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Solvent-free, one-step to the synthesis of sulfonic group functionalized mesoporous organosilica with ultra-high acid concentrations and excellent catalytic activities

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Abstract

We demonstrate here a novel solvent-free technique to the synthesis of sulfonic group functionalized mesoporous organosilica, which was achieved from self-assembly of block copolymer template with mercaptopropyltrimethoxysilane

Green Chemistry

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(MPTS) and tetramethoxysilane (TMOS) under melting condition without using additional solvents, and further condensation at high temperature (up to 140 °C). The resultant samples were designated as SMS-xs, where x stands for molar ratio of MPTS/(MPTS+TMOS). SMS-xs have relatively large BET surface areas, highly cross-linked framework, abundant and uniform mesopores with wormhole-like characteristics. Interestingly, MPTS could be used as the solo precursor to prepare mesoporous organosilica of SMS-1.0, which has controllable acidity and ultra-high concentration of sulfur (5.51 mmol g⁻¹, the highest acid densities to data), even higher than those of commercial Amberlyst 15 (4.7 mmol g⁻¹), HS-JLU-20-0.8 (4.61 mmol g⁻¹) and sulfonated carbon (CH_{0.30}O_{0.33}S_{0.16}, 4.90 mmol g⁻¹). The above structural characteristics make SMS-xs show excellent activities and good reusability in biomass conversions and fine chemicals synthesis, much better than various solid acids such as Amberlyst 15, H-form USY zeolite, sulfonic group functionalized ordered mesoporous silica.

Keywords: Solvent-free synthesis; Self-assembly; Solid acids; Biomass conversions; Mesoporous organosilica.

Introduction

Acid catalysis acts as one of the most important reaction has received extensive research interest in these years, which been widely used in the areas of oil refining, organic synthesis, biomass conversion and fine chemicals synthesis ¹⁻¹⁰. Within this regard, traditional acids such as sulfuric acid, hydrochloric acid, AlCl₃, and

HSO₃CF₃have been widely used in industry due to their advantages of low cost and excellent catalytic activities ^{4, 11-14}. However, the drawbacks such as volatile property, high toxicity, strong corrosion, intensive energy consumption for regeneration strongly constrain their widely industrial applications ⁵⁻¹⁴. Therefore, the exploring of suitable alternatives to liquid acids as the catalysts in various acid-catalyzed reactions is highly desired in these years.

For this purpose, extensive research works have been paid on the development of solid acids, and use them in a variety of acid-catalyzed reactions. The solid acids show the advantages including negligible volatility, environmentally friendliness, reduced corrosion, good activities and easy regeneration ⁵⁻¹⁶. From the point of view of supports, the solid acids could be divided into inorganic and organic frameworks⁴, ^{13, 14, 17-20}. Compared with inorganic solid acids, organic solid acids such as sulfonated porous organic polymers (POPs), metal organic frameworks (MOFs) based solid acids, acidic resins and sulfonated carbons exhibit unique characteristics of easy functionality, good chemical stability, diverse in building blocks, which show high concentrations of acid sites, further resulting in their enhanced catalytic activities ¹⁷, ²¹⁻²⁵. For instance, Bhaumik and coworkers successfully synthesized polymeric solid acids with enhanced acidity up to 4.4 mmol g⁻¹, which have been used in Hantzsch condensation and C-H activation ^{26, 27}. However, the low thermal stabilities of polymeric network strongly constrain them used as long-lived catalysts in various reactions. The solid acids with inorganic frameworks such as silica, zeolites, sulfonated metal oxides show much enhanced thermal stability in comparison with

Green Chemistry

organic solid acids ^{13, 28-31}, and the most reported inorganic solid acids are mesoporous organosilica such as sulfonic group functionalized mesoporous silica, which exhibit homogeneous dispersion and strong acid sites, large BET surface areas, abundant and controllable mesopores ^{20, 30-32}. The mentioned structural properties strongly enhance the accessibility of active site, and thus provide enhanced pathways for the fast diffusion of reactants and products in variously acid-catalyzed reactions.

Notably, the acid concentrations and accessibility of acid sites play key factors for their catalytic performances ^{21, 22, 33}. Therefore, the development of mesoporous organosilica with very high acid concentrations, abundant and controllable mesopores are highly desirable, which will largely enhance their catalytic performances. However, the reported mesoporous silica usually show limited concentrations of sulfonic group because of the large collapse of mesopores after introducing high contents of sulfonic groups ^{20, 30-32}. Xiao and coworkers successfully synthesized highly sulfonic group functionalized mesoporous silica by employing fluorocarbon-hydrocarbon surfactants as mixed templates at high temperature ³². However, inorganic silica precursor (TEOS) still needs to be introduced to prevent the collapse of mesopores. Moreover, nearly all of mesoporous organosilicas were synthesized in presence of abundant solvents such as water and alcohol, which generates large amount of wastes, results in complicated synthetic processes and high synthetic cost ^{34, 35}. The above disadvantages strongly constrain the wide applications of mesoporous silica based solid acids in industry ³⁶⁻⁴⁰.

