

Mesoporous Silica Materials with an Extremely High Content of Organic Sulfonic Groups and Their Comparable Activities with that of Concentrated Sulfuric Acid in Catalytic Esterification

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Received: March 24, 2006; In Final Form: May 22, 2006

Mesoporous silica materials (HS-JLU-20) with an extremely high content of mercaptopropyl groups have been successfully synthesized using fluorocarbon–hydrocarbon surfactant mixtures through a simple co-condensation approach of tetraethyl orthosilicate (TEOS) and (3-mercaptopropyl)trimethoxysilane (MPTS), which are characterized by X-ray diffraction (XRD), nitrogen adsorption and desorption isotherms, transmission electron microscopy (TEM), CHNS elemental analysis, thermogravimetry analysis (TGA), and ^{29}Si NMR spectroscopy. The results show that HS-JLU-20 samples with molar ratios of MPTS/(MPTS + TEOS) at 0.5–0.8 in the starting synthetic gels still show their mesostructures, while HS-SBA-15 with the molar ratio of MPTS/(MPTS + TEOS) at 0.50 completely loses its mesostructure in the absence of fluorocarbon surfactant. Possibly, fluorocarbon surfactant containing N^+ species with a positive charge could effectively interact with negatively charged mercapto groups in the synthesis of HS-JLU-20 materials, resulting in the formation of mesoporous silicas with good cross-linking of silica condensation even at an extremely high content of organic mercapto groups. More interestingly, after the treatment with hydrogen peroxide, $\text{HSO}_3\text{-JLU-20}$ materials with an extremely high content of organic sulfonic groups exhibit comparable activity with liquid concentrated sulfuric acid in catalytic esterification of cyclohexanol with acetic acid.

1. Introduction

Recently, mesoporous silica materials containing organic sulfonic groups have been paid much attention because of their potential use as solid acidic catalysts for chemical conversion of large molecules.^{1–13} Generally, the organic sulfonic groups are transformed from the oxidation of mercapto groups in mesoporous silica materials by H_2O_2 .^{1,3–5,7,9,10,12–14} Although there are a lot of successful examples for catalysis by solid mesoporous silica materials with organic sulfonic groups, their activities are still much lower than those of liquid concentrated sulfuric acid,¹⁵ which severely hinder their practical applications in catalytic reactions. The relatively low activities over mesoporous silicas with organic sulfonic groups, compared to liquid concentrated sulfuric acid, can be attributed to the low concentration of organic sulfonic groups in the samples.^{1,3,7,9,11–13} The increase of mercapto groups in the synthesis of mesoporous silica materials will significantly reduce the degree of cross-linking of silica condensation in the mesoporous walls to a level at which a stable ordered silica-based mesostructure cannot be formed.^{8,14,16–24} For example, when the molar ratio of organic mercapto species with the total silica sources in the starting gel is over 0.20, ordered mesoporous silica-based materials cannot be synthesized by using triblock polymer surfactant (P123, $\text{EO}_{20}\text{-PO}_{70}\text{EO}_{20}$) as a template in strongly acidic media.¹⁴ Therefore, mesoporous silica materials²⁵ with an extremely high content of organic mercapto groups are greatly desirable.

Here, we have demonstrated a simple and general route for the synthesis of ordered mesoporous silica-based materials²⁶

containing an extremely high content of mercaptopropyl groups using a surfactant mixture of fluorocarbon surfactant (FC-4) and block copolymer (P123).²⁷ After the treatment with hydrogen peroxide, the ordered mesoporous silica materials with an extremely high content of organic sulfonic groups exhibit comparable activities with liquid concentrated sulfuric acid in the catalytic esterification of cyclohexanol with acetic acid. This approach would open a door for the application of mesoporous silica materials²⁸ with an extremely high content of organic sulfonic groups as solid acidic catalysts on large molecular conversion with high activities.

2. Experimental Section

Mesoporous silica-based materials containing an extremely high content of mercaptopropyl groups (denoted as HS-JLU-20-X where X stands for the molar ratio of (3-mercaptopropyl)trimethoxysilane (MPTS) with the sum of MPTS and tetraethyl orthosilicate (TEOS)) were hydrothermally synthesized in strongly acidic media in the presence of surfactant mixtures of fluorocarbon surfactant (FC-4) and block copolymer (P123). In a typical run, 4 g of P123 and 12 g of FC-4 were dissolved in 240 mL of HCl solution (2.0 M) at 40 °C. After the addition of TEOS (9.8 g) and stirring at 40 °C for 45 min, a calculated amount of MPTS was slowly added into the solution, followed by stirring at 40 °C for 24 h and crystallizing at 100–140 °C for 48 h. The molar ratio of MPTS/(MPTS + TEOS) is varied from 0.5 to 0.8. After filtering, the solid product was washed with water and dried at room temperature. The surfactants in the solid products were extracted with acidified acetone solvent at 60 °C for 48 h.

