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# Sulfonic-acid-functionalized porous benzene phenol polymer and carbon for catalytic esterification of methanol with acetic acid

# Xiaoning Tian, Li Li Zhang, Peng Bai, X.S. Zhao\*

Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117576, Singapore

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# ABSTRACT

Porous benzene phenol polymer and carbon were synthesized in the presence of Pluronic P123 as template. Sulfonation of the porous structures yielded solids with sulfonic acid groups. The compositions of the solid acids were characterized using elemental analysis and thermogravimetric analysis methods. Their pore structures were investigated by physical adsorption of nitrogen. X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy were used to characterize surface functional groups. Carbonization of porous benzene phenol polymer at evaluated temperatures transferred the polymer to carbon as proven by X-ray diffraction and transmission electron microscope techniques. The catalytic properties of the solid acids were evaluated using esterification of methanol with acetic acid. Results showed that the catalytic activity for the sulfonated polymer increased with the increase in sulfonation temperature. Sulfonic acid groups on the polymer framework were observed to be more stable than those on the carbon framework.

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# 1. Introduction

Liquid sulfuric acid has been widely used as a catalyst in many chemical reaction processes, such as hydration, esterification, and hydrolysis. However, liquid sulfuric acid has several drawbacks, such as high toxicity, corrosion, and difficulty of separation from the reaction mixture. Therefore, design of environmentally friendly and efficient solid acid catalysts for replacing the liquid acid catalysts is highly desirable. Solid sulfonic acid catalysts based on silicas [1–5], solid organic/inorganic composites [6–10], and carbons [11,12] have been reported in the literature. Generally, organicbased solids are desirable over inorganic solids in terms of binding sulfonic acid (–SO<sub>3</sub>H) groups to create solid sulfonic acids because the former is in general more hydrophobic than the latter. This feature is important in catalyzing hydrocarbon conversions, especially when water is used as a solvent.

The synthesis of mesoporous benzene phenol polymer with block copolymer as a soft template has been described recently [13–17]. Subsequent carbonization of the mesoporous polymer readily leads to the formation of mesoporous carbon. In comparison with the traditional hard templating method [18,19] the soft route to prepare mesoporous carbon is simple and cost-effective. A recent study [20] showed that sulfonated mesoporous benzene phenol polymer displayed a good catalytic activity and recyclability. However, the activity and recyclability of both benzene phenol polymers and correlative carbons should be further evaluated for practical applications.

In this work, porous polymer was synthesized in the presence of soft template Pluronic P123. The polymer was then carbonized at evaluated temperatures to yield porous carbon. Subsequent sulfonation of the porous polymer and carbons yielded sulfonated solids with surface  $-SO_3H$  groups. Experimental results showed that the sulfonated benzene phenol polymer exhibited a better catalytic performance than the sulfonated carbon.

# 2. Experimental

#### 2.1. Preparation of porous benzene phenol polymer and carbons

Porous benzene phenol polymer was synthesized following the method described by Zhao et al. [15]. Soluble phenolic resin was synthesized by mixing 2 g of phenol and 7.0 ml of formaldehyde solution (38 wt%) in 50 ml of 0.1 mol/l NaOH solution at 70 °C for 30 min. Then, 50 ml of water with 8 g of Pluronic P123 ( $EO_{20}PO_{70}EO_{20}$ ) was added into the above phenolic resin solution. After stirring at 65 °C for 96 h and then at 70 °C for 24 h, the final solid was collected by sedimentation and dried in air. The sample thus obtained is designed as MP. Carbonization of MP was conducted in a quartz tube under pure nitrogen flow at different temperatures for 8 h with a heating rate of 1 °C/min. The resultant materials are donated as MC(x), where x stands for the temperatures used during carbonization, namely 350, 400, 500, 600, and 800 °C.



<sup>\*</sup> Corresponding author. Tel.: +65 65164727; fax: +65 67791936. E-mail address: chezxs@nus.edu.sg (X.S. Zhao).