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Recently, solvent free technique has been successfully realized for preparation of

4

Green Chemistry

zeolites and porous organic polymers, which strongly promotes their widely

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industrial applications ³⁷⁻⁴¹. However, there were still few reports on preparation of mesoporous silica especially for mesoporous organosilica based solid acids by using this state-of-the-art technique. In addition, it remains a great challenge to synthesize porous inorganic solid acids with ultra-high acid concentrations, which will largely improve their activities in various acid-catalyzed reactions. In this work, we innovatively expanded the solvent-free technique for preparation of sulfonic group functionalized mesoporous silica, where MPTS could be used as solo precursor. It is noteworthy that SMS-xs synthesized in this work show the highest acid density to data (See Table S1), controllable and strong acidity. Interestingly, SMS-xs show of acid-catalyzed reactions excellent activities in a variety including transesterification, esterification, and depolymerization of crystalline cellulose, higher than various solid acids including HS-JLU-20-0.8, H₃PW₁₂O₄₀, SBA-15-SO₃H-0.2, Amberlyst 15, carbonaceous solid acids of CH_{0.30}O_{0.33}S_{0.16} and H-USY. The preparation of SMS-xs open a cost-effective and sustainable approach for preparation of mesoporous organosilica based solid acids, which offers great opportunity for their wide applications in the industry.

Experimental section

Chemicals and reagents

All reagents were of analytical grade and used as purchased without further purification. Amberlyst 15, 5-hydroxymethylfurfural (HMF)

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1-*n*-butyl-3-methylimidazolium ([C₄mim]Cl), 3-mercaptopropyltrimethoxysilane (MPTS), tetramethoxysilane (TMOS), crystalline cellulose of Avicel, tripalmitin, nonionic block copolymer surfactant (Pluronic F127, M_w =12600) were purchased from Sigma-Aldrich Company, Ltd. (USA). Ethanol, methanol, *n*-dodecane, palmitic acid, HCl, H₂SO₄, sunflower oil were purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. H-form of Beta zeolite and ultra-stable Y zeolite (USY) were supplied by Sinopec Catalyst Co.

Synthesis of SMS-xs

As a typical run for the synthesis of SMS-1.0, 10.0 mmol of MPTS, 1.3 g of Pluronic F127 and 0.8 mL of HCl were mixed together, and stirring at room temperature for 2 h. The mixture was then transferred into an autoclave and cured at 140-180 °C for 24h, which gave the pristine products with yellow color. SMS-0.8 could be synthesized with similar procedures: 8.0 mmol of MPTS, 2.0 mmol of TMOS, 1.3 g of Pluronic F127 and 0.8 mL of HCl were mixed together, after stirring of the mixture at room temperature for 2 h, which was then transferred into an autoclave and cured at 140-180°C for 24 h, giving the pristine SMS-0.8 with yellow color. To obtain SMS-xs with opened mesopores, the F127templatecould be removed by extraction with the mixed solvent of ethanol and HCl. The extraction process was performed at 85 °C under refluxing condition for 48 h, and the volume ratio of ethanol to HCl was 7:1. Similarly, SMS-0.5 could also be synthesized with similar procedures as that of SMS-1.0 and SMS-0.8, where MPTS and TMOS with different molar ratio were employed as the mixed precursor. To transform thiol into sulfonic group in SMS-xs,

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1.0 g of extracted SMS-xs was dispersed into 20 mL of H_2O_2 , the suspension was stirred at 80 °C in a N_2 atmosphere for 24 h, which was then treated with 2M HNO₃ at 60 °C for another 24 h. The resultant samples could be obtained from centrifugation, washing with abundant water and drying at 80 °C for 12 h. Before catalytic applications, the SMS-xs was activated with following procedures: 0.5 g of extracted SMS-xs was dispersed into 50 mL of 1 M sulfuric acid. After stirring of the mixture for 24 h at room temperature, the sample was washed with abundant water to remove the residual sulfuric acid, and the ion exchange process was repeated for two times. Finally, the sample was dried at 80 °C for 12 h under vacuum condition before use. For comparison, SBA-15-SO₃H-0.2, HS-JLU-20-0.8and CH_{0.30}O_{0.33}S_{0.16} were synthesized as the literatures ^{30, 32, 42}.

Characterizations

Nitrogen adsorption-desorption isotherms were measured using a Micromeritics ASAP 3020M system. The samples were outgassed for 10 h at 180 °C before the measurements. The pore size distribution for mesopores was calculated using Barrett-Joyner-Halenda (BJH) model. FT-IR spectra were recorded by using a Bruker 66V FT-IR spectrometer. Thermogravimetric analysis (TGA) curves were determined on a Mettler-Toledo TGA/SDTA851e system under flowing air with a ramping rate of 20 °C min⁻¹. TEM images were performed on a JEM-2100F electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. XPS spectra were performed on a Thermo ESCALAB 250 with Al Kα radiation at y=901 for the X-ray sources, the binding energies were calibrated using the C1s peak at 284.9 eV. ¹³C solid state NMR

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experiments were carried out on a Varian Infinityplus-300 spectrometer at resonance frequencies of 75.38 MHz. The experiments were recorded using a 4 mm double-resonance MAS probe at a spinning rate of 10 kHz. The pulse width ($\pi/2$) for ¹³C was measured to be 4.1 µs. A contact time of 4 ms and a recycle delay of 3 s were used for the ¹H-¹³C CP/MAS measurement. ²⁹Si solid state NMR spectra were recorded on a Bruker MSL-400WB spectrometer, fitting the samples in a 7 mm ZrO₂ rotor, spinning at 8 kHz.

