

# Sulfonated porous biomass-derived carbon with superior recyclability for synthesizing ethyl levulinate biofuel

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# Abstract

The synthesis of ethyl levulinate (EL) via esterification of levulinic acid (LA) with ethanol, which can be derived from biomass, has become an attractive topic since EL can be applied in many fields, such as fuel additives for petroleum and biodiesel, food additives and fragrance. Herein, the sulfonated porous carbon catalysts derived from the rinds of corn stalk biomass wastes were prepared by using sulfuric acid and phosphoric acid as the sulfonating agent and activator, respectively. The preparation parameters were optimized based on the catalytic activity for LA esterification with ethanol and the acid density of the corresponding catalysts. Also, various reaction factors were optimized to improve the catalytic efficiency over the optimal sulfonated corn stalk-derived carbon (s-CSC). Under the conditions of reaction temperature 80 °C, catalyst dosage 5 wt%, ethanol-to-LA molar ratio 5.0:1 and reaction time 8 h, the LA conversion reached 94% and 93% catalyzed by s-CSC and the optimal porous catalyst (s-p-CSC), respectively. Noticeably, benefitting from the hierarchical porous structure with large surface area, s-p-CSC exhibited much better recyclability than s-CSC. This work offers a highly effective solid acid catalyst for the synthesis of biofuel.

**Keywords** Corn stalk biomass  $\cdot$  Sulfonated carbon  $\cdot$  Hierarchical porous structure  $\cdot$  Esterification  $\cdot$  Ethyl levulinate  $\cdot$  Biofuel

# Introduction

With the fast increase in urbanization and industrialization over the world, especially in China, energy is in high demand, which, in turn, leads to serious environmental pollution. Thus, it is necessary to develop practicable energy that could replace

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the traditional petroleum-based fuels [1, 2]. Among various renewable energies, biomass-based energy such as biodiesel is receiving much attention because of its unique characteristics including non-toxicity, low greenhouse gas emission, sustainability, biodegradability, etc. [3–7]. Notably, when used as fuel additive, ethyl levulinate (EL) may be added up to 5 wt% for the regular diesel engines to increase their lubricity, heat conductivity and ability of reducing particulate emissions [8]. Apart from this, EL also can be used in the fields of food additive and fragrance. In other words, the production of EL has a huge application market with obvious economic and social benefits.

Usually, EL is prepared with the esterification of levulinic acid (LA) with ethanol, which is an attractive green production process since both LA and ethanol can be obtained from renewable biomass. The reaction can be catalyzed not only by the soluble homogeneous acid catalysts (e.g.,  $H_2SO_4$ ,  $H_3PO_4$  and HCl) but also by the heterogeneous solid acid. Although the soluble catalysts exhibit high catalytic activity for LA esterification, they have serious deficiencies such as high equipment corrosion, environmental pollution and non-reusability [9], meaning that they cannot meet the requirements of green chemistry.

Solid acid catalysts possess unique advantages, such as easy separation, high reusability, low corrosion and environmental friendliness [10]. Therefore, various heterogeneous catalysts have been developed for the esterification LA with ethanol, such as the supported heteropolyacids [8–12], zeolite-based materials [13, 14] and sulfonated materials [15, 16]. Recently, sulfonated carbon has been found to be an effective catalyst for the conversion of LA to EL due to its good water tolerance, high thermal stability and superior catalytic performance [17–20]. In particular, the ones derived from biomass are of much interest since the low-cost biomasses are abundant and renewable apart from the aforementioned advantages [21–24]. Even so, the pristine biomass carbon cannot offer enough surface areas and pores to anchor the sulfonic acid groups firmly, leading to its unsatisfactory recyclability. Therefore, constructing a porous structure with high surface areas for sulfonated biomass-derived carbon catalysts is critical for their practical applications.

