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Preparation of sulfonated ordered mesoporous carbon and its use for the esterification of fatty acids

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ABSTRACT

Mesoporous carbon, which can be replicated from mesoporous silica and whose surface is hydrophobic, can be an ideal catalyst for the esterification of fatty acids. Here we report an easy and low cost way to prepare sulfonic acid group-functionalized mesoporous carbon. A sample of calcined mesoporous silica SBA-15 was added to an aqueous sucrose solution followed by drying and calcination at different temperatures. In contrast to existing procedures, the obtained hybrid Si/C material was then first sulfonated in H_2SO_4, before the final removal of the silica template in order to stabilize the porous structure towards the liquid phase sulfonation treatment. Thus the silica–carbon composites, instead of the mesoporous carbon, were successfully sulfonated to introduce $–SO_3H$ groups, while keeping the ordered mesoporous structure intact. The influence of carbonization temperature was investigated, suggesting an optimum temperature of 873 K. The SO_3H group-functionalized mesoporous carbon, denoted as CMK-3-873-SO_3H, was characterized by means of XRD, N_2 physisorption, SEM, FT-IR, elemental analysis and TEM. It followed that a uniform mesoporous carbon was obtained with an average pore size of 3.89 nm, a specific surface of 807 m^2/g and a $–SO_3H$ group loading of 0.39 meq/g of dry material. Compared with other solid acid catalysts, the resulting material shows enhanced activity in the acid-catalyzed esterification of oleic acid with methanol, and can be used repeatedly. The increased catalytic performance is attributed to the hydrophobic surface and larger pore size of the new catalyst. It can effectively accommodate long chain fatty acids and reject formed water, making the active sites easily accessible.

1. Introduction

Fatty acid esters are essential chemicals that are widely used in food, pharmaceutical, cosmetic and industrial applications. Currently industrial esterification processes are carried out in the presence of homogeneous Brønsted acids such as sulfuric acid or *p*-toluenesulfonic acid. However, these homogeneous acid catalysts are difficult to recycle, and also give rise to serious environmental and corrosion problems. Therefore, ester synthesis using solid catalysts instead of homogeneous liquid catalysts has gained much attention recently in view of their ease of separation and lack of corrosion or toxicity problems [1–7].

Inorganic-oxide solid acids such as zeolite and niobic acid have low densities of effective acid sites and thus cannot achieve adequate performance in acid-catalyzed reactions in the presence of water as a replacement for homogeneous acids in esterification [8]. Although strong acidic ion-exchange resins such as Amberlyst and Nafion have abundant sulfonic acid groups ($–SO_3H$), that function as strong acid sites, these resins are expensive and their catalytic activities are generally much lower than that of sulfuric acid. In addition, such resins show low operational stability and their catalytic activity is lost after a few cycles of reuse [2,8,9]. These limitations have restricted the practical utility of acidic cation-exchangeable resins. Sulfonated mesostructured silicas have also been used for the synthesis of fatty acid ester recently, and showed higher reactivity than acidic cation-exchangeable resins catalysts such as Amberlyst-15 and Nafion due to the higher accessibility of catalytic sites in the mesoporous structure [10,11]. However, the hydrophilic surface of silica makes effective sorption of long chain molecules difficult and the byproduct water is easily retained to the surface leading to deactivation of the silica-based catalysts. Recently, a new class of sulfonated carbons derived from incomplete carbonization of simple natural product such as sugar,

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starch or cellulose, has been reported to have better catalytic performance for esterification of fatty acids, and higher stability than sulfonated mesoporous silicas [12–14]. However, such materials were non-ordered or nonporous and exhibited low surface area, which may limit the accessibility to active sites. Thus mesoporous carbon, whose surface is hydrophobic while keeping the unique porous properties of mesoporous materials, is envisioned here as an ideal candidate for the development of esterification catalyst. Functionalization of mesoporous carbon with sulfonic acid groups is expected to allow high densities of functional groups and ensure good accessibility to active sites. Recently, Feng and co-workers firstly reported a method to prepare sulfonic acid-functionalized ordered mesoporous carbon [15,16]. In this method, ordered mesoporous carbon was first prepared, and then sulfonic acid-containing aryl radical was grafted on the carbon surface by covalent attachment; we feel the procedure is complicated and costly. Wu and co-workers also reported a vapour-phase transfer method to prepare sulfonic acid group-functionalized mesoporous carbon with the controlled carbonization degree [17]. However, a toxic and volatile 50 wt.% SO_3/H_2SO_4 was required for the sulfonation treatment, which increases the difficulty of operation. So it is important to find an easy, safe and low cost way to prepare sulfonic acid-functionalized ordered mesoporous carbons both in the practical and economic aspect.

