

# Synthesis and catalytic properties of mesoporous ethane-silicas containing phenyl-sulfonic acid group

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## Abstract

The synthesis and catalytic properties of the mesoporous ethane-silicas functionalized with phenyl-sulfonic acid were reported. The phenyl-sulfonic acid groups were generated by sulfonation of the mesoporous ethane-silicas functionalized with phenyl groups, which was synthesized via co-condensation of 1,2-bis (trimethoxysilyl)ethane (BTME) and phenyltrimethoxysilane (PTMS) using block co-polymer Pluronic 123 as template in acidic medium. The results of XRD and nitrogen sorption isotherms show that all materials remain their ordered two-dimensional hexagonal mesostructure after sulfonation. The existence of phenyl-sulfonic acid groups was confirmed by UV-Raman spectroscopy, acid–base titration method and ICP-AES. The acid exchange capacity of these materials is in the range of 0.49–0.86 mmol H<sup>+</sup> g<sup>-1</sup>. The sulfonated materials can effectively catalyze the condensation of phenol with acetone for the production of Bisphenol-A and the Claisen-Schmidt condensation of acetophenone with benzaldehyde to form chalcone. The catalytic results show that the catalytic activity of the mesoporous materials is not only affected by the amount of the phenyl-sulfonic acid group, but also by the structural order of the mesoporous materials.  
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## 1. Introduction

Sulfonic acid functionalized mesoporous materials have attracted much research attention because of their potential applications as solid acid catalysts. The synthesis and catalytic activities of the mesoporous silicas containing propyl-sulfonic acid group have been reported by different research groups recently [1–6]. The high catalytic activity of these materials can be attributed to their high surface area and the high accessibility of the acid centers to the reactants [1,3–6]. Anchoring sulfonic acid groups with different acid strength onto mesoporous materials might increase the potential catalytic applications of the mesoporous ethane-silicas functionalized with phenyl group. Previous studies show that phenyl-sulfonic acid group have stronger acid strength than propyl-sulfonic acid group [7,8]. Therefore, it is interesting to synthesize and investigate the catalytic properties of the mesoporous materials containing phenyl-sulfonic acid group.

The mesoporous materials containing phenyl-sulfonic acid group were synthesized by both the direct co-condensation of 2-(4-chlorosulfonylphenyl) ethyltrimethoxysilane and tetraethoxysilane in the presence of template and the sulfonation of the mesoporous materials containing phenyl group [7,9–12]. Compared with the direct co-condensation method, the sulfonation method provides a cheaper way for the synthesis of the mesoporous materials containing phenyl-sulfonic acid group. However, the sulfonation method always leads to mesoporous materials with disordered mesostructure and lower amounts of phenyl-sulfonic acid group (the acidity is lower than 0.5 mmol H<sup>+</sup> g<sup>-1</sup>) [11,12]. In this manuscript, we report on the synthesis of the high order mesoporous ethane-silicas functionalized with phenyl-sulfonic acid. The acidic exchange capacity of the material can reach as high as 0.86 mmol H<sup>+</sup> g<sup>-1</sup>. The mesoporous ethane-silicas functionalized with phenyl-sulfonic acid were first used as heterogeneous acid catalysts for the Claisen-Schmidt condensation of acetophenone with benzaldehyde to form chalcone. They are also efficient catalysts for the condensation of phenol with acetone to form Bisphenol-A.

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## 2. Experimental section

### 2.1. Chemicals

1,2-Bis (trimethoxysilyl)ethane (BTME), EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> (Pluronic 123) and phenyltrimethoxysilane (PTMS) were purchased from Sigma–Aldrich Company Ltd. (USA). Acetone was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. Other reagents are of analytic grade and used without further purification.

### 2.2. Synthesis of the mesoporous ethane-silicas functionalized with phenyl group (PEp-X%)

In a typical synthesis, 2.20 g of pluronic 123 and 13.98 g of KCl were dissolved in aqueous solution containing 2.0 M HCl (66.00 g) and deionized water (15.00 g) at 43 °C. Then a mixture (14.2 mmol) of BTME and PTMS was added to the above solution. After the mixture was stirred for 24 h at the same temperature, it was transferred to a Teflon lined autoclave and heated at 100 °C for additional 24 h under static conditions. The white powder was collected by filtration, washed thoroughly with deionized water, and dried at room temperature. Two kinds of methods were used for the surfactant extraction. Method A: the surfactant was extracted by refluxing of 1.0 g of as-synthesized sample in EtOH/HCl (2.5 g 37% HCl in 150 mL ethanol) for 24 h. After filtration, this process was repeated for one more time. Method B: after the surfactant was extracted by EtOH/HCl for 24 h as method A, the powder product after filtration was again refluxed in 200 mL HCl solution (2.0 M) at 95 °C for 6 h. After filtration and washed thoroughly with deionized water, the powder was dried at 80 °C overnight. The sample was denoted as PEp-X%, while X corresponds to the molar percent of PTMS in the initial silane precursors (X = 10, 20, 30).

