Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Catalysis 228 (2004) 265–272

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Synthesis, characterization, and catalytic activity of sulfonic acid-functionalized periodic mesoporous organosilicas

Qihua Yang [a,*], Jian Liu [a], Jie Yang [a], Mahendra P. Kapoor [b], Shinji Inagaki [b], Can Li [a]

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*
[b] *Toyota Central R&D Laboratories, Inc., Nagakute, Aichi 480-1192, Japan*

Received 26 May 2004; revised 27 August 2004; accepted 3 September 2004

Abstract

Sulfonic acid-functionalized periodic mesoporous organosilicas were synthesized directly by cocondensation of $(R'O)_3Si–R–Si(OR')_3$ ($R = CH_2CH_2$ and C_6H_4; $R' = CH_3$ and C_2H_5) with 3-mercaptopropyltrimethoxysilane $(MeO)_3SiCH_2CH_2CH_2SH$ in the presence of H_2O_2 using nonionic oligomeric polymer surfactant $C_{18}H_{37}(OCH_2CH_2)_{10}OH$ in acidic medium. The sulfonic acid functionalities ($–SO_3H$) were generated in situ by oxidation of the propylthiol using H_2O_2 as oxidant during the synthesis process. Powder X-ray diffraction patterns and nitrogen sorption indicate the formation of well-ordered mesoporous material with uniform porosity. The highest acid-exchange capacity (acid–base titration methods) was 1.72 H^+ mmol/g. Complete oxidation of –SH to $–SO_3H$ was observed as evidenced by X-ray photoelectron spectroscopy. For comparison, the sulfonic acid-functionalized mesoporous organosilicas were also prepared by a grafting method. The catalytic properties of the materials were investigated in liquid-phase condensation of phenol with acetone to form Bisphenol A. All sulfonic acid-functionalized mesoporous organosilicas show high catalytic activity. The highest TOF obtained for the mesoporous organosilica is 17.2.

Keywords: Sulfonic acid; Mesoporous bifunctional organosilica; Ethane bridged; Phenylene bridged; Bisphenol A

---

1. Introduction

The periodic mesoporous organosilicas (PMOs) attracted much attention and were recognized as potential candidates for applications in catalysis, enantioselective separation, chromatography, and sensing. PMOs synthesized from bridged organosilane precursors, $(R'O)_3Si–R–Si(OR')_3$, have uniformly distributed organic moiety in the framework. To date, only a limited number of organic moieties have been incorporated in the PMOs framework such as ethane, ethylene, benzene, biphenylene, and thiophene [1–5]. A versatile approach for the functionalization of PMOs is the development of bifunctionalized PMOs by cocondensation of trialkoxyorganosilanes with bridged silsesquioxane precursor in the presence of the surfactant. Ozin and co-workers [6] reported bifunctionalized periodic mesoporous organosilicas (BPMOs) having bridging ethyl groups in the walls and vinyl groups protruding into the channels. Later, a series of organic functionalities such as amine, thiol, diamine, imidazole, pyridine, benzyl, and phenethyl were incorporated into the channel of mesoporous organosilicas with the bridging ethyl groups in the framework [7]. In all reports basic medium along with cationic surfactant was employed. Markowitz and co-workers tried the synthesis of BPMOs in acidic medium using cetyltrimethylammonium chloride as surfactants [8]. Unfortunately, they could not succeed in getting the mesoporous structures. Still the study demonstrated that larger amounts of functional groups could be incorporated into the mesoporous organosilicas in acidic medium. The synthesis of ordered mesoporous material with high concentrations of functional groups is very important for applications. Recently, nonionic oligomeric surfactants were also successfully used for the synthesis of PMOs in acidic

---

[*] Corresponding author. Fax: +86 411 4694447.
E-mail address: yangqh@dicp.ac.cn (Q. Yang).

0021-9517/$ – see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2004.09.007

medium [9,10]; however, these surfactants have not yet been employed for the synthesis of BPMOs.

Sulfonic acid-functionalized mesoporous silicas have been successfully applied in a number of acid-catalyzed reactions, such as esterification and condensation [11–13]. Introducing sulfonic acid groups to PMOs is interesting since the surface properties (hydrophobicity/hydrophilicity) of PMOs can be modified by simply varying the nature of the bridging organic group in the framework. Recently, we have reported the sulfonic acid-functionalized mesoporous organosilicas by cocondensation of phenyl-bridged precursor $[(EtO)_3Si–C_6H_4–Si(OEt)_3]$ and 3-mercaptopropyltrimethoxysilane [MPTMS: $(MeO)_3Si–CH_2CH_2CH_2SH$] in the presence of octadecyltrimethylammonium chloride [C_{18}TMACl] surfactant followed by postsynthesis oxidation of –SH to $–SO_3H$ using concentrated HNO_3 as oxidant [14]. The postsynthesis oxidation method always leads to incomplete oxidation of –SH [15] and also the oxidation process using HNO_3 as oxidant is vigorous and accompanied by the generation of NO_2. In situ generation of $–SO_3H$ groups using H_2O_2 as oxidant in acidic medium was also reported [16].