Here we report a new and easy method to synthesise sulfonic acid-functionalized ordered mesoporous carbons. Sucrose was chosen as carbon source to fill the mesopores of mesoporous silica SBA-15 followed by carbonization at relativity low temperature to form interconnected rigid carbon framework while keeping certain amount of active groups available for the sulfonation. The obtained hybrid Si/C material was then sulfonated with concentrated H_2SO_4, followed by a final removal of the silica with HF to get sulfonated CMK-3 type mesoporous carbon material. The resulting material was examined as solid acid catalysts in the esterification of oleic acid with methanol, and its catalytic performance was compared with other commercial acidic catalysts. Successful reuse of the catalyst is demonstrated.

2. Experimental

2.1. Catalysts preparation

For the synthesis of CMK-3 type carbons, SBA-15 was employed as a hard template. SBA-15 was prepared according to a reported procedure [18]. Briefly, 12 g of P123 was dissolved in a mixture of 74.4 g of concentrated HCl and 375.6 g of distilled water at 311 K, followed by the addition of 31.5 g of TEOS with vigorous stirring for 30 min. The mixture was kept statically at the same temperature for 24 h, and then at 373 K for another 24 h. The solid was recovered by filtration, washed by water, and calcined at 823 K in air for 5 h.

The ordered mesoporous carbon CMK-3 was then synthesised by replication using SBA-15 as template and sucrose as carbon source. Briefly, 1.0 g of SBA-15 was impregnated with an aqueous solution obtained by dissolving 1.25 g of sucrose and 0.14 g of H_2SO_4 in 5.0 g of deionized water. The mixture was then dried at 373 K for 6 h, and subsequently at 433 K for 6 h. The silica sample, containing partially polymerized and carbonized sucrose, was treated again at 373 and 433 K after the addition of 0.8 g of sucrose, 90 mg of H_2SO_4 and 5.0 g of deionized water. The sucrose/silica composite was then heated at 673–873 K for 6 h under nitrogen to obtain carbon/silica composites. Sulfonation was carried out in a Teflon-lined autoclave where 1 g of carbon/silica composites powder was immersed in 10 ml concentrated H_2SO_4 (98%) at 423 K for 15 h. The sulfonated sample was rigorously washed with boiling deionized water to remove any physically adsorbed species until free of sulfate ions. Then, the resulting samples were dissolved with 40 wt.% hydrofluoric acid at room temperature to remove the silica template. The template-free carbon product, denoted as CMK-3-*T*-SO_3H (*T* denotes the carbonization temperature) thus obtained was filtered, washed with deionized water and acetone, and dried.

Amorphous sugar catalyst was prepared according to the procedure reported [12] with some change: sucrose, not D-glucose was used as starting material; the sulfonation was carried in a closed Teflon-lined autoclave rather than in the N_2 atmosphere. Typically, sucrose was pyrolyzed under dry N_2 at 673 K for 15 h. The resultant solid was ground and then sulfonated using concentrated sulfuric acid (1 g of solid/20 ml of H_2SO_4) at 423 K for 15 h in a Teflon-lined autoclave. The product was then washed with hot distilled water until no sulfate ions were detected in the wash water and dried.

2.2. Characterization methods

X-ray diffraction (XRD) patterns were obtained with a STOE STADI P transmission diffractometer using CuKα radiation. Nitrogen adsorption–desorption isotherms were measured at 77 K on a Micromeritics TriStar 3000 instrument. The pore size distribution was calculated using the Barrett–Joyner–Halenda (BJH) model. SEM images were obtained on a Philips XL30 FEG microscope. FT-IR spectra were recorded on a Nicolet 6700 Fourier transform infrared spectrometer using KBr technique. For TEM analysis the sulfonated CMK-3 powder was dispersed in ethanol followed by an ultrasonic treatment for about 10 min. The solution was then dropped onto a lacey carbon film supported by a TEM copper grid. TEM was performed using a Philips CM30 microscope operated at 300 kV. The sulfur contents of the sulfonated mesoporous carbon catalysts were determined by elemental analysis using ICP. The acidic groups concentrations of the catalyst sample were obtained using standard acid–base back-titration with bases of different strength: $NaHCO_3$ (sulfonic acid groups, carboxyl groups), Na_2CO_3 (sulfonic acid groups, lactones and carboxyls) and NaOH (sulfonic acid groups, phenols, lactones and carboxyls) [19]. Briefly, 30 mg of solid acid material was dispersed in 50 ml of 6×10^{-3} N alkali aqueous solution respectively for 24 h with stirring. Liquid was then separated, and titrated with 6×10^{-3} N HCl aqueous solution. The amount of acid groups in the solid acid was estimated by the NaOH consumed. Titration was performed three times and the average number was reported.