### 2.3. Sulfonation of the mesoporous ethane-silicas functionalized with phenyl group (S-PEp-X%)

The sulfonation process is according to the published method [11]. The PEp-X% (1.2 g) was added to the sample chamber of a glass apparatus shown in Fig. 1. The sample was dehy-

drated under vacuum (10<sup>-1</sup> Torr) at 150 °C for 16 h before it was allowed to contact with SO<sub>3</sub> (vaporized from 25 g 50% oleum) at 50 °C for 14 h. Then the sample was cooled to room temperature and the extra SO<sub>3</sub> was removed by a flow of argon. The sample was transferred to 500 mL of deionized water and stirred for 30 min. The powder product was recovered by filtration. This process was repeated for several times until the filtrate was neutral. Finally, the powder product was washed with 1,4-dioxane and ethanol, and dried at 80 °C overnight. The sample was denoted as S-PEp-X% (X = 10, 20, 30). For comparison, the mesoporous ethane-silicas without phenyl group were sulfonated under the identical conditions, the sample was denoted as S-PE.

### 2.4. Catalytic experiment

#### 2.4.1. Condensation of phenol with acetone to form Bisphenol-A

The reaction was performed in a 50 mL sealed glass vessel. A mixture of 70 mmol of phenol, 10 mmol of acetone and 70 mg of catalyst was stirred at 85 °C for 24 h. After reaction, biphenyl in acetonitrile was added as an external standard. The mixture was filtered and the filtrate was analyzed on an Agilent 6890 gas chromatography equipped with a flame ionization detector and a HP-5 capillary column (30 m × 0.32 mm × 0.25 μm).

#### 2.4.2. Condensation reaction between acetophenone and benzaldehyde

Typically, 50 mg of catalyst was stirred for 6 h at 150 °C in a mixture of 20 mmol of acetophenone and 20 mmol of benzaldehyde. The reaction products after filtration were analyzed by Agilent 6890 GC.

### 2.5. Characterization

X-ray powder diffraction (XRD) analyses were collected on a Rigaku D/Max 3400 powder diffraction system using Cu Kα radiation. The nitrogen sorption experiments were performed at 77 K on an ASAP 2000 system, the sample was outgassed at 100 °C for 10 h before the measurement. Surface area was cal-

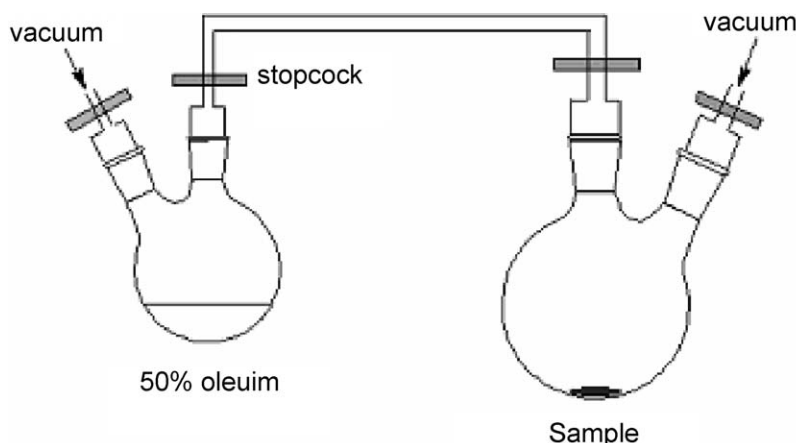


Fig. 1. Schematic diagram of the manifold used for sulfonation.

culated using Brunauer-Emmett-Teller (BET) method with the relative pressure in the range of 0.1–0.2. Pore diameters were determined from the adsorption branch of nitrogen isotherm using the Barrett-Joyner-Halenda (BJH) method. Transmission electron microscopy (TEM) was performed on a HITACHI 9000 electron microscope with an acceleration voltage of 200 kV. UV-Raman spectra were recorded on a home-made spectrometer, 244 nm laser line from Kimmon was used as the excitation source. Solid-state  $^{29}\text{Si}$  MAS (79.5 MHz) and  $^{13}\text{C}$  (100.5 MHz) CP MAS NMR experiments were obtained on a Bruker DRX-400 NMR spectrometer equipped with a magic angle spin probe using tetramethylsilane as external reference. Thermogravimetric analyses (TGA) were carried out on Perkin-Elmer Pyris Diamond TG analyzer with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  under a flow of nitrogen. The acid exchange capacity of S-PEP-X% was determined by titration with NaOH. 0.1 g of solid was added to 20 g of 2 M aqueous NaCl or 20 g of 1 M aqueous (*n*-Bu) $_4\text{NBr}$  solution. The resulting suspension was stirred at room temperature for 24 h until equilibrium was reached, and subsequently titrated potentiometrically by dropwise addition of 0.10 M NaOH.

