188 *Chem. Mater.* **2000,** *12,* 188−196

Direct Synthesis of Hybrid Organic−Inorganic Nanoporous Silica by a Neutral Amine Assembly Route: Structure−Function Control by Stoichiometric Incorporation of Organosiloxane Molecules

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Received August 16, 1999. Revised Manuscript Received November 8, 1999

The co-condensation of tetraethoxysilane (TEOS) and organotrialkoxysilane molecules by neutral alkylamine surfactant assembly (S^0I^0) is a convenient synthesis methodology for the one-step preparation of organically functionalized mesostructured materials. Two distinct approaches were considered for the formation of such hybrid inorganic−organic compounds, denoted as the *template substitution* and *direct addition* pathways. The template substitution pathway, involving the replacement of both surfactant and TEOS by an equivalent amount of organosilane (up to 11% substitution), was convenient for the functionalization of mesostructures with moieties whose size is comparable to that of the structure-directing amine surfactant. The direct addition method, involving the equimolar replacement of TEOS with organosilane (up to 9% of total silicon) while keeping the surfactant amount constant in the reaction mixture, was successful for the incorporation of organic groups whose sizes were smaller than that of the templating amine surfactant. Thus, the functionalization of mesostructured silica was demonstrated using a wide range of organosilane species, including octyltriethoxysilane, mercaptopropyltrimethoxysilane, phenyltriethoxysilane, butyltrimethoxysilane, and propyltrimethoxysilane. Short-chain functional groups such as ethyltriethoxysilane, however, appeared to become occluded within the framework walls of HMS silica, resulting in a lowering of the framework order and the porosity of the hybrid materials. A sufficiently long carbon chain (at least three methylene units) in the functional group of the organosilane allows an interaction with the hydrophobic core of the structure-directing micelle, thereby permitting the successful incorporation of the organosilane into the pore walls of the mesostructure.

Introduction

The proposed formation mechanism for the M41S family of mesoporous molecular sieves[1] involves charge matching between structure-directing alkylammonium ion surfactants (S^+) and framework-forming silicate oligomers (I^-) present in the reaction solution, producing materials with one of three possible lattice structures: hexagonal (MCM-41), cubic (MCM-48), or lamellar (MCM-50).[2,3] When the hexagonal or cubic derivatives are calcined at high temperatures (650 °C), the resulting silica matrices are characterized by a high degree of crystallographic ordering, very high surface areas (>800 m^2/g), and uniform mesoporosity (pore diameters ranging from 2 to 10 nm).

In addition to the S^+I^- pathway, other electrostatic assembly strategies have been employed to produce these materials. The complementary S^-I^+ anionic surfactant assembly pathway, involving the cross-linking of silicic acid precursors (I^+) at the interface of negatively charged structure-directing agents (S^-) such as alkylsulfonate surfactants, has been reported. In addition, the assembly of surfactants and inorganic species bearing identical charge (i.e., S^+ and I^+ or S^- and I^-) via counterion-mediated $S^+X^-I^+$ (where $X^- = Cl^-$ or Br^-) or $S^-M^+I^-$ (where $M^+ = Na^+$ or K^+) mechanisms have been demonstrated.[4,5]

Synthetic routes to mesostructured oxides by nonelectrostatic assembly pathways also are possible. Tanev and Pinnavaia reported the neutral (S^0I^0) templating route, where uncharged silica precursors such as tetraethyl orthosilicate (TEOS) (I^0) are assembled around

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10.1021/cm990532i CCC: $19.00

neutral amine surfactant micelles (S^0),[6−8] producing a class of mesoporous molecular sieves, denoted as HMS silicas, with wormholelike frameworks. Mesostructure formation was also achieved by nonionic surfactant assembly (N^0I^0), using alkylpoly(ethylene oxide) surfactants (N^0) as structure-directing agents,[9,10] forming another class of worm-hole frameworks, denoted the MSU-X family of oxides. For both HMS and MSU-X silicas, the assembly processes involve the association of partially hydrolyzed silica precursors (I^0) to the surfactant (S^0 or N^0) headgroups by hydrogen bonding, followed by their cross-linking around the micelle assembly. Although not crystallographically well-ordered as electrostatically assembled oxides, the wormhole motif structures of these materials nonetheless possess framework mesopores of uniform diameter. Moreover, the neutral charge on their frameworks allows for the removal of the structure-directing surfactants by solvent extraction and the formation of frameworks with a much higher surface silanol concentration compared to those of their electrostatically assembled and calcined counterparts.