2.3. Catalytic testing

An oleic acid content unlabelled industrial material was used for the catalyst test and it is assumed that oleic acid content was 100%. In a typical experiment, the esterification of oleic acid was conducted at 353 K by addition of sulfonated ordered mesoporous carbon to a stirred batch reflux system containing a methanol–oleic acid mixture (methanol: 250 mmol; oleic acid: 25 mmol) and 0.5 g heptadecane as an internal standard. Samples (100 μl) were withdrawn at specified time intervals from the reaction mixture, combined with *n*-octane, and then centrifuged. The upper layer was taken for GC analysis. For comparison, catalysis of concentrated sulfuric acid (>96%), protonated-Nafion (NR50), CBV-720 (H-USY, Si/Al = 15) and sugar catalyst was also examined. All tested catalysts except sulfuric acid were evacuated at 373 K for 1 h prior to reaction to remove adsorbed water, and the catalyst acid amount used in the reaction was always 1 mmol H^+. For the sulfonated ordered mesoporous carbon and sugar catalyst, the adding amount was based on the titration analysis.

The stability of OMC-SO_3H was investigated by performing the esterification reaction (methanol: 50 mmol; oleic acid: 5 mmol, CMK-3-873-SO_3H 0.1 g, 353 K for 6 h, sealed vial) with the same catalyst five times. After each use, the catalyst was recycled by centrifugation, followed by washing with acetone and drying in an oven at 373 K in the vacuum oven overnight.

3. Results and discussion

3.1. Preparation and characterization of samples

The procedures for preparing sulfonic acid-functionalized mesoporous carbon materials are illustrated in Fig. 1. The calcined SBA-15 was impregnated with aqueous solution of sucrose containing trace sulfuric acid as catalyst for sucrose polymerization. After drying treatment, the sample turned dark brown, containing partially polymerized and carbonized sucrose. The impregnate and dry procedures were repeated another time to make the pores of SBA-15 completely filled. The resultant composite was subject to a thermal treatment in a quartz tuber under N_2 to carbonize sucrose at a temperature range from 673 to 873 K which is lower than that of normal mesoporous carbon preparation (973–1173 K). The low pyrolysis temperature is expected to form rigid carbon framework, while at the same time keeping certain amount of large polycyclic aromatic carbon sheets, required for introducing sulfonic acid groups [20,21]. The carbon–silica composite obtained after pyrolysis was then heated in concentrated H_2SO_4 to introduce sulfonate groups (–SO_3H) followed by removing the silica template with HF to get a pure sulfonated ordered mesoporous carbon material. Sulfonation of the silica–carbon hybrid composite rather than sulfonation of the purified mesoporous carbon is a key step for the preparation of stable CMK-3-SO_3H. It seems that the silica template serves as a support for the carbon to keep its mesoporous structure intact during the sulfonation process, while in our hands the pure mesoporous carbon material (after silica removal) totally loses its mesostructure after such acid treatment (see later from the XRD reflections in Fig. 2). We feel our method is practical and more general applicable than existing procedures [15–17]. This method can for instance also be used to introduce other functional groups on the surface of mesoporous carbon. For example, oxygen-containing functional groups can be introduced into carbonatized mesoporous silica–carbon hybrid by refluxing with nitric acid, followed by washing with HF to remove the silica, while keeping intact the ordered mesoporous structure. As we mentioned before, direct functionalization of template-free mesoporous carbon in our hands with such harsh oxidation conditions always led to the degradation of the structural order of the mesopores.

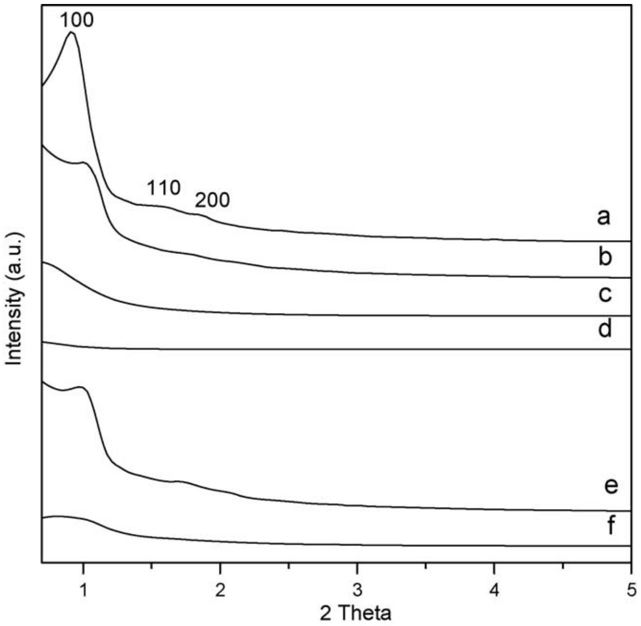

Fig. 2. XRD patterns of (a) SBA-15, (b) CMK-3-873-SO_3H, (c) CMK-3-773-SO_3H, (d) CMK-3-673-SO_3H, (e) CMK-3-873 and (f) CMK-3-873 after sulfonation.