### 3. Results and discussion

#### 3.1. Characterization of the mesoporous ethane-silicas functionalized with phenyl group by solid-state NMR technique

$^{13}\text{C}$  CP MAS NMR spectrum of PEP-30% extracted by EtOH/HCl is displayed in Fig. 2a. The strong resonance at 5.2 ppm is derived from carbon of  $-\text{CH}_2\text{CH}_2-$  [13,14]. The resonances at 134.2 and 128.2 ppm are unambiguously attributed to the carbon of phenyl group. The peak at 71.5 ppm is due to the carbon species of the surfactant residue and the peaks at 58.2 and 17.0 ppm can be assigned to the carbon of surface ethoxy groups ( $\text{Si}-\text{OCH}_2\text{CH}_3$ ) formed in the course of solvent extraction. The

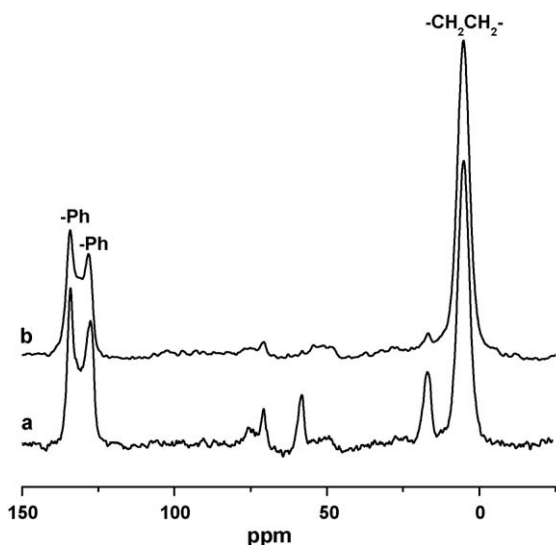


Fig. 2.  $^{13}\text{C}$  CP MAS NMR spectra for PEP-30% extracted with EtOH/HCl for two times (a), extracted with EtOH/HCl followed by 2 M HCl (b).

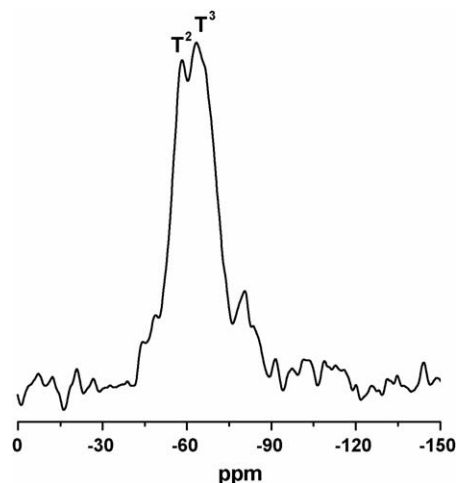


Fig. 3.  $^{29}\text{Si}$  MAS NMR spectrum of PEP-30%.

result of  $^{13}\text{C}$  CP MAS NMR shows that the surfactant cannot be removed completely by extraction with EtOH/HCl. For the mesoporous ethane-silicas synthesized using P123 as template in acidic medium, the surfactant could be removed completely by refluxing the as-synthesized materials in EtOH/HCl [13]. However, this is not the case for the mesoporous ethane-silicas functionalized with phenyl group. This may be because that the hydrophobic phenyl group can interact with P123 surfactant more tightly. Thus the remaining surfactant was further extracted by 2 M HCl aqueous solution. Three strong resonances (5.2, 128.2 and 134.2 ppm) were observed in  $^{13}\text{C}$  CP MAS NMR spectrum of PEP-30% extracted by 2 M HCl aqueous solution, which could be assigned to the carbon species of bridged ethane moiety and pendant phenyl moiety (Fig. 2b). The peak related with surfactant at 71.5 ppm is very weak, indicating almost complete removal of the surfactant by 2 M HCl aqueous solution.

Solid-state  $^{29}\text{Si}$  MAS NMR spectrum of PEP-30% is depicted in Fig. 3.  $^{29}\text{Si}$  MAS NMR spectrum clearly exhibits the resonances of silicon species connected with carbon in the range of  $-70$  to  $-50$  ppm. Distinct resonances at  $-58.3$  and  $-63.3$  ppm could be assigned to  $\text{T}^2$  [ $\text{SiC}(\text{OH})(\text{OSi})_2$ ] and  $\text{T}^3$  [ $\text{SiC}(\text{OSi})_3$ ] sites, respectively. The absence of signals between  $-90$  and  $-120$  ppm indicates that no silicon-carbon bond cleavage occurred during the synthesis and surfactant removal process.

$^{29}\text{Si}$  MAS and  $^{13}\text{C}$  CP MAS NMR analyses of PEP-30% confirm the integrity of the ethane groups and phenyl functionalities in the material.

