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Ph-SO₃H-modified mesoporous carbon as an efficient catalyst for the esterification of oleic acid

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ABSTRACT

Mesoporous carbon materials with thin pore walls (~1.7 nm) were synthesized using low-cost γ -Al₂O₃ as a hard template and *in situ* polymerized resorcinol–furfural resin as the carbon precursor. Compared with sugar, resin, a widely used carbon precursor, has higher carbon yield and simplifies the synthetic process. Ph-SO₃H modified mesoporous carbon was synthesized by covalent grafting of Ph-SO₃H groups on mesoporous carbon via the diazonium salt. The resulting materials were characterized by means of nitrogen adsorption analysis, TEM, ¹³C NMR, XRD, FTIR and sulfur elemental analysis. The modified carbons were shown to possess high surface area (~1000 m²/g), a bimodal pore size distribution and high strong acid density (1.86 mmol H⁺/g). These sulfonated carbons were used as solid acid catalysts in the esterification of oleic acid and methanol, a key reaction in biodiesel production. Compared with the traditional solid acid Amberlyst-15, the optimized carbon catalyst exhibited much higher activity with a rate constant (1.34 h⁻¹) three times to that of Amberlyt-15 and a turnover frequency (TOF) of 128 h⁻¹ eight times that of Amberlyst-15. The efficient catalytic ability was attributed to the high surface area and a proper mesopore texture. This carbon catalyst could then be easily separated from the product by filtration. The catalyst was reused six times, and no distinct activity drop was observed after the initial deactivation.

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1. Introduction

Due to its renewable feedstock and low CO_2 emission, biodiesel produced from vegetable oil is considered a sustainable fuel to replace conventional diesel [1]. The production of biodiesel usually involves the transesterification of triglycerides catalyzed by a homogeneous base, such as NaOH, KOH or NaOCH₃ [1–3]. However, the free fatty acid (FFA) contained in the crude vegetable oil will be saponified by the basic catalysts. Therefore, a pre-esterification process is necessary to convert FFA into the corresponding esters before transesterification. Conventionally, the catalysts for preesterification are liquid H₂SO₄, which is toxic, corrosive and costly to neutralize, separate and recycle. Therefore, the development of a green and easily separated acid catalyst has received much attention [4].

Among heterogeneous catalysts, carbon-based solid acid is ideal for many reactions owing to such advantages as chemical inertness, mechanical stability, structural diversity and surface hydrophobicity. For the pre-esterification of FFA, much work has focused on sulfonated carbon as the solid acid [5–16]. Using inexpensive biomass (sucrose [6], glucose [7,9], starch [10,11] or biochar [12]) as the carbon precursor, the pioneering work in this area synthesized carbon catalysts through direct carbonization of precursors followed by sulfonation in concentrated H_2SO_4 [5–16]. Such catalysts performed well in the esterification of fatty acid, but direct carbonization led to carbon catalysts with low porosity and low surface area, which is unfavorable for reactant accessibility to active sites. Moreover, the carbon yield of sugar is low. For instance, the theoretical carbon yield of sucrose is 40%, while the actual yield is only approximately 20% [17].

A new type of sulfonated ordered mesoporous carbon (OMC) has been developed for FFA pre-esterification [18–21]. In this work, the organic precursors were first impregnated into the pores of an ordered mesoporous silica template (typically SBA-15) and carbonized, and then the template was removed by treatment with HF solution. The remaining carbon materials were sulfonated by concentrated H₂SO₄ [18,19] or 4-benzene-diazoniumsulfonate (4-BDS) [20,21] to yield OMC-based solid acids with high surface area and large pores. This improved texture facilitates the diffusion of fatty acid molecules with long carbon chains to the active site, thereby increasing the catalytic efficiency. In most cases, silica templates must be prepared beforehand through multiple steps, which inevitably increase the cost of this type of catalysts.

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Our previous work reported the synthesis of carbon-based solid acid with sucrose as the carbon precursor, commercial γ -Al₂O₃ as the template and 4-BDS as the sulfonating agent [22–25]. Owing to delicate control of the sucrose loading on the template surface, such catalysts consist of small and thin carbon sheets. They can readily disperse in methanol to efficiently catalyze the esterification of oleic acid with methanol. The highest turnover frequency (TOF) observed was seven times that of Amberlyst-15. However, due to the low carbon yield of sucrose, repeated impregnation and carbonization was necessary in the synthesis of such catalysts.