The solid-state ³¹P NMR spectra over SMS-xs catalysts were performed as the following procedures: prior to the sorption of trimethylphosphine oxide (TMPO) probe molecule, the samples were placed in glass tubes, which were connected to a vacuum line for dehydration. The samples were kept at a final temperature at 453 K for 24 h, with the pressure below 10^{-3} Pa. Then, they were cooled. The preparation of TMPO adsorbed samples was performed according to the method proposed by Zheng and coworkers ⁴³. Prior to the NMR experiments, the sealed sample tubes were opened and the samples were transferred into NMR rotors with a Kel-F end cap under a dry nitrogen atmosphere in a glove box. ³¹P NMR experiments were performed on a Bruker Ascend-500 spectrometer at a resonance frequency of 202.34 MHz for ³¹P nucleus, with a 4 mm triple-resonance MAS probe at a spinning rate of 12 kHz. Pulse width ($\pi/2$) for ³¹P was measured to be 4.5 μ s. ³¹P MAS NMR spectra with high power proton decoupling were recorded with a recycle delay of 30 s. The chemical shift of ${}^{31}P$ resonance was externally referenced to 1 M aqueous H₃PO₄.

Catalytic reactions

Esterification of palmitic acid with methanol

As a typical run for esterification of the palmitic acid with methanol: 1.282 g of palmitic acid (5 mmol), 2.5 mL of methanol and 0.1 g of catalyst were mixed together into a flask equipped with a condenser and a magnetic stirrer. Then, the reaction was performed at 65 °C for 5 h under vigorous stirring. At different time intervals, samples were withdrawn and analyzed by using gas chromatography. The product in the reaction was methyl palmitate with selectivity near 100 %, which was analyzed by using Agilent 7890A gas chromatography equipped with a flame ionization detector (FID). The column was HP-INNOWax capillary column (30 m); The initial temperature was 100 °C, the ramping rate was 20 °C min⁻¹, and the final temperature was 280 °C; the temperature of the FID detector was 300 °C. In this reaction, the yield of methyl palmitate was calculated by using the internal standard (dodecane) method and established the corresponding correction factor.

Transesterification

As a typical run for transesterification of tripalmitin with methanol: 0.84 g (1.04 mmol) of tripalmitin and 0.10 g of catalyst were mixed well in a flask equipped with a condenser and magnetic stirrer at 70 °C, followed by the addition of 3.71 mL (93.6 mmol) of methanol. The reaction was lasted for 16 h under vigorous stirring and refluxing. The catalysts could be regenerated from centrifugation, washing with abundant CH₂Cl₂ for removing of the absorbed reactants and products, and drying at 60 °C under vacuum condition. The product in this reaction was methyl palmitate with selectivity near 100 %. In this reaction, the yield of biodiesel was evaluated by

using internal standard method, where dodecane was used as internal standard.

Transesterification of sunflower oil with methanol was performed as the following procedure: 1.0 g of sunflower oil (1.16 mmol) and 0.15 g of catalyst were added into a three-necked round flask equipped with a condenser and a magnetic stirrer, and the reaction temperature was rapidly increased to 80 °C. Then, 3.5 mL of methanol (86.3 mmol) was quickly introduced under vigorous stirring, the reaction was lasted for 18 h. The molar ratio of sunflower oil/methanol was 1/72.1 and the mass ratio of catalyst/sunflower oil was 0.15. The main products in this reaction were methyl palmitate ($C_{16:0}$), methyl stearate ($C_{18:1}$), methyl oleate ($C_{18:2}$), methyl linoleate $(C_{18:3})$, methyl arachidate $(C_{20:0})$, 11-eicosenoic methyl $(C_{20:1})$, methyldocosanoate $(C_{22:0})$ and methyltetracosanoate $(C_{24:0})$. The quantitative analysis of these products was performed on an Agilent GC/MS instrument (Agilent 6890N/5975I) equipped with a programmable split/splitless injector. The injector-port temperature was set at 270 °C. The oven-temperature program was initially set at 140 °C and ramped to 270 °C with the ramping rate of 10 °C min⁻¹. The sample could be easily recovered from filtration, washed with abundant methanol and drying at 60 °C for 12 h under vacuum condition. Before recycling, the catalyst was activated with $0.1M H_2SO_4$ for 12 h, and washed with abundant water for removing absorbed H₂SO₄, which was then used for the next time.

Depolymerization of Avicel cellulose

100 mg of Avicel cellulose was dissolved into 2.0 g of [C₄mim]Cl ionic liquid at 100 °C for 5 h under vigorous stirring, which gave a clear cellulose solution. Then, 20

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mg of specific catalyst was introduced into the mixture, after stirring of the mixture for 40 min, then 600 μL of water was added into the reaction system with a very slow rate. The reaction temperature was kept at 100 °C. At different time intervals, the samples were withdrawn, weighed (recorded as M1), quenched immediately with cold water, and centrifuged at 14,800 rpm for 5 min for removing of catalysts and unreacted cellulose. The resultant reaction mixtures were subsequently analyzed, the volume of which was measured and recorded as V1. Unreacted Avicel was separated, washed, dried and weighed.

Preparation of DNS Reagent

DNS reagent was prepared as following procedures: 182 g of potassium sodium tartrate was added into 500 mL of hot deionized water at 50 °C, followed by addition of 6.3 g of 3,5-dinitrosalicylic acid (DNS) and 262 mL of 2 M NaOH. 5 g of phenol and 5 g of sodium sulfite were then introduced into the solution under vigorous stirring to obtain homogeneous solution. The solution was cooled down to room temperature and diluted with deionized water to 1000 mL to give the DNS reagent.

Total Reducing Sugar (TRS) tests

TRS value was measured by DNS method as literature ^{8, 42}. 0.5 mL of DNS regent was mixed with 0.5 mL of the reaction solution and heated at 100 °C for 5 min. The mixture was then cooled down to room temperature, and 4 mL of deionized water was added to dilute the solution for five times. The adsorption at 540 nm was measured in a calibrated NanoDrop2000 UV-spectrophotometer. The value of TRS was then determined based on a standard curve, which was built from standard glucose solution.