The use of functionalized mesoporous oxides as high-surface-area adsorbents[11,12] and catalysts[13−17] has recently received much attention, in particular because of their exceptionally high surface areas, which allow the binding of a large number of surface chemical moieties. Moreover, the large diameter and wormhole nature of the pore channels in these oxides are conducive to the formation of functional materials in which the reactive species are highly dispersed within the framework and quantitatively accessible for reaction with adsorbate molecules.[11]

The grafting of functional groups to the pore walls of mesoporous molecular sieves can be achieved by the covalent fixation of hydrolyzable moieties (of the type $RSiX_3$, where X = Cl or OCH_3 and R = functional organic group) to the surface Si−OH groups lining the pores of the mesostructures.[18,19] This strategy has already opened up new prospects for the design of promising new adsorbents and catalysts whose properties clearly surpass those of materials designed by the grafting of nonporous or amorphous supports such as silica gels. For instance, the grafting of metal ion-binding thiol groups in HMS silica and MCM-41 has resulted in materials with unprecedented heavy metal ion-loading capacities that afford total access of the metal ions to all of the ligating sites in the materials.[11,12] The anchoring of isolated metal centers onto the pore channels of MCM-41 has also been demonstrated as being a viable approach to the preparation of catalysts with improved efficiency.[14] A significant drawback of the chemical-grafting approach, however, is the inability to adequately control the loading of the anchored guest species. Moreover, the steps required to obtained the functionalized product may be somewhat extensive, often requiring, for instance, the complete drying of both the mesostructure and the reaction solvent prior to the grafting reaction in order to avoid the formation of unwanted polycondensation byproducts.

The direct incorporation of organosiloxane moieties in mesostructured silica has recently offered a promising alternate route for the preparation of such materials that is quicker and offers greater synthetic ability than the grafting process. Burkett et al. have reported the one-step synthesis of hybrid organic−inorganic mesoporous frameworks by the co-condensation of siloxane and organosiloxane precursors during the synthesis of MCM-41.[20] Although the authors demonstrate the incorporation of organic groups into the MCM-41 framework, in some instances the functionalized mesostructure decomposed upon removal of the templating surfactant from the pores through acid leaching. This observation clearly illustrates a general disadvantage of electrostatic S^+I^- assembly for direct functionalization, namely, that removal of the charged surfactant molecules from the framework by extraction techniques is problematic.

Macquarrie[21] and, most recently, Corriu et al.[22] and Bossaert et al. [23] utilized the S^0I^0 assembly pathway for HMS molecular sieves as an alternate strategy for the synthesis of such hybrid materials. Likewise, Richer and Mercier have recently demonstrated the use of the N^0I^0 pathway as yet another means of producing functionalized mesostructures.[24] In both of these cases, the surfactant molecules could be easily extracted from the mesostructures by ethanol extraction without damaging the frameworks, resulting in mesoporous structures containing incorporated functional groups dispersed within the materials' pore channels. The use of nonelectrostatic templating pathways is thus a promising strategy for the rapid and convenient synthesis of functionalized mesoporous molecular sieves.

In this work, a variety of functional organosiloxane groups were incorporated into mesoporous HMS molecular sieves silicas through the neutral amine (S^0I^0) assembly pathway. Although this study emphasizes derivatives prepared using octylamine as a structure-directing agent (producing the mesoporous molecular sieve denoted as HMS-C8), the incorporation of functionalities into the larger pores of dodecylamine-assembled silica (denoted HMS-C12) also is examined. Emphasis is placed on controlling the organosiloxane