#### 3.2. Mesopore structure of PEP-X%

The X-ray diffraction patterns of PEP-10% and PEP-20% exhibit three well resolved diffraction peaks corresponding to (1 0 0), (1 1 0), (2 0 0) reflection, indicating that the materials have highly ordered two-dimensional hexagonal mesopore structure (Fig. 4). TEM images of PEP-10%, which shows hexagonal symmetry mesopores throughout the sample, are consistent with the powder X-ray diffraction results and further confirm the two-dimensional hexagonal structure of the material (Fig. 5). The X-ray diffraction pattern of PEP-30% displays one sharp (1 0 0)

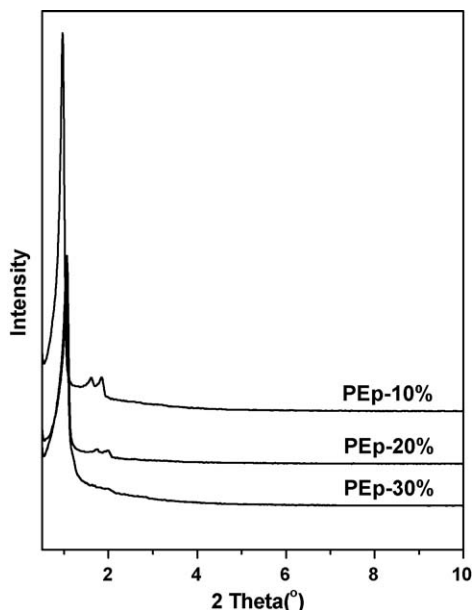


Fig. 4. XRD patterns of surfactant-free PEp-X%.

and a weak (1 1 0) reflection peaks, showing that the mesostructure of PEp-30% is not as well ordered as that of PEp-10% and PEp-20%. XRD results indicate that the meso-structural order of PEp is decreased with the molar fraction of PTMS increasing.

Nitrogen sorption analyses of all PEp-X% display typical type IV isotherm patterns with a sharp capillary condensation step, indicating that PEp-X% materials have uniformly distributed mesopores (Fig. 6). H1-type hysteresis loop at relative pressures in the range of 0.4–0.8 was observed for all samples, which is characteristic of the ordered mesoporous materials with one-dimensional cylindrical channels [13,15]. The capillary condensation step of nitrogen adsorption branch shifted to lower relative pressure. The above results imply that the mesopore of PEp-X% becomes smaller and less regular with the molar fraction of PTMS increasing.

XRD and nitrogen sorption analyses show that ordered mesoporous ethane-silicas functionalized with phenyl group could be obtained by using P123 as template in acidic medium with the aid of KCl.

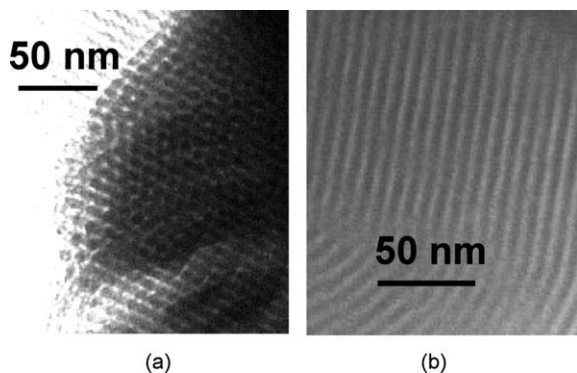


Fig. 5. TEM images of surfactant-free PEp-10% (a) in the direction of the pore axis and (b) in the direction perpendicular to the pore axis.

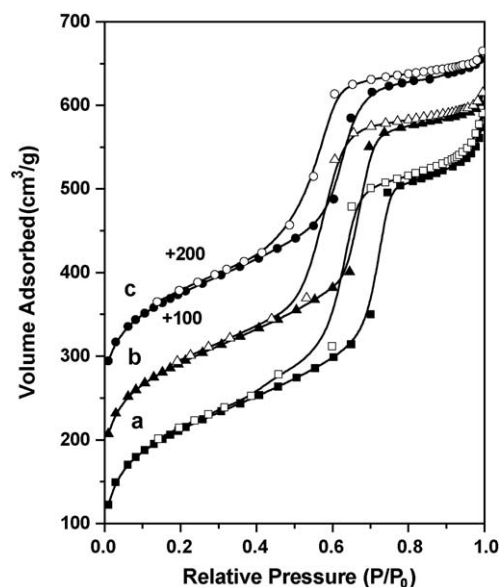


Fig. 6. N<sub>2</sub> sorption isotherms of PEp-X%. (a) PEp-10%, (b) PEp-20%, and (c) PEp-30%.