Here, we report the direct synthesis of the sulfonic acid-functionalized mesoporous organosilicas with high concentrations of $–SO_3H$ functionalities by cocondensation of ethane- or benzene-bridged organosilane with 3-mercaptopropyltrimethoxysilane in the presence of H_2O_2 using nonionic oligomeric polymer surfactant (Brij-76) in acidic medium. The catalytic activity of these sulfonic acid-functionalized mesoporous organosilicas was tested for the liquid-phase condensation of phenol with acetone to form Bisphenol A, which is a very important raw material for synthesis of resins and polymers. In the industrial process, ion-exchanged resins are used as catalysts for the synthesis of Bisphenol A. However the thermal stability of resins is limited. The search for effective solid acids with high thermal stability continues. It was found that the sulfonic acid-functionalized mesoporous organosilicas synthesized in this work show high catalytic activity and stability. It was shown by others [17,18] that PMOs exhibit very good mechanical and hydrothermal stability. These new materials could serve as solid acid catalysts with potential in many acid-catalyzed reactions.

2. Experimental

2.1. Chemicals and reagents

All materials were analytical grade and used as purchased without further purification. 3-Mercaptopropyltrimethoxysilane, $C_{18}H_{37}(OCH_2CH_2)_{10}OH$ [Brij-76], and 1,2-bis(trimethoxysilyl)ethane [BTME] were purchased from Sigma-Aldrich Company Ltd. (USA). 1,4-Bis(triethoxysilyl)benzene [BTEB] was synthesized according to the literature [19].

2.2. Synthesis of sulfonic acid-functionalized mesoporous organosilicas

2.2.1. Direct synthesis of sulfonic acid-functionalized ethane silica (EPMO)

Brij-76 (1.0 g) was dissolved in HCl solution (16 g, 2 M) at 50 °C under vigorous stirring. A mixture of BTME (3.5 mmol) and MPTMS (1.5 mmol) was added to the above solution, followed by slow addition of H_2O_2 (8 g). The reaction mixture was kept stirring at 50 °C for 24 h. After filtration, the white precipitate was recovered by filtration followed by thoroughly washing with deionized water. The solid was dried at room temperature. The surfactant was extracted by refluxing 0.5 g of as-synthesized material in 200 ml ethanol for 12 h. The sulfur contents of the sample are listed in Table 2.

2.2.2. Direct synthesis of sulfonic acid-functionalized benzene silica

The synthesis procedure was similar to that described above. A mixture of BTEB (3.5 mmol) and MPTMS (1.5 mmol) was used along with 0.8 g Brij-76. The sulfur contents of the sample are listed in Table 2.

2.2.3. Preparation of sulfonic acid-functionalized organosilicas by grafting

In a typical grafting procedure, MPTMS (2 mL) was added dropwise into the previously dispersed mesoporous benzene silica [3] or ethane silica [1] mesoporous material (1.28 g) in chloroform (100 mL). The suspension was stirred at room temperature for 5 consecutive days. The thiol-functionalized mesoporous organosilica material obtained after filtration was washed with copious amounts of chloroform and dried at room temperature. The transformation of –SH to $–SO_3H$ was accomplished by treatment of thiol-functionalized ethane silica and benzene silica with 65 wt% HNO_3 [14] to give GEPMO and GBPMO, respectively. The sulfur contents of the samples are listed in Table 2.

2.3. Catalytic experiment

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

2.4. Characterization

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/Max 3400 powder diffraction system using

Cu$K\alpha$ radiation. The nitrogen sorption experiments were performed at 77 K on an ASAP 2000 system. The samples were evacuated at 100 °C for 10 h prior to the measurement. BET surface area was calculated from adsorption data in the relative pressure range from 0.01 to 0.3. Pore diameters were determined from adsorption branches using the Barret–Joyner–Halenda (BJH) method. The solid-state NMR spectra were obtained with a Bruker DRX 400 spectrometer equipped with a magic-angle spin probe using a 4-mm ZrO_2 rotor. ^{13}C (100.6 MHz) cross-polarization magic-angle spinning (CP-MAS) spectra were measured under experimental conditions of 5-ms contact time, 3-s pulse delay, and 7.0 kHz spin rate. X-ray photoelectron spectra (XPS) were measured on VG ESCALAB MK-2 X-ray spectrometer equipped with a hemispherical electron analyzer and an Al anode X-ray exciting source (Al$K\alpha$ energy $= 1486.6$ eV). Binding energies were corrected for charge effects by referencing to the C1s peak at 284.6 eV. Thermal gravimetric analysis (TGA) was performed with Perkin–Elmer Pyris Diamond TG analyzer under nitrogen atmosphere with a heating rate of 10 °C/min. The acid-exchange capacity was determined by titration with NaOH. In a typical procedure, 0.1 g of solid was suspended in 20 g of 2 M aqueous NaCl solution. The resulting suspension was stirred at room temperature for 24 h until equilibrium was reached and potentiometrically titrated by dropwise addition of 0.1 M NaOH.

