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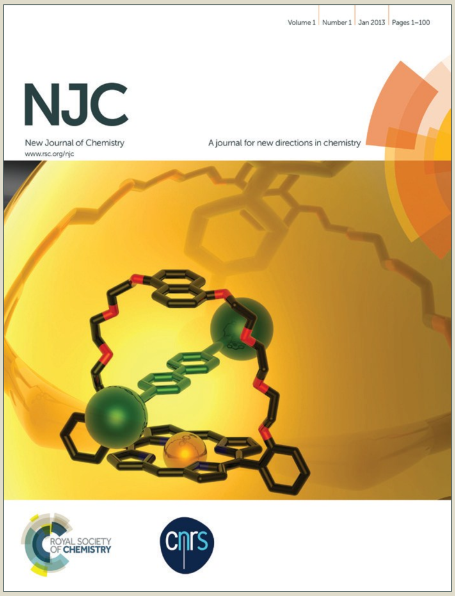

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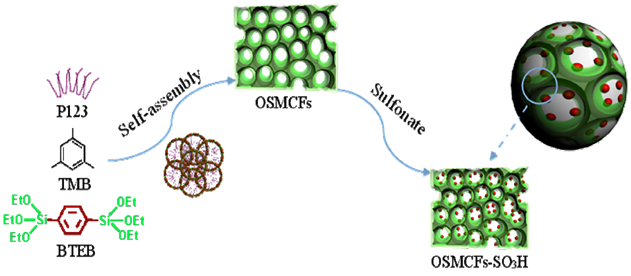
Sulfonated Organosilica Mesocellular Foam for Catalyzing Bulky Molecules

Sihan Chu, Guorui Cai, Ziting Tan , Daoping Xiang, Chunrong Xiong *

Organosilica mesocellular foam (OSMCF), a large-pore material, was successfully fabricated with 1,4-bis(triethoxysilyl)-benzene (BTEB) as a precursor, Pluronic P123 as a template, and 1,3,5-trimethylbenzene (TMB) as a swelling agent. The cell size is tailorable by changing the weight ratio of TMB to P123. Thermogravimetry (TG) analysis revealed that the material had a high thermal stability. FT-IR spectra and chemical titration suggested that sulfonic acid might be grafted onto the OSMCF by treating with sulfuric acid (98 wt%) and potassium disulfate. After sulfonation, the large-pore acidic catalysts exhibited very high catalysis activities for bulky reactants. The catalysts were evaluated in hydrolysis of lab-extracted natural fibers or commercial microcrystalline cellulose, and esterification of oleic acid (OA).

The advantages of solid acids over liquid acids include easy separation of the catalyst, reductive corrosion, recyclability, simple handling requirements, and environmentally friendly nature.[1–5] They have been widely applied in acid-catalyzed reactions such as esterification, isomerization, alkylation and Friedel−Crafts reactions.[6-10] Recently, sulfonation of various polymer materials have attracted a lot of attentions. For examples, Wu et al[11] sulfated FDU-type mesoporous phenol–formaldehyde resins with a pore size of ~ 3 nm and a surface area of ~ 540 m^2/g, but the acidic concentration was still blocked by the limitation to sulfonation of the phenolic rings due to the strong steric hindrance. Xiao et al[12] prepared mesoporous polydivinylbenzene (PDVB) solid acid with a BET surface area of 376 m^2/g and a pore size of ~ 20 nm. In addition, polymeric organic species have been introduced into mesoporous silicas by surface initiated atom transfer radical polymerization (ATRP) techniques.[13-16] However, it is difficult to avoid potential pore clogging associated with polymerization using porous materials as the supports,[16] or the pore sizes would be reduced to some extent. Moreover, these polymer-based solid acids might be softened and deformed in some solvent or upon stringent heating. Comparatively, mesoporous organic-inorganic hybrid materials have higher thermal and solvent stabilities. Rhijn et al[17] firstly prepared mesoporous sulfonic acid-containing hybrid solids by both grafting and co-condensation methods. However, it is difficult to obtain a large amount of sulfonic groups on the surface of silicas, because the increase of mercapto groups in the synthesis will significantly reduce the crosslinking degree of silica in the mesoporous walls.