The synthesis of HOOC-JLU-20 and $\text{NH}_2\text{-JLU-20}$ samples was almost the same as that of HS-JLU-20 except for the use

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TABLE 1: Physical Parameters and $\Sigma T^m/\Sigma(T^m + Q^n)$ of As-Extracted HS-JLU-20 and HS-SBA-15 Samples

sample	$d(100)$ (Å)	pore size (Å)	pore volume (cm ³ /g)	surface area (m ² /g)	a_0^a (Å)	wall thickness ^b (Å)	$\Sigma T^m/\Sigma(T^m + Q^n)$ (%)
HS-JLU-20-0.5	110	39	0.24	400	127	88	68
HS-JLU-20-0.6	110	38	0.15	277	127	89	81
HS-JLU-20-0.7	113	23	0.10	202	130	107	89
HS-JLU-20-0.8	110	17	0.05	109	127	110	91
HS-SBA-15-0.2	113	70	0.70	551	130	60	28

^a a_0 (lattice parameter) = $2d_{100}/3^{1/2}$. ^b Wall thickness = a_0 - pore size.

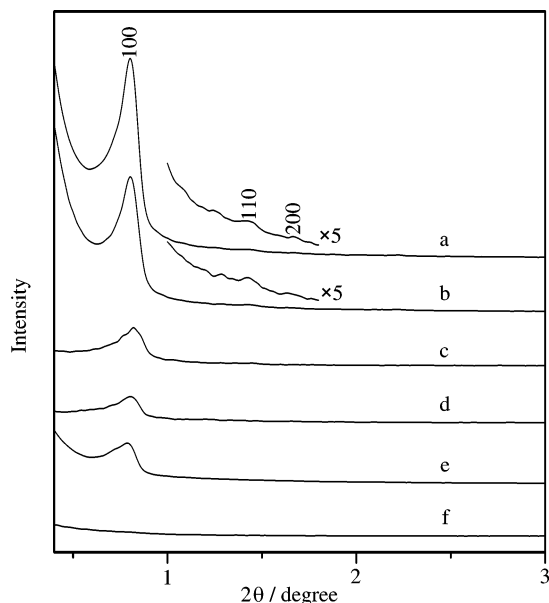


Figure 1. XRD patterns of as-extracted HS-JLU-20 and HS-SBA-15 samples: (a) HS-JLU-20-0.50; (b) HS-JLU-20-0.60; (c) HS-JLU-20-0.70; (d) HS-JLU-20-0.80; (e) HS-SBA-15-0.20; (f) HS-SBA-15-0.50.

of 11-triethoxysilanylundecanoic acid ethyl ester (11-triethoxysilanylundecanoic acid ethyl ester) and 3-aminopropyl triethoxysilane (3-aminopropyl triethoxysilane) replacing MPTS. HS-SBA-15 was synthesized according to the published literature.¹⁴

Mesoporous silica materials with mercaptopropyl groups (HS-JLU-20) were further oxidized with H₂O₂ to form sulfonic-functional mesoporous silica materials (HSO₃-JLU-20).¹³ Typically, 2.04 g of 35% H₂O₂ was mixed with 1 g of HS-JLU-20, followed by the addition of 6.12 g of methanol. After stirring at room temperature for 24 h, the suspension was filtered and washed with water and ethanol. The wet material was restirred again (1 wt %) in acidified H₂O (H₂SO₄; 0.1 M) for another 4 h. Finally, the materials were extensively washed with H₂O and then dried at room temperature, denoted as HSO₃-JLU-20.

As a model reaction, catalytic esterification of cyclohexanol with acetic acid over various sulfonic-functionalized mesoporous silicas was carried out. Typically, 0.2 g of catalyst was added into 11.2 mL of cyclohexanol in the reactor. After heating the reactor in an oil bath to 100 °C, 17.35 mL of acetic acid was rapidly added, followed by reaction for 6 h. In this reaction, the molar ratio of cyclohexanol/acetic acid was 2.6 and the mass ratio of catalyst/cyclohexanol was 0.018. The products were then analyzed by gas chromatography (Varian CP-3800) with a flame ionization detector (FID).