It has been verified that phosphoric acid ( $H_3PO_4$ ) activation for carbon may construct an ideal structure, which leads to the enhanced catalytic performance of the corresponding solid acid catalysts. Also, such strategy can sharply reduce the carbonization temperature of the biomass due to the excellent water absorptivity of  $H_3PO_4$ , resulting in low energy consumption in practical applications. Tang and Niu found the biodiesel yield may reach as high as 97.3% over the sulfonated bambooderived carbon activated by  $H_3PO_4$  [25]. Xue et al. prepared the sulfonated peanut shell-derived carbon activated by  $H_3PO_4$ , which possessed a specific surface area of 387 m<sup>2</sup> g<sup>-1</sup> and exhibited excellent stability for the hydrolysis of cyclohexyl acetate [26]. Zhong et al. also prepared the sulfonated peanut hull-derived carbon activated by  $H_3PO_4$ , whose surface area could reach up to 953 m<sup>2</sup> g<sup>-1</sup> [27]. Fu et al. found that the previous impregnation with  $H_3PO_4$  facilitates the pore formation in the sulfonated pulp fibers-derived carbon catalysts, whose specific surface area could be 118 m<sup>2</sup> g<sup>-1</sup> [28]. Nonetheless, the limited literature has reported on the sulfonated corn stalk-derived carbon activated by  $H_3PO_4$  to date. Corn is one of the main crops and widely planted in the world. Correspondingly, abundant corn stalks become agricultural waste every year, causing serious environmental pollution. Therefore, it is necessary to develop new techniques for the efficient use of corn stalks, which could support the sustainable development of human society. In fact, corn stalks have been used to produce biogas [29, 30], bioethanol [31, 32], solid biofuel [33], etc. However, those utilizations are far from being enough to consume huge amounts of corn stalks at present. Considering the fact that corn stalk contains cellulose, hemicellulose and lignin, corn stalk-derived carbon materials have attracted considerable attention and have been applied in many fields such as absorbents [34, 35], electrode materials [36, 37] and solid acid catalysts [38]. Nevertheless, there are only a few reports about the preparation of sulfonated porous corn stalk-derived carbon for LA esterification.

Inspired by the aforementioned insights, we, herein, focus on the sulfonated porous carbon prepared from corn stalks by using  $H_3PO_4$  as an activator for LA esterification with ethanol. In order to verify the influence of the activation, a series of sulfonated corn stalk-based carbon catalysts without using  $H_3PO_4$  are also prepared. The as-prepared materials are characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR), scanning electron microscope (SEM), thermogravimetric analysis (TGA),  $N_2$  adsorption–desorption experiment, temperature programmed desorption of ammonia ( $NH_3$ -TPD) and Raman spectra. The preparation parameters such as carbonization temperature and time, sulfonation temperature and time and  $H_3PO_4$  dosage are optimized based on the corresponding LA conversion and the acid density. Moreover, the catalytic reaction factors such as temperature, mole ratio of ethanol to LA, time and catalyst dosage are optimized to improve the catalytic efficiency. Also, the recycling behaviors of the as-prepared solid acid catalysts are comparatively explored.

## **Experimental section**

#### Preparation of the sulfonated corn stalk-derived carbon

The mature corn stalks collected on the farmlands in September (Wuyang County, Henan Province, China) were cut into about 20 cm, the rinds were stripped out, washed with deionized (DI) water to remove the impurities and dried at 110 °C in an oven. Then, these rinds were carbonized at 240 °C for 0.5 h in air atmosphere (muf-fle furnace, 20 °C min<sup>-1</sup>) and mixed evenly. Finally, the black solids were ground and partially carbonized at certain temperatures (400–900 °C) in a tube furnace under nitrogen atmosphere (with 2 °C min<sup>-1</sup> temperature varying rate) for certain time (30–180 min) to get the corresponding corn stalk-derived carbon materials.

1 g of corn stalk-derived carbon materials were blended with concentrated sulfuric acid (98%, 15 mL) and hydrothermally treated at designed temperatures (100–200 °C) for certain time (9–24 h). To remove the residual sulfuric acids, the resulting black solids were washed with hot DI water (80 °C) until it reached neutral pH, followed by drying at 110 °C in an oven. Unless otherwise specified, CSC cited in this work were the optimal one calcined at 600 °C for 120 min and s-CSC was the CSC-based catalysts sulfonated at 140 °C for 18 h.

## Preparation of the sulfonated porous corn stalk-derived carbon

2 g of the corn stalk rind powders (<0.25 mm in diameter) were dispersed evenly into phosphoric acid solution (30%, 10–70 mL) via ultrasonication, followed by drying at 110 °C in an oven. Then, the resultant black viscous solid was calcined at certain temperatures (200–600 °C) under nitrogen atmosphere (tube furnace, 5 °C min<sup>-1</sup>) for certain time (30–270 min) and washed with DI water to bring pH=7, resulting in the corresponding porous corn stalk-derived carbon materials. Unless otherwise specified, p-CSC referred to below was the optimal one treated with 30 mL of phosphoric acid solution and calcined at 300 °C for 150 min.

The sulfonated procedure for the porous corn stalk-derived carbon was similar to that for the aforementioned one. Unless otherwise specified, s-p-CSC referred to below was the porous catalyst prepared from p-CSC sulfonated at 140 °C for 18 h.

## Characterization

The samples were characterized by XRD (Panalytical XPert-Pro diffractometer, Cu K $\alpha$  radiation), XPS (RBD upgraded PHI-5000C ESCA system), IR (Thermo scientific Nicolet 380 Fourier transform spectrometer), SEM (SU8010 scanning electron microscope), Raman (Renishaw in Via-Reflex spectrometer,  $\lambda$ =633 nm), TGA (STA 409 PC simultaneous thermogravimetric analyzer–differential scanning calorimeter, 5 °C min<sup>-1</sup>, N<sub>2</sub> flow), N<sub>2</sub> adsorption–desorption (Micromeritics ASAP 2420-4MP automated surface area and pore size analyzer) and NH<sub>3</sub>-TPD (Quantachrome Autosorb-IQ gas adsorption analyzer).