Fig. 2 shows the XRD patterns of SBA-15 hard template and corresponding sulfonated mesoporous carbon replicas obtained after the carbonation was performed on the SBA-15/sucrose composite at various temperatures (673–873 K). SBA-15 exhibited an intense diffraction peak together with two weak peaks, that can be indexed as 100, 110 and 200 planes of 2D hexagonal structure

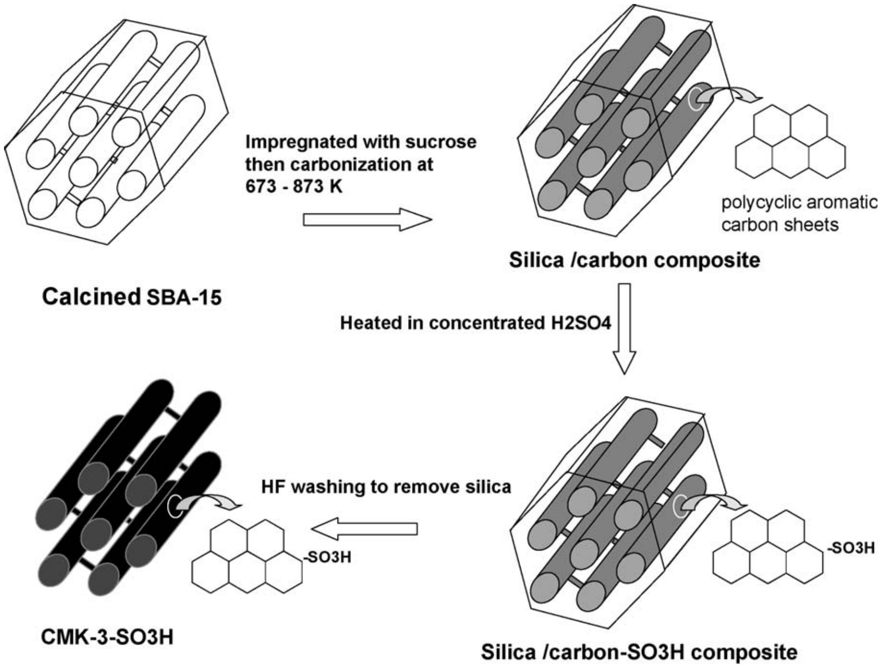

Fig. 1. Schematic illustration for the successful preparation of CMK-SO_3H mesoporous solid acid materials.

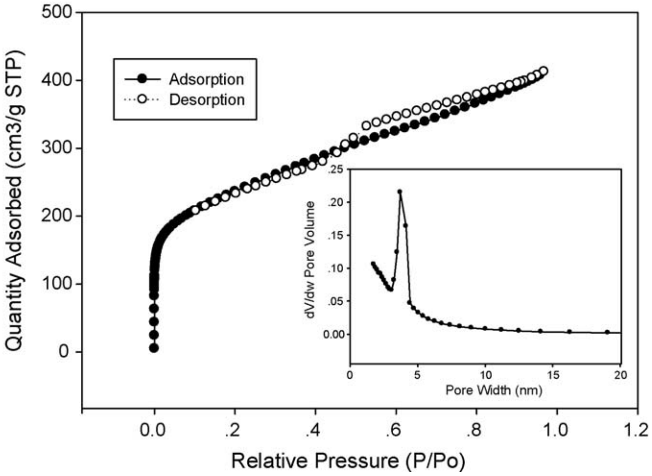

Fig. 3. N_2 adsorption isotherms and pore size distribution of CMK-3-873-SO_3H.

(*p*6*mm*) (Fig. 2a), which indicated a well-ordered structuring of the mesopores. The samples carbonatized at 673 and 773 K (Fig. 2c and d) did not show any clear reflection peaks due to a too low carbonization temperature to develop a rigid carbon mesostructure. By increasing the carbonization temperature to 873 K, a well-ordered mesoporous carbon was obtained (Fig. 2b). This material is clearly stable enough to withstand the harsh sulfonation treatment. Although higher carbonization temperatures are helpful to increase the mesostructure order of the carbon material even more, it is not beneficial to introduce the sulfonic acid groups. It has been reported that the content of sulfur achieved through the functionalization of polycyclic aromatic carbons decreased greatly at carbonization temperatures higher than 873 K [20]. So, for the synthesis of sulfonic acid-functionalized mesoporous carbon, the optimum carbonization temperature is 873 K. It is high enough to fabricate a still well-ordered mesoporous structure, while keeping a considerable amount of polycyclic aromatic carbon to functionalize with –SO_3H. Very surprisingly, we were not able to sulfonate the mesoporous carbon CMK-3 after removal of the silica template, without destroying the mesopores' organization of the material. Hence, the silica exercises a protective role during the sulfonation procedure, keeping the mesoporous structure intact, as suggested in the XRD reflection pattern (compare Fig. 2e with Fig. 2f).