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Table 1. Reagent Stoichiometries Used to Incorporate Organosilane into Octylamine-Assembled HMS-C8 Mesostructures by the Template Substitution Process

organosiloxane substituent	sample annotation	TEOS substitution (mol %)	octylamine (mmol)	organosiloxane (mmol)	TEO (mmol)
none	HMS-C8	0	23.2	0	106
octyltriethoxysilane (OctTEOS)	Oct−HMS-C8-2.2	2.2	20.9	2.3	103
	Oct−HMS-C8-4.3	4.3	18.6	4.6	101
	Oct−HMS-C8-6.6	6.6	16.2	7.0	98.9
	Oct−HMS-C8-11	11	11.6	11.6	94.1
mercaptpropyltrimethoxysilane (MP TMS)	MP−HMS-C8-2.3	2.3	23.2	2.4	104
	MP−HMS-C8-4.5	4.5	23.2	4.8	101
	MP−HMS-C8-6.9	6.9	23.2	7.3	98.9
	MP−HMS-C8-9.0	9.0	23.2	9.2	92.2
phenyltriethoxysilane (PhTEOS)	Ph−HMS-C8-2.0	2.0	23.2	2.0	104
	Ph−HMS-C8-3.8	3.8	23.2	4.0	102
	Ph−HMS-C8-5.7	5.7	23.2	6.0	100
	Ph−HMS-C8-7.5	7.5	23.2	8.0	98.0
butyltrimethoxysilane (BuTMS)	Bu−HMS-C8-2.0	2.0	23.2	2.1	104
	Bu−HMS-C8-3.8	3.8	23.2	4.0	102
	Bu−HMS-C8-5.6	5.6	23.2	5.9	100
	Bu−HMS-C8-7.5	7.5	23.2	8.0	98.0
propyltrimethoxysilane (PrTMS)	Pr−HMS-C8-0.9	0.9	23.2	0.9	103
	Pr−HMS-C8-1.7	1.7	23.2	1.8	101
	Pr−HMS-C8-2.7	2.7	23.2	3.0	99.0
	Pr−HMS-C8-5.0	5.0	23.2	5.4	97.0
ethyltriethoxysilane (EtTEOS)	Et−HMS-C8-2.0	2.0	23.2	2.1	104
	Et−HMS-C8-4.0	4.0	23.2	4.2	102
	Et−HMS-C8-6.0	6.0	23.2	6.4	100
	Et−HMS-C8-8.0	8.0	23.2	8.5	98.0

loading in the mesostructures in order to regulate the extent of incorporation and to adjust the channel pore dimensions of the resulting inorganic−organic hybrid compounds. The effect of the chemical nature and the size of the incorporated organic groups on the functionalized structures also is discussed.

Experimental Section

Chemicals. The silica source was tetraethoxysilane (TEOS, $Si(OCH_2CH_3)_3$), purchased from Aldrich. The surfactants (*n*-dodecylamine, $CH_3(CH_2)_{11}NH_2$, and *n*-octylamine, $CH_3(CH_2)_7NH_2$) were also obtained from Aldrich, as was 1,3,5-trimethylbenzene (TMB, $C_6H_3(CH_3)_3$) and 3-mercaptopropyltrimethoxysilane (MPTMS, $(CH_3O)_3Si(CH_2)_3SH$). Octyltriethoxysilane (OctTEOS, $(CH_3CH_2O)_3Si(CH_2)_7CH_3$) was supplied by Dow-Corning, Inc. Phenyltriethoxysilane (PhTEOS, $(CH_3CH_2O)_3SiC_6H_5$), butyltrimethoxysilane (BuTMS, $(CH_3O)_3Si(CH_2)_3CH_3$), propyltrimethoxysilane (PrTMS, $(CH_3O)_3Si(CH_2)_2CH_3$), and ethyltriethoxysilane (EtTMS, $(CH_3CH_2O)_3SiCH_2CH_3$) were procured from United Chemical Technologies, Inc. Deionized water and absolute ethanol were used in the syntheses and extraction processes.

Synthesis. *HMS-C8*. This parent mesostructure was prepared by stirring octylamine (23.2 mmol) in 200 mL water for 30 min until an opalescent solution was obtained. TEOS (106 mmol) was then added, and the mixture stirred for 24 h. The resulting precipitate was filtered and dried in air for 24 h. The mesostructure was then washed free from surfactant by Soxhlet extraction over ethanol for 48 h.