Recently, we successfully synthesized mesoporous carbon materials with thin walls and large surface areas using resorcinol-furfural resin, which in situ polymerized on an alumina surface, as the carbon precursor [17]. Owing to the carbon yield of resorcinol-furfural resin being as high as 50%, one polymerization-carbonization process was sufficient. Moreover, resorcinol-furfural resin tends to form complete carbon frameworks that are stable enough to support themselves. In this paper, Ph-SO₃H groups were attached on the surface of these carbon materials via 4-BDS. N₂ adsorption analysis showed these modified materials still possessed the mesoporous structure and a large surface area ($\sim 1000 \, \text{m}^2/\text{g}$), and their strong acid density, determined by sulfur elemental analysis, reached 1.86 mmol H⁺/g. The optimal carbon catalyst was identified with a TOF of 128 h^{-1} , eight times that of Amberlysts-15 and even higher than that of previously reported sucrose catalysts $(109 h^{-1})$ [25]. Due to the complete carbon framework, the catalyst was easy to separate from the liquid reaction system by filtration. The optimal catalyst was reused several times with no significant drop in activity after the initial deactivation.

2. Experimental

2.1. Catalyst preparation

2.1.1. Source of alumina template

Three types of alumina were used as template: (a) commercial alumina SBA150 (Engelhard Corp., USA), denoted AI; (b) alumina prepared by calcination of pseudoboehmite (Shandong Aluminum Corp., China) at 550 °C for 4 h, denoted AII; and c) alumina prepared by calcination of aluminum hydroxide dried gel (Sinopec Corp., China) at 550 °C for 4 h, denoted AIII. All alumina templates were calcined at 800 °C for 4 h before use.

2.1.2. Preparation of mesoporous carbon materials

Mesoporous carbon materials were prepared according to a previously reported procedure [17]. The alumina templates (AI, AII or AIII) were mixed and thoroughly ground with resorcinol. The weight ratio of alumina to resorcinol, m_c , was calculated according to the empirical formula below.

$$m_{c} = 1.05 \times 1.5 \times \frac{S_{\text{BET,A}} \times 2 \times 12.0}{3 \times (\sqrt{3}/2) \times (1.42 \times 10^{-10})^{2} \times 6.02 \times 10^{23}}$$
(1)

where $S_{BET,A}$ is the Brunauer–Emmett–Teller (BET) surface area of the alumina template. Typically, 7 g of alumina AI was ground with 1.12 g of resorcinol for at least 20 min. Then, the mixture was transferred to a round bottom flask containing 30 ml of mesitylene, 2.5 ml of furfural and 3 drops of 1,2-ethylenediamine. After stirring at 90 °C for 4 h, the alumina/resorcinol–furfural resin composite was filtered, washed with ethanol three times and dried in an oven at 130 °C.

To obtain the mesoporous carbon, the composite was carbonized under N₂ for 3 h at 500 °C, 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C, respectively, and then immersed in a 24% hydrofluoric acid (HF) solution at room temperature for 3 h to dissolve the alumina.

The remaining carbon materials, denoted C-Ax-*T* (Ax denotes the alumina template, *T* denotes the carbonization temperature), were washed repeatedly with water and dried at $110 \degree$ C.

2.1.3. Sulfonation

The sulfonation of C-Ax-Ts was carried out using a previously reported method [25]. In a typical procedure, 0.22 g of 4-aminobenzene sulfonic acid was dissolved in a 0.05 M HCl aqueous solution and cooled to $5 \,^{\circ}$ C. Then, 90 mg of NaNO₂ was added to 4-aminobenzene sulfonic acid to produce 4-BDS. The sulfonation was achieved by mixing the 4-BDS solution prepared above with 0.4 g of C-Ax-T and holding the suspension at $5 \,^{\circ}$ C for 3 h. After filtration and thorough washing with water, dimethylformamide (DMF) and acetone, the sulfonated mesoporous carbon catalysts were obtained and denoted SC-Ax-T.

Amberlyst-15 (Acros Organics) was ground into a powder for use as a control catalyst and was degassed at 100 °C for 7 h before catalytic tests.