Fig. 3 shows the N_2 adsorption–desorption isotherms and corresponding pore size distribution curves (using the BJH method) for CMK-3-873-SO_3H. The isotherm is of type IV with a clear hysteresis loop in the relative pressure range of ~0.4–0.9. The pore size distribution indicates the presence of uniform mesopores (~3.9 nm) in a narrow range. The BET surface area and the pore volume analysis show the following values, 808 m^2/g and 0.47 cm^3/g, respectively. The N_2 adsorption data along with the result obtained from XRD thus indicate that the CMK-3-873-SO_3H materials typically possess an ordered hexagonal mesostructure, induced by the replication of the silica template. High resolution TEM images, presented in Fig. 4, indeed prove the presence of

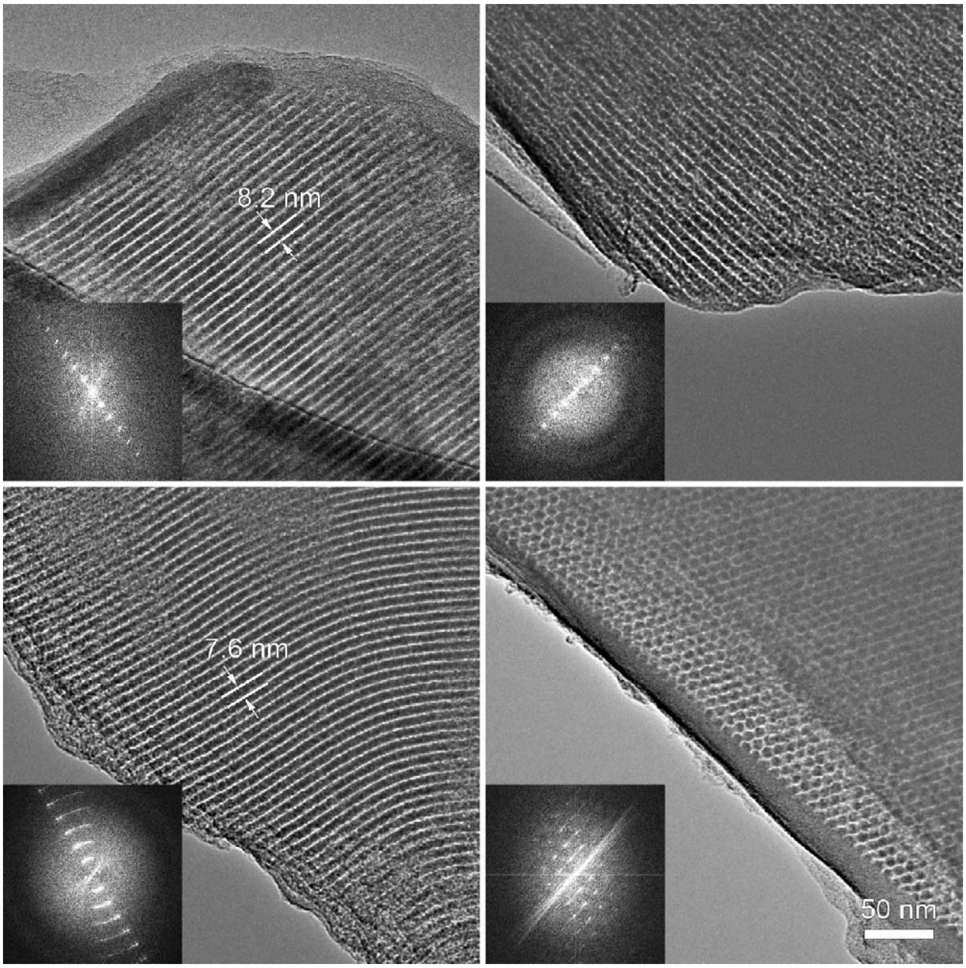

Fig. 4. Various HRTEM images of the CMK-3-873-SO_3H, viewed perpendicularly to and along the channel direction.