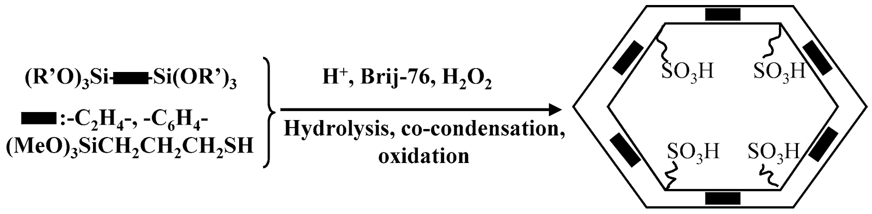
3. Results and discussion

3.1. Preparation of sulfonic acid-functionalized mesoporous organosilicas

Non-ionic oligomeric alkylethylene oxide surfactants are useful because of their high interfacial stability. They are nontoxic, biodegradable, and inexpensive. Their effective use in the synthesis of mesoporous ethane silicas with well-ordered hexagonal structures was already demonstrated [9,10]. In the present study non-ionic oligomeric alkylethylene oxide surfactants [Brij-76] in acidic medium in combination with in situ generation of $–SO_3H$ groups were investigated. The hydrolysis and condensation of the organosilane precursor in the presence of H_2O_2 enable the formation of highly ordered mesoporous EPMO and BPMO with high concentrations of $–SO_3H$ functionalities (Scheme 1). The structural, textural, and compositional information including the titration results of both sulfonic acid-functionalized mesoporous organosilicas are listed in Table 1. The results on sulfonic acid-functionalized mesoporous organosilicas synthesized using grafting are also included.

3.2. Mesostructure and porosity

Powder X-ray diffraction patterns of surfactant-free sulfonic acid-functionalized benzene silica display three reflection peaks, indicating the formation of a well-ordered two-dimensional hexagonal structure (Fig. 1a). A very small and broad peak centered around 12° 2θ with a d spacing of 0.76 nm was also observed, suggesting the existence of some periodicity in the pore walls. Similar pore wall periodicity reported previously [3,14] was attributed to the organization of benzene moiety bridged in the mesoporous framework in basic medium. However, the extent of periodicity observed in the case of BPMO synthesized under acidic medium is lower than that in similar materials synthesized under basic conditions. A similar tendency of the periodicity was also observed for the relatively large-pore benzene-bridged mesoporous organosilicas synthesized with triblock copolymer surfactants in



Scheme 1. Direct synthesis of sulfonic acid-functionalized mesoporous organosilicas.

Table 1
Structural, textural, and compositional information of sulfonic acid-functionalized organosilicas

Sample	d_{100} (nm)	BET surface area (m^2/g)	Pore diameter (nm)[a]	Total pore volume (cm^3/g)	a_0 (nm)[b]	Wall thickness (nm)[c]
EPMO	6.05	1401	3.10	1.11	6.99	3.89
BPMO	5.77	1056	3.50	0.88	6.66	3.16
GEPMO	5.10	756	2.39	0.52	5.89	3.50
GBPMO	4.69	665	2.10	0.41	5.41	3.31

[a] Pore diameter was calculated from adsorption branch.
[b] $a_0 = 2d_{100}/\sqrt{3}$.
[c] Wall thickness $= a_0$-pore size.

Table 2
Comparison of sulfur content in organosilicas prepared by a cocondensation method and a grafting method

Sample	Initial mole percent of MPTMS (mol%)	S content (wt%)[a]
EPMO	30	5.5
BPMO	30	3.3
GEPMO	–	2.6
GBPMO	–	2.8

[a] Sulfur contents were obtained by elemental analysis.

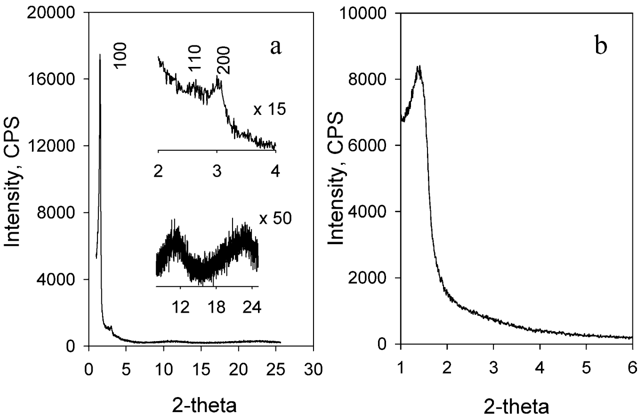


Fig. 1. XRD patterns of surfactant-free sulfonic acid-functionalized organosilicas synthesized in acidic medium in the presence of H_2O_2: (a) BPMO; (b) EPMO.