2.2. Characterization

Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2100 high-resolution microscope (Japan) at an acceleration voltage of 200 kV. The N₂ sorption analysis was performed on a Micromeritics ASAP 2010 volumetric adsorption system (US) at 77 K. All samples were degassed at 150 °C prior to measurements. The specific surface area was determined using the BET method based on the adsorption data in the relative pressure (P/P_0) range 0.05–0.20. Pore size distribution (PSD) was evaluated by the Barrett–Joyner–Halenda method from the desorption branch of the isotherm (additional note will be present when evaluated from the adsorption branch). The total pore volume was estimated from the amount of N₂ adsorbed at a relative pressure of 0.99.

Fourier transform infrared (FT-IR) absorbance spectra in the range of 600–4000 cm⁻¹ were recorded on a Nicolet iN10 FT-IR Microscope (USA) using pure samples. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX0200 powder diffractometer (Japan) using Ni-filtered Cu K_{α} radiation at 40 kV and 100 mA. ¹³C solid state NMR spectra were recorded on a Bruker AVANCE III WB Solid-State NMR Spectrometer with a WVT 4 mm CP/MAS double resonance probe head. The spin rate was 8.0 kHz. Sulfur and carbon elemental analyses were carried out on an Elementar Vario Micro Cube (Germany).

2.3. Catalytic tests

The esterification of oleic acid and methanol was performed in a stirred 20-ml autoclave at 65 °C. Typically, 20 mg of solid acid catalyst or 1.82 mg of H_2SO_4 (contain identical H⁺ amount to SC-AI-900) was added to 1 g of oleic acid (99%, TCI) and 8 ml of methanol. At selected reaction times, the autoclave was rapidly cooled in a room-temperature water bath. The catalyst was then removed by filtration, and the product was extracted and diluted with *n*-hexane to 100 ml. The yield of methyl oleate was analyzed by gas chromatography equipped with a FID detector and a BD-5 capillary column, where methyl heptadecanoate (AccuStandard, 10.0 mg/l in hexane) was used as the internal standard.

The stability of SC-AI-900 was investigated by performing the esterification reaction six times with 20 mg of SC-AI-900, 1 g of oleic acid and 8 ml of methanol at 65 °C for 1 h. After each use, the catalyst was recycled by filtration and washed with methanol. After recovery, the catalysts were activated in 0.1 M H_2SO_4 at room temperature, washed with deionized water and dried at 110 °C.

For kinetic studies, the conversion results were fitted to a pseudo-first order rate equation to determine the rate constant, *k*. TOF was calculated according to the equation below.

$$\text{TOF} = k \frac{n_{0,\text{OA}}}{n_{\text{H}^+}} \tag{2}$$

where $n_{0,OA}$ is the initial amount of oleic acid and n_{H^+} is the amount of strong acid sites on the catalyst, as determined by sulfur elemental analysis.

3. Results and discussion

3.1. Preparation and characterization of sulfonated mesoporous carbon catalysts

Mesoporous carbon materials were prepared by a previously published method using low-cost γ -alumina as the template and resorcinol-furfural resin as the carbon precursor [17]. Rather than direct impregnation, the precursor was generated in situ on the alumina surface. First, resorcinol was mechanically mixed with alumina and ground thoroughly at room temperature, which enabled resorcinol to uniformly disperse on the alumina surface. Then, after the introduction of furfural, the polymerization occurred in the presence of the basic catalyst 1,2-ethylenediamine to form resin layers uniformly covering the alumina surface. The empirical formula (1) was used to determine the weight ratio of resorcinol and alumina, m_c , on the basis that the carbon materials prepared according to m_c possess an ideal graphene structure and a thickness of 1.5 graphene layers. Our previous work demonstrated that 1.5 nominal graphene layers was thin enough to reserve the mesopores in the alumina but also tough enough to support itself as a stable framework when alumina was removed by HF [17].

The resin/alumina composite was carbonized under N₂ in a temperature range from 500 °C to 1000 °C to investigate the effect of carbon surface properties on catalytic performance. The resulting carbon/alumina composite was immersed in HF solution to dissolve alumina and obtain the carbon material C-Ax-Ts.

C-Ax-Ts displayed a distinct mesoporous structure, thin pore walls and a high BET surface area. Taking C-AI-900 as an example (Fig. 1), the sample exhibited a typical type IV adsorption isotherm with a hysteresis loop and peaks in the mesopore range in the PSD curve. Furthermore, a PSD peak for C-AI-900 resided close to that of its alumina template, AI (vertical dotted line in Fig. 1). The difference between the most probable pore size of C-AI-900 (10.1 nm) and AI (11.8 nm), 1.7 nm, could be approximately viewed as the



Fig. 1. N₂ sorption isotherms and pore size distribution plots (inset) of C-AI-900 and SC-AI-900. The vertical dotted line represents the most probable pore size of the alumina template AI.

average thickness of the carbon walls. Thin carbon walls could also be observed in the TEM image of C-AI-900 (Fig. 2a).