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# 2.2. Sulfonation of porous benzene phenol polymer and carbons

About 0.15 g of a solid sample was combined with 50 ml of concentrated  $H_2SO_4$  (>98%, Merck) at a given temperature. After 4 h, the sample was cooled down to room temperature. Then, 1000 ml of deionized water (DI water) was added to the mixture to form a black precipitate, which was then washed repeatedly using DI water till no sulfate ion in the filtrate was detectable. The resultant sulfonated solid was donated as MC(*x*,*y*), where *y* stands for the sulfonation temperature.

#### 2.3. Characterization

The pore structure of porous polymer and carbon materials was investigated using physical adsorption of nitrogen at -196°C on an automatic volumetric sorption analyzer (Quantachrome, NOVA 1000). Prior to each measurement, a sample was degassed at 120 °C for 3 h under vacuum. The specific surface area was determined according to the Brunauer-Enmett-Teller (BET) method in the relative pressure range of 0.05-0.2. The total pore volume was obtained from the volume of nitrogen adsorbed at relative pressure of 0.99. Pore size distribution (PSD) curves were obtained using the density functional theory (DFT) method, which allows the determination of pore size for both micropores and mesopores using a single analysis method [21-23]. The CO<sub>2</sub> adsorption was detected using physical adsorption of CO<sub>2</sub> at 0°C on a Mircomeritics ASAP 2020 instrument. X-ray diffraction (XRD) patterns were collected on an XRD-6000 (Shimadzu, Japan) with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). Field-emission scanning electron microscope (FESEM) images were obtained from JSM-6700F (JEOL Japan) operated at 10 kV. High-resolution transmission electron microscope (HRTEM) images were obtained from JEM 2010F (JEOL, Japan) operated at 200 kV. X-ray photoelectron spectroscopy (XPS) spectra were recorded on an AXIS HIS 165 spectrometer (Kratos Analytical) with a monochromatized Al K $\alpha$  X-ray source. Thermogravimetric analysis (TGA) was conducted on a thermogravimetric analyzer TGA 2050 (Thermal Analysis Instrument, USA) in nitrogen with a flow rate of 100 ml/min. The elemental compositions of the samples were detected using a CHNS-O Analyzer (FLASH EA 1112 series, Thermo electron corporation). Fourier-transform infrared (FT-IR) spectra were acquired using the KBr technique on a Shidmazu 8400 by averaging 64 scans in the frequency range of  $4000-400 \text{ cm}^{-1}$  with a resolution of 8 cm<sup>-1</sup>. Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) was carried out on a Quantachrome instrument (ChemBET Pulsar TPR/TPD).

# 2.4. Esterification of methanol with acetic acid

The catalytic activity of the sulfonated solids was evaluated using the esterification reaction of methanol with acetic acid. The reaction was carried out in a round bottom flask immersed in a silicon oil bath at 55 °C. 0.4 mol of methanol, 0.04 mol of acetic acid and 0.08 g of solid catalyst were added into the flask. Quantitative analysis was carried out after 5 h of reaction using a gas chromatograph (HP 6890 series GC) mass spectrometer (HP 5973 Mass selective detector) with a capillary column (HP 5MS, L 30 m, I.D. 0.25 mm, Film 0.25  $\mu$ m). A used catalyst was collected, washed using DI water, and dried at 100 °C for the next reaction cycle.

The deactivation nature of the sulfonated solids were studied by using a BaCl<sub>2</sub> solution to detect  $H_2SO_4$  due to the hydrolysis of -SO<sub>3</sub>H groups [24,25] using a UV-vis spectrometer (UV-1601PC, Shimhdzu) to detected the leaching of carbon sheets connected with -SO<sub>3</sub>H groups [26].



Fig. 1.  $N_2$  adsorption/desorption isotherms of (a) MC(350), (b) MC(400), (c) MC(500), (d) MC(600), and (e) MC(800).