The acid density of the as-prepared carbon catalysts was calculated by Eq. (1) according to an ion-exchange titration method. 0.05 g of the catalysts were dispersed into NaCl solution (2 mol  $L^{-1}$ , 15 mL) under ultrasonic to reach the exchange equilibrium between H<sup>+</sup> and Na<sup>+</sup>. The solid was filtered and washed thoroughly with DI water. The resultant filtrate was titrated with NaOH solution (0.01 mol  $L^{-1}$ ) using phenolphthalein as an indicator for pH neutral condition.

Acid density (mmol g<sup>-1</sup>) = 
$$\frac{\Delta V_{\text{NaOH}} \times c_{\text{NaOH}}}{m}$$
, (1)

where  $\Delta V_{\text{NaOH}}$  was the consumed volume of NaOH solution (mL),  $c_{\text{NaOH}}$  was the molar concentration of NaOH solution (0.01 mol L<sup>-1</sup>) and *m* was the dosage of the catalyst (0.05 g).

# **Catalytic performance**

Esterification of LA with ethanol was used to investigate the catalytic performance of the solid acid catalysts obtained. LA (4.00 g, 34.0 mmol) and certain amounts of

catalyst measured with the mass percentage of LA were blended with ethanol in a 50-mL round bottom flask equipped with a water-cooled condenser in an oil bath. Under magnetic stirring (600 rpm), the mixture was heated at predefined temperature for certain time. Then, the solid acid catalysts were separated out by vacuum filtration and washed with ethanol. The remaining ethanol and water produced in the filtrate were removed out by rotary evaporation. The final products were analyzed by a gas chromatograph (GC2010 II, FID detector, 30 m × 0.53 mm × 0.33 mm OV-1701 capillary column). LA conversion was calculated by using Eq. (1).

LA conversion (%) = 
$$\frac{n_0 - n}{n_0} \times 100,$$
 (2)

where  $n_0$  is the initial amount of LA (mmol) and *n* is the final amount of LA (mmol).

The esterification reaction catalyzed by s-CSC were optimized from the aspects of temperature (40–90 °C), ethanol-to-LA molar ratio ((2.5–12.5):1), catalyst dosage (0–12.5 wt%) and time (2–12 h) to improve the catalytic efficiency.

The catalytic reaction was performed for six runs under the optimized conditions to evaluate the recyclability of s-CSC and s-p-CSC. After each esterification run, the catalysts were washed with hot DI water (80 °C) and ethanol to eliminate LA and EL attached during esterification, followed by drying at 110 °C for the next cycle.

# **Results and discussion**

#### **Optimization of the fabrication conditions**

As for sulfonated carbon materials, different preparation parameters of both carbonization and sulfonation procedures may affect the microstructure, the anchored amounts and existed state of sulfonic acid groups, leading to different catalytic performances. Thus, it is necessary to optimize the preparation conditions to improve LA conversion catalyzed by the sulfonated corn stalk-based carbon catalysts. In this section, the esterification reaction is performed under the conditions as follows: the reaction temperature of 80 °C, reaction time of 8 h, catalyst dosage of 5.0 wt% and ethanol-to-LA molar ratio of 5.0:1.

Figures 1a and 2a show the influence of different carbonization temperatures on catalytic activity and acid density of the corresponding sulfonated corn stalk-derived carbon and porous carbon catalysts, respectively. We can see that the increase in carbonization temperature improves the LA conversion and acid density to some extent. Further increasing carbonization temperature leads to opposite behaviors in both cases. It is because that high carbonization temperature may produce more polycyclic aromatic hydrocarbons to bond more sulfonic acid groups. At a further elevated temperature, corn stalks are carbonized severely, leading to the formation of macromolecular fused ring aromatic planar carbon, which deceases their binding ability with the sulfonic acid groups [24]. For the un-activated carbon catalysts, the one carbonized at 600 °C possesses the largest acid density (1.94 mmol  $g^{-1}$ ) and offers the highest catalytic activity (LA conversion=89%) under the present conditions



Fig. 1 Effects of carbonization temperature (a), carbonization time (b), sulfonation temperature (c) and sulfonation time (d) on the catalytic activity and acid density of the corresponding sulfonated carbon catalysts



Fig. 2 Effects of carbonization temperature (a), carbonization time (b), sulfonation temperature (c) and sulfonation time (d) on the catalytic activity and acid density of the corresponding sulfonated porous carbon catalysts

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(carbonization time 150 min, sulfonation temperature 180 °C and sulfonation time 24 h). For the activated porous carbon catalysts, the optimal carbonization temperature is 300 °C. Under the applied conditions (carbonization time 90 min,  $H_3PO_4$  solution dosage 30 mL, sulfonation temperature 140 °C and sulfonation time 24 h), LA conversion and acid density could reach 90% and 1.94 mmol g<sup>-1</sup>, respectively (Fig. 2a). Moreover, compared with that of the un-activated catalysts, the optimal carbonization temperature of the porous catalysts decreases from 600 to 300 °C, which is mainly related to the strong water absorptivity of phosphoric acid, resulting in low energy consumption in the practical applications.