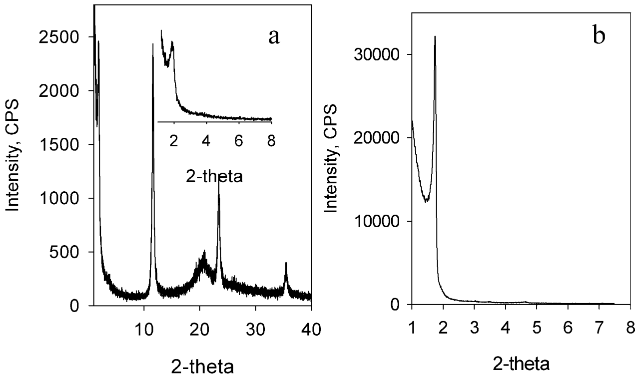


Fig. 2. XRD patterns of sulfonic acid-functionalized organosilicas prepared by grafting (a) GBPMO; (b) GEPMO.

acidic medium [20]. The X-ray patterns of ethane-bridged organosilicas (EPMO) clearly exhibit one diffraction peak indicating that the material has an ordered mesostructure (Fig. 1b).

The X-ray diffraction pattern of GBPMO (Fig. 2a) resembles the parent mesoporous benzene silica reported elsewhere [3] that was prepared under basic conditions. In addition to a peak in the lower angle diffraction regime ($2\theta < 10°$), three additional peaks at 12, 23, and 35° 2θ (with d spacings of 0.76, 0.38, and 0.25 nm) also appeared in the medium-angle diffraction regime ($10 < 2\theta < 40$). These peaks are assigned to a periodic arrangement of hydrophobic benzene layers and hydrophilic silica layers within the pore walls. It is noteworthy that the additional broad reflection at 20° 2θ ($d = 0.42$ nm), that was also observed in the original mesoporous benzene silica is not due to any contamination of the amorphous materials but due to the amorphous nature of atomic arrangements of Si and O in the silica layers of the benzene silica materials. The XRD pattern of GEPMO (Fig. 2b) is almost similar to that reported for the mesoporous ethane silica.

The nitrogen adsorption isotherms of sulfonic acid-functionalized organosilicas (BPMO and EPMO) were of type IV with a typical capillary condensation step in the relative pressure (P/P_0) range of 0.3–0.5 (Fig. 3). This indicates that both BPMO and EPMO possess well-defined mesoporous structures and relatively narrow pore-size distributions. Similar type IV isotherms were also observed for GEPMO and GBPMO, indicating that the mesostructures survived both the grafting and the oxidation process. It is worth noting that EPMO and BPMO synthesized directly in acidic medium show higher BET surface areas and larger pore diameters than the samples prepared by grafting (Table 1).

3.3. Compositional and structural information in the framework

Four resonances were observed in ^{13}C CP MAS NMR spectrum of EPMO (Fig. 4). The resonance at 5.9 ppm is due to the C species of ethane moiety [1] while the resonance at 12.5, 19.1 and 54.6 ppm are assigned to ^1C, ^2C, and ^3C carbon species of $\equiv Si–{}^1CH_2{}^2CH_2{}^3CH_2–SO_3H$, respectively (Fig. 4a) [16]. The ^{13}C NMR spectrum of BPMO displays the signal of benzene moiety at 133.2 ppm [3]. Signals coming from the propylsulfonic acid moiety appeared at 13.0 (^1C), 18.9 (^2C), and 54.8 (^3C) ppm [14]. The signal at 30.4 ppm may be due to the residue surfactant (Fig. 4b). ^{13}C CP MAS NMR spectra of both GEPMO and GBPMO synthesized by grafting method are shown in Fig. 5. For GBPMO, the signals of carbon species of $\equiv Si–{}^1CH_2{}^2CH_2{}^3CH_2–SO_3H$ and -Ph- were clearly observed with almost the same chemical shift as that of BPMO. For GEPMO; the signals of ^2C and ^3C of $\equiv Si–{}^1CH_2{}^2CH_2{}^3CH_2–SO_3H$ appeared at 19.1 and 54.6 ppm, respectively. The broad peak centered at 5.9 ppm masks the ^1C carbon of $\equiv Si–{}^1CH_2{}^2\mathit{C}H_2{}^3CH_2–SO_3H$ and carbon of the $–\mathit{C}H_2\mathit{C}H_2–$moiety. ^{13}C CP MAS NMR results clearly demonstrate the integrity of propylsulfonic acid functionality on the mesoporous organosilicas synthesized by both the cocondensation method and the grafting method.