Generally speaking, the most reported mesoporous molecular sieves have a pore size less than 8 nm. Grafting of -SO$_3$H or other groups would further lower the mesoporosity.[14-16] The resulting materials could hinder the diffusion of reactants and products when used to treat bulky reactants. Some bulky molecules, such as cellulose or fatty acids, could not get access to the inside active sites through the relatively small pores. Mesostructured cellular foam (MCF) represents a new class of aerogel-like and ultralarge-pore materials. In previous publications, silica foams were synthesized by changing the hydrophobic volumes of the templates,[18-19] and the pore sizes range from 20 to 50 nm. Herein, the strategy was extented to prepare a benzene containing hybrid organosilica foam, in which benzene rings were further sulfated to obtain soild acid as presented in Scheme 1. The obtained catalyst could exhibit higher thermal and solvent stabilities as compared to the polymer-based solid acids. Moreover, it possesses a larger pore size and a higher pore volume with respect to the conventional mesoporous molecular sieves. Since the bulky reactants make the transport to the catalytic sites a highly demanding process, the organosilica foam practically fulfill the requirements. Hydrolysis of cellulose and esterification of long chain carboxylic acids were used to evaluate the catalytic performance of the sulfonated organosilica MCF.



Scheme 1 Preparation of sulfonated organosilica mesocellular foam

In Scheme 1, 1,4-bis(triethoxysilyl)-benzene (BTEB) was used as a precursor to prepare organosilica mesocellular foam (OSMCF) with Pluronic P123 as a template, and 1,3,5-trimethylbenzene (TMB) as a swelling agent for expansion of the pore size. The as-prepared OSMCF powder was refluxed in a solution composed of HCl and ethanol to remove the P123 and TMB. The OSMCF was then treated with sulfuric acid (98 wt%) and potassium disulfate to graft sulfonate groups.

Two kinds of OSMCFs were prepared with a different weight ratio of TMB to P123. OSMCF-0.75 means that the ratio was 0.75 in the preparation, and OSMCF-1.00 was for a ratio of 1.00. The SEM images are shown in Fig. 1. They have an approximately spheric shape. The diameter of the spheres was not uniform as seen in Fig. 1a and 1c. The OSMCF-0.75 has a biggest diameter of ~ 3 µm, and it was ~ 4 µm for the OSMCF-1.00. The high magnificant SEM images of the spheres show a porous structure for both samples as seen in Fig. 1b and 1d. The TEM images in Fig. 1e and 1f also demonstrated that mesocellular organosilica foam were successfully prepared. The OSMCF-0.75 has a cell diameter of ~ 30 nm, and the OSMCF-1.00 was ~ 50 nm. The sizes were further verified by nitrogen physisorption analysis. The BET surface area of the OSMCF-0.75 was 582 m^2/g, and its pore volume was 0.46 cm^3/g.

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For the OSMCF-1.00, the BET surface area and the pore volume were enhanced to 597 m^2/g and 0.55 cm^3/g, respectively. These indicated that the cell size and the BET surface area of the OSMCF might be also tailorable by changing the weight ratio of TMB to P123.

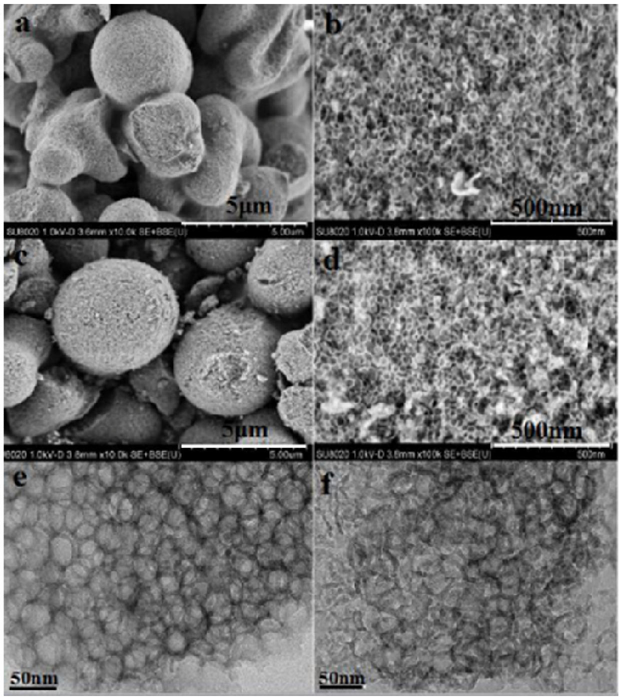

Fig. 1 SEM images of (a, b) OSMCF-0.75, (c, d) OSMCF-1.00; TEM images of (e) OSMCF-0.75, (f) OSMCF-1.00.