Figures 1b and 2b show the influences of different carbonization time on catalytic activity and acid density of the corresponding catalysts, respectively. Prolonging suitably the carbonization time could facilitate the increase in the catalytic activity and acid density for both as-prepared solid acid catalysts. Further increasing carbonization time does not lead to the increase in the LA conversion and acid density anymore, which even decrease slightly. This can be explained that the carbonization degree of forming the polycyclic aromatic hydrocarbon structure increases with increasing carbonization time, which anchors the sulfonic acid groups. Once the carbon skeleton structure is finally formed, the additional carbonization time may be unnecessary. Therefore, the optimal carbonization time for the sulfonated carbon is 120 min under the conditions of carbonization temperature 600 °C, sulfonation temperature 180 °C and sulfonation time 24 h. The corresponding LA conversion and acid density are 91% and 2.06 mmol  $g^{-1}$ , respectively (Fig. 1b). For the sulfonated porous carbon, the optimal carbonization time is 150 min under the conditions (carbonization temperature 300 °C, H<sub>3</sub>PO<sub>4</sub> solution dosage 30 mL, sulfonation temperature 140 °C and sulfonation time 24 h), over which the LA conversion and acid density are 90% and 2.00 mmol  $g^{-1}$ , respectively (Fig. 2b).

Figures 1c and 2c show the influence of different sulfonation temperatures on catalytic activity and acid density of the corresponding sulfonated corn stalk-derived carbon and porous carbon catalysts, respectively. We can see the LA conversion and acid density first increase with increasing sulfonation temperature and then keep almost constants or even decrease when the temperature is above 140 °C, mostly resulting from the occurrence of side reactions such as sulfone and multi-sulfonation [21]. Therefore, the optimal sulfonation temperature is 140 °C for the sulfonated carbon catalysts and the porous ones. For the former, under the conditions (carbonization temperature 600 °C, carbonization time 120 min and sulfonation time 24 h), the maximum LA conversion and acid density are 92% and 2.08 mmol g<sup>-1</sup>, respectively (Fig. 1c). For the latter, under the conditions (carbonization temperature 300 °C, carbonization time 150 min,  $H_3PO_4$  solution dosage 30 mL and sulfonation time 24 h), the maximum LA conversion and acid density are 93% and 2.00 mmol g<sup>-1</sup>, respectively (Fig. 2c).

Figures 1d and 2d show the influences of different sulfonation time on catalytic activity and acid density of the corresponding sulfonated corn stalk-derived carbon and porous carbon catalysts, respectively. We can see that both LA conversion and acid density increase obviously when the time is within 18 h. Further extending the sulfonation time cannot lead to positive influences anymore. Therefore, the optimal sulfonation time is 18 h for the sulfonated carbon catalysts and

the porous ones. For the former, under the conditions (carbonization temperature 600 °C, carbonization time 120 min and sulfonation temperature 140 °C), the maximum LA conversion and acid density are 92% and 2.10 mmol g<sup>-1</sup>, respectively (Fig. 1d). For the latter, under the conditions (carbonization temperature 300 °C, carbonization time 150 min,  $H_3PO_4$  solution dosage 30 mL and sulfonation temperature 140 °C), the maximum LA conversion and acid density are 94% and 2.02 mmol g<sup>-1</sup>, respectively (Fig. 2d).

 $H_3PO_4$  is expected to construct porous structure in the sulfonated carbon with high surface area, which are favorable for tightly anchoring the  $-SO_3H$  groups. However, too much  $H_3PO_4$  dosage may increase the degree of graphitization and induce the collapse of the etched pores. Therefore, it is necessary to optimize the dosage of  $H_3PO_4$ . As shown in Fig. 3, LA conversion reaches the highest value (93%) catalyzed by the sulfonated porous carbon prepared with 30 mL of  $H_3PO_4$ solution. The corresponding acid density is up to 2.00 mmol g<sup>-1</sup>. In other words, Fig. 3 verifies the optimal  $H_3PO_4$  solution dosage is 30 mL under the present conditions (carbonization temperature 300 °C, carbonization time 150 min, sulfonation temperature 140 °C and sulfonation time 18 h).