# 3. Results and discussion

# 3.1. Pore structure

The N<sub>2</sub> adsorption-desorption isotherms of the MC samples are shown in Fig. 1. The adsorption isotherm of sample MC(350) appears both Type I and Type IV, suggesting a porous structure with both micropores and mesopores. The adsorption and desorption isotherms are irreversible nearly in the whole relative pressure region. This is a typical behavior of polymer materials because of the swelling of the polymer in condensed nitrogen [13,14]. Polymers possess a large amount of void space, referred to as free volume. As nitrogen condenses in the free volume, the structure of the polymer relaxes, allowing nitrogen access to the void space at high relative pressures. In desorption, those nitrogen molecules having swollen polymer cannot be desorbed, causing such a hysteresis behavior in a wide range of relative pressure. It is also seen from Fig. 1 that samples MC(400), MC(500), MC(600) and MC(800) all exhibited a Type I isotherm, indicating a microporous structure [27], which is consist with the pore size distribution results (see Fig. 2b-e). The adsorption and desorption branches for these samples were irreversible almost throughout the whole relative pressure range. This observation may be due to the swelling of carbon microparticles by nitrogen during adsorption and/or the strong interaction between nitrogen molecules and carbon surface [23,29-31]. As the oxygen content measured using elemental analysis (see Table 1) for these carbon samples were all very high, they must contain a large number of oxygen-containing functional groups, which may provide the interaction with nitrogen molecules. Moreover the N<sub>2</sub> (see Fig. 1e) and CO<sub>2</sub> (see Fig. S1 in Supporting Information) adsorption isotherms of sample MC(800) revealed that the micropore network was accessible to  $N_2$  and  $CO_2$  at -196 and 0 °C respectively. Therefore, sample MC(800) is not an ultramicroporous material [28].

Sample MP consists of small pellets (see Fig. S2a in Supporting Information). After carbonization at 350 °C, the pellets particle size of MC(350) became smaller (see Fig. S2b in Supporting Information). As is known, thermal treatment causes shrinkage of the polymer framework [13]. After high-temperature carbonization treatment, more obvious size shrinkage can be found for MC(800) (see Fig. S2c in Supporting Information). Synthesized MP pallets are

Table 1



Fig. 2. DFT pore size distribution of (a) MC(350), (b) MC(400), (c) MC(500), (d) MC(600), and (e) MC(800).

dark red, whereas MC(350) appeared a darker color and MC(800) showed a bright black color. This color change is mainly caused by the carbonization process, because the sample compositions changed during the carbonization process, which are analyzed in details in the compositions part.

Fig. 2 shows the pore size distribution curves of the carbonized samples. It can be seen that the pore size decreased with the increase in carbonization temperature from 350 to  $800 \degree$ C. At the carbonization temperature of 400, 500, 600 and  $800 \degree$ C, most of the mesopores disappeared while micropores dominated. From the textural parameters of the samples (see Table 2), it can be seen that at low carbonization temperatures ( $350-400\degree$ C), the surface area and total pore volume decreased with the increase in carbonization temperature, which is due to the shrinkage of the polymer framework during the carbonization process. MC(400) and MC(500) show the similar surface area and total pore volume, which means no big difference of framework shrinkage happened when carbonization temperature increased from 400 to  $500\degree$ C. However, the surface area and total pore volume increased with the further increase in the carbonization temperature from 500 to 600 °C. Such