### 3.3. Characterization of S-PEp-X%

The phenyl-sulfonic acid functionalities were generated by gas phase reaction of SO<sub>3</sub> with the mesoporous ethane-silicas functionalized with phenyl group. The same strategy was also employed for the successful synthesis of beta-type zeolite-phenylsulfonic-acid and MCM-41-phenylsulfonic-acid [11,12]. The acid exchange capacity of S-PEp-X% was measured by acid-base titration method. The acid exchange capacity of S-PEp-X% is increased from 0.49 to 0.86 mmol H<sup>+</sup> g<sup>-1</sup> as the molar fraction of PTMS increasing from 10 to 30 (determined using NaCl as ion exchanger). The similar acid exchange capacity was obtained using (*n*-Bu)<sub>4</sub>NBr (with larger cationic ions) as ion exchanger (Table 2). This result implies that the phenyl-sulfonic acid groups are accessible by guest molecules with similar or smaller size as that of (*n*-BuN)<sup>+</sup>. The S content of S-PEp-X% analysed by ICP-AES is listed in Table 2. The acidity of S-PEp-X% measured by acid-base titration method is higher than that analysed by ICP-AES. The sample S-PE synthesized by sulfonation of pure mesoporous ethane-silica under identical conditions as that of S-PEp-X% shows an acidity of 0.10 mmol H<sup>+</sup> g<sup>-1</sup> measured by acid-base titration method using NaCl as ion exchanger. The above results indicate that the existence of physisorbed H<sup>+</sup> species on S-PEp-X% is the main reason for the higher acidity obtained by the titration method.

The mesostructure of S-PEp-X% was investigated by XRD and nitrogen sorption technique. The XRD patterns of S-PEp-10% and S-PEp-20% clearly exhibit (1 0 0), (1 1 0) and (2 0 0) reflection peaks, while S-PEp-30% gives one sharp (1 0 0) reflection peak (Fig. 7). TEM image of S-PEp-30% clearly shows the ordered arrangement of the mesopore throughout the sample (Fig. 8). The results of XRD and TEM suggest that the mesostructure of PEp-X% (X = 10, 20, 30) remains to be well ordered after sulfonation process.



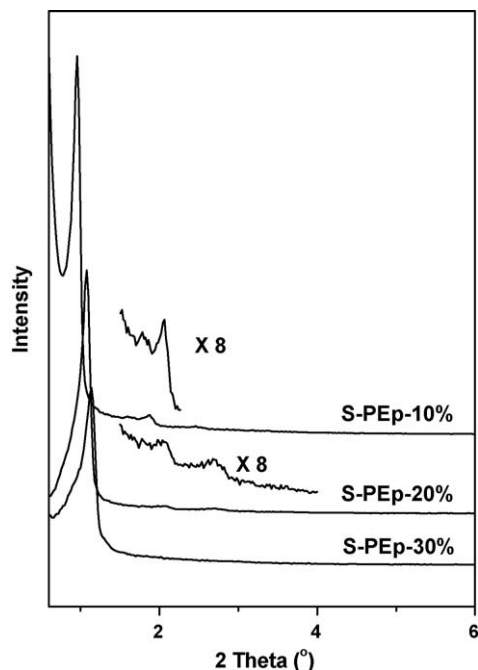


Fig. 7. XRD patterns of S-PEp-X%.

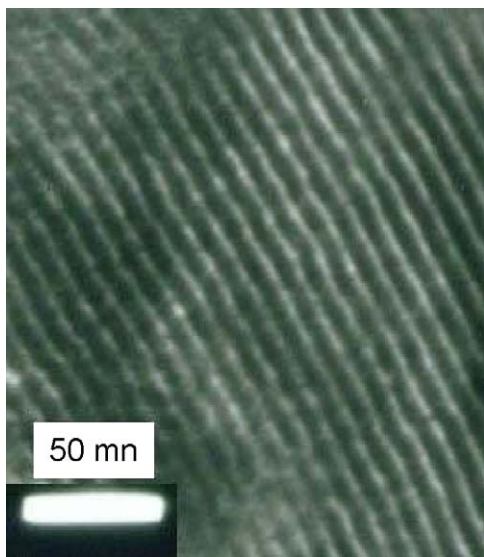


Fig. 8. TEM image of S-PEp-30%.

Nitrogen sorption isotherms of S-PEp-10%, S-PEp-20% and S-PEp-30% are of typical type IV with sharp capillary condensation step, characteristic of mesoporous materials with uniform pore size distributions (Fig. 9). This result shows that the

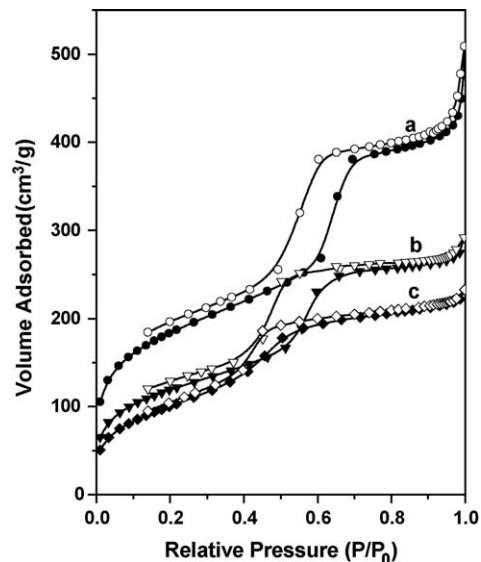
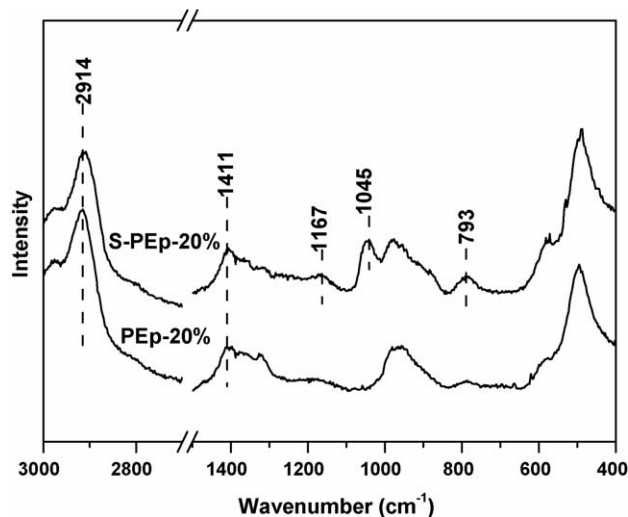
Fig. 9. N<sub>2</sub> sorption isotherms of S-PEp-X%. (a) S-PEp-10%, (b) S-PEp-20% and (c) S-PEp-30%.