Organosilane Incorporation in HMS-C8. Derivatives of HMS-C8 functionalized with OctTEOS, MPTMS, PhTEOS, BuTMS, PrTMS, and EtTEOS were prepared using the reagent quantities given in Table 1, according to the following general protocol. Octylamine was stirred in 200 mL of water for 30 min until an opalescent mixture was obtained. TEOS and organosilane were then mixed together and added to the stirred amine solution (in the case of OctTEOS only, the organosilane was first added to the amine solution, and then TEOS was added after 30 s of stirring). The mixture was then stirred for 24 h, and the resulting precipitate was filtered. After air-drying for 24 h, the white powder was then transferred to a cellulose extraction thimble and washed with Soxhlet extraction over ethanol for 48 h.

HMS-C12. This unfunctionalized mesostructure was prepared by dissolving dodecylamine (6.74 mmol) in 10 mL of ethanol and adding the solution to 90 mL of water. The mixture was stirred for 30 min, and TEOS (30.3 mmol) was added. After 30 s of vigorous stirring, TMB (6.7 mmol) was added, and the mixture stirred for 24 h. The resulting precipitate was filtered and dried in air for 24 h. The mesostructure was then washed free of surfactant by Soxhlet extraction over ethanol for 48 h.

Mercaptoproylsilane Incorporation in HMS-C12. An 8% MPTMS-substituted HMS-C12 derivative (denoted MP−HMS-C12-8%) was prepared following the same synthesis protocol as that of HMS-C12, except that a mixture of TEOS (27.9 mmol) and MPTMS (2.4 mmol) was added to the amine solution.

Characterization Techniques. Powder X-ray diffraction patterns were measured on a Rigaku Rotaflex diffractometer equipped with a rotating anode and using Cu Kα radiation.

The N_2 adsorption isotherms were measured at −196 °C on a Coulter Omnisorp 360 CX sorptometer using standard continuous adsorption procedures. Prior to measurement, all samples were outgassed at 110 °C at 10^{-6} Torr. BET surface areas were calculated from the linear part of the BET plot. Pore size distributions were calculated using the Horvath−Kawazoe method.[25]

^{29}Si MAS NMR spectra were obtained on a Varian VXR solid-state NMR spectrometer at 79.5 MHz using 7 mm zirconia rotors and a sample spinning frequency of 4 kHz. A delay of 870 s was applied between pulses, allowing the complete magnetic relaxation of the Si nuclei to give signal intensities that are proportional to the amount of each site in the samples. The chemical shifts for all of the spectra were referenced to TMS (tetramethylsilane).

C, H, N, and S analyses were performed in duplicate by the Microanalysis Laboratory at the University of Illinois at Urbana-Champaign.

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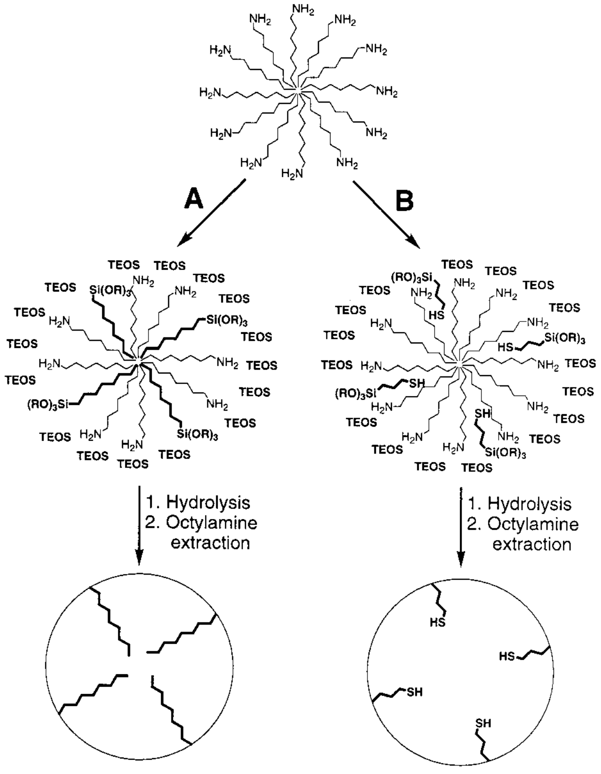
Scheme 1. Representation of Organosilane Functionalization of HMS Silicas with Octylamine as the Structure-Directing Surfactant