Composition of samples analyzed using elemental analysis.								
Sample	C (wt%)	O (wt%)	H (wt%)	S (wt%)				
MC(350)	74.3	21.2	4.5	0				
MC(350,40)	60.9	30.4	4.2	4.5				
MC(350,40) <sup>a</sup>	66.5	26.9	4.2	2.4				
MC(350,100)	56.9	33.5	3.9	5.7				
MC(350,100) <sup>a</sup>	62.1	29.6	4.1	4.2				
MC(400)	79.3	16.2	4.5	0				
MC(400,40)	71.1	23.3	3.9	1.7				
MC(400,40) <sup>a</sup>	74.5	21.1	4.2	0.2				
MC(500)	88.5	7.8	3.7	0				
MC(500,40)	79.9	16.2	3.3	0.6				
MC(500,40) <sup>a</sup>	83.4	12.7	3.5	0.4				
MC(600)	91.3	7.2	1.5	0				
MC(600,40)	76.9	19.6	2.3	1.2				
MC(600,40) <sup>a</sup>	82.9	14.9	1.9	0.3				
MC(800)	89.5	9.9	0.6	0				
MC(800,40)	78.6	18.3	1.1	2.0				
MC(800,40) <sup>a</sup>	80.4	15.5	3.3	0.8				

<sup>a</sup> Catalyst after the 4th reaction cycle.

an increase in porosity is probably due to the formation of more micropores because of the release of small molecules (CO, CO<sub>2</sub> and H<sub>2</sub>O) at high carbonization temperatures [29,32–34] as revealed by the TGA data (see Fig. S3 in Supporting Information). As can be seen, sample MP showed a weight loss of about 52% in the temperature range of 350–400 °C under nitrogen, which was assigned mainly to the removal of P123 template [13]. About 7% weight loss was observed in the temperature range of 500–800 °C, which was mainly caused by the release of small molecules.

After sulfonation, though mesopore channels can still be observed over sample MC(350,100) (see Fig. 3a), the surface area and pore size distribution of samples MC(350,40) and MC(350,100) decreased (see Fig. S4 in Supporting Information and Fig. 2a) due to the damage of pore channels and shrinkage of framework during the sulfonation process [34]. After sulfonation, the surface areas of sample MC(400,40), MC(500,40), MC(600,40) and MC(800,40) all decreased (see Table 2), indicating that the pore structure of the carbon sample was partially destroyed during the sulfonation process.

Fig. 4 shows the XRD patterns of all carbonized samples. It should be noted that the peaks at around 37 and 44 degrees two theta are attributed to the Al holder (see Fig. S5 in Supporting Information). It is seen that samples MC(350), MC(400) and MC(500) all exhibited a broad peak at around 23 degrees two theta, indicating amorphous structures with little graphite domains. Samples MC(600) and MC(800) showed two broad peaks at around 23 and 43 degrees two theta, attributed to the (002) and (101) planes



Fig. 3. HRTEM images for (a) MC(350,100) and (b) MC(800).

Table 2	
Pore properties obtained from N2 sorpt	ion isotherms.

Sample	$S_{\text{BET}}^{a}(m^{2}/g)$	$V^{\rm b}$ (cm <sup>3</sup> /g)	Sample	$S_{\text{BET}}^{a}(m^{2}/g)$	$V^{\rm b}$ (cm <sup>3</sup> /g)
MC(350)	421	0.26	MC(350,40)	44	0.04
MC(400)	314	0.16	MC(350,100)	64	0.04
MC(500)	287	0.17	MC(400,40)	-	-
MC(600)	350	0.20	MC(500,40)	-	-
MC(800)	514	0.26	MC(600,40)	-	-
			MC(800,40)	-	-

<sup>a</sup> BET surface area calculated from the linear part of the BET plot ( $P/P_0 = 0.05 - 0.2$ ).

<sup>b</sup> Total pore volume, taken from the volume of N<sub>2</sub> adsorbed at  $P/P_0 = 0.99$ .

of graphitic carbon, respectively. These two peaks for MC(800) was more intense than that of sample MC(600), showing an increase in the degree of stacking of graphene layers caused by the increase in carbonization temperature [35]. From the peak at around 23 degrees two theta, the layer-to-layer distance (d-spacing) was estimated to be about 0.37 nm [36], consistent with that obtained from the HRTEM image shown in Fig. S6 (see Supporting Information). The HRTEM image of MC(800)(Fig. 3b) indeed showed the presence of flat graphene carbon sheets of graphitic nature [37]. It can be concluded that graphite structure formed during the high-temperature carbonization process.