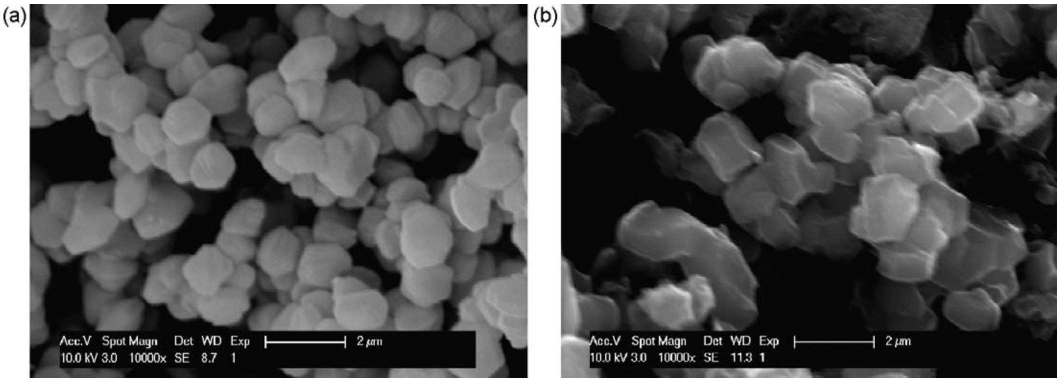

Fig. 5. SEM images of SBA-15 (a) and CMK-3-873-SO_3H (b).

hexagonal arrays of mesopores as a result of the *p*6*mm* mesostructure of the parent SBA-15. The size of the carbon-filled channels, *i.e.* the black parts in the TEM images, approaches a value of 7.9 ± 0.3 nm, in agreement with the original pore diameter of the SBA-15 starting material, while the white parts in the images represents the available porosity of the CMK-3-873-SO_3H in which the acid groups are located. SEM images show that, CMK-3-873-SO_3H (Fig. 5b) consists of fairly uniform block-like particles, which truly reflects the morphology of the parent SBA-15 silica (Fig. 5a).

Acid loadings obtained by titration with bases of different strength are 1.3 ($NaHCO_3$), 2.17 (Na_2CO_3) and 2.34 (NaOH) mmol g^{-1}, respectively. According to Boehm [19], $NaHCO_3$ (p*K*a = 6.37) neutralizes the sulfonic acid groups (–SO_3H) and carboxylic groups (–COOH), Na_2CO_3 (p*K*a = 10.25) balances the sulfonic acid groups (–SO_3H), carboxylic (–COOH), and lactonic groups (–COO–), whereas NaOH (p*K*a = 15.74) neutralizes all the groups mentioned above including phenolic (–OH) structures. The densities of the SO_3H groups were estimated based on the sulfur content (1.27 wt.%) determined from sample compositions obtained by elemental analysis, assuming all S atoms in the catalysts are in the –SO_3H form, as proposed by Hara's group, who found only a single S_{2p} peak at 168 eV, diagnostic for SO_3H groups, in their XPS study for various sulfonated carbon catalysts [20]. Using the data from the series of titration experiments together with the elemental analysis for SO_3H determination, allows the calculation of the amounts of SO_3H, COOH, –COO– and phenolic –OH groups in CMK-3-873-SO_3H. The respective values amount to 0.39, 0.91, 0.87 and 0.17 mmol g^{-1}.

The FT-IR spectra for both sulfonated and raw carbon material, pyrolyzed at 873 K, are shown in Fig. 6. The vibration bands at 1040 cm^{-1} (S═O symmetric stretching), 1080 cm^{-1} (S═O asymmetric stretching) and 1397 cm^{-1} (asymmetric SO_2 stretching in SO_3H) are clearly visible in the FT-IR spectrum, proving the presence of SO_3H groups [22,23]. The band at 1719 cm^{-1} was assigned to the C═O stretching mode of the –COOH and –COO– groups, while the intense, broad envelop centered at 3440 cm^{-1} was assigned to the O–H stretching modes of the –COOH and phenolic OH groups. The band at 1610 cm^{-1} was assigned to the aromatic-like C═C stretching mode in polyaromatics and graphite-like material [17]. The overlapping peaks, which form an absorption band in the 1300–1000 cm^{-1} region, can be assigned to ether (symmetrical stretching vibrations) and phenolic structures existing in different structural environments [23–27].