X-ray photoelectron spectroscopy analyses of surfactant-free BPMO and EPMO are shown in Fig. 6. S2p binding energy was found to be 169.2 and 169.3 eV for BPMO and EPMO, respectively. This binding energy was attributed to the oxidized sulfur ($–SO_3H$) [21]. No S2p binding energy at 164 eV (corresponding to –SH) was observed, further confirming the complete oxidation of –SH to $–SO_3H$. The O1s

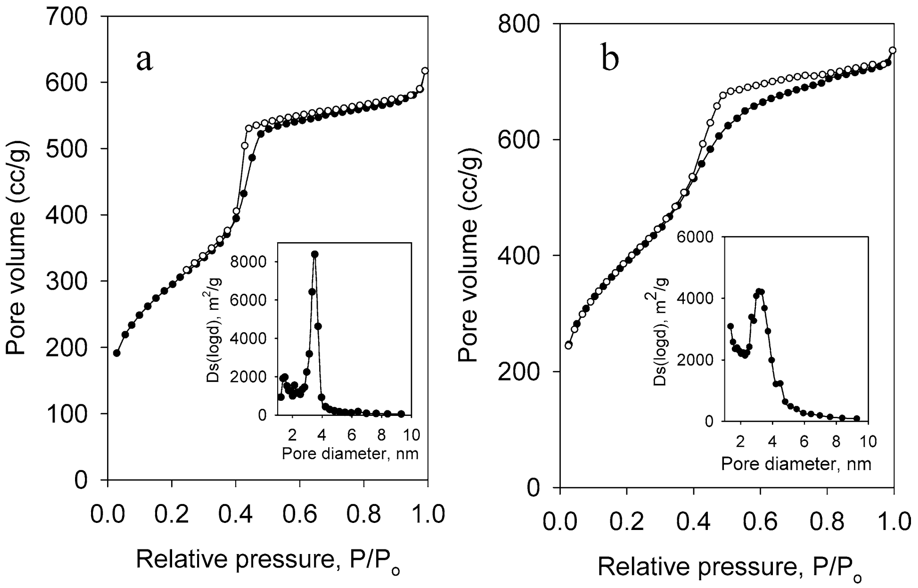


Fig. 3. Nitrogen sorption isotherms of surfactant free sulfonic acid-functionalized organosilicas synthesized in acidic medium in the presence of H_2O_2: (a) BPMO; (b) EPMO.

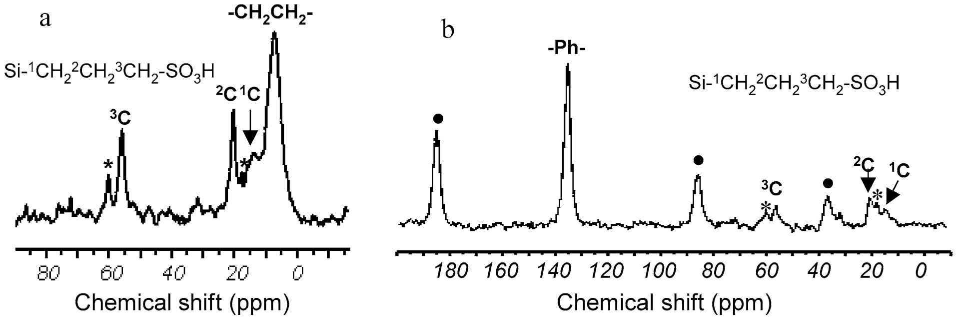


Fig. 4. ^{13}C CP MAS NMR spectra of surfactant-free sulfonic acid-functionalized organosilicas synthesized in acidic medium in the presence of H_2O_2. ∗ Refers to –OCH_2CH_3 formed during the surfactant removal process; ● refers to spinning side band: (a) EPMO; (b) BPMO.

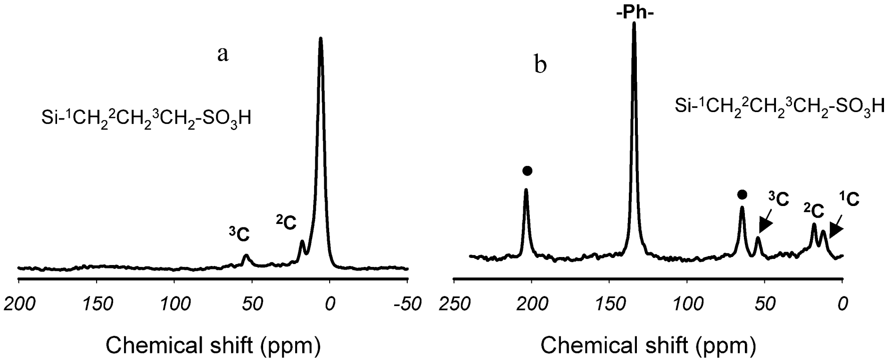


Fig. 5. ^{13}C CP MAS NMR spectra of sulfonic acid-functionalized organosilicas synthesized by grafting method. ● Refers to the side band: (a) GEPMO; (b) GBPMO.

binding energy was found at 532.3 eV for both BPMO and EPMO while the Si2p biding energy at 102.7 eV for BPMO and 102.8 eV for EPMO was obtained from an overlap of Si2p$_{3/2}$ and Si2p$_{1/2}$ binding energy. XPS results imply that the oxidation during the synthesis process lead to complete oxidation of –SH to –SO_3H.