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Measuring the yields of glucose, cellobiose and HMF

The concentrations of glucose, cellobiose and HMF in the reaction mixture were measured by a Shimadzu LC-20A high-performance liquid chromatography (HPLC) system equipped with both refractive index detector (RID) and ultraviolet detector (UVD) based on the standard curve methods; Separation was carried out with an SCR-101N column using extra-pure water during the mobile phase at a flow rate of 0.5 mL min⁻¹. The column temperature was set to 50 °C, and the volume of each injection was 10 µL. Pre-measured glucose, cellobiose and HMF were used to establish the calibration curves for the HPLC. The concentrations of soluble sugars from the reactions were then determined from the calibration curves (e.g., glucose yield %=carbon mass of glucose/carbon mass of cellulose, equation 2).

 $Yield_{Glucose} = \frac{M_{Glucose}}{M_{Cellulose}} \times 100\%$ (1)

 $Yield_{Cellobiose} = \frac{M_{Cellobiose}}{M_{Cellulose}} \times 100\%$ (2)

Results and discussion

Porosity characterizations

Figure S1 shows small angle XRD patterns of various SMS-xs samples, which was a classical and reliable technique for investigating the regularity of mesoporous materials. Notably, SMS-0.2, SMS-0.5 and SMS-0.8 show a well resolved diffraction

Green Chemistry

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peak centered at 0.91° indexed as (100) reflection, indicating the worm-like mesopores with certain ordering in these samples ³⁴. In contrast, a very weak and broad peak diffraction peaks could be observed in SMS-1.0, suggesting its much decreased ordering of mesopores in comparison with other samples ³⁴.

The textural properties of synthesized SMS-xs samples were determined by using N₂ as the probing molecule. Figure 1 shows the N₂ adsorption-desorption isotherms at -196 °C and the mesopore size distributions of SMS-xs. Notably, all the three samples of SMS-1.0. SMS-0.8 and SMS-0.5 show typical type-IV isotherms with relatively high volume adsorption, which increases steeply at the relative pressure of $P/P_0=0.5-0.85$, indicating the presence of abundant mesopores in these samples. The corresponding mesopore size distribution covers a broad range of 4.5-10.0 nm. The calculated textural parameters of SMS-xs are also illustrated in Table 1. It is found that SMS-xs have relatively large BET surface areas and total pore volumes (214~589 m² g⁻¹, 0.29~0.81 cm³ g⁻¹, Table 1), which are higher than variously reported solid acids ^{32, 44}. It is noteworthy that the BET surface areas and total pore volumes of SMS-xs decrease with the increasing of sulfur contents. For instance, SMS-0.2 with lowest sulfur content, has the largest BET surface area and total pore volume at 589 $m^2 g^{-1}$ and 0.81 cm³ g⁻¹ respectively, larger than those of SMS-0.5, SMS-0.8 and SMS-1.0. This phenomenon should be attributed to the loaded sulfur largely increases the weight of the framework of SMS-xs, which has negative effect on their BET surface areas and pore volumes. Similar results could also be found in mesopore size distribution, the higher sulfur contents results in the decreased mesopore sizes. For instance, SMS-0.5 shows the mesopore size at 10.0 nm, larger than those of SMS-0.8 (6.9 nm) and SMS-1.0 (4.6 nm). The decreased mesopore sizes in SMS-0.8 and SMS-1.0 was resulted from the blocking of their mesopores by sulfonic group ⁴⁵. Therefore, the mesoporosity and BET surface areas of SMS-*x*s can be easily tuned by adjusting the ratio of MPTS/TMOS.

Furthermore, SMS-xs show the highest acid concentrations among various solid acids to data. For instance, the sulfur content of SMS-1.0 was as high as 5.51 mmol g⁻¹, and its acid capacity was up to 5.59 mmol g⁻¹ (Table 1), much higher than variously reported solid acids (Table S1). In fact, both hydroxyl and sulfonic groups in SMS-xs contribute the acidity, and SMS-xs contain large amount of silicon hydroxyl group besides sulfonic group (³¹P NMR spectra). However, a high density of sulfonic acid groups can cause the formation of pairs that after the ion exchange treatment retains a bridged H⁺ besides a Na⁺ ion, apart from the accessibility. Furthermore, the disulfide bonds should also be formed in the high sulfonated samples ^{46,47}. Although the presence of the mentioned two negative effects on the acidity, the presence of large amount of silicon hydroxyl group still results in relatively higher acidity than the S content in SMS-xs samples (Table 1). The high acid density plays key factor for the activities of solid acids in a variety of acid-catalyzed reactions such as biomass conversions and fine chemicals synthesis.

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Figure 2 shows the high-resolved scanning electron microscope (SEM) images of SMS-0.5 and SMS-0.8 with high magnifications. Both samples show rough surface characteristics with abundant aggregated and worm-hole like mesoporosity, and the

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packed pore sizes were distributed in the range of 20-50 nm, while the worm-like mesopores were distributed in the range of 5-20 nm. Compared with SMS-0.5, the building unit in SMS-0.8 shows more uniform spherical morphology, which was resulted from its high contents of organosilica ³². In contrast, SMS-0.5 monolith was formed from the aggregation of the SiO₂ nanoparticles with irregular shapes. The above mentioned phenomenon results in the more uniform mesopores of SMS-0.8 in comparison with SMS-0.5, which agrees well with N₂ adsorption-desorption results (Figure 1).