Thin walls lead to high BET surface area. As shown in Table 1, entry 4, the specific surface area of C-AI-900 was as high as $1671 \text{ m}^2/\text{g}$ and its pore volume reached $3.60 \text{ cm}^3/\text{g}$. Additionally, two peaks were distinguishable in the PSD curve of C-AI-900 (Fig. 1). In accordance with previous results, the texture of C-AI-900 duplicated the pore size of the alumina templates, corresponding to one PSD peak close to that of AI. After the template was removed, however, another type of pore with the size of the alumina particles emerged, corresponding to the other PSD peak centered at 6.6 nm. Because the most probable size of the alumina pores and particles was discrepant, a bimodal PSD was observed for C-AI-900.

The sulfonations of C-Ax-*T*s were achieved through reacting the mesoporous carbon materials with diazonium salt 4-BDS at 5 °C. This method efficiently grafted benzenesulfonic acid groups onto the carbon surface [20], transforming the carbon materials into excellent solid acid catalysts. Compared with the traditional sulfonation method (*i.e.*, boiling in concentrated H_2SO_4), diazonium-salt modification is carried out under relatively mild conditions [26,27]. In the interest of keeping the mesoporous structure intact, this method seems to be more suitable for the functionalization of carbon materials with large pores, thin walls and large BET areas. As shown in the TEM images (Fig. 2), the morphology of sulfonated



Fig. 2. TEM images of C-AI-900 (a) and SC-AI-900 (b).

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Table	1

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Entry	Sample	BET area (m ² /g)	D ^a (nm)	<i>V</i> ^b (cm ³ /g)	Strong acid density (mmol H ⁺ /g)	Conv. ^c (%)	$k(\mathbf{h}^{-1})$	$TOF(h^{-1})$
1	AI	127	15.4	0.49				
2	AII	176	9.0	0.40				
3	AIII	208	19.7	1.02				
4	C-AI-900	1671	8.63	3.60				
5	SC-AI-900	1118	8.16	2.39	1.86	77.7	1.34	128
6	SC-AII-900	1175	5.96	1.75	1.84	66.5		
7	SC-AIII-900	996	9.77	2.43	1.83	66.1		
8	SC-AI-1000	1170	8.16	2.39	1.88	76.7		
9	SC-AI-800	1114	7.88	2.20	1.61	72.8		
10	SC-AI-700	1036	7.50	1.94	1.58	64.6		
11	SC-AI-600	886	5.72	1.27	1.47	53.9		
12	SC-AI-500	636	3.74	0.59	1.16	34.4		
13	Amberlyst-15	43	29.1	0.31	5.03	40.5	0.43	15
14	H ₂ SO ₄				20.4	90.7 ^d	2.25	214

^a Average pore diameter.

^b Pore volume.

^c Conversion of oleic acid. Reaction conditions: 1 g of oleic acid, 8 ml of methanol, 20 mg of catalyst, and 65 °C for 1.25 h.

 d Catalytic acid amount (H⁺) of H₂SO₄ equal to that of SC-AI-900.

carbon SC-AI-900 had a similar disordered mesoporous structure to that of C-AI-900. In addition, the texture of SC-AI-900 preserved the bimodal PSD observed in C-AI-900. The ¹³C NMR spectra of SC-AI-900 (Fig. 3a) showed resonance peak at 128 ppm, 155 ppm and 171 ppm, which are attributed to aromatic carbon, phenolic-OH and COOH, respectively [13]. The XRD patterns (Fig. 3b) also showed that both C-AI-900 and SC-AI-900 were poorly crystallized.

The successful attachment of benzenesulfonic acid groups onto the carbon matrix was confirmed by FT-IR spectra (Fig. 3c). Compared with raw carbon material C-AI-900, the S=O vibration bands at 1010 cm^{-1} (symmetric stretching) and 1034 cm^{-1} (asymmetric stretching) could be distinguished in the FT-IR spectra of sulfonated SC-AI-900, proving the presence of SO₃H on the catalyst surface [28]. The vibrational band at 837 cm⁻¹ could be attributed to the out-plane bending of the C–H of 1,4-disubstituted benzene, suggesting the Ph-SO₃H groups were attached to the carbon surface *para* to SO₃H. This conformation was consistent with the molecular structure of the sulfonating agent 4-BDS.