Pathway A describes the template substitution process, where surfactant molecules in the micelle are substituted for long-chain organosilane moieties such as octyltriethoxysilane. Pathway B depicts the direct addition process, where short-chain organosilane substituents are included into the micelle without decreasing the number of octylamine molecules available for micelle formation (pathway B). Both tetraethyl orthosilicate (TEOS) and organosilane molecules hydrolyze to form the cross-linked framework, and then the amine surfactant is removed by ethanol extraction to yield a functionalized nanoporous mesostructured silica.

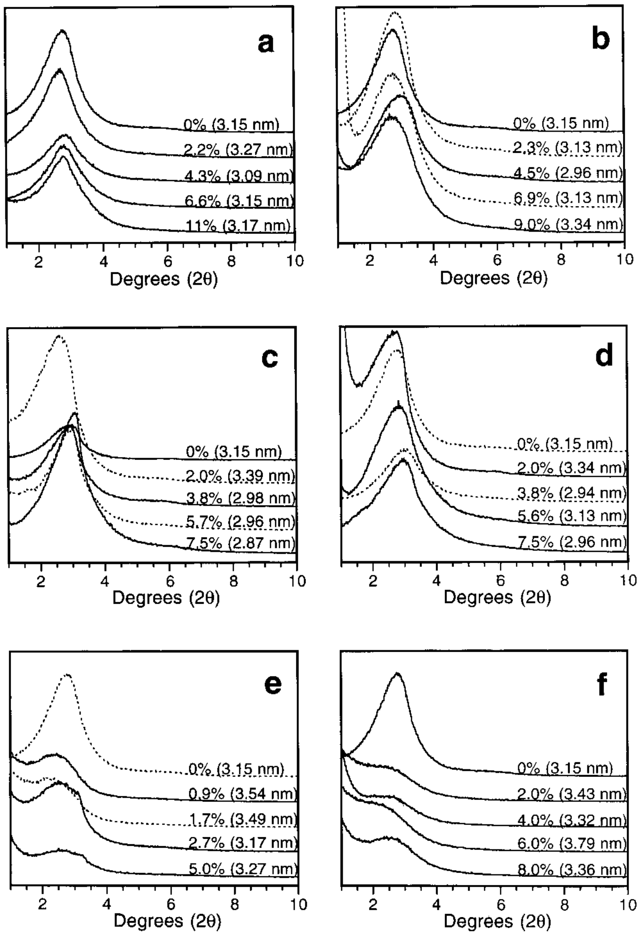


Figure 1. Powder X-ray diffraction patterns for octylamine-assembled HMS-C8 silica derivatives functionalized with (a) OctTEOS, (b) MPTMS, (c) PhTEOS, (d) BuTMS, (e) PrTMS, and (f) EtTEOS. The percentage of organosilane molar substitution for each material series is indicated. The d_{100} spacings for the materials are shown in parentheses.

Results and Discussion

Functionalized Framework Formation and Structure. Scheme 1 illustrates the two distinct functionalization strategies considered for the preparation of hybrid inorganic–organic frameworks. The first incorporation approach, denoted as the *template substitution pathway*, involves the replacement of both framework-forming TEOS and structure-directing amine surfactant with an equimolar quantity of organosilane. In this way, when the size of the incorporated organic groups matches that of the surfactant molecules, the morphology of the structure-directing micelle is expected to remain unperturbed by the inclusion of the relatively large functional moieties. An example of this route has been demonstrated by the incorporation of octylsilane groups into a HMS-C8 framework (Scheme 1, pathway A), in which the size of the organic group is the same as that of the hydrophobic chain of the templating amine. The second incorporation approach, denoted as the *direct addition pathway*, entails the incorporation of organic groups in the mesostructure synthesis while retaining the same ratio of amine surfactant to TEOS used to form the parent, unfunctionalized mesostructure. This latter strategy is expected to favor the incorporation of organic moieties whose dimensions are significantly smaller that those of the amine surfactant. For instance, a short chain functionality (i.e., mercaptopropylsilane) may fit into the void spaces between the surfactant chains without disturbing the structure of the micelle assembly (Scheme 1, pathway B). This synthesis pathway was utilized for the preparation of HMS-C8 derivatives functionalized with mercaptopropyl, phenyl, butyl, and ethyl moieties.