X-ray diffraction (XRD) patterns were obtained with a Siemens D5005 diffractometer using Cu Kα radiation. Transmission electron microscopy (TEM) experiments were performed on a JEM-3010 electron microscope (JEOL, Japan) with

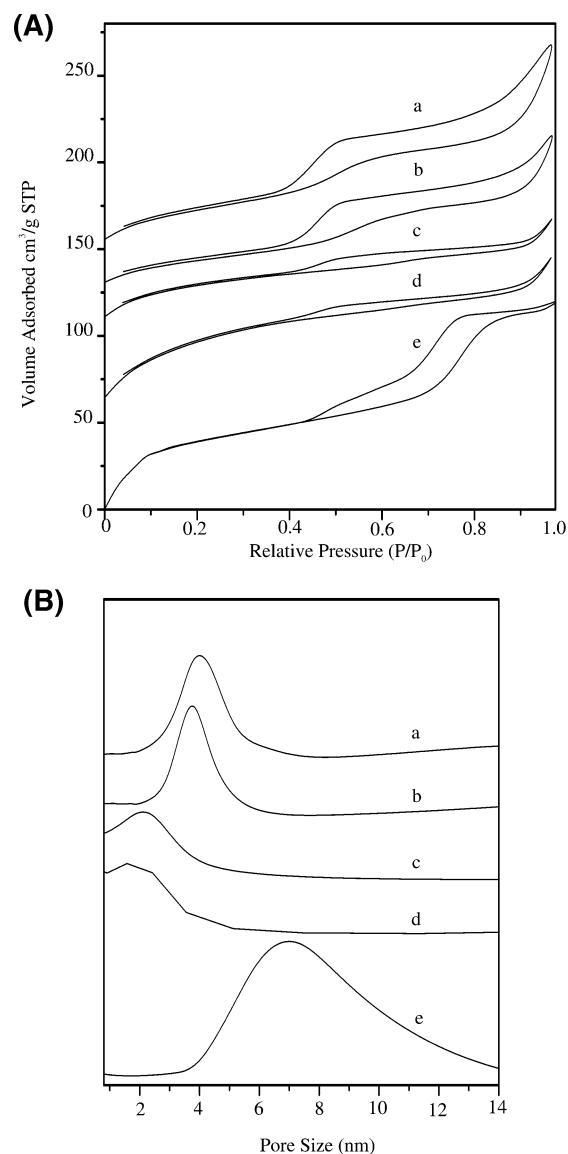


Figure 2. (A) Nitrogen adsorption-desorption isotherms and (B) BJH pore-size distribution of as-extracted HS-JLU-20 and HS-SBA-15 samples: (a) HS-JLU-20-0.50; (b) HS-JLU-20-0.60; (c) HS-JLU-20-0.70; (d) HS-JLU-20-0.80; (e) HS-SBA-15-0.20. The isotherms for parts b, c, d, and e are offset by 10, 30, 60, and 100 cm³/g, respectively.

an acceleration voltage of 300 kV. The nitrogen adsorption and desorption isotherms at the temperature of liquid nitrogen were measured using a Micromeritics ASAP 2020M system. The samples were outgassed for 10 h at 300 °C before the measurements. The pore-size distribution for mesopores was calculated using the Barrett-Joyner-Halenda (BJH) model. ²⁹Si NMR spectra were recorded on a Bruker MSL-400WB spectrometer, fitting the samples in a 7 mm ZrO₂ rotor, spinning at 8 kHz. CHNS elemental analyses were performed on a Perkin-Elmer series II CHNS analyzer 2400. A Perkin-Elmer TGA 7