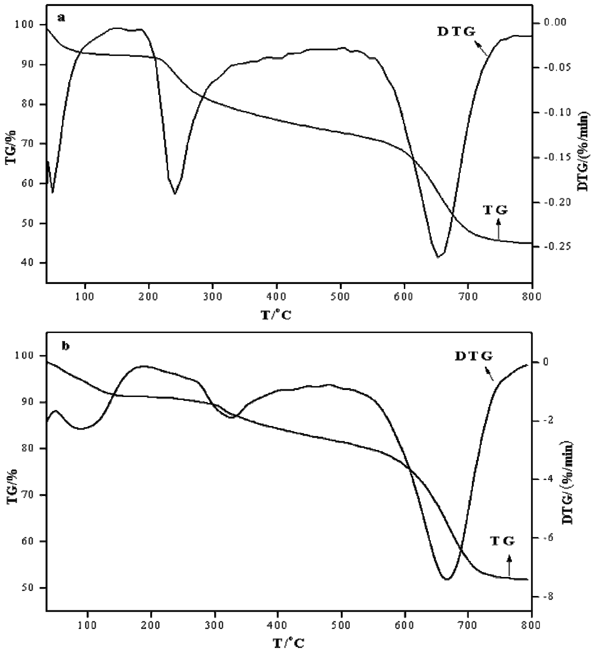

Fig. 2 Thermal stability analysis of (a) OSMCF-0.75; (b) OSMCF-1.00

Thermogravimetry (TG) analysis in Fig. 2 were performed to evaluate the thermal stability of the OSMCFs. Three weight loss peaks were observed for both the OSMCF-0.75 and the OSMCF-1.00. The one at ~ 100 °C was attributed to physisorbed water. The second occurred between 250 and 350 °C corresponded to the loss of residual surfactant molecules. Whereas the most obvious weight lost between 600 and 700 °C could be assigned to the decomposition of benzene bridges in OSMCFs. Comparatively, some polymer based porous materials would decompose at around 300 °C. Therefore, the OSMCFs are very thermostable. The amounts of sulfonic acid grafted onto the organosilica foams were determined by chemical titration. It was 0.778 mmol/g for the OSMCF-0.75, and 0.952 mmol/g for the OSMCF-1.00 due to the relatively higher BET surface area.

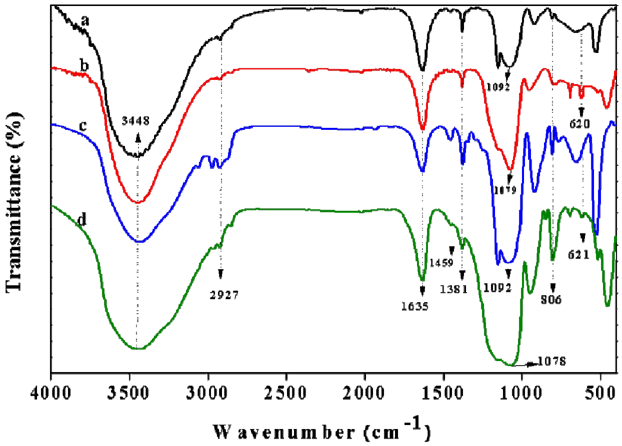

Fig. 3 FT-IR spectra of (a) OSMCF-0.75, (b) SMCF-0.75-SO$_3$H, (c) OSMCF-1.00, (d) OSMCF-1.00-SO$_3$H.

Fig. 3 displays FT-IR spectra of the samples. The broad band at 3448 cm^{-1} is assigned to the stretching vibration of the silanol groups.[20] Hydrolysis of BTEB generated six silanol groups, some of them did not completely condensed as the silane was connected at the surface of the OSMCF. The weak band at 2927 cm^{-1} were assigned to the stretching vibrations of C-H in -CH$_2$CH$_2$-,[20] indicating that trace amounts of P123 present in OSMCF. The stretching vibration of C=C in benzene ring was found at 1635 cm^{-1}, and the band at 1381 cm^{-1} was due to the in-plane C-H bending vibration.[21] The bands at 1155 and 1092 cm^{-1} corresponded to asymmetric and symmetric stretching vibrations of the Si-O–Si,[22] respectively. In addition, the Si-O stretching modes were observed at 809 cm^{-1}.[23] Compared to the OSMCFs, the OSMCF-SO$_3$H samples displayed characteristic vibrations of sulfonic acid groups as shown in Fig. 3b and 3d. The band around 620 cm^{-1} was ascribed to the stretching vibration of the S-O in sulfonate groups.[24] Since the symmetric vibration of O=S=O at 1078 cm^{-1} was overlapped with that at 1092 cm^{-1} for the Si-O–Si, the band was widened and shifted to low wavenumber.