The grafting of benzenesulfonic acid groups could also be confirmed by N₂ absorption analysis. As seen in Fig. 1 and Table 1 (entries 4 and 5), the BET area, average pore diameter and pore volume of C-AI-900 dramatically decreased after sulfonation. It was therefore reasonable to infer that Ph-SO₃H groups on the carbon surface occupied a part of the porous space, leading to an obvious reduction in porosity. However, the mesopores of carbon materials were not seriously blocked by these groups. As shown in Table 1, most SC-Ax-Ts still exhibited mesoporous structures and large BET areas approximately 1000 m²/g.

The acid density of carbon-based solid acids is a key factor for determining the catalytic activity. In terms of sulfonated carbon catalysts, there are two types of acidic sites: (1) the strong acid sites (i.e., the introduced SO₃H groups) and (2) the weak acid sites, including COOH and OH from incomplete carbonization of the organic precursor. Generally, the acid density of carbon-based solid acids is determined by titration with NaOH or Na₂CO₃ [29], which are not able to distinguish the strong acid sites from the weak acid sites. Given that the esterification of oleic acid is poorly catalyzed by COOH and OH, only the strong acid sites will affect the performance of the carbon catalysts. Therefore, the strong acid densities of SC-Ax-Ts were calculated from the content of elemental sulfur and are listed in Table 1, assuming all sulfur atoms were in the form SO₃H. The effectiveness of sulfonation via the diazonium salt was confirmed by the strong acid density of SC-AI-900 (1.86 mmol/g), which was higher than any reported carbon catalyst sulfonated by H_2SO_4 .

3.2. Effect of catalyst texture on catalytic activity

Since the BET area, pore size and pore volume of the carbon catalysts are associated with the accessibility of reactant molecules to the catalytic active sites, it is necessary to investigate the effect of catalyst texture on catalytic activity to find the optimal catalyst. The texture of Ph-SO₃H-modified carbon catalysts was tuned using three types of alumina templates (AI, AII and AIII) with different porous structures. Fig. 4 displays adsorption isotherms and PSD curves for the three alumina templates, and the textural properties are listed in Table 1 (entries 1, 2 and 3). All three templates were mesoporous materials, but their PSDs were different. AI and AII exhibited concentrated PSD with the most probable pore sizes of 11.8 nm (AI) and 6.2 nm (AII), respectively. Meanwhile, AIII exhibited a wide PSD peak, and the most probable pore size was 14.9 nm, indicating AIII had considerably larger pores.

Carbonized at the same temperature (900 °C), the carbon catalysts were prepared using the three templates. As shown in Fig. 5 and Table 1 (entries 5, 6 and 7), SC-AI-900, SC-AII-900 and SC-AIII-900 not only duplicated the PSD of their respective templates but also exhibited pores from the template particles (bimodal PSD). The two peaks of SC-AII-900 overlapped each other because the particle size of AII was close to its pore size.

Different templates led to carbon catalysts with different textures. First, the three carbon catalysts revealed different pore sizes. The PSD of SC-AI-900 was in the range of 6-10 nm, SC-AII-900 mainly possessed smaller pores of 4–5 nm and SC-AIII-900 was rich in pores larger than 10 nm, but small pores approximately 4 nm were also visible. Second, SC-AII-900 and SC-AIII-900 contained inkbottle shaped pores, which could be inferred from the presence of false peaks on the PSD curves. These curves were obtained from the desorption branch of the isotherm, where N₂ desorption takes place. Thus, the bottle necks of the inkbottle pores will bring about the so-called tensile strength effect (TSE) and result in a false peak on the PSD curves at a pore size of 3-4 nm [30]. In PSD curves for both SC-AII-900 and SC-AIII-900, a sharp peak could be seen at a pore size of 3.6 nm. To prove they were indeed false peaks, PSD curves were calculated from the adsorption branch of isotherms and are shown in Fig. 5c. On these curves, no peak was observed at a pore size of 3.6 nm. Therefore, the presence of the false peak was confirmed, suggesting the two carbon catalysts SC-AII-900 and SC-AIII-900 contained pores shaped like ink bottles.