3.4. Thermogravimetric properties

Thermogravimetric analysis of sulfonic acid-functionalized mesoporous organosilicas was conducted from 30 to 900 °C under nitrogen atmosphere (Fig. 7). A weight loss below 120 °C was observed for all materials, which is due

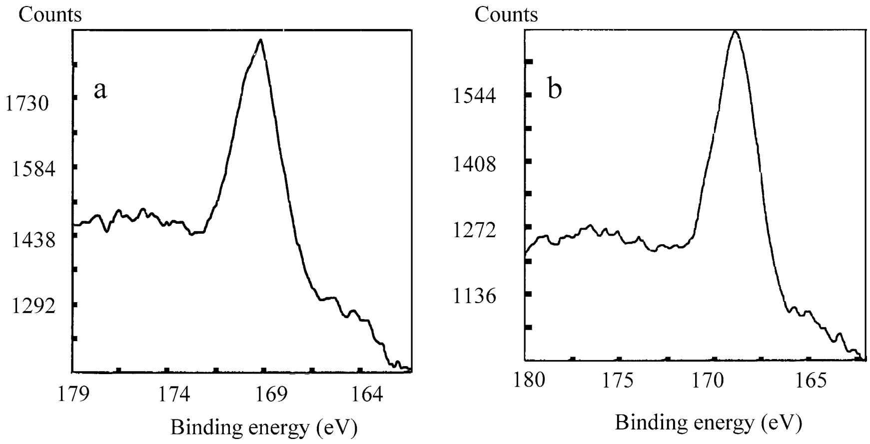


Fig. 6. S2p XPS binding energy peak of sulfonic acid-functionalized organosilicas synthesized in acidic medium in the presence of H_2O_2: (a) EPMO; (b) BPMO.

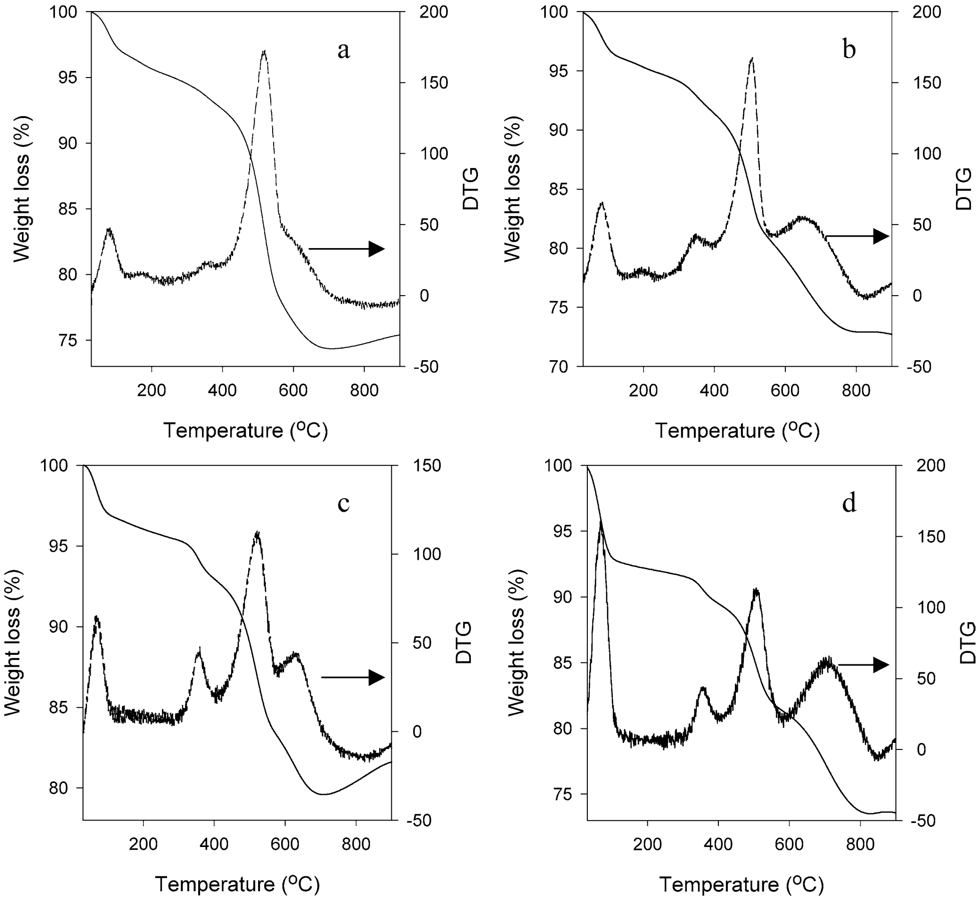
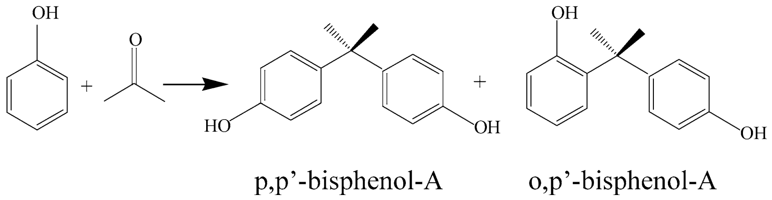