Fig. 10. UV-Raman spectra of PEp-20% and S-PEp-20%.

mesostructure of the materials synthesized with  $\leq 30$  mol% of PTMS is stable enough to survive the sulfonation process. However, the decrease of BET surface area and pore diameter was observed for all PEp-X% after sulfonation (Table 1).

UV-Raman spectrum of PEp-20% displays vibrations at 2914 and 1411  $\text{cm}^{-1}$ , which could be assigned to ethane group (Fig. 10). Besides the vibrations of ethane group, new bands at 1167, 1045 and 793  $\text{cm}^{-1}$  were observed in the UV-Raman

Table 1  
Physical properties of PEp-X% and S-PEp-X%<sup>a</sup>

Sample	<i>d</i> spacing <sup>a</sup> (nm)	Surface area ( $\text{m}^2 \text{g}^{-1}$ )	Pore diameter (nm)	Pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	Wall thickness <sup>b</sup> (nm)
PEp-10%	9.20 (9.22)	752 (653)	5.56 (4.30)	0.87(0.69)	5.06 (6.35)
PEp-20%	8.34 (8.18)	686 (427)	4.91 (3.89)	0.78 (0.42)	4.72 (5.56)
PEp-30%	8.59 (7.75)	630 (371)	4.96 (3.93)	0.70 (0.34)	4.96 (5.46)

<sup>a</sup> Values in parentheses are for S-PEp-X%.

<sup>b</sup> Wall thickness =  $2d/\sqrt{3}$  pore diameter.

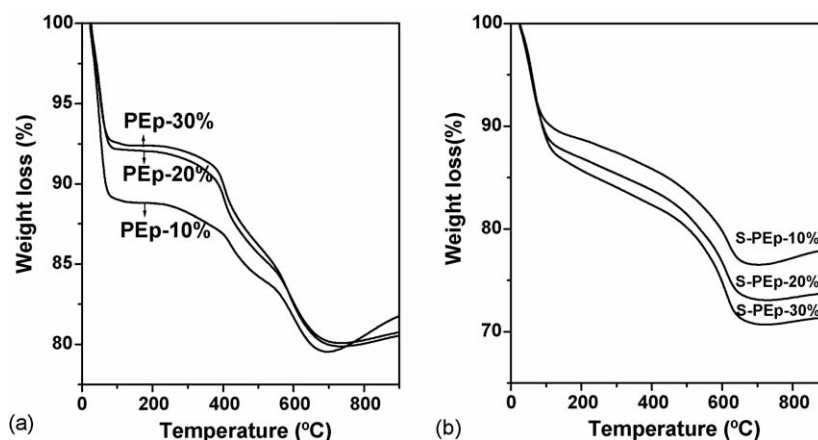


Fig. 11. Thermogravimetric analyses of (a) PEp-X% and (b) S-PEp-X%.

spectrum of S-PEp-20%. The bands at 1167 and 1045  $\text{cm}^{-1}$  can be assigned to sulfonic acid group. The band at 793  $\text{cm}^{-1}$  can be assigned to the sulfonated phenyl group. The UV-Raman results indicate the successful sulfonation of the phenyl groups in the mesoporous ethane-silicas.

Thermogravimetric analyses of PEp-X% and S-PEp-X% are carried out under nitrogen atmosphere (Fig. 11). The weight loss before 120 °C is due to the removal of the physisorbed water. For PEp-X%, this weight loss is decreased from PEp-10% to PEp-30%, indicating the enhanced surface hydrophobicity by the incorporation of phenyl group in the materials. In the range of 400–700 °C, two successive steps of weight loss were observed for PEp-X%. The decomposition of ethane group starts at 400 °C [9], while the phenyl group begin to decompose at 500 °C. The weight loss between 500 and 700 °C is increased from PEp-10% to PEp-30%, which implies that more amount of phenyl group was incorporated in the materials with the molar fraction of PTMS increasing. After sulfonation, the weight loss before 120 °C is increased from S-PEp-10% to S-PEp-30%, suggesting that the surface hydrophilicity of the materials is increased in the following order: S-PEp-10% < S-PEp-20% < S-PEp-30%. The increased surface hydrophilicity from S-PEp-10% to S-PEp-30% may be an evidence for the existence of  $-\text{SO}_3\text{H}$  group

because  $-\text{SO}_3\text{H}$  has a tendency to adsorb water through the formation of hydrogen bond. One major weight loss in the temperature range of 120–700 °C is seen. This is mainly due to the removal of chemisorbed water (120–400 °C) and decomposition of ethane, phenyl and sulfonic acid groups (400–700 °C) [9].