Figure 3 shows transmission electron microscopy (TEM) images of SMS-0.5 and SMS-0.8. Notably, both samples show abundant and uniform mesopores with a wormhole like characteristics. Compared with SMS-0.8, SMS-0.5 shows enhanced ordering of mesopores (Figure 2C), suggesting high sulfur content disturbs the self-assembly and condensation processes, which has negative effect on the ordering of mesopores. The mesopore sizes of SMS-0.8 and SMS-0.5 estimated from TEM images, were distributed in the range of 5.0-10.0 nm, which agree well with N₂ adsorption-desorption isotherms results. TEM images confirm that abundant and worm-hole like mesopores could be introduced into SMS-*xs via* the novel solvent free technique exploited by us in this work, which was consistent with small angle XRD results (Figure S1).

Structural and acidity characterizations

Figure 4 shows ¹³C and ²⁹Si solid state NMR spectra of SMS-0.5 and SMS-1.0, which is an effective and reliable technique for investigating the chemical structures

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of various solid materials. SMS-0.5 shows two groups of peaks in the range from -50 to -80 ppm and -100 to 130 ppm, which are attributed to the signals of organosiloxane $[T^m, RSi(OSi)_m(OH)_{3-m}, m=1-3; T^3 at -68 ppm and T^2 at -60 ppm]$ and siloxane $[Q^n, Si(OSi)_n(OH)_{4-n}, n=2-4; Q^4 at -111 ppm and Q^3 at -101 ppm], respectively$ ^{30, 32}. Notably, the signals associated with T group are stronger than that of Q group, indicating large amount of organic sulfonate group has been successfully introduced into SMS-0.5. Furthermore, the obviously stronger intensity of T^3 and Q^4 in SMS-0.5 indicate its high condensation degree of framework, which strongly enhance their hydrothermal stability in the water-contained reactions ⁴⁸. Interestingly, only one peak at around -68 ppm associated with T³ was observed in SMS-1.0, which confirms its completely organic silica network with ultra-high condensation degree, further resulting in its ultra-high concentration of sulfonic group and good hydroyhermal stability ^{30, 32, 48}. Additionally, ¹³C solid-state NMR spectrum further confirms the successful and controllable incorporation of sulfonic group in SMS-0.5. For instance, the resultant extracted sample show the signals centered at around 11, 18, 27, 41, 48, 57, 65, 75 and 177 ppm. The peaks at around 11 (¹C), 18 (¹C), 27 (¹C), 41 (²C) and 48 (^{2}C) ppm should be attributed to the signals of alkyl chain in organo sulfonic groups $^{30-32}$; The peaks at around 57 (³C) and 65 (⁴C) should be attributed to the carbon connected with sulfonic group and hydroxyl group ³⁰⁻³², the peak at around 177 ppm should be attributed to the carbon connected with carboxylic group ⁴⁹⁻⁵¹. The presence of hydroxyl group and carboxylic group should be resulted from the partial oxidation of alkyl chain by HNO₃ and H₂O₂. Notably, a small and broad peak centered

at around 75 ppm should be attributed to the carbon atoms in the residual F127 template ⁴⁹⁻⁵¹, which could not be completely removed from SMS-*x*s samples by solvent-extraction approach, similar phenomenon has also been reported previously ⁴⁹⁻⁵¹

Figure 5 shows XPS spectra of SMS-0.8. The survey spectrum shows the signals of Si_{2p} , S_{2p} , C_{1s} and O_{1s} in SMS-0.8. The high resolved peaks of Si_{2p} and S_{2p} were centered at around 103 and 169 eV ^{11, 21, 22, 30}, which were assigned to the signals of SiO_2 framework and sulfonic group. Correspondingly, the peak of C_{1s} could be fitted and deconvoluted into three peaks centered at around 284.4, 285.9 and 287.5 eV, which were assigned to C-C, C-S and C-O bonds. These results further confirmed the successful introduction of sulfonic group in SMS-0.8, in good agreement with NMR results.

To further confirm the successful and controllable introduction of sulfonic group in SMS-xs via the solvent free technique. FT-IR spectra of SMS-0.5, SMS-0.8 and SMS-1.0 were also investigated in Figure 6. It can be seen that the strong vibration at around 2900 cm⁻¹ associated with C-H stretch vibrations (of the propyl chains) increases as the MPTS/(MPTS+TEOS) molar ratio was increased. The vibration at around 926 cm⁻¹ was assigned to the signal of V_s (S-O), the vibration at around 1036 cm⁻¹ was assigned to the signal of C-S bond, and the vibration at around 1370 and 1289 cm⁻¹ were assigned to the signals of V_s (S=O) and V_{As} (S=O), respectively ^{11, 21, 22, ^{30, 52}. From SMS-0.5 to SMS-1.0, the signals associated with sulfonic group became more resolved because of the increased concentrations of sulfonic group. The} combination of NMR, XPS and FT-IR results, we can conclude that mesoporous organosilica with high contents of sulfonic group and highly cross-linked framework could be extensively prepared *via* the novel high temperature, solvent free technique in this work.