The XRD patterns of HMS-C8 and the corresponding octylsilane-functionalized analogues produced by the surfactant substitution pathway (Figure 1a) were characteristic of typical wormhole motif mesostructured HMS phases.[6–8] Both the unfunctionalized and functionalized products featured dominant d_{100} reflections corresponding in all cases to nearly identical lattice spacings in the range 30.9–32.7 Å (cf. Table 2). The similarity between the XRD pattern for this series of functionalized mesostructures confirms the success of the amine substitution strategy in producing isostructural compounds, as expected when the total molar quantity of octylamine and octylsilane has been kept constant in each preparation. The decrease in XRD peak intensities observed in the compounds with high incorporation (20–50%) can be attributed to increased contrast matching between the mesostructure framework and the alkyl chains present in the pore channels.

Table 2. Physical Characteristics of Octylamine-Assembled Functionalized HMS-C8 Derivatives Prepared by the Direct Addition Process

substituent	TEOS sub. (mol %)	lattice spac. (nm)	surf. area ($m^2\ g^{-1}$)	pore vol ($cm^3\ g^{-1}$)	pore size (nm)
none	0	3.15	1408	0.46	1.95
OctTEOS	2.2	3.27	1055	0.36	1.46
	4.3	3.09	655	0.26	1.14
	6.6	3.15	534	0.22	1.08
	11	3.17	468	0.22	<1.0
MPTMS	2.3	3.13	1221	0.43	1.75
	4.5	2.96	1331	0.50	1.65
	6.9	3.13	1087	0.42	1.51
	9.0	3.34	1063	0.41	1.48
PhTEOS	2.0	3.39	1772	0.63	1.67
	3.8	2.98	1088	0.40	1.50
	5.7	2.96	972	0.36	1.40
	7.5	2.87	1168	0.43	1.32
BuTMS	2.0	3.34	981	0.35	1.79
	3.8	2.94	1165	0.45	1.72
	5.6	3.13	920	0.33	1.61
	7.5	2.96	1039	0.36	1.60
PrTMS	0.9	3.54	1114	0.43	1.90
	1.7	3.49	852	0.33	1.80
	2.7	3.17	1121	0.43	1.76
	5.0	3.27	809	0.37	1.65
EtTEOS	2.0	3.43	937	0.41	1.80
	4.0	3.32	384	0.17	1.80
	6.0	3.79	517	0.22	1.80
	8.0	3.36	649	0.28	1.80

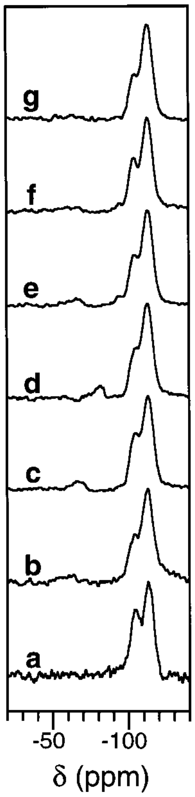


Figure 2. ^{29}Si MAS NMR spectra for octylamine-assembled (a) HMS-C8 silica, and its derivatives functionalized with (b) OctTEOS, (c) MPTMS, (d) PhTEOS, (e) BuTMS, (f) PrTMS, and (g) EtTEOS.