In summary, the optimal synthesis parameters for the production of sulfonated corn stalk-derived carbon are as follows: calcination temperature of 600 °C, calcination time of 120 min, sulfonation temperature of 140 °C and sulfonation time of 18 h. While the optimal synthesis parameters for the production of sulfonated corn stalk-derived porous carbon are as follows: calcination temperature of 300 °C, calcination time of 150 min,  $H_3PO_4$  solution (30%) dosage of 30 mL, sulfonation temperature of 140 °C and sulfonation time of 18 h.



Fig. 3 Effects of phosphoric acid solution dosage on LA conversion and acid density for the corresponding sulfonated porous corn stalk carbon

#### Characterization

In order to investigate the relationship between the microstructure and catalytic property, we characterize the samples prepared under the aforementioned optimal conditions with various techniques.

Figure 4a illustrates the IR spectra of CSC, s-CSC, p-CSC and s-p-CSC. On the one hand, the sulfonated solid acid catalysts (s-CSC and s-p-CSC) maintain the characteristic IR absorption peaks of the corresponding pristine carbon materials. On the other hand, compared with those of the pristine carbon materials, three new absorption peaks appear at ca. 580, 1040 and 1163 cm<sup>-1</sup> in the IR spectra of s-CSC and s-p-CSC. Those peaks are attributed to the weak absorption of C–S bonds, the symmetric and asymmetric stretching of O=S=O, respectively, confirming the successful incorporation of –SO<sub>3</sub>H group into the pristine carbon structure.

The thermal stability of the sulfonated catalysts is measured using TGA technique under nitrogen atmosphere (Fig. 4b). The weight loss of 3% for s-p-CSC and 8% for s-CSC below 170 °C is caused by the evaporation of water adsorbed. At elevated temperatures, s-CSC and s-p-CSC show different weight loss characteristics. For s-CSC, two obvious decomposition processes occur at 250–380 °C and 450–800 °C, respectively. For s-p-CSC, a continuous weight loss is seen at 250–800 °C. These losses are related to the gradual decompositions of various components presented in the catalysts, such as the cellulose component (C–C, C–O and –OH bonding) and the anchored –SO<sub>3</sub>H groups [39]. Their different decomposition of H<sub>3</sub>PO<sub>4</sub>, which is favorable for the decompositions of cellulose component. Based on their similar acid density representing the nearly same amounts of anchored –SO<sub>3</sub>H groups in the catalysts, s-p-CSC shows a larger residual char yield (~42%) than s-CSC (~32%) even deducing their difference in the aforementioned water adsorbed.

Figure 5 shows the XPS spectra of s-CSC and s-p-CSC. The survey spectra shown in Fig. 5a verify that they contain the elements of O, C and S. Among them, the element of C and part of O originate from the corn stalk biomass, while S and part of O come from the anchored  $-SO_3H$  groups in the catalysts. In addition, no P element is detected, meaning that the  $H_3PO_4$  activator has been washed out thoroughly



Fig. 4 IR spectra (a) and TG curves (b) of the as-prepared materials



Fig. 5 XPS survey spectra (a) and the corresponding high-resolution C 1s (b), O 1s (c) and S 2p (d) spectra of s-CSC and s-p-CSC

during the preparation procedure. As presented in Fig. 5b for the C 1s spectrum, the peak at 284.8 eV is assigned to the C–C and/or C=C of graphitic carbon. The one centered at 286.8 eV is assigned to the carbon in C–O, whereas the peaks centered at 288.8 and 291.2 eV are assigned to C in C=O and O–C=O, respectively [21]. For the high-resolution O 1s spectrum shown in Fig. 5c, the peak centered at about 533 eV originates from O in C–O and HO–C=O. The peak centered at about 532 eV is assigned to O in C=O and –SO<sub>3</sub>H groups. The peaks at 168.7 eV and 169.9 eV in the high-resolution S 2p spectrum shown in Fig. 5d can be attributed to S  $2p_{3/2}$  and S  $2p_{1/2}$ , respectively, further confirming the successful introduction of –SO<sub>3</sub>H groups [40].

Figure 6a displays the XRD patterns of CSC, s-CSC, p-CSC and s-p-CSC. It is observed that either the pristine carbon materials (CSC and p-CSC) or the sulfonated catalysts (s-CSC and s-p-CSC) exhibit a broad diffraction peak ( $2\theta = 15^{\circ}-37^{\circ}$ ) and one weak peak ( $2\theta = 38^{\circ}-50^{\circ}$ ), corresponding with the (002) and (100) planes of graphite carbon, respectively [41, 42]. Compared with that for CSC, the (002) plane for other samples shift about 2° to higher  $2\theta$  angle. Meanwhile, the peak intensity, especially that of the (100) plane, decreases. The results prove that the activation of H<sub>3</sub>PO<sub>4</sub> and the anchored  $-SO_3H$  groups increase the defects of the carbon materials and further promote the formation of the layered graphite structure with a decreased inter-layer distance.