To investigate the effect of catalyst texture on catalytic activity, SC-Ax-900s were tested as solid acids in the esterification of oleic acid and methanol under identical reaction conditions. The catalytic performance was evaluated based on the conversion of oleic



Fig. 3. 13 C NMR spectra of SC-AI-900 (a), and XRD patterns (b) and FT-IR spectra (c) of C-AI-900 and SC-AI-900.

acid at 1.25 h, and the results are listed in Table 1 (entries 5, 6 and 7). Among the three carbon catalysts, SC-AI-900 displayed the highest activity with an oleic acid conversion of 78%. Meanwhile, the activities on SC-AII-900 and SC-AIII-900 were similar to each other and relatively low (~66%). Because the strong acid density of the three carbon catalysts was almost the same (~1.8 mmol H⁺/g), the higher activity on SC-AI-900 was attributed to the catalyst texture.

The SC-AI-900 PSD curve has a much smaller false peak than the other two catalysts (Fig. 5b), suggesting this sulfonated carbon catalyst did not possess significant inkbottle pores. The bottleneck of such pores would prevent oleic acid from diffusing into the "ink bottle" to reach the active sites. Therefore, the presence of such pores is unfavorable for catalytic reactions involving large molecules, and



Fig. 4. $N_{\rm 2}$ sorption isotherms and pore size distribution plots (inset) of Al, AlI and AlII.

the absence of inkbottle pores in SC-AI-900 should be viewed as the primary reason for its superior catalytic performance.

The effect of catalyst pore size on activity is not clear. The length of an oleic acid molecule is roughly 2 nm, smaller than the pore size of all three SC-Ax-900s (8.16 nm, 5.96 nm and 9.77 nm, respectively), so diffusion should be easy. Previous work on mesoporous carbon catalysts reported that a large pore size would enhance catalytic activity [15], but this work focused on carbon catalysts with 2–4 nm pores. It is therefore possible that catalyst frameworks with too large of pores (*e.g.*, approximately 10 nm in SC-AIII-900) are not suitable for catalysis, as they reduce the effective BET surface area.

3.3. Effect of carbonization temperature on catalytic activity

Besides texture, carbonization temperature is another important concern for carbon-based catalysts. To investigate its influence, resorcinol-furfural resin was carbonized under N₂ gas at 500 °C, 600 °C, 700 °C, 800 °C, 900 °C and 1000 °C using AI as the template. First, the carbonization temperature directly determines the amount of oxygen-containing groups on the carbon matrix. Carbon materials pyrolyzed from organic precursors always possess these groups (e.g., OH and COOH). Increasing the carbonization temperature could eliminate these groups to some extent. As shown in Table 2, the elemental analysis of raw C-AI-Ts demonstrated this effect. As carbonization temperature increased, the carbon content of SC-AI-Ts increased, while oxygen and hydrogen content decreased. The atom ratios of carbon to oxygen also clearly revealed this trend. When the temperature was higher than 700 °C, however, the reduction of oxygen content was not clear, and the carbon content of C-AI-900 (92.56%) and C-AI-1000 (92.88%) were almost identical.

Through affecting oxygen content of the carbon matrix, carbonization temperature influences the acid density of carbon catalysts. As seen in Table 1 (entries 5 and 8–12), the strong acid densities of SC-AI-Ts increased with carbonization temperature.

Fable 2				
Elemental	content	of C-	AI-Ts	

Sample	Elemental	Elemental content (wt.%)				
	С	Н	0			
C-AI-1000	92.88	0.66	6.46	19.2		
C-AI-900	92.56	0.76	6.68	18.5		
C-AI-800	91.64	0.98	7.38	16.6		
C-AI-700	90.39	1.85	7.76	15.5		
C-AI-600	86.63	2.52	10.85	10.6		
C-AI-500	81.22	3.14	15.64	6.9		



Fig. 5. N_2 sorption isotherms (a) and pore size distribution plots of SC-Ax-900s calculated from both the desorption branch (b) and the adsorption branch (c) of isotherms.

When resin was carbonized at low temperature, a large number of oxygen-containing groups remained on the edge of the carbon planes, occupying positions that would otherwise be attached to Ph-SO₃H and hindering the diazonium modification of the carbon surface.