The acidity properties of SMS-xs were further investigated by using ^{31}P solid-state NMR techniques involving trimethylphosphine oxide (TMPO) as probe molecule, which could interact with the acid sites on the SMS-xs samples. Notably, the ³¹P NMR probe technique is a *state-of-the-art* approach to determine the acid type (Brønsted or Lewis acid) and acid strength (strong or weak acid) of various kinds of acid catalysts with different stabilities ⁵³⁻⁵⁸. Figure 7 illustrates the ³¹P solid-state MAS NMR spectra of TMPO adsorbed on various SMS-xs samples. SMS-0.5 shows multiple ³¹P resonance peaks centered at around 49, 62, 76, and 89 ppm, while SMS-1.0 exerts that at approximately 49, 64, 81, and 89 ppm, which indicates the presence of various acid sites with different acid strengths in these samples. The peaks below 64 ppm may be assigned to the signals of weakly acidic sites such as silicon hydroxyl group, while the resonances above 76 ppm can be attributed to the relatively strong ones. Interestingly, the relative amount of ³¹P peaks for the strong acid sites (above 76 ppm) is dramatically increased from SMS-0.5 to SMS-1.0, which should be attributed to the higher sulfonic group content of SMS-1.0 sample. The grafted sulfonic groups were confined into the nanopores of SMS-1.0 with different chemical environments, hence directly resulting in the higher degree of exposure of acid sites. In contrast, the weaker acidity of SMS-0.5 may be attributed to its

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18

Green Chemistry

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relatively lower sulfonic group contents, since large amount of acid sites were embedded into the framework and remained inaccessible due to the large usage of inert silica precursor of TMOS. Whatever, the aforementioned results showed the comparable strong acidity of SMS-*x*s with 100 % H₂SO₄ (89 ppm) ⁵⁸. The strong acidity of SMS-*x*s could also be confirmed by NH₃-TPD technique (Figure S2). The strong and controllable acidity was favorable for the large enhancement of their catalytic activities in various acid-catalyzed reactions such as biomass conversions.

Thermal stability

The thermal stability of solid acids is very important for their applications in the area of acid catalysis. Figure 8 shows TG curves of SMS-1.0, SMS-0.8 and SMS-0.5, which was a reliable technique for evaluating thermal stability of different kinds of materials. The TG curves of SMS-xs could be divided into three temperature ranges of 50-130, 320-490, and 490-700 °C. The weight loss in the temperature range of 50-130 °C should be attributed to desorption of the adsorbed water. The weight loss in the temperature range of 320-490 °C should be attributed to the destruction of sulfonic group. The weight loss in the temperature range of 490-700 °C should be attributed to the decomposition of alkyl chain in SMS-xs samples. The high decomposition temperatures verify the good thermal stability of sulfonic group confined in SMS-xs, which was favorable for them used as stable catalysts in various reactions. Notably, SMS-1.0, SMS-0.8 and SMS-0.5 showed different weight residuals of 55.7, 41.3 and 38.1 *wt*% because of their different concentrations. The TG analyses

are in consistent with elemental analysis and solid NMR results.

Catalytic performances

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Figure 9 shows the kinetic behaviors of various solid acids in the esterification of palmitic acid with methanol, the esterification of fatty acids was an important reaction for the production of high quality biodiesel. Notably, SMS-1.0 and SMS-0.8 show much better catalytic performances than those of HS-JLU-20-0.8, SBA-15-SO₃H-0.2, and Amberlyst 15. For instance, the yields of methyl palmitate catalyzed by SMS-1.0 and SMS-0.8 exceeded 40 % within 20 min; WhileHS-JLU-20-0.8, SBA-15-SO₃H-0.2, and Amberlyst 15 give relatively lower yields at 30.5, 18.8 and 16.3 %, respectively. Further prolong the reaction time to 120 min, SMS-1.0 and SMS-0.8 gave the product yields at 90.5 and 86.7 %, which were much higher than those of HS-JLU-20-0.8 (77.2 %), SBA-15-SO₃H-0.2 (63.2 %), and Amberlyst 15 (56.6 %). Compared with HS-JLU-20-0.8, SBA-15-SO₃H-0.2 and Amberlyst 15, the synergistic effects of high concentrations of sulfonic group, strong acidity, and abundant porosity result in their better activities in esterification.

Except for esterification, the excellent activities of SMS-xs could also be observed in transesterification, which was an important reaction to transform low cost oil such as plant or animal oils into biodiesel ^{59, 60}. Figure 10 shows kinetic curves in transesterification of tripalmitin with methanol catalyzed by SMS-1.0, SMS-0.8, HS-JLU-20-0.8, SBA-15-SO₃H-0.2 and Amberlyst 15, and the yields of methyl palmitate steadily increase with the reaction time. Notably, the catalytic activities of SMS-1.0 and SMS-0.8 were much better than those of HS-JLU-20-0.8,

SBA-15-SO₃H-0.2 and Amberlyst 15. For instance, the yields of methyl palmitate catalyzed by SMS-1.0 and SMS-0.8 were all higher than HS-JLU-20-0.8, SBA-15-SO₃H-0.2 and Amberlyst 15 at every time point. After reacting for 16 h, SMS-1.0 and SMS-0.8 gave the product yields at 85.6 and 82.1 %, respectively; While HS-JLU-20-0.8, SBA-15-SO₃H-0.2 and Amberlyst 15 gave relatively lower product yields at 70.2, 52.3 and 49.7 %.

