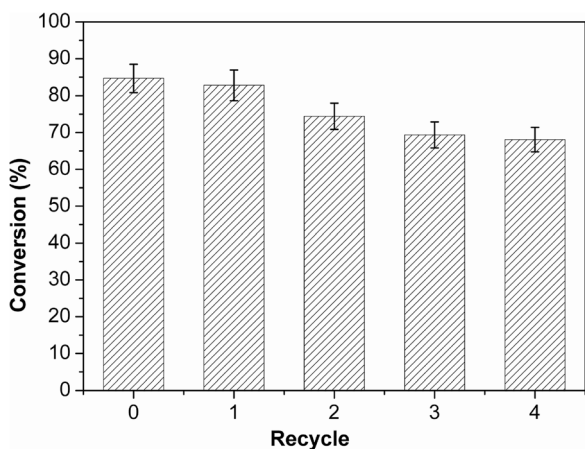
**Table 2** A comparison of esterification of oleic acid with methanol over various catalysts

Catalyst	Sulfonating agent	Catalyst dosage (g/g acid)	Alcohol/acid (molar ratio)	Temperature (°C)	Time (h)	Conversion <sup>a</sup> (%)
Mesoporous SO <sub>3</sub> H-carbon	H <sub>2</sub> SO <sub>4</sub>	0.07	10	80	10	58 (Peng <i>et al.</i> , 2010)
protonated Nafion	—	0.07	10	80	10	51 (Peng <i>et al.</i> , 2010)
HY zeolite	—	—	6	70	2	78 (Alismaeel <i>et al.</i> , 2018)
Amberlyst-15	—	0.02	55	65	4	79 (Geng <i>et al.</i> , 2012)
sulfonated carbon	H <sub>2</sub> SO <sub>4</sub>	0.10	20	65	6	90 (Flores <i>et al.</i> , 2019)
SC-Plg-5	TsOH	0.02	55	65	4	84.68 (Present study)
SBA-15-C-SO <sub>3</sub> H	TsOH, H <sub>2</sub> SO <sub>4</sub>	0.036	10	80	5	85.2 (Wang <i>et al.</i> , 2015)

<sup>a</sup> Conversion of oleic acid

greater than over HY zeolite, mesoporous SO<sub>3</sub>H-carbon, or protonated Nafion, despite the higher reaction temperature used for the latter catalysts (Peng *et al.*, 2010; Alismaeel *et al.*, 2018). Its oleic acid conversion was also greater than that of Amberlyst-15 under the same reaction conditions but was slightly less than that of sulfonated carbon and SBA-15-C-SO<sub>3</sub>H prepared using H<sub>2</sub>SO<sub>4</sub> as the sulfonating agent (Geng *et al.*, 2012; Wang *et al.*, 2015; Flores *et al.*, 2019). The results illustrated that the naturally occurring Plg can replace the more expensive SBA-15 mesoporous molecular sieve as a catalyst carrier.

The SC-Plg-5 catalyst retained most of its initial catalytic performance and displayed an oleic acid conversion of 68.09% after the fifth cycle (Fig. 7). This is greater than that of sugarcane bagasse-derived sulfonated carbon (66.6%) (Flores *et al.*, 2019). The results indicated that SC-Plg possessed excellent catalytic activity and stability. The S content in SC-Plg-5 decreased from 0.547 to 0.181 mmol/g after the fifth cycle, which suggests that the decreased catalytic activity of SC-Plg-5 was caused by the loss of -SO<sub>3</sub>H groups from the carbonaceous material during the reaction (Jiang *et al.*, 2012).

**Fig. 7** Reusability of the SC-Plg-5 catalyst

## CONCLUSIONS

SC-Plg was prepared conveniently via the simultaneous carbonization-sulfonation of a mixture of sucrose, TsOH, and Plg. Plg nanofibers were used mainly as the carriers of sulfonated carbon materials. The inexpensive Plg replaced sucrose-derived carbon and increased the surface area of the catalyst. The introduction of Plg did not affect significantly the catalytic activity of the SC catalyst. SC-Plg exhibited high catalytic performance and excellent stability despite lower -SO<sub>3</sub>H content when used for the esterification of oleic acid with methanol. Excess TsOH did not improve the catalytic activity of SC-Plg because the -SO<sub>3</sub>H groups were encapsulated in the carbonaceous material, and were not completely released in the subsequent reaction. Natural Plg nanofibers were economic and efficient carriers of carbon-based, solid-acid, composite catalysts.