Fig. 6 XRD patterns (a) and Raman spectra (b) of the as-prepared materials

The graphitization is characterized by Raman spectroscopy. Two typical peaks attributed to amorphous carbon appear in all the spectra at around 1370 and 1590 cm<sup>-1</sup>, which are corresponded with the *D*- and *G*-bands, respectively (Fig. 6b). The *D*-band is attributed to the vibration of carbon with dangling bonds for the in-plane terminations of defects and disordered graphite, whereas the G-band is assigned to the vibration of  $sp^2$  carbon in the two-dimensional hexagonal lattice [43, 44]. The corresponding peak intensity ratios of the *D*- and *G*-bands are 0.74, 0.81, 0.77 and 0.79. The results reveal that the activation of H<sub>3</sub>PO<sub>4</sub> and the anchored –SO<sub>3</sub>H groups could generate some new defects and increase the disorder in the pristine carbon sheets.

Figures 7 and 8 illustrate the SEM images and EDX elemental mappings of s-CSC and s-p-CSC, respectively. From Figs. 7a and 8a, we can observe clearly that both of them display a sheet structure in addition to an irregular and heterogeneous surface morphology containing obvious crevices and cracks. Moreover, compared with s-CSC, s-p-CSC has a much rougher surface with holes in various sizes and shapes due to the phosphoric acid activation. After the chemical reaction between



Fig. 7 SEM image (a) and EDX elemental mapping (b) of s-CSC



Fig. 8 SEM image (a) and EDX elemental mapping (b) of s-p-CSC

 $H_3PO_4$  and the cellulose, lignin and other components in corn stalks, such as dehydration condensation and cross-linking, pores could be formed in the catalyst [45] which in turn provide large surface area to firmly anchor the sulfonic groups. Also, the catalyst with porous structure and high surface area is advantageous to the heterogeneous catalysis because of the decreased mass transfer resistance. The elemental mappings shown in Figs. 7b and 8b reveal that the S, C and O elements exist in both catalysts, implying that the  $-SO_3H$  groups are homogeneously loaded onto the surfaces of CSC and p-CSC in the employed hydrothermal sulfonation process, respectively.

The textural properties of CSC, s-CSC, p-CSC and s-p-CSC are characterized by  $N_2$  adsorption-desorption analysis. First, as presented in Fig. 9a, all materials exhibit type IV isotherms with H3-type hysteresis loops, confirming that mesoporous structures are constructed in the materials. Second, the obvious steep rise of  $N_2$  uptake in their adsorption-desorption isotherms, except for that of s-CSC, reveals the presence of abundant micropores [46]. This also can be found in their pore size distribution curves shown in Fig. 9b and their large t-Plot micropore areas



Fig.9  $N_2$  adsorption-desorption isotherms (a) and pore size distribution curves (b) of the materials obtained

and micropore volumes (Table 1). Third, p-CSC and s-p-CSC possess much larger  $N_2$  volume adsorbed than CSC and s-CSC due to the construction of abundant pores through the etching of  $H_3PO_4$  mentioned above, implying the higher surface area of catalysts. As presented in Table 1, the Langmuir surface area (S<sub>Langmuir</sub>) and Brunauer–Emmet–Teller (BET) surface area  $(S_{BET})$  for p-CSC are as high as 685.7 and 484.7 m<sup>2</sup> g<sup>-1</sup>, respectively. The corresponding values for CSC are only 35.9 and 28.9 m<sup>2</sup> g<sup>-1</sup>, respectively. Four,  $S_{\text{Langmuir}}$ ,  $S_{\text{BET}}$  and pore volume ( $V_{\text{p}}$ ) of the sulfonated solid acid catalysts are lower than that of the corresponding pristine carbon. For s-CSC,  $S_{\text{Langmuir}}$ ,  $S_{\text{BET}}$  and  $V_{p}$  dramatically decrease by 52.1% (from 35.9 to  $17.2 \text{ m}^2 \text{ g}^{-1}$ ), 57.1% (from 28.9 to 12.4 m<sup>2</sup> g<sup>-1</sup>) and 21.7% (from 0.023 to 0.018 cm<sup>3</sup>) g<sup>-1</sup>), respectively, in comparison with those of CSC. For s-p-CSC, S<sub>Langmuir</sub>, S<sub>BET</sub> and  $V_p$  dramatically decrease by 8.5% (from 685.7 to 627.2 m<sup>2</sup> g<sup>-1</sup>), 12.1% (from 484.7 to 426.0 m<sup>2</sup> g<sup>-1</sup>) and 49.2% (from 0.459 to 0.233 cm<sup>3</sup> g<sup>-1</sup>), respectively, in comparison with those of p-CSC. The results also indicate the successful attachment of -SO<sub>3</sub>H groups onto the CSC and p-CSC matrix, including partial occupation and obstruction of pore space of the pristine carbon. Besides, the destruction of part of the pore structure of pristine carbon during the sulfonation process also contributes to the changes in textural structures [47].