Furthermore, the carbonization temperature also affects catalyst texture. Because redundant oxygen-containing groups would soften the carbon matrix, the higher the carbonization temperature, the tougher the carbon framework formed and the less liable the porous structure is to collapse. As seen in Fig. 6 and Table 1 (entries 5 and 8–12), when resin was pyrolyzed at temperatures higher than 700 °C, the carbon framework was rigid enough to support itself and displayed a bimodal PSD. In these cases, the BET surface areas were all above 1000 m²/g. However, when the

carbonization temperature fell below 600 °C, the whole network tended to collapse to denser structures characterized by lower BET areas and smaller pores. Notably, the high false peak in the PSD curves indicated the emergence of many inkbottle pores.

To investigate the effect of carbonization temperature on catalytic activity, SC-AI-Ts were tested in the esterification of oleic acid under identical conditions. The activity was compared based on oleic acid conversion at 1.25 h. As seen in Table 1 (entries 5 and 8–12), catalysts carbonized at higher temperatures displayed better catalytic activities. For example, the activities of SC-AI-900 and SC-AI-1000 were close, suggesting limited improvement of catalytic performance through elevating the carbonization temperature.

Among the SC-AI-Ts, SC-AI-900 stands out as the best catalyst. The first factor likely contributing to this activity was the high carbonization temperature, which tends to increase the strong acid density of a carbon catalyst. It is well known that the acid density of sulfonated carbon is the key factor in determining catalytic activity. The more SO₃H attached to the carbon surface, the better performance the catalyst will show. The strong acid density of SC-AI-900 was as high as 1.86 mmol H⁺/g, supporting the highest observed activity among the SC-AI-Ts. Second, a high carbonization temperature helps stabilize the carbon framework to maintain the optimal mesoporous texture. When the carbonization temperature was higher than 700 °C, inkbottle pores were negligible. Structural shrinkage and a large quantity of inkbottle pores are unfavorable for reactant transportation and give lower catalytic activity. Third, a high carbonization temperature promotes the surface hydrophobility of the catalysts. For carbon-based solid acids, fewer oxygen-containing groups are related to higher hydrophobility, which is favorable for water, a product of esterification, to desorb from the active site and promote reaction. Hence, compared with SC-AI-Ts carbonized at lower temperatures, the hydrophobility of SC-AI-900 should also be one of the reasons for its excellent activity.

3.4. Catalytic performance of SC-AI-900

As discussed above, through adjusting template texture and carbonization temperature, SC-AI-900 was developed as the optimal catalyst. Intensive study of its catalytic activity and stability was thus subsequently carried out. The catalytic performance of SC-AI-900 in the esterification of oleic acid with methanol is shown in Fig. 7. The equilibrium conversion of oleic acid after 5 h of reaction was close to 100%. Because the amount of methanol was 66 times that of oleic acid, the reaction could be viewed as following pseudo first order kinetics, in which reaction rate depends solely on the amount of oleic acid. Such a first-order kinetic plot was fit (Fig. 7) and the rate constant *k* was determined to be $1.34 h^{-1}$. Based on the strong acid density of SC-AI-900 (1.86 mmol H⁺/g, Table 1, entry 5), the TOF was calculated using formula (2) and found to be $128 h^{-1}$.

As shown in Fig. 7, sulfuric acid, a homogeneous catalyst, has the highest activity, with the highest $k(2.25 \text{ h}^{-1})$ and TOF (214 h^{-1}) . But the kinetic plot of SC-AI-900 is quite close to that of sulfuric acid, showing the good activity of this solid acid. Compared with the commercial solid acid Amberlyst-15, SC-AI-900 exhibited higher catalytic activity and efficiency. Amberlyst-15 was tested in this esterification reaction under identical conditions. The time course and kinetic plot are shown in Fig. 7, and k and TOF were determined to be $0.43 h^{-1}$ and $15 h^{-1}$, respectively (Table 1 entry 13). Although the strong acid density of SC-AI-900 (1.86 mmol H⁺/g) was much lower than Amberlyst-15 (5.03 mmol H^+/g), the rate constant on SC-AI-900 was three times that of Amberlyst-15, underlining the excellent catalytic ability of Ph-SO₃H-modified mesoporous carbon. Notably, the TOF on SC-AI-900 reached eight times that of Amberlyst-15, further demonstrating the superior catalytic efficiency of the sulfonated carbon catalyst.



Fig. 6. N₂ sorption isotherms and pore size distribution plots of SC-AI-Ts.