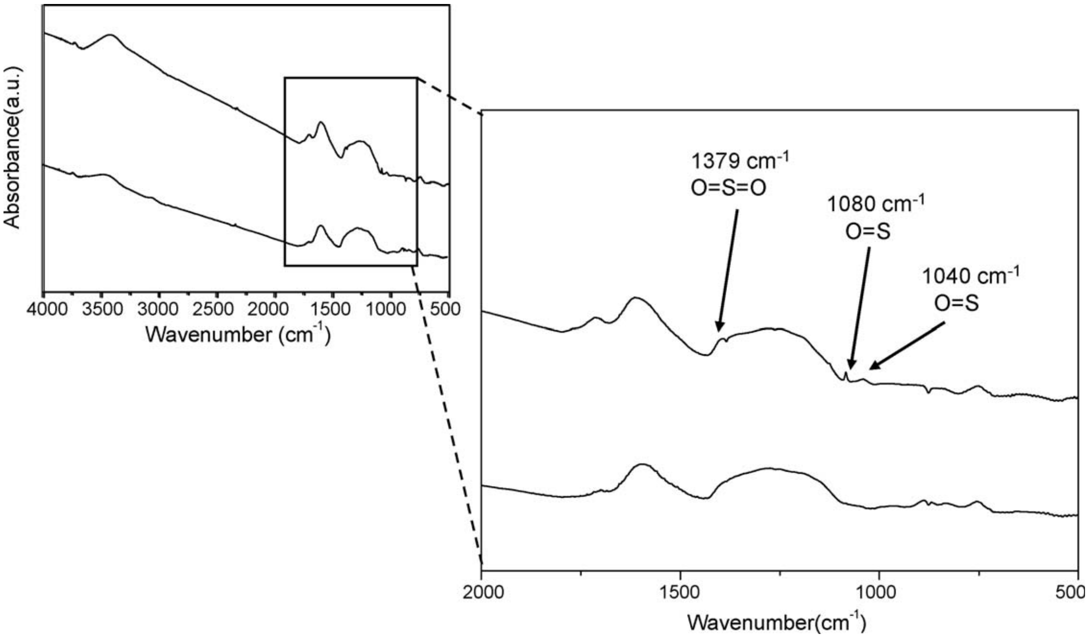

Fig. 6. FT-IR spectra of CMK-3-873-SO_3H (up) and CMK-3-873 (below).

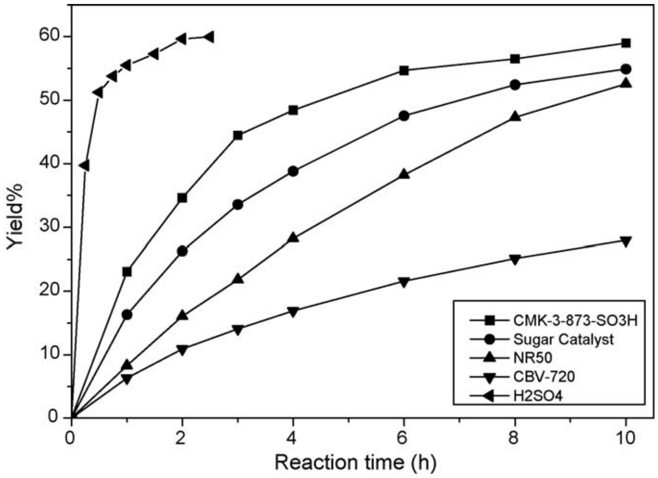

Fig. 7. Comparison of catalytic activity for conversion of oleic acid over different catalysts.

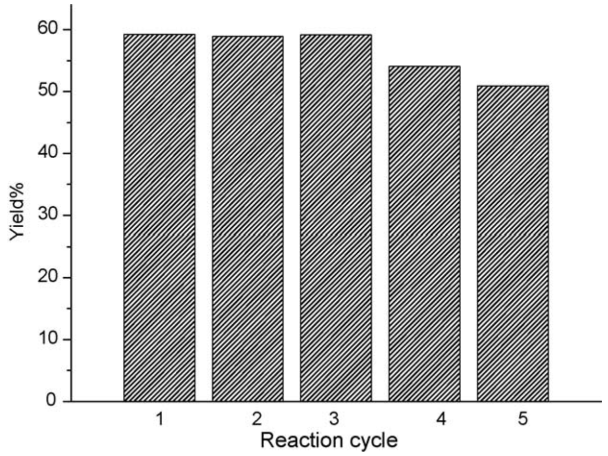

Fig. 8. The reuse of CMK-3-873-SO_3H in the esterification of oleic acid (0.005 mol) with ethanol (0.05 mol) at 353 K. The yields of ethyl oleate produced after reaction for 6 h are shown.

3.2. Fatty acid esters formation by solid acid catalysts

The catalytic performance of CMK-3-873-SO_3H in biodiesel synthesis was investigated by esterification of oleic acid with methanol at 353 K. In order to rationally evaluate the activity of CMK-3-873-SO_3 catalyst in this reaction, a comparative study was made with three solid acid catalysts (amorphous sugar catalyst, protonated Nafion (NR50, and zeolite CBV-720) and homogeneous acid catalyst H_2SO_4. Fig. 7 shows time profiles of oleic acid conversion on these catalysts and their surface areas, acid densities, added amount, and catalytic activities (rate of methyl oleate formation) are summarized in Table 1.

