

Short communication

## Sulfonic acid catalyst based on silica foam supported copolymer for hydrolysis of cellulose

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## ABSTRACT

Mesocellular silicon foam supported poly(chloromethylstyrene-co-divinylbenzene) (MCF-copolymer) was synthesized. It has a pore size of 24.2 nm. The pore volume and the surface area were 0.84 cm<sup>3</sup>/g and 246.9 m<sup>2</sup>/g, respectively. MCF-copolymer supported sulfonic acid was accomplished via sulfonation with concentrated sulfuric acid. The acid amount on the MCF-copolymer was 2.03 mmol/g. Hydrolysis of banana pseudo-stem fibers and microcrystalline cellulose was carried out over the catalyst. The large pore size favors the diffusion of molecules in catalyzing bulky molecules. The corresponding catalytic turnover frequencies (TOF) were 5.57 h<sup>-1</sup> and 8.066 h<sup>-1</sup>.

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## 1. Introduction

Solid acids have emerged as green substitutes for traditional liquid acids because of their easy recovery, lower pollution and lack of corrosiveness [1,2]. Among them, zeolites have attracted a lot of attention, but the narrow pore size has been considered as an important drawback [3,4]. To host bulky molecules, great efforts have been made to design large pore sizes aiming to expand the applications. The most investigated and effective route for this purpose is the micelle templated synthesis of ordered mesoporous materials, such as MCM-41 or SBA-15 [5,6]. In the past years, some strategies have also been developed to synthesize organic-inorganic hybrid mesoporous materials. For example, the silica surface was post-grafted with organosilanes [7–9]. Tetraalkoxysilanes ((RO)<sub>4</sub>Si) and trialkoxyorganosilanes ((RO)<sub>3</sub>SiR) were co-condensed to prepare periodic mesoporous organosilicas (PMOs) with bridging organic groups in the framework [10,11]. In both cases, the organic groups were further functionalized with sulfonic acid. However, an important limitation is the saturation of the mesoporous structure by the organic species [3].

Surface initiated atom transfer radical polymerization (ATRP) is one of the most powerful and commonly used techniques to introduce uniform polymer layers on solid surfaces [3,12–15]. A poly(vinylsulfonic acid)-grafted poly(styrene) resin has also been investigated via surface initiated radical polymerization of vinylsulfonic acid and used for catalytic esterification reactions [16]. In the recent literatures [3,17],

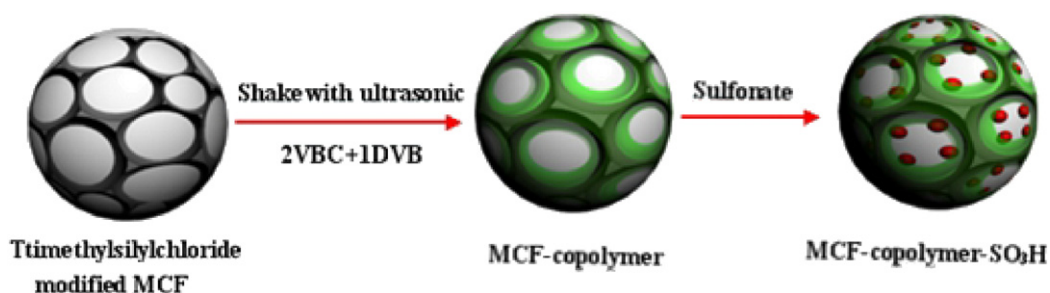
poly(sodium styrene sulfonate) has been grafted onto SBA-15 via ATRP of sodium styrene sulfonate. However, low organic loadings and acidities were achieved. To achieve a high content of organic groups on the surface, Jones et al. reported a polymer brush supported sulfonic acid via surface initiated ATRP of styrene followed by sulfonation of the polymer brush [12]. In this case, Cab-O-Sil M5, a nonporous silica, is used as the support to avoid potential pore clogging issues associated with polymerization with porous materials as the supports [18,19].

In terms of the traditional mesoporous supports, such as MCM-41 or SBA-15, the relatively small pore size (~6 nm) of the resulting hybrid materials could hinder the diffusion of reactants and products when used to treat bulky molecules. For example, production of biodiesel typically involves transesterification of triglycerides with short chain alcohols and esterification of free fatty acids from feedstocks. Comparatively, silica foam has a pore size range of 20–50 nm, which would alleviate pore clogging issues. Herein, lab-prepared silica foam was used to support polymer layer via surface initiated polymerization.

In this work, mesocellular silica foam (MCF) was first grafted with chlorotrimethylsilane to enhance hydrophobicity of the surface, then loaded with chloromethylstyrene and divinylbenzene under ultrasonic shake followed by radical polymerization as illustrated in Scheme 1. The thickness of the grafted film can be controlled to 2 nm. Sulfonic acid-grafted silica foam was obtained via sulfonation with concentrated sulfuric acid. Because the bulky molecular chains make the transport of substrates to the catalytic sites a highly demanding process, hydrolysis of banana pseudo-stem fibers or microcrystalline cellulose is used to evaluate performance of the supported sulfonic acid catalyst. Besides, cellulose dissolved in ionic liquids is very viscous, which makes the transport of cellulose chains to the catalytic sites more difficult.

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**Scheme 1.** Preparation of silica foam supported sulfonated copolymer.

## 2. Experimental

### 2.1. Materials

3,5-Dinitrosalicylic acid (DNS) and 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl], >98%) were obtained from TCI (Shanghai); 1,3,5-trimethylbenzene (TMB), Pluronic P123 (PEO<sub>20</sub>PPO<sub>70</sub>PEO<sub>20</sub>), tetraethoxysilane (TEOS), chlorotrimethylsilane (TMCS) and microcrystalline cellulose (20 μm) were purchased from Sigma-Aldrich; chloromethylstyrene, divinylbenzene, dichloromethane, azobisisobutyronitrile, toluene and ethanol were supplied by Guangzhou Chemical Reagent Co.