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## Declarations

## Conflict of Interest

The authors declare that they have no conflict of interest.

## REFERENCES

- Alismael, Z. T., Abbas, A. S., Albayati, T. M., & Doyle, A. M. (2018). Biodiesel from batch and continuous oleic acid esterification using zeolite catalysts. *Fuel*, *234*, 170–176.
- Araújo Melo, D. M., Ruiz, J. A. C., Melo, M. A. F., Sobrinho, E. V., & Martinelli, A. E. (2002). Preparation and characterization of lanthanum palygorskite clays as acid catalysts. *Journal of Alloys and Compounds*, *344*, 352–355.
- Budarin, V., Clark, J. H., Hardy, J. J. E., Luque, R., Milkowski, K., Tavener, S. J., & Wilson, A. J. (2006). Starbons: new starch-derived mesoporous carbonaceous materials with tunable properties. *Angewandte Chemie International Edition*, *45*, 3782–3786.
- De Vyver, S. V., Peng, L., Geboers, J., Schepers, H., de Clippel, F. C., Gommès, J., Goderis, B., Jacobs, P. A., & Sels, B. F. (2010). Sulfonated silica/carbon nanocomposites as novel catalysts for hydrolysis of cellulose to glucose. *Green Chemistry*, *12*, 1560–1563.
- Flores, K. P., Omega, J. L. O., Cabatingan, L. K., Go, A. W., Agapay, R. C., & Ju, Y. H. (2019). Simultaneously carbonized and sulfonated sugarcane bagasse as solid acid catalyst for the esterification of oleic acid with methanol. *Renewable Energy*, *130*, 510–523.
- Geng, L., Wang, Y., Yu, G., & Zhu, Y. (2011). Efficient carbon-based solid acid catalysts for the esterification of oleic acid. *Catalysis Communications*, *13*, 26–30.
- Geng, L., Yu, G., Wang, Y., & Zhu, Y. (2012). Ph-SO<sub>3</sub>H-modified mesoporous carbon as an efficient catalyst for the esterification of oleic acid. *Applied Catalysis A: General*, *427–428*, 137–144.
- Guo, M. L., Yin, X. Y., & Huang, J. (2017). Preparation of novel carbonaceous solid acids from rice husk and phenol. *Materials Letters*, *196*, 23–25.
- Jiang, J., Xu, Y., Duanmu, C., Gu, X., & Chen, J. (2012). Preparation and catalytic properties of sulfonated carbon-palygorskite solid acid catalyst. *Applied Clay Science*, *95*, 260–264.
- Laohapornchaiphon, J., Smith, C. B., & Smith, S. M. (2017). One-step preparation of carbon-based solid acid catalyst from water hyacinth leaves for esterification of oleic acid and dehydration of xylose. *Chemistry - An Asian Journal*, *12*, 3178–3186.
- Ma, H., Li, J., Liu, W., Cheng, B., Cao, X., Mao, J., & Zhu, S. (2014). Hydrothermal preparation and characterization of novel corn-cob-derived solid acid catalysts. *Journal of Agricultural and Food Chemistry*, *62*, 5345–5353.
- Nakajima, K., & Hara, M. (2012). Amorphous carbon with SO<sub>3</sub>H groups as a solid Brønsted acid catalyst. *ACS Catalysis*, *2*, 1296–1304.
- Nandan, D., Sreenivasulu, P., Saxena, S. K., & Viswanadham, N. (2011). Facile synthesis of sulfonated carbon-silica-meso composite and mesoporous silica. *Catalysis Communications*, *47*, 11537–11539.
- Ngaosuwan, K., Goodwin Jr., J. G., & Prasertdham, P. (2016). A green sulfonated carbon-based catalyst derived from coffee residue for esterification. *Renewable Energy*, *86*, 262–269.
- Okuhara, T. (2002). Water-tolerant solid acid catalysts. *Chemical Reviews*, *102*, 3641–3666.
- Peng, L., Philippaerts, A., Ke, X., Noyen, J. V., Clippel, F. D., Tendeloo, G. V., Jacobs, P. A., & Sels, B. F. (2010). Preparation of sulfonated ordered mesoporous carbon and its use for the esterification of fatty acids. *Catalysis Today*, *150*, 140–146.