Fig. 7. Representative thermogravimetric weight loss curves for sulfonic acid-functionalized organosilicas under nitrogen flow: (a) EPMO; (b) BPMO; (c) GEPMO; (d) GBPMO.

to the removal of the physisorbed water. Minor weight loss in the range of 120 to 210 °C was observed for EPMO and BPMO synthesized by cocondensation. This weight loss could be assigned to the decomposition of the surfactant residue. No weight loss in this range was found for GEPMO and GBPMO synthesized by a grafting method, indicating complete removal of the surfactant in these materials. The decomposition of propylsulfonic acid functionality occurred at 380 °C for all materials [16]. The weight loss in the range of 400–800 °C is due to the decomposition of the propylsulfonic acid residue and the bridged organic moiety. Thermogravimetric analysis results reveal that the sulfonic acid-functionalized mesoporous organosilicas are stable up to 380 °C in a nitrogen flow atmosphere.



Scheme 2. Condensation of phenol with acetone to form Bisphenol A.

3.5. *Catalytic condensation of phenol with acetone to form Bisphenol A*

To evaluate the catalytic properties of sulfonic acid-functionalized mesoporous organosilicas and to investigate the influence of the bridging ethane or benzene moieties, the condensation of phenol with acetone to form Bisphenol A was performed (Scheme 2). The effect of the preparation method on the catalytic properties was evaluated by comparing sulfonic acid-functionalized mesoporous organosilicas synthesized by cocondensation and grafting. All sulfonic acid-functionalized mesoporous organosilicas were efficient catalysts for the condensation of phenol with acetone (Table 3). The active site for the reaction is the –SO_3H group. The surface area and average pore diameter of the materials may also cause the different catalytic activity. Therefore the acidity of the materials was normalized with the surface area (Table 3). From the TOF, it can be seen that the samples (GEPMO and GBPMO) prepared by grafting exhibit higher catalytic activity than samples (EPMO and BPMO) synthesized by cocondensation in acidic medium. The acidity of the materials based on surface area is in the range of 0.9×10^{-3} to 1.4×10^{-3} mmol H^+/m^2, which cannot explain the significant difference of activities. The diffusion of the reactants and products during the reaction process may be one of the main reasons for different activities of the materials. The functionalities introduced to the mesoporous material by grafting always lead to irregularly distributed functionalities, and thus most of the functionalities are distributed on the surface or near the pore mouth of the mesoporous material [22]. The higher catalytic activity of GEPMO and GBPMO may be due to the fact that sulfonic acid sites on the surface or near the pore mouth are easily accessible for the reactants in the catalytic reactions. In contrast, mesoporous organosilicas synthesized by cocondensation have uniformly distributed sulfonic acid sites. In addition it might be that the reactants cannot reach some of the sulfonic acid sites buried in the wall of the materials synthesized by cocondensation.

The catalytic activity of sulfonic acid-functionalized mesoporous organosilicas also differs with different bridging organic moieties in the framework. The activity of GEPMO was higher than that of GBPMO and the same tendency was observed for organosilicas synthesized by a direct cocondensation method in acidic medium. One of the reasons for the observed trend that ethylene-bridged PMO showed higher catalytic activity than the phenyl-bridged PMO is the larger specific surface areas and average pore diameters of the former.

Table 3
Acidity and catalytic properties of sulfonic acid-functionalized mesoporous organosilicas in the catalytic condensation of phenol with acetone to form Bisphenol A[a]

Sample	Acidity (mmol H^+/g)	Acidity (mmol H^+/m^2)	TOF[b]	$p,p'/o,p'$ molar ratio
EPMO	1.72	1.3×10^{-3}	4.6	3.1
BPMO	0.93	0.9×10^{-3}	2.7	3.4
GEPMO	0.80	1.1×10^{-3}	17.2	3.5
GBPMO	0.90	1.4×10^{-3}	7.6	3.2
SBA-propyl-SO_3H[12]	–	–	8.8	10.0

[a] 70 mmol, phenol; 10 mmol, acetone; 70 mg, catalyst; reaction temperature, 85 °C; reaction time, 24 h.