The results of thermogravimetric analyses show that PEp-X% and S-PEp-X% is thermally stable up to 400 °C under nitrogen atmosphere.

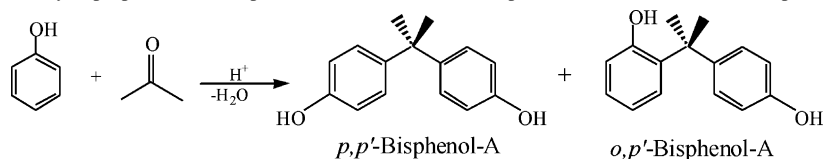
### 3.4. Catalytic properties of S-PEp-X%

#### 3.4.1. Condensation of acetone with phenol to form Bisphenol-A

Bisphenol-A is a very important raw material for the production of epoxy resins and other polymers. Industrially, ion-exchange resins such as Amberlysts are used as catalysts for this reaction [16]. However, due to their limited thermal stability, it is necessary to develop new solid acid catalysts with high catalytic activity and thermal stability. The higher thermal stability and strong acid sites of the mesoporous ethane-silicas functionalized with phenyl-sulfonic acid may be potential catalysts for this reaction. The catalytic results of these materials are listed in Table 2.

Table 2

Catalytic properties of S-PEp-X% for the condensation of phenol with acetone to form Bisphenol-A<sup>a</sup>



Catalyst	Acidic capacity ( $\text{mmol H}^+ \text{g}^{-1}$ )		Acidic capacity ( $\text{mmol H}^+ \text{m}^{-2}$ )	S content ( $\text{mmol} [\text{g SiO}_2]^{-1}$ ) <sup>b</sup>	TOF <sup>c</sup>	p,p'/o,p' (mol ratio)
	NaCl	( <i>n</i> -Bu) <sub>4</sub> NBr				
S-PE	0.10	–	–	–	–	–
S-PEp-10%	0.49	0.45	$7.5 \times 10^{-4}$	0.29	8.3	1.9
S-PEp-20%	0.69	0.60	$1.6 \times 10^{-3}$	0.58	17.4	2.0
S-PEp-30%	0.86	0.90	$2.3 \times 10^{-3}$	0.77	16.4	2.1

<sup>a</sup> Reagents and conditions: 70 mmol of phenol; 10 mmol of acetone; 70 mg of catalyst; reaction temperature, 85 °C; reaction time, 24 h.

<sup>b</sup> S content was analysed by ICP-AES.

<sup>c</sup> Mol of Bisphenol-A/mol of active site.

Table 3  
Catalytic activity of S-PEp-20% for the condensation of phenol with acetone to form Bisphenol-A at different temperature<sup>a</sup>

Reaction temperature (°C)	TOF <sup>b</sup>	p,p'/o,p' (mol ratio)
60	3.9	2.5
85	17.4	2.0
110	29.6	1.9

<sup>a</sup> Reagents and conditions: 70 mmol of phenol; 10 mmol of acetone; 70 mg of S-PEp-20%; reaction time, 24 h.

<sup>b</sup> Mol of Bisphenol-A/mol of active site.

Under identical conditions, no products were detected in the absence of catalysts. Also, no products were observed with S-PE (the acidity is 0.10 mmol H<sup>+</sup> g<sup>-1</sup>) as the catalyst, indicating that the physisorbed H<sup>+</sup> has no catalytic activity for the reaction. All S-PEp-X% exhibit catalytic activities for the condensation of phenol with acetone. The catalytic activity of S-PEp is mainly attributed to the phenyl-sulfonic acid group. The lowest catalytic activity was found on S-PEp-10%, which is due to the low concentration of active sites ( $7.5 \times 10^{-4}$  mmol H<sup>+</sup> m<sup>-2</sup>). S-PEp-30% has the highest concentration of phenyl-sulfonic acid group, however, its catalytic activity is slightly lower than that of S-PEp-20%. This may be due to the lower surface area and pore volume of S-PEp-30%. Two structural isomers p,p'-Bisphenol-A and o,p'-Bisphenol-A were formed as the only products. The ratio of p,p'-Bisphenol-A to o,p'-Bisphenol-A is about 2 for all catalysts, which is almost the same as that for para-toluene sulfonic acid.