- Suganuma, S., Nakajima, K., Kitano, M., Yamaguchi, D., Kato, H., Hayashi, S., & Hara, M. (2008). Hydrolysis of cellulose by amorphous carbon bearing SO<sub>3</sub>H, COOH, and OH groups. *Journal of the American Chemical Society*, *130*, 12787–12793.
- Tang, X., & Niu, S. (2019). Preparation of carbon-based solid acid with large surface area to catalyze esterification for biodiesel production. *Journal of Industrial and Engineering Chemistry*, *69*, 187–195.
- Tao, M. L., Guan, H. Y., Wang, X. H., Liu, Y. C., & Louh, R. F. (2015). Fabrication of sulfonated carbon catalyst from biomass waste and its use for glycerol esterification. *Fuel Processing Technology*, *138*, 355–360.
- Toda, M., Takagaki, A., Okamura, M., Kondo, J. N., Hayashi, S., Domen, K., & Hara, M. (2005). Biodiesel made with sugar catalyst. *Nature*, *438*, 178.
- Valle-Vigón, P., Sevilla, M., & Fuertes, A. B. (2012). Sulfonated mesoporous silica-carbon composites and their use as solid acid catalysts. *Applied Surface Science*, *261*, 574–583.
- Wang, J., Xu, W., Ren, J., Liu, X., Lu, G., & Wang, Y. (2011a). Efficient catalytic conversion of fructose into hydroxymethylfurfural by a novel carbon-based solid acid. *Green Chemistry*, *13*, 2678–2681.
- Wang, R., Jia, J., Li, H., Li, X., Wang, H., Chang, Y., Kang, J., & Lei, Z. (2011b). Nitrogen-doped carbon coated palygorskite as an efficient electrocatalyst support for oxygen reduction reaction. *Electrochimica Acta*, *56*, 4526–4531.
- Wang, Y., Wang, D., Tan, M., Jiang, B., Zheng, J., Tsubaki, N., & Wu, M. (2015). Monodispersed hollow SO<sub>3</sub>H-functionalized carbon/silica as efficient solid acid catalyst for esterification of oleic acid. *ACS Applied Materials & Interfaces*, *7*, 26767–26775.
- Xiao, H., Guo, Y., & Liang, X. (2010). One-step synthesis of a novel carbon-based strong acid catalyst through hydrothermal carbonization. *Monatshfte für Chemie*, *141*, 929–932.
- Xu, Y., Li, X., Zhang, X., Wang, W., Liu, S., Qi, W., Zhuang, X., Luo, Y., & Yuan, Z. (2016). Hydrolysis of corn-cob using a modified carbon-based solid acid catalyst. *BioResources*, *11*, 10469–10482.
- Yang, Z., Niu, L., Jia, X., Kang, Q., Ma, Z., & Lei, Z. (2011). Preparation of silica-supported sulfate and its application as a stable and highly active solid acid catalyst. *Catalysis Communications*, *12*, 798–802.
- Yang, J., Zhang, H., Ao, Z., & Zhang, S. (2019). Hydrothermal carbon enriched with sulfonic and carboxyl groups as an efficient solid acid catalyst for butanolysis of furfuryl alcohol. *Catalysis Communications*, *123*, 109–113.
- Zhan, S., Tao, X., Cai, L., Liua, X., & Liu, T. (2014). The carbon material functionalized with NH<sup>2+</sup> and SO<sub>3</sub>H groups catalyzed esterification with high activity and selectivity. *Green Chemistry*, *16*, 4649–4653.
- Zhang, B., Ren, J., Liu, X., Guo, Y., Guo, Y., Lu, G., & Wang, Y. (2010a). Novel sulfonated carbonaceous materials from *p*-toluenesulfonic acid/glucose as a high-performance solid-acid catalyst. *Catalysis Communications*, *11*, 629–632.
- Zhang, L., Jin, Q., Shan, L., Liu, Y., Wang, X., & Huang, J. (2010b). H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> immobilized on silylated palygorskite and catalytic activity in esterification reactions. *Applied Clay Science*, *47*, 229–234.
- Zhang, W., Tao, H., Zhang, B., Ren, J., Lu, G., & Wang, Y. (2011). One-pot synthesis of carbonaceous monolith with surface sulfonic groups and its carbonization/activation. *Carbon*, *49*, 1811–1820.

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