Firstly, the catalytic hydrolysis of lab-extracted natural fibers was carried out over the OSMCF-SO$_3$H. The natural fibers were chemically extracted from dried banana pseudo-stem as described in the supporting information. The fibers has a cellulose content ~ 81 %, and other major components were ligin and hemicelluloses. The catalytic hydrolysis of the fibers proceeded at 110 °C. The plot of TRS yield vs time was seen in Fig. 4. The total reducing sugars (TRS) yield reached 62.1 % for the OSMCF-1.00-SO_3H with a reaction time of 1.5 h. The corresponding catalytic turnover frequency (TOF) was 14.78 h^{-1}. The catalytic reaction was not optimized but already showed an interesting activity for hydrolysis of natural fibers. However, the TRS yield has only a slight increase after 1 h, probably because the residual cellulose was protected by the ligin in fibers. Meanwhile, hydrolysis of the fibers was also tested over the OSMCF-0.75-SO_3H with a same amount of acid. Despite the OSMCF-0.75-SO_3H has a big pore size of ~30 nm, the effect of pore size on the catalytic reaction of bulky molecule can still be observed. The obtained TRS yields were slightly lower than those observed over the OSMCF-1.00-SO_3H at the same time intervals. When the reaction duration was 1.5 h, the TRS yield was 58.9 % with a TOF value of 11.46 h^{-1} for the OSMCF-0.75-SO_3H. Cai et al.[25] investigated the effect of pore size on hydrolysis of microcrystalline cellulose over four kinds of zeolites. The results revealed that HY, HBeta, HZSM-5 and SAPO-34 had a TRS yield of 50 %, 33.3 %, 18.1 % and 2.9 %, respectively. The TRS yield decreased with the reduction of the pore size under the same reaction conditions.

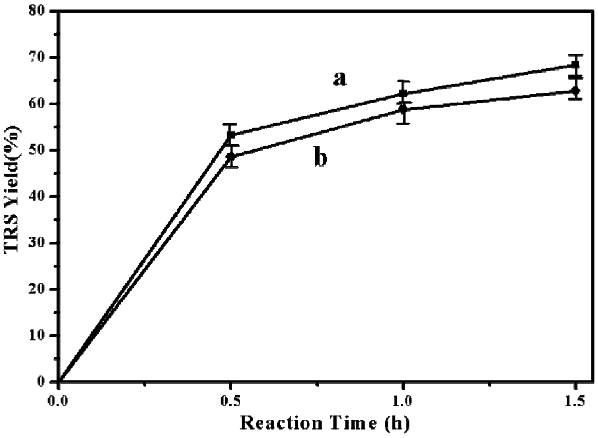

Fig. 4 Plot of TRS yield vs time for hydrolysis of the banana pseudo-stem fibers catalyzed over (a) OSMCF-1.00-SO_3H, (b) OSMCF-0.75-SO_3H.

For comparison, depolymerization of microcrystalline cellulose were run over the OSMCF-SO_3H under the same reaction conditions. The results showed that the microcrystalline cellulose might produce more TRS over both catalysts. They are 75.6 % and 66.4 % for the OSMCF-1.00-SO_3H and the OSMCF-0.75-SO_3H, respectively.

In addition, the esterification of oleic acid (OA) with methanol was further evaluated over the OSMCF-SO_3H. OA presents in major oil crops such as soybean, jatropha curcas, sunflower, rapeseed, pongamia, palm and sea mango. Biodiesel, an alternative diesel fuel derived from vegetable oils or animal fats by esterification, has been paid great attentions. Within 6 hours of reaction duration at 100 °C, Amaximum yields of methyloleate reached 89.7 % and 93.3 % for the OSMCF-0.75-SO_3H and OSMCF-1.00-SO_3H, respectively. Comparatively, a commercial ZSM-5 with a silica-alumina ratio of 40 exihited a methyloleate yield of only 28%. It further suggested that pore size of solid acid catalysts significantly affect the catalytic conversion of bulky molecules. Therefore, the sulfonated organosilica mesocellular foams should be a suitable and practical soild acid catalyst for many bulky reactants.