### 2.2. Preparation of MCF

In a typical preparation, 3.2 g of P123 was dissolved in 66 mL of 1.5 M HCl aqueous solution. Next, 4.6 mL of TMB was slowly added to the flask. The mixture was stirred at 40 °C for 2 h, then 7.4 g of TEOS was added dropwise to the mixture with vigorous stirring for 5 min. The resulting mixture was transferred into an autoclave and aged at 40 °C for 20 h. Afterwards, 1 mL of 1 M NH<sub>4</sub>F was added, and the autoclave was heated to 140 °C for one day. The precipitate was separated by suction filtration and washed with water and ethanol, and dried at 80 °C. The white powder was then calcined in air at 550 °C for 5 h.

### 2.3. Preparation of trimethylsilane functionalized MCF

1 g of MCF was degassed at 100 °C overnight, and mixed with 50 mL of toluene with stirring for 15 min. 0.5 g of TMCS was then added dropwise and refluxed at 110 °C for 24 h under nitrogen atmosphere. The mixture was filtered and washed with toluene and ethanol. The physically adsorbed TMCS on the MCF was extracted with ethanol in a Soxhlet extractor for 24 h, then vacuum filtrated and dried at 70 °C for 7 h.

### 2.4. Fabrication of MCF loaded poly(chloromethylstyrene-co-divinylbenzene) (MCF-copolymer)

1.5 mL of mixture comprised of chloromethylstyrene and divinylbenzene with a molar ratio of 2:1 was dissolved in 4 mL of dichloromethane, and then 0.02 g of azobisisobutyronitrile was added, and then followed by adding 1 g of trimethylsilane functionalized MCF which was degassed at 100 °C. The resulting mixture was shaken with ultrasonic for 10 min. Dichloromethane was removed by vacuum evaporation at room temperature for 4 h. Then the powder was heated in an oven at 65 °C for 20 h, and 100 °C for 1 h, followed by 150 °C for another 1 h.

### 2.5. Sulfonation of MCF-copolymer

0.1 g of MCF-copolymer was suspended in 3 mL of dichloromethane. The slurry was then added into 10 mL of concentrated sulfuric acid. The mixture was stirred under N<sub>2</sub> atmosphere at 100 °C for 5 h. After cooling

down, the mixture was slowly added into excess deionized (DI) water. The solid was recovered by filtration, and was washed repeatedly with boiling DI water until the pH of the filtrate was above 6. The catalyst was dried under vacuum at 100 °C overnight.

### 2.6. Characterization

FT-IR spectra were obtained on a Bruker Tensor 27 spectrometer using KBr Pellets. Surface areas and pore sizes of the samples were assessed via nitrogen physisorption analysis using a Micromeritics ASAP 2400. Before measurement, the samples were degassed overnight under vacuum around 110 °C. The microstructures were observed by transmission electron microscopy (TEM) performed on JEOL JEM-2010. The morphologies were evaluated by scanning electron microscopy (SEM) on Hitachi S-4800 from Au coated samples. Thermogravimetry analysis (TGA) was performed on TA Q600 at a heating rate of 10 °C/min under N<sub>2</sub> atmosphere. The Brønsted acid amounts of the catalysts were determined by chemical titration. Typically, 0.02 g of catalyst was added into 20 mL of 0.01 M NaOH aqueous solution, stirred at room temperature for 2 h, then titrated with 0.01 M HCl aqueous solution with phenolphthalein as indicator.

### 2.7. Hydrolysis of cellulose

Cellulose hydrolysis was carried out in a Teflon-lined autoclave under self-generated pressure. Typically, 50 mg of banana pseudo-stem fibers or microcrystalline cellulose, 1.5 mg of H<sub>2</sub>O and 1 g of [BMIM][Cl] were stirred at 100 °C for 1 h, then 15 mg of the catalyst was added. The catalytic hydrolysis of cellulose proceeded at 110 °C for 1 h. At the end of reaction, 10 mL of deionized water was used to dilute the reaction liquid and stirred for 20 min at room temperature. The filtrate was recovered by centrifugation. Reducing sugar equivalents were estimated based on the reduction of 3,5-dinitrosalicylic acid (DNS) to 3-amino-5-nitro-salicylic acid (ANS) [20]. 0.25 mL of supernatant filtrate, 1.5 mL of DNS reagent and 1.75 mL of water were heated in water bath at 100 °C for 5 min, then cooled down and diluted by 6.5 mL of water. The concentrations of total reducing sugar (TRS) were measured at 540 nm using a StellarNet Inc EPP2000 UV-vis spectrometer. All reactions were repeated twice and each sample was measured three times to achieve an average value.

## 3. Results and discussion

A SEM image of the as-synthesized silica MCF is shown in Fig. 1a. The particles have a spherical morphology. The particle size varies in range from 2 to 5 μm. Dense and opening pores might be observed on the surface from the high magnification SEM as shown in Fig. 1b. The TEM image in Fig. 2a clearly shows a mesocellular structure. After polymerization of chloromethylstyrene and divinylbenzene inside the MCF, the spherical morphology was still kept for MCF-copolymer as shown in Fig. 2c. Meanwhile, an opening mesoporous structure was demonstrated as shown in the SEM image in Fig. 1d, indicating that chloromethylstyrene and divinylbenzene penetrate inside the pores of

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