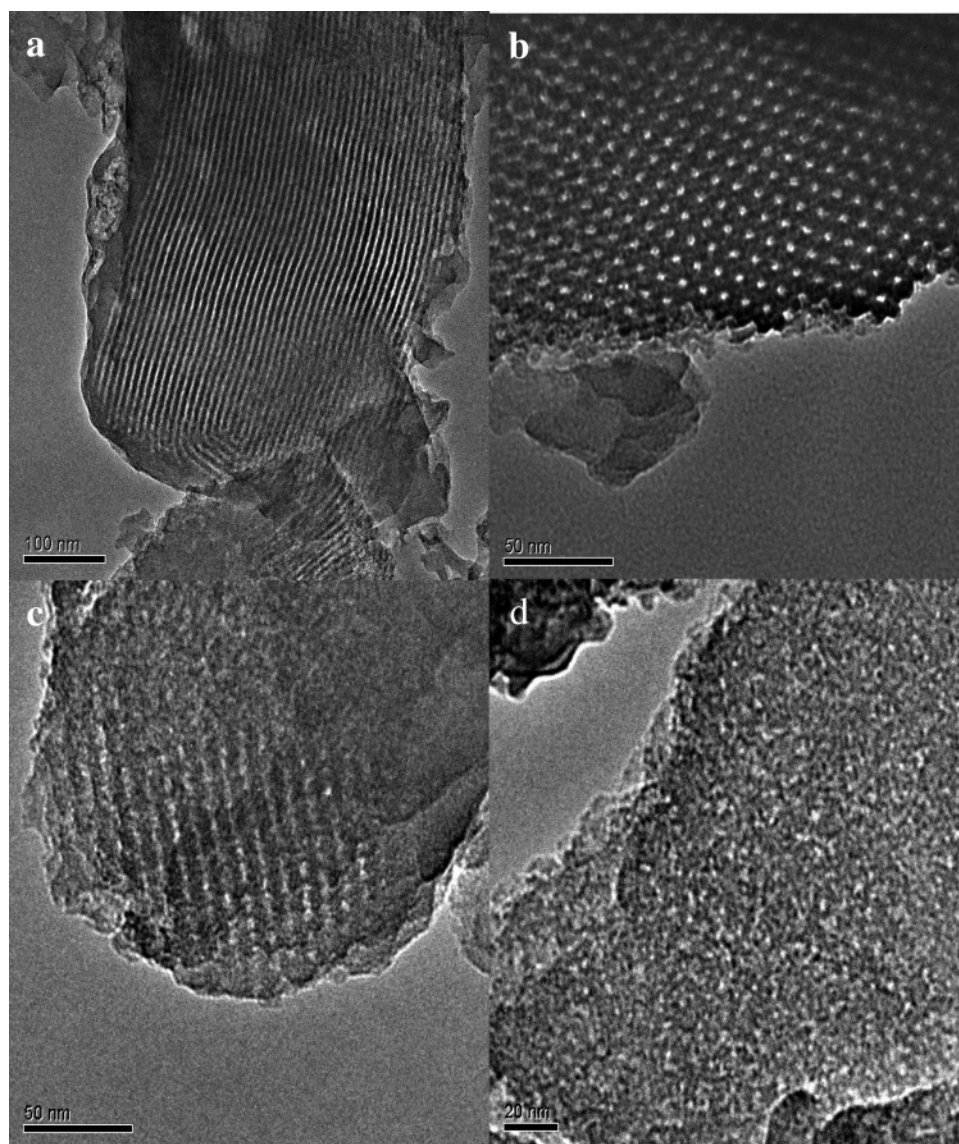


Figure 3. TEM images of as-extracted HS-JLU-20-0.50 (a and b) and HS-JLU-20-0.80 (c and d).

unit was used to carry out the thermogravimetric analysis (TGA) in air at a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$.

3. Results and Discussion

Figure 1 shows XRD patterns for as-extracted HS-JLU-20 and HS-SBA-15 with various ratios of MPTS/(MPTS + TEOS) in starting synthetic gels. Notably, as-extracted HS-JLU-20-0.50 and HS-JLU-20-0.60 (Figure 1a and b) exhibit clearly well-resolved peaks that can be indexed as (100), (110), and (200) diffractions associated with the *p6mm* hexagonal symmetry.³⁰ Interestingly, at least one peak could be observed for as-extracted HS-JLU-20-0.80 (Figure 1d), implying the maintenance of its mesostructure. In contrast, as-extracted HS-SBA-15-0.50 completely loses its mesostructure in the absence of fluorocarbon surfactant (Figure 1f). Obviously, the presence of fluorocarbon surfactant plays an important role in the synthesis of ordered mesoporous silica materials with an extremely high content of mercaptopropyl groups.