Sulfuric acid, as a homogeneous acid catalyst, has the highest activity, reaching 60% yield of methyl oleate (based on oleic acid) after 2 h of reaction. Except for the CBV-720, the other three solid acid catalysts require at least 10 h to obtain a similar methyl oleate yield. Compared with the commercial protonated Nafion, a well-known polymer-based strong solid acid, the sulfonated carbon-based solid acid, CMK-3-873-SO_3 and amorphous sugar catalyst clearly show higher catalytic activity with much higher initial methyl oleate formation rates (96.1 μmol min^{-1} and 67.9 μmol min^{-1} *vs.* 34.4 μmol min^{-1}, respectively) using the same equivalent H^+ in the reaction. The hydrophobic substrate of carbon-based catalyst is believed to contribute to the superior performance on catalyzed formation of methyl oleate, because it can lead to effective adsorption of the long chain fatty acid molecules, while it has a low affinity for the byproduct water, especially at the beginning stage. The enhancement of catalytic performance of the CMK-3-873-SO_3 in comparison with the amorphous sugar-derived catalyst is due to its large pore size, favoring the fast diffusion of large organic molecules to the active sites.

For evaluation of the operational stability of the CMK-3-873-SO_3H catalyst, the catalyst was recovered and recycled for further reaction. After each use, the catalyst was recycled by washing with acetone and centrifugation twice and drying at 373 K in the vacuum oven overnight. The yield of methyl oleate for CMK-3-873-SO_3H catalysts almost remained unchanged for the first three cycles, and only gradually decreases. After four cycles, the material still gives a notable high yield of methyl oleate of 51%, as shown in Fig. 8. We suppose the small loss in activity is not due to acid leaching in the solution, as filtrate tests showed no significant activity. Although previous reports claim that sulfonated carbons prepared from the pyrolysis of D-glucose followed by sulfonation are insoluble in solvents including water, methanol, ethanol, and benzene [20], recent research have suggested that solid polycyclic aromatic hydrocarbons are not completely insoluble in common solvents [28]. The leaching of polycyclic aromatic hydrocarbons containing –SO_3H groups has been reported recently for sulfonated amorphous carbon catalysts during the reaction and washing procedure [29]. For the CMK-3-873-SO_3H catalyst, the activity was stable at the first three reaction cycles and began to lose some active site during the forth run. Based on the catalyst activity for oleic acid esterification after four cycles of reaction and wash, we estimated that around 85–90% of the catalytic sites of a freshly prepared sulfonated mesoporous carbon catalyst should remain on the catalyst under the reaction conditions used in this study. Another explanation might be the physical loss of some catalyst powder during the recycle step. During the washing step of CMK-3-873-SO_3H after three cycles, the centrifugate was indeed not clear, but rather looks like a suspension containing some fine black solid carbon species, explaining the unavoidable loss of catalyst during the recycle step. Finally, after reusing the catalyst several times, we need to include possible catalyst deactivation due to accumulation of impurities or byproducts. Further work is now in progress to investigate the lowering in activity in more detail in order to clearly distinguish between the different options.

Table 1
Catalytic activity of the tested catalysts[a].

Catalyst	Total surface area (m^2/g)	Acid density[b] (mmol H^+/g)	Added amount (g)	Initial formation rate (μmol min^{-1})
CMK-3-873-SO_3H	807.8	2.3[a]	0.43	96.1
Amorphous sugar catalyst	<5	3.4[a]	0.3	67.9
Protonated-Nafion (NR50)	–	0.8	1.25	34.4
CBV-720	780	1.0	2	26.3
H_2SO_4	–	20.4	0.05	165.4

[a] Reaction condition: acid-catalyzed (H^+ = 1 mmol) esterification of oleic acid (25 mmol) with methanol (250 mmol) at 353 K for 10 h.

[b] Determined by titration with NaOH.

4. Conclusions

A new solid acid, mesoporous carbon material with sulfonic acid group, has been prepared through first sulfonating in liquid phase the carbon/SBA-15 hybrid composite prior to silica removal. In our hands, sulfonation before silica removal is crucial in order to keep the ordering in the porous structure. Soft carbonization is important in order to be able to introduce enough acid sites. The optimal mesoporous SO_3H–carbon material (CMK-3-873-SO_3H) exhibits a high surface area and a uniform pore size. The large pore size and hydrophobic surface property of CMK-3-873-SO_3H make it a highly efficient esterification catalyst. A unique feature of CMK-3-873-SO_3H is its reusability; a high activity was observed even after four recycles. While esterification catalysis is explored here, the application of the sulfonated mesoporous carbon materials can easily be extended to other acid-catalyzed reaction types.

Acknowledgments

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