In addition, the decrease in surface area for p-CSC and s-p-CSC is much lower than that for CSC and s-CSC. Meanwhile, the percentages of t-Plot micropore area  $(S_{\text{Micro}})$  and t-Plot micropore volume  $(V_{\text{Micro}})$  increase drastically, which are opposite to those for CSC and s-CSC. Such phenomenon confirms that p-CSC retains abundant pores to anchor the  $-SO_3H$  groups and form new micropores. Figure 9b shows their pore size distribution curves detected with the nonlocal density functional theory (NLDFT) method using the one-dimensional slit pore model, which also verifies that both p-CSC and s-p-CSC possess hierarchical pores with sizes of 0.15–50 nm, while CSC and s-CSC only display very weak pore signals (inset in Fig. 9b). The generated porous structure with large surface areas may promote the molecular accessibility to active sites of the sulfonated catalysts.

In summary, the analytic results reveal the -SO<sub>3</sub>H groups are successfully anchored to the corresponding pristine carbon. Moreover, compared with s-CSC, s-p-CSC with a hierarchical porous structure possesses much higher surface area and larger pore volume.

#### Optimization of the catalytic reaction conditions

In order to verify suitable factors for the catalysis, various reaction parameters including temperature, ethanol-to-LA molar ratio, time and catalyst dosage are optimized over s-CSC.

Due to that reaction temperature influences the reaction rate and the production cost, and the influence of temperature ranging in 40–90 °C on the catalytic activity is first studied under the following reaction conditions: ethanol-to-LA molar ratio 5.0:1, reaction time 8 h and catalyst dosage 5.0 wt%. Figure 10a depicts the significant increase in LA conversion from 36 to 90% when the reaction temperature increases from 40 to 80 °C. It is because the esterification reaction is endothermic,

Table 1 Por	parameters of the as-pre-	pared materials					
Material	$S^{\rm a}_{ m Langmuir}({ m m}^2{ m g}^{-1})$	$S^{\rm b}_{\rm BET}~({ m m}^2~{ m g}^{-1})$	$S^{\rm c}_{ m Micro}~({ m m^2~g^{-1}})$	$V_{\rm p}^{\rm d}  ({\rm cm}^3  {\rm g}^{-1})$	$V_{\rm Micro}^{\rm e}({ m cm}^3{ m g}^{-1})$	$S_{ m Micro}/S_{ m BET}$ (%)	$V_{ m Micro}/V_{ m p}$ (%)
csc	35.9	28.9	19.7	0.023	0.01	68.2	43.5
s-CSC	17.2	12.4	2.8	0.018	0.001	22.6	5.6
p-CSC	685.7	484.7	83.9	0.459	0.042	17.3	9.2
s-p-CSC	627.2	426.0	288.9	0.233	0.133	67.8	57.1
<sup>a</sup> S <sub>Langmuir</sub> , sp	ecific surface area calcula	ted by the Langmuir m	lethod				
be consit	in antena area antena	by the Dannes Emmet	<ul> <li>Tollor (DET) mothod</li> </ul>				

 $^{b}S_{\rm BET}$  specific surface area calculated by the Bruner–Emmett–Teller (BET) method

 $^{\rm c}S_{\rm Micro},$  Micropore area calculated by the t-plot method

 $^{\rm d}V_{\rm p},$  Total pore volume determined at  $P/P_0\!=\!0.99$ 

 $^{\rm e}V_{\rm Micro},$  Micropore volume calculated by the t-plot method



Fig. 10 Effects of reaction temperature (a), ethanol-to-LA molar ratio (b), catalyst dosage (c) and reaction time on LA conversion over the s-CSC catalysts

and increasing reaction temperatures may offer sufficient kinetic energy to accelerate the mass transfer rate among LA, ethanol and catalyst phases, enhancing the reaction rate and resulting in the enhanced conversion. When further increasing the temperature to 90 °C, LA conversion decreases to 86%. It is because the evaporation decreases the content of liquid ethanol in the reaction system since 90 °C is far above 78.3 °C, which is the boiling point of ethanol. Therefore, 80 °C, herein, is the optimal reaction temperature.

The esterification reaction requires high molar ratio (ethanol to LA) in driving the reaction toward the formation of EL, which is reversible. Essentially, the effects of the molar ratio of ethanol to LA ranging from 2.5:1 to 12.5:1 on the catalytic activity of s-CSC are also investigated under the following reaction conditions: reaction temperature 80 °C, reaction time 8 h and catalyst dosage 5.0 wt%. Figure 10b shows that the lowest LA conversion (62%) is obtained when the ethanol-to-LA molar ratio is 2.5:1. With increasing the molar ratio, LA conversion increases and the maximum value (94%) is obtained in the ratio of 5.0:1. However, as the molar ratio further increases, LA conversion exhibits an opposite behavior. As shown in Fig. 10b, the conversion decreases to 79% when the ratio rises up to 12.5:1. It may be attributed to the facts that the excess of ethanol up to the optimum level tends to increase the dispersion ability of s-CSC and enhances the diffusion and miscibility among the reactants, resulting in less interactions among LA, ethanol and CSC [48–50].