The reaction temperature has an important effect on the catalytic activity (Table 3). With reaction temperature increasing from 60 to 110 °C, the TOF is increased from 3.9 to 29.6 with only slightly decreasing of p,p'-Bisphenol-A to o,p'-Bisphenol-A ratio.

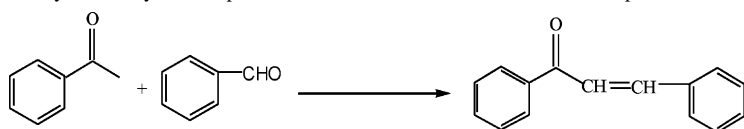
#### 3.4.2. Claisen-Schmidt condensation of acetophenone with benzaldehyde to form chalcone

Chalcones constitute important key intermediates, especially in the synthesis of naturally occurring heterocyclic compounds of the flavonoid family. The most general preparation procedure for these types of organic substrates is the Claisen-Schmidt con-

densation of aryl ketones with benzaldehyde derivatives [17]. Basic catalysts are usually employed for this reaction. However, the competitive Cannizzaro reaction of the aldehyde and other undesired side reaction might occur when base-sensitive groups are involved. Here, we tried for the first time to use the mesoporous materials containing phenyl-sulfonic acid as catalysts for this reaction.

Under the reaction conditions, the product yield of 12.9% and 12.2% was observed for the reaction performed without catalyst and with S-PE as the catalyst, respectively. This result indicates that physisorbed H<sup>+</sup> shows almost no catalytic activity, which is consistent with the results of the condensation reaction between acetone and phenol. All S-PEp-X% exhibit catalytic activities for the condensation of acetophenone with benzaldehyde in the absence of solvent (Table 4). The selectivity of chalcone is above 95% for all materials. Within 6 h, the conversion of acetophenone can reach 61.7% on S-PEp-10%. The conversion of acetophenone can reach as high as ~75% on both S-PEp-20% and S-PEp-30% with higher amount of phenyl-sulfonic acid group. Although the concentration of acid sites of S-PEp-30% is higher than that of S-PEp-20%, the S-PEp-30% does not exhibit higher catalytic activity than S-PEp-20%. The similar tendency was also observed in the condensation of acetone with phenol. The above catalytic results indicate that the catalytic activity of the mesoporous ethane-silicas functionalized with phenyl-sulfonic acid is not only determined by the amount of the active sites but also by their structural order. The stability of the catalyst during the reaction process is one of the most important factors for the practical application. Therefore, the reuse ability of the material was tested using S-PEp-20% as model catalyst. The conversion of acetophenone is decreased to 46% after the first cycle of S-PEp-20%. The second cycle of the catalyst gives the acetophenone conversion of 31%. Because the physisorbed H<sup>+</sup> has no catalytic activity, the decreasing of the catalytic activity of S-PEp-20% during the recycling process is due to the leaching of the sulfonic acid from the catalyst, which is also observed for the mesoporous materials containing phenyl-sulfonic acid group [7]. Recently, a stable and highly active hybrid mesoporous solid acid catalyst was reported [10]. The solid acid catalyst was synthesized by Diels-Alder reac-

Table 4  
Catalytic activity of S-PEp-X% for condensation reaction between acetophenone with benzaldehyde<sup>a</sup>



Sample	Conversion <sup>b</sup> (%)	Yield (%)	Selectivity (%)
Blank	13.1	12.9	98.5
S-PE	12.4	12.2	98.4
S-PEp-10%	61.7	59.1	95.8
S-PEp-20%	74.7	71.8	96.1
S-PEp-20% (run 1)	46.4	45.8	98.7
S-PEp-20% (run 2)	32.3	31.2	96.6
S-PEp-30%	75.8	72.0	95.0

<sup>a</sup> Reagents and conditions: 50 mg of catalyst; 20 mmol of acetophenone; 20 mmol benzaldehyde; reaction temperature, 150 °C; reaction time, 6 h.

<sup>b</sup> Conversion is based on the acetophenone.

tion of –CH=CH– bridging in the framework of mesoporous organosilica with benzocyclobutene, followed by the sulfonation of the phenylene group. The resultant materials can be recycled in the esterification of ethanol with acetic acid for at least four times without obvious loss of catalytic activity (the reaction was performed at 70 °C). The loss of the sulfonic acid sites in our case may be due to the high reaction temperature used for the catalysis (150 °C).

#### 4. Conclusion

Mesoporous ethane-silicas functionalized with phenyl-sulfonic acid were synthesized by sulfonation of the mesoporous ethane-silicas functionalized with phenyl group. The decreasing of structural order was observed for materials with higher amounts of phenyl group incorporated. The highest acid exchange capacity of the material is 0.86 mmol H<sup>+</sup> g<sup>-1</sup>. The mesoporous ethane-silicas functionalized with phenyl-sulfonic acid are efficient solid acid catalysts for the production of Bisphenol-A and chalcone. The catalytic activity of the mesoporous ethane-silicas functionalized with phenyl-sulfonic acid is not only affected by the amount of the phenyl-sulfonic acid group, but also by the structural order of the mesoporous materials.

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