### 3.2. Chemical compositions

The C/H/O molar ratio of sample MC(350) was measured to be about 6.2/4.5/1, confirming that the sample is polymer-based material with a phenolic resin framework [13]. Samples MC(400), MC(500), MC(600) and MC(800) showed a lower oxygen content compared with sample MC(350) due to the removal of template and the release of small molecules. The carbon content for sample MC(400) was about 80%, indicating an low temperature incomplete carbonization. Therefore MC(400) is an incomplete carbon-based material and exhibits a transition status from polymer to carbon during carbonization process. With the increase of carbonization temperature, the carbon contents for samples MC(500), MC(600) and MC(800) increased to about 90%, which is much higher than that of MC(350), implying a carbon-based material [13]. Therefore, it can be concluded that during the carbonization process the polymer framework released small molecules through pyrolysis to result in the formation of aromatic rings connected together to form carbon sheets, through which the framework was trans-



Fig. 4. XRD patterns for (a) MC(350), (b) MC(400), (c) MC(500), (d) MC(600), and (e) MC(800).

ferred from polymer to carbon, in agree with the results of XRD and HRTEM.

It is seen from Table 1 that MC(350,40) possessed higher sulfur content than samples MC(400,40) and MC(500,40). This may come from two reasons. First, with the increase in carbonization temperature, more aromatic rings connected together to form large carbon sheets, resulting in a decrease in the density of  $-SO_3H$  groups as  $-SO_3H$  groups are attached on the edges of carbon sheets [38]. Second, with the increase in carbonization temperature, the carbon sheets grew larger and larger, thus the carbon framework became denser and denser, leading to a lower density of  $-SO_3H$  groups because compact carbon structures are more difficult to be sulfonated than polymers [11,38].

It is also seen from Table 1 that the sulfur content for sulfonated carbon-based samples, i.e. MC(500,40), MC(600,40) and MC(800,40), increased with the increase in carbonization temperature. The data in Table 2 show that the surface area and pore volume increased with the increase in the carbonization temperature. This increase was caused by the release of small molecules (CO, CO<sub>2</sub> and H<sub>2</sub>O) during the carbonization process. From the results of physical adsorption of nitrogen it can be seen that mesopores disappeared with the increase of carbonization temperature and micropores dominated the main pore size distribution. The increase in micropores increased the area for the attachment of -SO<sub>3</sub>H groups. However, the micropores partially collapsed during the sulfonation process. The collapsed aromatic carbon sheets with attached -SO<sub>3</sub>H groups may be trapped inside the carbon particles during the sulfonation and subsequent washing processes. This can explain why the sulfur content increased for the sample carbonized at higher temperatures in spite of larger aromatic carbon sheets formed at high carbonization temperatures.

The XPS spectra for samples MC(350,40), MC(350,100), MC(400,40) and MC(800,40) are shown in Fig. 5. All samples exhibited a single S2p peak at about 168.8 eV, which is assigned to aromatic carbon atoms in connection with  $-SO_3H$  groups [11,38]. The S2p spectra can be deconvoluted into two peak with binding energies of 168.5 and 169.4 eV, which are assigned to S2p<sub>3/2</sub> and S2p<sub>1/2</sub> of the sulfur in  $-SO_3H$ , respectively [39,40].

The sulfur content measured using the elemental analysis method (see Table 1) is higher than that measured using the XPS technique (see Table S1 in Supporting Information) for sulfonated polymer-based samples i.e. MC(350,40) and MC(350,100), indicating that the surface density of  $-SO_3H$  groups is higher than that of the outer. However for sulfonated incomplete carbon-based sample i.e. MC(400,40) and sulfonated carbon-based samples i.e. MC(500,40), MC(600,40), MC(800,40) the sulfur content detected using the elemental analysis method is lower than that measured using XPS technique, implying that the inner  $-SO_3H$  group density is lower than that of the outer.