Meanwhile, the production cost increases with too much ethanol. Therefore, 5.0:1 is the optimal molar ratio under the present conditions.

The influence of various catalyst dosages on LA esterification is further investigated under the conditions of reaction temperature 80 °C, reaction time 8 h and ethanol-to-LA molar ratio 5.0:1. Figure 10c reveals that the presence of s-CSC obviously accelerates LA esterification through reducing the activation energy, in comparison with the blank case (LA conversion = 8%). Furthermore, LA conversion increases with increasing catalyst dosage due to the presence of hydrophilic surface functional groups of  $-SO_3H$  acting as anchoring sites that attach LA and ethanol. The highest conversion (94%) is achieved using a catalyst dosage of 5.0 wt%. Larger dosage leads to opposite effects because of the poor mass transfer. As a result, the most suitable s-CSC dosage, herein, is found to be 5.0 wt%.

The influence of different reaction time (2-12 h) on the catalytic activity of s-CSC is depicted in Fig. 10d under the following reaction conditions: reaction temperature 80 °C, catalyst dosage 5.0 wt% and ethanol-to-LA molar ratio 5.0:1. The conversion of LA increases obviously from 38 to 94% when the reaction time increases from 2 h to 8 h. Further prolonging time cannot lead to further increment of the LA conversion. Therefore, 8 h is selected as the optimal reaction time.

In summary, the optimal catalytic reaction parameters are as follows: reaction temperature 80 °C, ethanol-to-LA molar ratio 5.0:1, catalyst dosage 5.0 wt% and reaction time 8 h, which are consistent with those catalyzed by our previously developed sulfonated carbon catalysts derived from loofah sponges [21] and pine needles [24].

## The recycling performance of the sulfonated solid acid catalysts

The recyclability of a catalyst is essential for its practical applications. Thus, the recycling performance of s-CSC and s-p-CSC for LA esterification with ethanol is investigated under the aforementioned optimal reaction conditions. As presented in Fig. 11, in the first run, LA conversions reach up to 94% and 93% catalyzed by s-CSC and s-p-CSC, respectively. However, the conversion is sharply





Fig. 13 NH<sub>3</sub>-TPD profiles of s-CSAC (a), s-p-CSAC (b) and the corresponding reused catalysts

dropped in the subsequent runs over s-CSC, which is similar to our previously developed sulfonated carbon catalysts [21, 24]. The LA conversion is as low as 36% in the sixth run. It is worthy noted that the LA conversion is always satisfactory over s-p-CSC, which is still as high as 84% even in the sixth run, revealing its superior recyclability.

The reduced catalytic activity is mainly ascribed to the leaching of  $-SO_3H$  groups anchored to the pristine carbon, which could be confirmed by the FT-IR spectroscopy (Fig. 12) and NH<sub>3</sub>-TPD analysis (Fig. 13). As shown in Fig. 12, compared with the fresh catalysts, the intensities of the characteristic absorption bands of the  $-SO_3H$  groups for the reused s-CSC are obviously weakened, while those for the reused s-p-CSC have not obviously changed. Similar phenomenon also can be found in their NH<sub>3</sub>-TPD curves (Fig. 13). The total acid content decreases sharply from 2.01 mmol g<sup>-1</sup> for the fresh s-CSC to 1.51 mmol g<sup>-1</sup> for the reused one, while the value changes from 2.06 mmol g<sup>-1</sup> for the fresh s-p-CSC to 1.95 mmol g<sup>-1</sup> for the reused one. In our opinion, the hierarchical porous

structure of p-CSC with high specific surface area facilitates firmly anchoring the  $-SO_3H$  groups, endowing s-p-CSC with excellent recyclability.

# Conclusions

In summary, the sulfonated corn stalk rinds-derived porous carbon catalysts are successfully prepared by using phosphoric acid as the activator. Compared with the unactivated s-CSC, the resulting s-p-CSC not only exhibits similar catalytic activity for LA esterification with ethanol but also possesses much superior recyclability. This is presumably due to that the activation of phosphoric acid endows s-p-CSC a hierarchical porous structure with high surface area ( $S_{\text{Langmuir}} = 627.2 \text{ m}^2 \text{ g}^{-1}$ ,  $S_{\text{BET}} = 426.0 \text{ m}^2 \text{ g}^{-1}$ ,  $V_p = 0.233 \text{ cm}^3 \text{ g}^{-1}$ ), which is beneficial to firmly anchoring the -SO<sub>3</sub>H groups. This work offers a new strategy for using the corn stalk biomass wastes in the environmentally friendly synthesis of biofuel.

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