Figure 2A shows N_2 isotherms of as-extracted HS-JLU-20 and HS-SBA-15 with various molar ratios of MPTS/(MPTS + TEOS) in the starting synthetic gels. Notably, with increasing content of mercaptopropyl groups in the synthetic gels, the sample isotherms are gradually changed from type IV-like to

type I-like.³⁰ These results suggest that the pore sizes are gradually reduced by increasing the content of mercaptopropyl groups, which are confirmed by the estimation of pore-size distribution calculated from nitrogen adsorption data using the BJH method (Figure 2B). From XRD and N_2 adsorption data, the wall thickness and pore size of various samples are estimated (Table 1). Interestingly, the pore sizes of as-extracted HS-JLU-20 samples gradually decrease from about 39 to 17 Å with an increase in the molar ratios of MPTS/(MPTS + TEOS) in the synthetic gels from 0.50 to 0.80. Correspondingly, the samples' wall thicknesses gradually increase from 88 to 107 Å. This phenomenon is unique and quite different from other routes reported previously.^{31,32} These results suggest that organic mercaptopropyl groups might be gradually enriched inside of mesopores with an increase in the ratios of MPTS/(MPTS + TEOS) in the starting synthetic gels, and result in the reduction of pore size.

TEM images of as-extracted HS-JLU-20-0.50 (Figure 3a and b) exhibit ordered hexagonal arrays of mesopores with one-dimensional channels and further confirm that HS-JLU-20-0.50 has a 2-D hexagonal (*P6mm*) mesostructure. Particularly, as observed from high-dark contrast in the TEM images of the sample (Figure 3a and b), the distance between mesopores is