Fig. 6 shows the FT-IR spectra of sulfonated polymer-based samples, namely samples MC(350), MC(350,100), and MC(350,40). The peaks at around 1464 and 1623 cm<sup>-1</sup> are attributed to C=C stretching vibrations. The peak at around 1209 cm<sup>-1</sup> is attributed to the presence of Ar–OH [20]. The sulfonated samples, namely



Fig. 5. S2p XPS spectra for (a) MC(350,100), (b) MC(350,40), (c) MC(400,40), and (d) MC(800,40).

MC(350,100) and MC(350,40), displayed two new peaks at around 1032 and  $610 \, \text{cm}^{-1}$  (see Fig. 6b–d), which are assigned to symmetric stretching vibrations of S=O and –OH in –SO<sub>3</sub>H groups (see Figs. S7B and S7D in Supporting Information), respectively [20]. The S–O stretching band is seen at around  $704 \, \text{cm}^{-1}$  while the peak at round  $630 \, \text{cm}^{-1}$  is responsible for the C–S stretching vibration [26,41]. The same peaks attributed to –SO<sub>3</sub>H groups attached to aromatic carbon atoms can also be found for sample MC(350,100) after the 4th reaction run (see Fig. S7C), indicating a stable attachment of sulfonic acid groups. The sulfonated carbon-based sample, MC(800,40), also showed peaks attributed to C–S ( $630 \, \text{cm}^{-1}$ ), S=O ( $1048 \, \text{cm}^{-1}$ ) [26,41], and S–O ( $704 \, \text{cm}^{-1}$ ) stretching vibrations (see Fig. S8). The intensity for these peaks is lower than that of the polymer-based samples, indicating a lower density of –SO<sub>3</sub>H groups.



Fig. 6. FT-IR spectra of (a) MC(350), (b) MC(350,100), (c) MC(350,100) after the 4th reaction cycle, (d) MC(350,40).



**Scheme 1.** The formation of  $-SO_3H$  group on (a) polymer framework, (b) carbon framework with small carbon sheets, and (c) carbon framework with big carbon sheets.

# 3.3. The formation of $-SO_3H$ groups

Xing et al. [20] and Okamura et al. [38] showed that  $-SO_3H$  groups are attached on those carbon atoms in aromatic rings in both polymer and carbon frameworks. On the basis of the previous works and our own XPS and FT-IR results, it is believed that  $-SO_3H$  groups were attached to aromatic carbon atoms in the porous polymer as illustrated in Scheme 1a. During carbonization, the aromatic rings connected together to form carbon sheets by releasing small molecules, resulting in the attachment of the  $-SO_3H$  groups to the aromatic carbon atoms in the carbon sheets (see Scheme 1b). The carbon sheets further grew with the increase in carbonization temperature (see Scheme 1c).



Fig. 7. Catalytic conversion of acetic acid over resultant sulfonic acid catalyst.

#### 3.4. Thermal gravimetric analysis and NH<sub>3</sub>-TPD

The TGA–DrTGA curves for MC(350,100) are shown in Fig. S9 (see Supporting Information). The main weight loss event in the temperature range between 150 and 350 °C is mainly attributed to the decomposition of functional groups, such as –OH, –CH<sub>2</sub>OH and –SO<sub>3</sub>H [11]. The NH<sub>3</sub>–TPD profile for sample MC(350,100) shown in Fig. S10 (see Supporting Information) demonstrated that there is a intensive peak at about 300 °C, which was due to the desorption of ammonia from sulfonic acid groups. Using elemental analysis method allows one to estimate the density of sulfonic acid groups [42].