To further reduce the cost of biodiesel, the selecting of low cost feedstock such as plant oil has received considerable attention in these years, which was very important for the industrial application of biodiesel ^{59, 60}. Therefore, we further investigate the catalytic activities of SMS-xs solid acids for catalyzing conversion of sunflower oil into biodiesel, and the main products in this reaction were methyl palmitate $(C_{16:0})$, methyl stearate $(C_{18:1})$, methyl oleate $(C_{18:2})$, methyl linoleate $(C_{18:3})$, methyl arachidate ($C_{20:0}$), methyl 11-eicosenoate ($C_{20:1}$), methyldocosanoate ($C_{22:0}$) and methyltetracosanoate ($C_{24:0}$), which were summarized in Table 2. For comparison, the activities of a variety of acid catalysts were also summarized in Table 2, which include H₂SO₄, HS-JLU-20-0.8, carbonaceous solid acid of CH_{0.30}O_{0.33}S_{0.16}, H₃PW₁₂O₄₀, SBA-15-SO₃H-0.2, Amberlyst 15 and H-USY. Interestingly, SMS-xs show much improved catalytic activities in comparison with these solid acids, and the efficiency of acid center in SMS-xs was a little lower than H₂SO₄. For instance, SMS-xs show relatively high yields of C_{16:0} (75.7-83.4 %), C_{18:1} (74.8-82.3 %), C_{18:2} (76.3-80.1 %), C_{18:3} (76.2-81.8 %), C_{20:0} (75.5-81.1 %), C_{20:1} (78.3-82.3 %), C_{22:0} (76.7-81.3 %) and C_{24:0} (75.4-81.8%, Table 2, run 1-3), which were as comparable as that of H₂SO₄ with the

same acid number (C_{16:0}: 83.2 %, C_{18:1}: 82.6 %, C_{18:2}: 80.4 %, C_{18:3}: 82.3 %, C_{20:0}: 80.5 %, C_{20:1}:81.7 %, C_{22:0}: 80.9 % and C_{24:0}: 80.7 %, Table 2, run 4). The activities of SMS-xs were higher than various solid acids including HS-JLU-20-0.8, carbonaceous solid acid of $CH_{0.30}O_{0.33}S_{0.16}$, $H_3PW_{12}O_{40}$, much higher than those of SBA-15-SO₃H-0.2, Amberlyst 15 and H-USY (Table 2, run 5-10). More importantly, SMS-xs show very good reusability, and the decreasing of activities cannot be observed even after five times recycling (Table 2, run 11). The excellent activities and good reusability were attributed to their ultra-high acid concentrations, strong acid strength and good hydrothermal stability ^{30, 32, 45}.

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Besides the catalytic production of biodiesel, we also investigate the catalytic activities of SMS-xs in depolymerization of crystalline cellulose (DCC, Table 3), and the main products were glucose, cellobiose and HMF. For comparison, the activities of commercial acid resin of Amberlyst 15 and HCl were also summarized in Table 3. Notably, DCC has received extensive research interests in the area of biomass conversion in these years, which transforms low cost and waste biomass into useful chemicals. Acid catalysts have been widely used in this reaction due to their advantages such as low cost, mild reaction conditions, good activities and enhanced reusability ^{1, 2, 7, 8}. Interestingly, SMS-xs were very active in DCC, much better than that of commercial acid resin of Amberlyst 15, which were as comparable as HCl with the same acid number. For instance, the yields of glucose, cellobiose and HMF catalyzed by SMS-xs were in the range of 30.8-40.7, 19.1-22.3 and 5.9-10.5 %, which were as comparable as HCl (41.5, 22.7 and 9.8 %). In contrast, Amberlyst 15 shows

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very low yields at 14.1, 17.8 and 3.9 %. Correspondingly, the TRS values of SMS-xs were ranged from 70.5-86.3 %, a little lower than that of HCl (88.2 %), much higher than that of Amberlyst 15 (39.8 %). Compared with SMS-0.5, SMS-1.0 and SMS-0.8 show higher activities because of their enhanced acid concentrations and acid strength. Based on the above-mentioned results, SMS-xs could be used as highly efficient and reusable solid acids for catalyzing production of biofuels and fine chemicals, much better than variously reported solid acids. Their excellent catalytic performances were resulted from their structural characteristics such as large BET surface areas, abundant mesopores, good hydrothermal stabilities, ultra high acid concentrations and controllable acid strength.

Conclusion

In summary, a series of mesoporous organosilica of SMS-xs with large BET surface areas, abundant nanopores, highly cross-linked framework, ultra high acid concentrations and controllable acid strength were prepared *via* a novel high temperature, solvent free induced self-assembly technique. The synthesized SMS-xs could be used as highly efficient and reusable solid acids in esterification of fatty acid with methanol, transesterification of plant oil with methanol and depolymerization of crystalline cellulose into fine chemicals, and their catalytic activities were much better than a variety of reported solid acids. This work develops a sustainable and low cost approach for preparation of highly efficient and stable mesoporous silica solid acids, which offers great opportunity for the wide applications of mesoporous organosilica based solid acids in the areas of biomass conversions and fine chemicals

synthesis in the industry.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21573150, 21203122, U1662108, 21473244, 11575117), Natural Science Foundation of Zhejiang Province (LY15B030002).

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Samples	S contents (mmol S	Acid capacity (mmol	$S_{BET} (m^2 g^{-1})^{c}$	$V_{t} (cm^{3}g^{-1})^{d}$	Pore
	g ⁻¹ sample) ^a	H ⁺ g ⁻¹ sample) ^b			diameter ^e
SMS-0.2	1.97	2.00	589	0.81	9.1
SMS-0.5	3.98	4.02	421	0.80	10.0
SMS-0.8	5.01	5.07	378	0.53	6.9
SMS-1.0	5.51	5.59	214	0.29	4.6

Table 1. Textual properties of variously synthesized SMS-xs.