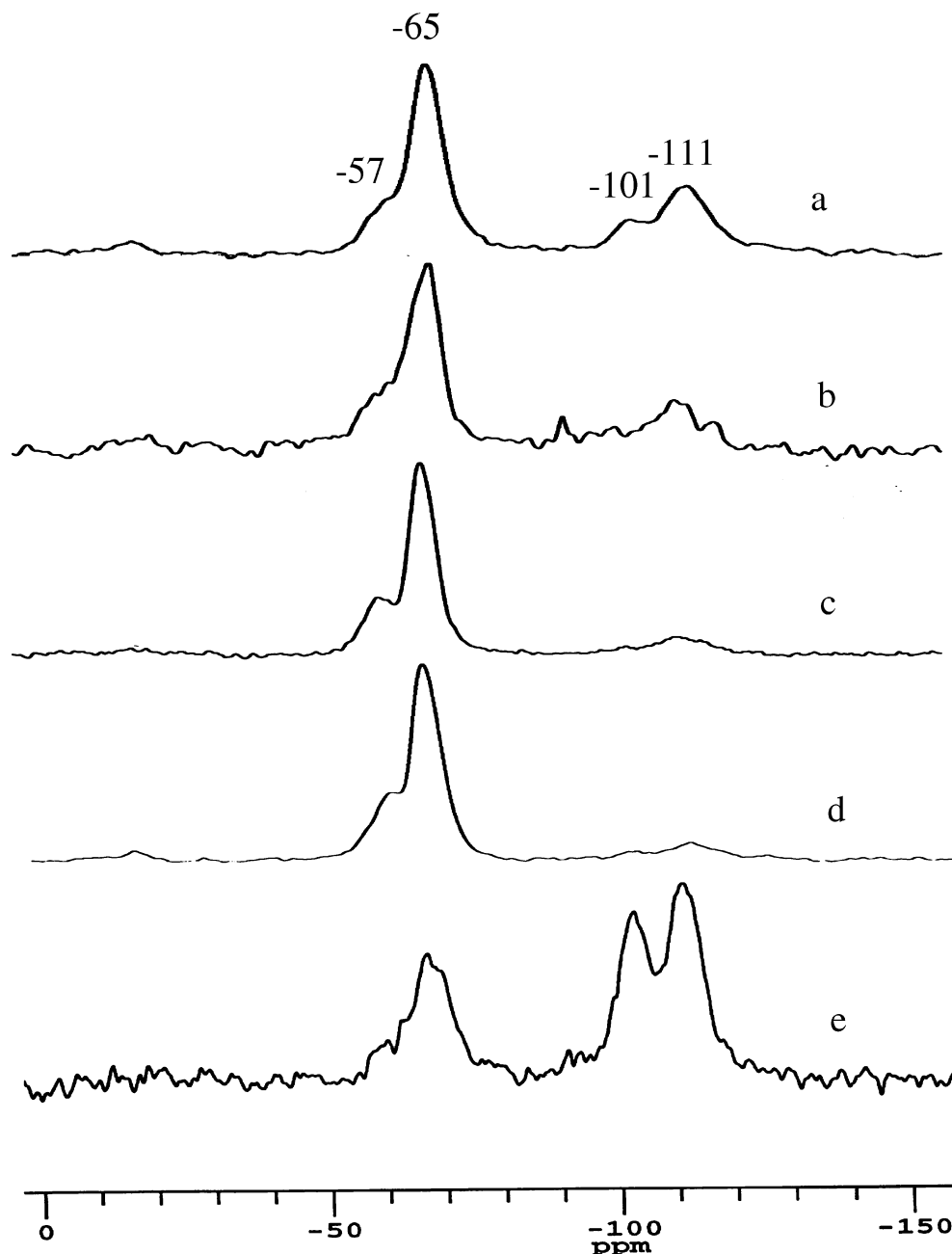


Figure 4. ^{29}Si MAS NMR spectra of as-extracted HS-JLU-20 samples: (a) HS-JLU-20-0.50; (b) HS-JLU-20-0.60; (c) HS-JLU-20-0.70; (d) HS-JLU-20-0.80; (e) HS-SBA-15-0.20.

estimated to be 85 Å, in good agreement with the value determined from XRD. More interestingly, HS-JLU-20-0.8 (Figure 3c and d) still exhibits a good mesostructure when the sample has an extremely high content (80%) of organic groups.

Figure 4 shows ^{29}Si MAS NMR spectra of as-extracted HS-JLU-20 and HS-SBA-15 samples, giving two group peaks at -100 to -120 ppm and -55 to -80 ppm, which are typically attributed to siloxane [Q^n , $\text{Si}(\text{OSi})_n(\text{OH})_{4-n}$, $n = 1-4$] and organosiloxane [T^m , $\text{RSi}(\text{OSi})_m(\text{OH})_{3-m}$, $m = 1-3$] species in the mesoporous walls, respectively. Notably, the signals assigned to T groups (T^2 and T^3) are much stronger than those assigned to Q groups (Q^3 and Q^4) in HS-JLU-20 samples, indicating that organic mercapto groups have been efficiently introduced into the walls of mesoporous materials. Furthermore, the signals assigned to Q groups stepwise decrease with increasing organic mercapto groups in the starting synthetic gels, and only a very small amount of Q^n species is observed in the HS-JLU-20-0.80 sample, which demonstrates that the content of organic mercapto

groups in HS-JLU-20 samples increases with the organic groups in the starting synthetic gels. Moreover, the ratios of $\Sigma \text{T}^m / \Sigma (\text{T}^m + \text{Q}^n)$ estimated from ^{29}Si MAS NMR spectra (Figure 4) of HS-JLU-20 samples are 0.68, 0.81, 0.89, and 0.91, which are in good agreement with the content of organic groups in starting synthetic gels (Table 1). As compared with HS-JLU-20 samples, HS-SBA-15-0.20 shows relatively weak signals associated with T^m species (Figure 4e and Table 1), indicating the low concentration of organic groups in the mesoporous walls.¹⁴ From the elemental analysis for C, H, and S over as-extracted HS-JLU-20 and HS-SBA-15 samples (Supporting Information Table 1), we can see that the sulfur contents in the mesoporous materials are basically consistent with those in the starting synthetic gels, confirming the extremely high concentration of organic groups in the mesoporous walls.

The synthesis of HS-JLU-20 samples with an extremely high content of organic groups should be directly attributed to the use of fluorocarbon surfactant rather than other synthetic

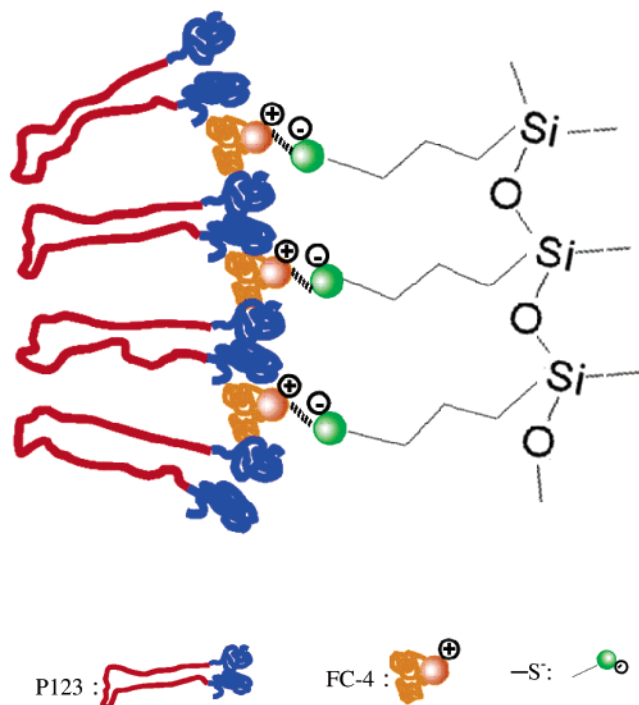


Figure 5. Proposed scheme for synthesis of HS-JLU-20 with an extremely high content of mercaptopropyl groups.