#### 3.5. Catalytic properties

Fig. 7 shows the catalytic activity of the sulfonated materials after different reaction runs. It is seen that catalyst MC(350,100) showed the highest conversion in the first reaction run. After the fourth reaction run, the sulfur content of MC(350,100) decreased from 5.7 to 4.2 wt%, indicating a stable attachment of -SO<sub>3</sub>H groups. Fig. 8 shows the conversion of acetic acid versus time catalyzed by MC(350,100) at 55 °C in the second reaction run. The activity and recyclability for MC(350,100) are better than those of sulfonated polypyrrole spheres [26], indicating easier and more stable attachment of sulfonic acid groups on the benzene phenol rings than that on pyrrole rings. A nafion resin catalyst has been evaluated under the same reaction conditions. The conversion of acetic acid for the first reaction run was about 98%, which is higher than that of the sulfonated catalysts. However, significant swelling phenomenon was observed for the nafion resin catalyst. The swollen nafion resin was crashed into invisible small parts during stirring. Therefore, the recyclability for the sulfonated polymer is better than that of the nafion resin.

It is also seen from Fig. 7 that the catalytic activity for all sulfonated catalysts decreased with the increase in reaction times. This may be due to two reasons. One is the hydrolysis of  $-SO_3H$ groups [24,25]. When BaCl<sub>2</sub> solution was added to the filtrate after catalytic reaction, white precipitate (BaSO<sub>4</sub>) was found. The other one is the leaching of aromatic carbon sheets attached with  $-SO_3H$ groups, similar to the leaching of polycyclic aromatic hydrocarbons [26,43], which was detected using the UV technique [26]. For the filtrate after catalytic reaction, a UV peak at about 250 nm was found for both polymer and carbon-based catalysts. This peak is attributed



Fig. 8. Acetic acid conversion vs time for esterification reaction catalyzed by MC(350,100) at 55 °C for the 2nd cycle.

to the decomposition of catalysts during the catalytic reaction (see Fig. S11).

Sample MC(800,40) exhibited the highest catalytic activity among the sulfonated carbon-based materials in the first run due to the high sulfur content. However, the conversion of acetic acid in the second run decreased to 40%. Because the micropores of sample MC(800) partially collapsed during the sulfonation process, the attached sulfonic acid groups might be trapped inside the sample. The significant drop of conversion in the second run should thus be due to the leaching of collapsed carbon sheets, which attached with sulfonic acid groups. This was detected using the UV method the results are shown in Fig. S11. Increasing carbonization temperature enhanced the formation of compact carbon structure, which is difficult to be sulfonated [11,38].

For sample MC(600,40), however, no obvious decrease in catalytic activity was observed after the second reaction run, indicating the attached  $-SO_3H$  groups are stable. The main deactivation reason for sample MC(600,40) is thus due to the hydrolysis of  $-SO_3H$  groups. While MC(600,40) possessed a higher sulfur content than MC(500,40) did, the activity of MC(600,40) is lower than that of MC(500,40). Therefore, it can be assumed that the hydrolysis of  $-SO_3H$  groups in MC(600,40) is easier than that in MC(500,40).

The initial catalytic activity in esterification of methanol with acetic acid catalyzed by MC(350,100) was investigated. An apparent reaction order was determined by varying the concentration of one reactant while keeping the other one in excess. The results are given in Table S2. The concentrations of both acetic acid and methanol had positive effect on the reaction rate with increasing reactant concentration. Using a power law approximation, the apparent reaction orders were determined to be 0.8 for methanol and 0.7 for acetic acid, respectively.

# 4. Conclusions

Sulfonic-acid-functionalized porous polymer and carbon were successfully prepared. Characterization results showed that the aromatic rings in the polymer bonded together to form carbon sheets during the carbonization process. The size of the carbon sheets increased with the increase in carbonization temperature. As a result, the polymer framework transferred to carbon. Graphite carbon structure was observed over the carbon samples prepared at high carbonization temperatures. large carbon sheets and compact carbon structure were found to be not favorable for the attachment of -SO<sub>3</sub>H groups during sulfonation. The density and stability of attached –SO<sub>3</sub>H groups on the polymer framework were observed to be higher than those on the carbon framework. Therefore, the sulfonated porous polymer catalytically performed better than the sulfonated porous carbons in the reaction of esterification of methanol with acetic acid.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2010.03.082.

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