SC-AI-900 outperformed the traditional catalyst Amberlyst-15 to a large extent because of its unique texture. Amberlyst-15, an ion exchange resin, is composed of macropores with low BET surface area $(43 \text{ m}^2/\text{g})$ and high acid density (5.03 mmol H⁺/g) (Table 1, entry 13). Such a texture indicates that most of the acid sites of Amberlyst-15 are located inside the resin network, which is not capable of swelling well enough to be penetrated by large molecules such as oleic acid. On the other hand, the texture of SC-AI-900 features mesopores with thin carbon walls, a high BET surface area (1118 m²/g, 26 times that of Amberlyst-15) and relatively low acid density (1.86 mmol H⁺/g). These characteristics suggest that most acid sites reside on the catalyst surface and are readily accessible for large substrate molecules. Therefore, SC-AI-900 shows a much higher catalytic efficiency in the esterification of oleic acid than Amberlyst-15.

Previously, we reported a sucrose-carbon catalyst showing high efficiency in the esterification of oleic acid and methanol (TOF $109 h^{-1}$). This catalyst consisted of thin and small carbon sheets able to disperse in methanol, promoting the catalytic process [25]. However, SC-AI-900 from resorcinol–furfural resin exhibited an even higher catalytic efficiency (TOF $128 h^{-1}$). Moreover, unlike the sucrose-carbon catalyst, the monolithic carbon framework of SC-AI-900 facilitated catalyst separation and recycling.

Due to its superior reactivity, the stability of SC-AI-900 was evaluated by running the esterification reaction six times with the same catalyst. As shown in Fig. 8, the conversion of oleic acid gradually decreased in the first four cycles, but no distinct drop in catalytic ability was observed after three cycles (conversion of



Fig. 7. Esterification of oleic acid with methanol over H_2SO_4 , SC-Al-900 and Amberlyst-15. Kinetic plot was fitted to first order reaction kinetics. Reaction conditions: 1 g of oleic acid, 8 ml of methanol, 20 mg of solid catalyst or 1.82 mg H_2SO_4 , and 65 °C.



Fig. 8. Recycling of SC-AI-900 for the esterification of oleic acid (1 g) with methanol (8 ml) at 65 °C. The conversions of oleic acid at 1 h are shown.

oleic acid near 60%). To investigate this deactivation, the strong acid density of SC-AI-900 after six reaction cycles was determined for comparison with freshly prepared SC-AI-900. The results of the sulfur element analysis showed that after six reaction cycles, the strong acid density of SC-AI-900 was reduced from 1.86 mmol H⁺/g to 1.34 mmol H⁺/g. Since the catalytic ability of sulfonated carbon largely depends on the acid density, the loss of acid sites was likely the main reason for catalyst deactivation. As described in the literature, the leaching of polycyclic aromatic hydrocarbons bearing SO₃H groups was observed on sulfonated carbon catalysts and led to deactivation [31,32]. However, the remaining active sites, approximately 72% of the freshly prepared SC-AI-900, still attached to the carbon surface after six reaction cycles and were able to give a high conversion of oleic acid. This observation suggested that the Ph-SO₃H-modified mesoporous carbon was a stable solid acid catalyst.

4. Conclusion

Ph-SO₃H-modified mesoporous carbon was prepared using γ -Al₂O₃ as the hard template, resorcinol–furfural resin *in situ* polymerized on an alumina surface as the carbon precursor and 4-BDS as the sulfonating agent via diazonium chemistry. Using inexpensive γ -Al₂O₃ reduced the catalyst cost, resorcinol–furfural resin, instead of sucrose, simplified the catalyst preparation process, and the diazonium modification replaced H₂SO₄ sulfonation while increasing strong acid density and keeping the carbon mesoporous network intact. The Ph-SO₃H-modified carbon materials had a distinct mesoporous structure with bimodal PSD, thin pore

walls, ultra-high BET area and high strong acid density. These materials showed superior catalytic performance in the esterification of oleic acid and methanol. The optimal catalyst, SC-AI-900, displayed much higher activity than the traditional solid acid catalyst Amberlyst-15 with a rate constant of $1.34 \, h^{-1}$, three times that of Amberlyt-15, and a TOF of $128 \, h^{-1}$, eight times that of Amberlyt-15. In addition, SC-AI-900 could be easily separated from the reaction system by filtration and reused. There was no distinct activity drop during recycling after the initial deactivation, suggesting Ph-SO₃H-modified mesoporous carbon is a stable and efficient solid acid catalyst. Such carbon-based solid acids could also be useful for many other acid-catalyzed reactions involving large reactant molecules.

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