parameters, because all parameters between HS-JLU-20 and HS-SBA-15 in the synthesis are the same except for the use of fluorocarbon surfactant. Therefore, it is proposed that the use of fluorocarbon surfactant in the synthesis plays an important role for the formation of mesoporous silica materials with an extremely high content of organic mercapto groups. Possibly, fluorocarbon surfactant containing N^+ species with a positive charge could effectively interact with negatively charged mercapto groups in the synthesis of HS-JLU-20 materials,²⁷ resulting in the formation of mesoporous silica materials with good cross-linking of silica condensation even at an extremely high content of organic mercapto groups (Figure 5). As observed in Table 1 and Figure 2, the decrease of the pore size from about 39 to 17 Å in HS-JLU-20 samples with an increase in the ratio of MPTS/(MPTS + TEOS) from 0.50 to 0.80 in the synthetic gels supports the interaction between fluorocarbon surfactant and mercapto groups. To further prove this idea, a silica source containing negatively charged $-\text{COOH}$ (11-triethoxysilanylundecanoic acid ethyl ester) and a silica source containing a neutral organic group of $-\text{NH}_2$ (3-aminopropyl triethoxysilane) are used to assemble with a mixture of fluorocarbon surfactant and triblock polymer, and the obtained results show that ordered mesoporous samples of HOOC-JLU-20 have an extremely high content of $-\text{COOH}$ groups (Figure 6a–d). In contrast, it is very difficult to synthesize NH_2 -JLU-20 samples with a high content of aminopropyl groups (Figure 6e).

After the treatment of mesoporous silicas with mercapto groups by hydrogen peroxide, mesoporous silicas with sulfonic groups are formed.¹³ Figure 7 shows XRD patterns of HS-JLU-20 samples treated by hydrogen peroxide (HSO_3 -JLU-20), giving clear peaks associated with characteristic mesostructures. These results indicate that HSO_3 -JLU-20 samples with an extremely high content of sulfonic groups basically keep their mesostructures even after the treatment of hydrogen peroxide. The TGA analyses (Supporting Information Figure 1) show that the as-extracted sample HS-JLU-20-0.5 decomposed with a peak centered at 350 °C while HSO_3 -JLU-20-0.5 decomposed with

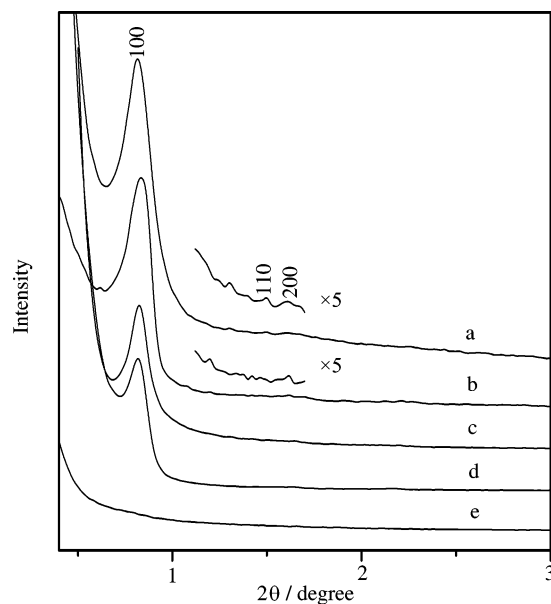


Figure 6. XRD patterns of as-extracted HOOC-JLU-20 samples: (a) HOOC-JLU-20-0.50; (b) HOOC-JLU-20-0.60; (c) HOOC-JLU-20-0.70; (d) HOOC-JLU-20-0.80; (e) NH_2 -JLU-20-0.50.