[b] TOF is based on mmol of Bisphenol A/mmol of active site.

A SBA-15 material functionalized with propylsulfonic groups was tested for the same reaction by others [12]. The preparation involved the grafting of MPTMS on purely siliceous SBA-15 followed by oxidation of the thiol group with H_2O_2. A TOF of 8.8 was obtained with this material (Table 3). It is worth noting that only two structural isomers of Bisphenol A were formed. No other by-products such as chroman and trisphenol were detected. For most of the sulfonic acid-functionalized organosilicas, the ratio of *p,p'*-Bisphenol A to *o,p'*-Bisphenol A was around 3 that is substantially lower than the ratio for SBA-propyl-SO_3H.

4. Conclusion

Sulfonic acid-functionalized periodic mesoporous organosilicas with well-ordered mesoporous structure were synthesized directly by cocondensation of ethane- or benzene-bridged silsesquioxanes precursors with MPTMS in acidic medium in the presence of H_2O_2. The complete oxidation of –SH to –SO_3H was achieved with this in situ oxidation method. The highest acidity of the mesoporous organosilicas synthesized by this direct method is 1.72 H^+ mmol/g. These sulfonic acid-functionalized organosilicas are efficient catalysts for the condensation reaction of phenol with acetone to form Bisphenol A. Ethane-bridged mesoporous organosilicas exhibit higher catalytic activity than benzene-bridged organosilicas.

Acknowledgments

Financial support of this work was provided by the National Science Foundation of China (20303020), National Basic Research Program of China (2003CB615803), and Talent Science Program of the Chinese Academy of Sciences.

References

[1] S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, O. Terasaki, J. Am. Chem. Soc. 121 (1999) 9611.

[2] T. Asefa, M.J. MacLachlan, N. Coombs, G.A. Ozin, Nature 402 (1999) 867.

[3] S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, Nature 416 (2002) 304.

[4] B.J. Melde, B.T. Holland, C.F. Blanford, A. Stein, Chem. Mater. 11 (1999) 3302.

[5] C. Yoshina-Ishii, T. Asefa, N. Coombs, M.J.G. MacLachlan, A. Ozin, Chem. Commun. (1999) 2539.

[6] T. Asefa, M. Kruk, M.J. MacLachlan, N. Coombs, H. Grondey, M. Jaroniec, G.A. Ozin, J. Am. Chem. Soc. 123 (2001) 8520.

[7] M.C. Burleigh, M.A. Markowitz, M.S. Spector, B.P. Gaber, J. Phys. Chem. B 105 (2001) 9935.

[8] M.C. Burleigh, M.A. Markowitz, M.S. Spector, B.P. Gaber, Langmuir 17 (2001) 7923.

[9] S. Hamoudi, S. Kaliaguine, Chem. Commun. (2002) 2118.

[10] A. Sayari, Y. Yang, Chem. Commun. (2002) 2582.

[11] D. Das, J.F. Lee, S. Cheng, Chem. Commun. (2001) 2178.

[12] V. Dufaud, M.E. Davis, J. Am. Chem. Soc. 125 (2003) 9403.

[13] I. Díaz, C. Márquez-Alvarez, F. Mohino, J. Pérez-Pariente, E. Sastre, J. Catal. 193 (2000) 295.

[14] Q.H. Yang, M.P. Kapoor, S. Inagaki, J. Am. Chem. Soc. 124 (2002) 9694.

[15] I. Díaz, C. Márquez-Alvarez, F. Mohino, J. Pérez-Pariente, E. Sastre, J. Catal. 193 (2000) 283.

[16] D. Margolese, J.A. Melero, S.C. Christiansen, B.F. Chmelka, G.D. Stucky, Chem. Mater. 12 (2000) 2448.

[17] M.C. Burleigh, M.A. Markowitz, S. Jayasundera, M.S. Spector, C.W. Thomas, B.P. Gaber, J. Phys. Chem. 107 (2003) 12628.

[18] Q. Yang, Y. Li, L. Zhang, J. Yang, J. Liu, C. Li, J. Phys. Chem. B 108 (2004) 7934.

[19] K.J. Shea, D.A. Loy, O. Webster, J. Am. Chem. Soc. 114 (1992) 6700.

[20] Y. Goto, S. Inagaki, Chem. Commun. (2002) 2410.

[21] J.G.C. Shen, R.G. Herman, K. Klier, J. Phys. Chem. B 106 (2002) 9975.

[22] M.H. Lim, A. Stein, Chem. Mater. 11 (1999) 3285.