Sulfonated organosilica mesocellular foams were successfully fabricated. The pore sizes were over 30 nm. Compared to the strategy that introduce polymeric organic species into mesoporous molecular sieves by ATRP technique, OSMCF may avoid potential pore clogging associated with polymerization in the pores. Moreover, OSMCF would be less vulnerable under the thermal and organic solvent conditions. The sulfonated OSMCF, a large-pore acidic material, exhibited a relatively high catalysis activity in catalyzing bulky molecules. Therefore, for some reactions with a difficulty of diffusion, the sulfonated OSMCF would be a very practical and efficient solid acidic catalyst.

Experimental section

Materials

3,5-Dinitrosalicylic acid (DNS) and 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl], > 98 %) were purchased from TCI (Shanghai); 1,3,5-trimethylbenzene (TMB), Pluronic P123 (Mn=5800), 1,4-bis(triethoxysilyl)-benzene (BTEB) and microcrystalline cellulose (20 μm) were purchased from Sigma-Aldrich; Hydrogen chroride (37 %), oleic acid (OA), concentrated sulfuric acid, potassium disulfate, sodium hydroxide, ammonium floride and ethanol were supplied by Guangzhou chemical reagent Co.

Preparation of organosilica mesocellular foam (OSMCF)

0.25 g of P123 were dissolved in 9 mL of 0.07 M HCl aqueous solution with vigorous stirring, followed by adding dropwise some weights of TMB. The mixture was stirred at 40 °C for 2 h, then 0.25 g of BTEB was added slowly within 5 min and kept stirring for another 5 min. The resulting mixture was transferred to a Teflon-lined autoclave and aged at 40 °C for 20 h without stirring. After that, 1 mL of 0.05 M NH_4F was added, and the mixture was aged at 100 °C for 24 h. The final product was isolated by suction filtration, washed with deionized water and dried at 90 °C. Template was removed by refluxing the obtained powder in a solution with 2.5 mL HCl (37 %) in 62.5 mL of ethanol at 70 °C for 8 h.

Sulfonation of OSMCF

0.1 g of OSMCF upon drying at 100 °C overnight, 10 mL of sulfuric acid (98 wt%) and 5 g potassium disulfate were mixed and refluxed at 105 °C for 14 h under nitrogen atmosphere. The resulting solid (OSMCF-SO_3H) was recovered by suction filtration, washed with boiling water until the filtrate became neutral, dried at 80 °C overnight.

Characterization

FT-IR spectra were obtained on 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. Transmission electron microscopy (TEM) measurements were performed on JEOL JEM-2010. The morphologies were evaluated by scanning electron microscopy (SEM) on Hitachi S-4800 from Au coated samples. TA Q600 was used for thermogravimetry analysis (TGA) under nitrogen atmosphere with a heating rate of 10 °C/ min. The acid loading on 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 0.01M HCl aqueous solution with phenolphthalein as indicator.

Hydrolysis of cellulose

Cellulose hydrolysis was carried out in a Teflon-lined autoclave. Typically, 50 mg of lab-extracted natural fibers from banana pseudo-stem or commercial microcrystalline cellulose, 2.0 mg of H_2O and 1 g of [BMIM][Cl] were stirred at 100 °C for 1 h, then 15.0 mg of OSMCF-1.00-SO_3H or 18.3 mg of OSMCF-0.75-SO_3H was added. The catalytic hydrolysis of cellulose proceeded at 100 °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).[26] 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 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.

Esterification of oleic acid (OA)

0.10 g of OSMCF-1.00-SO_3H or 0.12 g of OSMCF-0.75-SO_3H, 0.2 g of OA and 0.7 g methanol were mixed in a 25 mL round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The mixture was stirred at 100 ° C until the reaction was completed. The solid catalyst was separated by centrifugation at 2000 rpm for 20min. The liquid phase was diluted with 20 mL of ethanol. The unreacted OA was titrated by 0.153 M KOH aqueous solution at 70 ° C with phenolphthalein as an indicator.

Chemical extraction of banana pseudo-stem fibers was detailed in the Supporting information

Acknowledgements

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Graphic abstract

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