As was the case for the octyl-functionalized derivatives, the XRD patterns of HMS-C8 derivatives containing mercaptopropyl (cf. Figure 1b), phenyl (cf. Figure 1c), or butyl groups (cf. Figure 1d) do not show significant differences in their lattice spacing values (cf. Table 2). This indicates that little or no perturbation occurred in the octylamine micelle structure as a result of the inclusion of these organic moieties through the direct addition approach (pathway B). These relatively short organic chains are therefore able to fit in the spaces present between the amine surfactant molecules without significantly disturbing the micelle assembly, as depicted in Scheme 1, pathway B. Only in the case of the phenyl−HMS-C8 series is a slight lattice contraction observed at TEOS substitutions of 3.8% and greater (Figure 1c). This can be explained by the steric repulsion of this relatively large group, which forces the octylamine headgroups apart in the micelle, causing the curvature of the micelle assembly to increase, thus decreasing its diameter. The hydrolysis of silica at the interface of this contracted micelle therefore results in a mesostructure with a diminished lattice spacing.

The XRD peaks for the propyl-modified HMS-C8 compounds (Figure 1e) were significantly lower in intensity than those of the other hybrid materials (Figure 1a−d). Greater framework disorder is likely in these materials, although the lattice spacings were reasonably close to those of the other mesostructures.

Unlike the other functionalized HMS-C8 compounds, the broad, low-intensity d_{100} reflections observed in the XRD pattern for the Et−HMS-C8 series (cf. Figure 1f) indicated substantial framework disorder relative to the other functionalized derivatives. Moreover, an expansion of the lattice spacing with respect to HMS-C8 is observed in all of these compounds. It can be postulated that ethyltriethoxysilane (EtTEOS) is not sufficiently hydrophobic to allow efficient incorporation of the short ethyl chains into the micelle core. Thus, EtTEOS becomes essentially chemically indistinguishable from TEOS under the synthesis conditions. This results in the occlusion of at least some EtTEOS within the framework walls of the mesostructure, causing an increase in the wall thickness. Moreover, the presence of only three hydrolyzable $Si-OCH_2CH_3$ bonds in such intraframework EtTEOS is likely to impede the complete cross-linking of the silica network, resulting in the observed perturbation in the framework ordering. From these results, it can be inferred that sufficiently long carbon chains (i.e., those containing at least three methylene units) in the organosilane functional groups are needed for interaction with the hydrophobic core of the structure-directing micelle. These organosilane−surfactant interactions allow the incorporation of the organosilane moieties into the pore walls of the mesostructure with retention of the wormhole framework.

^{29}Si MAS NMR spectra were recorded for HMS-C8 and the most highly functionalized samples of each HMS-C8 derivatives (Figure 2). The HMS-C8 spectra featured the typical silica (Q^4) signal at −113 ppm and that of the surface Si−OH (Q^3) signal at −103 ppm.[7] The appearance of organosilane signals between −65 and −69 ppm (−82 ppm for Ph−HMS-C8-7.5%) in the organic HMS-C8 derivatives are characteristic of fully cross-linked organosiloxane species,[20] demonstrating the incorporation of the functional groups *within* the framework walls of the mesostructures. Moreover, the apparent decrease in the Q^3 signals of the organic derivatives with respect to HMS-C8 signify the replacement of surface Si−OH sites on the walls of the mesostructures by the incorporated functional groups. These results

Table 3. Extent of Organosilane Incorporation into Alkylamine-Assembled HMS Derivatives As Evidenced by ^{29}Si MAS NMR

sample	calculated organosilane/total Si ratio	measured organosilane/total Si ratio	measured organosilane substitution (%)
Oct−HMS-C8-6.6	0.066	0.057	5.7
Oct−HMS-C8-11	0.11	0.054	5.4
MP−HMS-C8-9.0	0.090	0.057	5.7
Ph−HMS-C8-7.5	0.075	0.053	5.3
Bu−HMS-C8-7.5	0.075	0.056	5.6
Pr−HMS-C8-5.0	0.050	0.042	4.2
Et−HMS-C8-8	0.080	0.018	1.8
MP−HMS-C12−8	0.080	0.080	8.0

indicate that mesostructure functionalization proceeds via the simultaneous cooperative assembly of both TEOS and organosiloxane at the structure-directing micelle interface.