^{*a*} Sulfur contents determined by elemental analysis. ^{*b*} Acid–base titration using Na⁺ as exchange-cation. ^{*c*} Surface area calculated from the BET equation in the relative pressure range of $0.05\sim0.20$. ^{*d*} Single point total pore volume calculated at the relative pressure of 0.99. ^{*e*} Pore size determined using the BJH approach, and calculated from the adsorption branch.

Run	Catalysts	Yields of methyl esters (%)							
		Methyl	Methy	Methyl	Methyl	Methyl	Methyl	Methyl	Methyl
		palmitat	I	oleate	linolea	arachi	11-eicos	docosa	tetraco
		e (C _{16:0})	stearat	(C _{18:2})	te	date	enoate	noate	sanoat
			е		(C _{18:3})	(C _{20:0})	(C _{20:1})	(C _{22:0})	е
			(C _{18:1})						(C _{24:0})
1	SMS-1.0	82.8	81.2	79.6	80.3	81.1	82.3	80.5	81.8
2	SMS-0.8	83.4	82.3	80.1	81.8	78.6	80.7	81.3	80.6
3	SMS-0.5	75.7	74.8	76.3	76.2	75.5	78.3	76.7	75.4
4	H ₂ SO ₄ ^b	83.2	82.6	80.4	82.3	80.5	81.7	80.9	80.7
5	HS-JLU-20-0.8 ^c	69.4	70.2	72.7	74.3	70.9	72.7	71.3	68.8
6	$CH_{0.30}O_{0.33}S_{0.16}^{\ \ d}$	63.9	61.7	69.1	70.8	68.3	63.7	63.3	65.7
7	$H_3PW_{12}O_{40}$	72.8	70.9	71.1	72.3	69.2	70.5	72.8	73.5
8	SBA-15-SO ₃ H-0.2	56.5	58.1	53.4	55.1	44.8	34.1	41.7	41.3
	е								
9	Amberlyst 15	51.6	49.4	43.7	47.6	30.2	31.5	37.3	18.7
10	H-USY ^f	18.2	15.3	22.1	16.9	14.5	10.7	13.1	8.9
11	SMS-1.0 ^g	81.8	81.3	78.9	81.3	79.8	80.4	78.6	79.8

Table 2. Catalytic data in transesterification of sunflower oil with methanol over various acid

^{*a*} 1.0 g of sunflower oil (1.16 mmol); 3.5 mL of methanol (86.3 mmol); 0.1 g of catalyst; Reaction temperature 80 °C; Reaction time 18 h. The catalytic activity of the catalyst was characterized quantitatively by the conversion of fatty acid methyl esters (FAME, Y %), which was calculated as follows: Yield=(M_D/M_T)×100 %, where M_D and M_T are the number of moles of each FAME produced and expected, respectively. In this section, M_T is the number of moles of FAME catalyzed by 0.1 g of H₂SO₄ in 24 h, performed at 80 °C with the same content of feedstock as that of SMS-*x*s solid acids. ^{*b*} The same acid number as that of SMS-0.8. ^{*c-e*} Synthesized from ref. 28,30,40. ^{*f*} Supplied by Sinopec Catalyst Co. ^{*g*} The sample has been recycled for five times.

catalysts ^a.

Table 3. Yields of sugars and dehydration products in the depolymerization of Avicel catalyzed by

various acid catalysts.

Run	Samples	Glucose	Cellobiose	HMF	TRS (%) ^b
		yield (%) ^{<i>a</i>}	yield (%) ^a	yield (%) ^a	
1	Amberlyst 15	14.1	17.8	3.9	39.8
2	HCI ^c	41.5	22.3	9.8	88.2
3	SMS-1.0	40.1	22.4	10.5	86.3
4	SMS-0.8	40.1	21.2	8.6	84.5
5	SMS-0.5	30.8	19.1	5.9	70.5

^{*a*} Measured by HPLC method.

^b Measured by DNS method.

^c The same acid number as that of SMS-0.8.



Figure 1. N_2 adsorption-desorption isotherms and pore size distribution of various SMS-xs

samples.



Figure 2. SEM images of various (A&B) SMS-0.8 and (C&D) SMS-0.5.

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Figure 3. TEM images of various (A&B) SMS-0.8 and (C&D) SMS-0.5.



Figure 4. (A) ²⁹Si solid state NMR spectra of (a) SMS-1.0 and (b) SMS-0.5, (B) ¹³C solid state NMR

spectra of SMS-0.5.

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Figure 5. XPS spectra of (A) survey, (B) Si_{2p} , (C) S_{2p} and (D) C_{1s} of SMS-0.8.



Figure 6. FT-IR spectra of (a) SMS-0.5, (b) SMS-0.8 and (c) SMS-1.0.



Figure 7. Room temperature ³¹P MAS NMR spectra of TMPO adsorbed on (a) SMS-0.5, and (b)

SMS-1.0.



Figure 8. TG curves of various SMS-xs samples.

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Figure 9. Dependence of methyl palmitate yields on reaction time in the esterification of palmitic acid with methanol over (a) SMS-1.0, (b) SMS-0.8, (c) HS-JLU-20-0.8, (d) SBA-15-SO₃H-0.2, and (e) Amberlyst 15.



Figure 10. Catalytic kinetic curves in transesterification of tripalmitin with methanol over by (a)

SMS-1.0, (b) SMS-0.8, (c) HS-JLU-20-0.8, (d) SBA-15-SO₃H-0.2, and (e) Amberlyst 15.

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Graphical Abstract:



Green, solvent free to the fast synthesis of highly sulfonic group functionalized, hydrothermally stable mesoporous organosilicas (SMS), which could be used as efficient and reusable solid acids for catalyzing production of biofuels and fine chemicals.