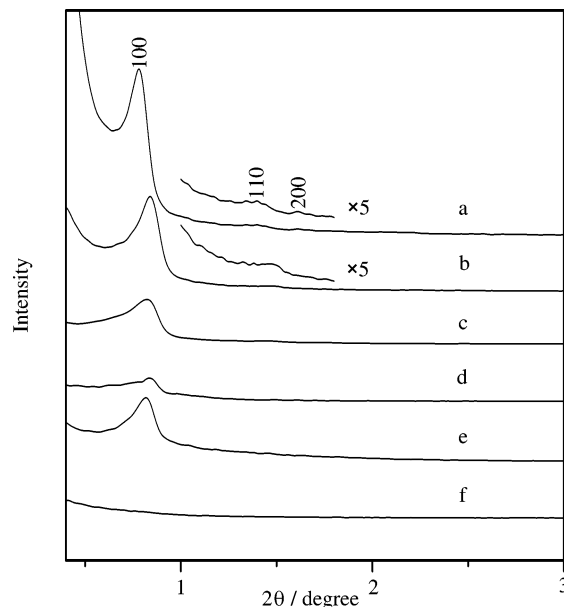


Figure 7. XRD patterns of HS-JLU-20 and HS-SBA-15 samples treated with H_2O_2 (HSO_3 -JLU-20 samples): (a) HSO_3 -JLU-20-0.50; (b) HSO_3 -JLU-20-0.60; (c) HSO_3 -JLU-20-0.70; (d) HSO_3 -JLU-20-0.80; (e) HSO_3 -SBA-15-0.20; (f) HSO_3 -SBA-15-0.50.

a peak centered at 405 °C, which indicates that the catalysts have a relatively good thermal stability.

As a model reaction, catalytic esterification of cyclohexanol with acetic acid over various sulfonic-functionalized mesoporous silicas was carried out. The measurement of the products shows that the cyclohexyl acetate is the only product for this reaction. Notably, from Table 2, we can see that the concentrated sulfuric acid exhibits the conversion at 96.5%, and HSO_3 -SBA-15-0.20 gives the conversion at 41.1%. Interestingly, HSO_3 -JLU-20 samples show much higher catalytic activities than that of HSO_3 -SBA-15-0.20. From the HSO_3 -JLU-20-0.5 with an activity of 77.5% to the HSO_3 -JLU-20-0.8 with an activity of 92.5%, the activities are significantly increased with the concentration of sulfonic groups in HSO_3 -JLU-20 samples. Particularly, HSO_3 -JLU-20-0.80 exhibits the conversion at 92.5%, which is almost

TABLE 2: Catalytic Esterification of Cyclohexanol with Acetic Acid over HSO₃-SBA-15, HSO₃-JLU-20, and Concentrated Sulfuric Acid

sample	conversion (%)
HSO ₃ -SBA-15-0.20	41.1
HSO ₃ -JLU-20-0.50	77.5
HSO ₃ -JLU-20-0.60	79.1
HSO ₃ -JLU-20-0.70	84.1
HSO ₃ -JLU-20-0.80	92.5
concentrated sulfuric acid	96.5

the same as that of concentrated sulfuric acid (96.5%). Considering the advantages for solid acidic catalysts such as recycle and avoidance of cauterization for chemical reactor, solid acidic catalysts of HSO₃-JLU-20 samples with an extremely high concentration of sulfonic groups would be potentially important for industrial reactions catalyzed by liquid acids.

It is worth mentioning that the synthesis of mesoporous silica materials with an extremely high content of organic sulfonic groups is not limited to the use of a surfactant mixture of P123 and FC-4, and many surfactant mixtures of polymer and fluorocarbon compounds such as F127 and FC-4²⁹ might be useful. It is believed that the strategy developed here provides a unique, effective, and potentially general approach for synthesis of mesoporous silica materials with an extremely high content of organic sulfonic groups.

4. Conclusions

Mesoporous materials with an extremely high content of mercaptopropyl groups have been successfully synthesized from a simple co-condensation approach of tetraethyl orthosilicate (TEOS) and (3-mercaptopropyl)trimethoxysilane (MPTS) using a fluorocarbon-hydrocarbon surfactant mixture as a template. After the treatment with hydrogen peroxide, HSO₃-JLU-20 materials with an extremely high content of organic sulfonic groups exhibit comparable activities with liquid concentrated sulfuric acid in the catalytic esterification of cyclohexanol with acetic acid, which would be potentially important for industrial reactions catalyzed by liquid acids.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (20233030, 20373018, 20573044), State Basic Research Project of China (2004CB217804 and 2003CB615802), and the Ministry of Education, China.

Supporting Information Available: Table showing the CHNS elemental analysis data of as-extracted HS-JLU-20 and HS-SBA-15 samples and figure showing TGA measurements of (A) as-extracted sample HS-JLU-20-0.5 and (B) HSO₃-JLU-20-0.5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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