The relative integrated intensities of the organosilane NMR signals allow the quantitative assessment of the extent of organosilane incorporation into each functionalized framework. Thus, as shown in Table 3, there is an apparent leveling off in the organosilane content in the functionalized HMS-C8 compounds to between 5.3 and 5.7% loading. This value represents the maximum possible surface coverage of the mesostructures with the incorporated organic groups, beyond which relatively little organosilane incorporation can occur. In the case of the ethyl-incorporated materials, only 1.8% organosilane loading was achieved, once again demonstrating the inability of this organosilane to suitably form a hybrid mesostructured derivative. The organosilane quantities listed in Table 2 were confirmed by elemental analysis. Moreover, the lack of detectable nitrogen levels in any of the samples demonstrates the efficiency of the ethanol extraction technique in removing all of the amine surfactant form the pore channels, while the framework-incorporated organic functionalities remained in the structures.

Surface Characteristics and Porosity. The surface properties of the functionalized HMS-C8 derivatives (BET surface area, pore volume, and pore diameters) were determined from the N_2 adsorption isotherms (Figure 3) and are given in Table 2.

For the octylsilane-incorporated HMS-C8 compounds, a systematic decrease in both adsorption volume and surface area is observed as a function of increasing octylsilane substitution (Figure 3a, Table 2). In addition, the decrease in the Horvath−Kawazoe pore diameters and the broadening of the pore size distribution profile as a function of octylsilane incorporation is also observed (Figure 4a, Table 2). The variation in the content of octyl by regulation of the TEOS:OctTEOS:octylamine molar quantities results in a systematic change in the pore diameter−pore size distribution. Thus, by varying the relative OctTEOS/TEOS molar ratio while keeping the total molar amounts of silicon (viz., OctTEOS + TEOS) and octyl chain (viz., Octylamine + OctTEOS) constant, one obtains mesostructured materials with very similar lattice spacings and controlled loading of the octyl chains inside their pore channels. These results demonstrate the versatility of the template substitution pathway (Scheme 1, pathway A) for the preparation of functionalized mesostructured materials with accurately controlled surface and porosity characteristics.

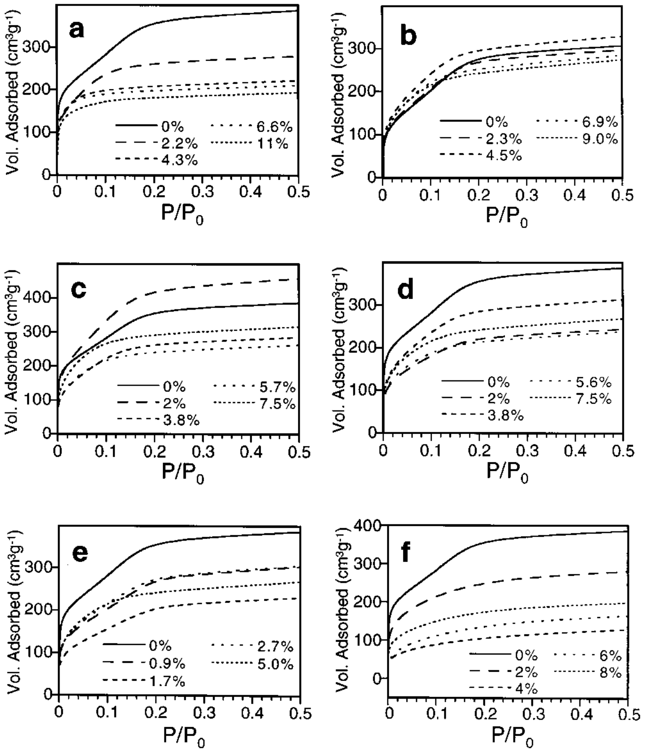


Figure 3. Nitrogen adsorption isotherms for octylamine-assembled HMS-C8 silica derivatives functionalized with (a) OctTEOS, (b) MPTMS, (c) PhTEOS, (d) BuTMS, (e) PrTMS, and (f) EtTEOS. P/P_0 is the relative pressure, where P is the equilibrium pressure of the adsorbate and P_0 its saturation pressure at the adsorbent temperature.

HMS-C8 derivatives functionalized with mercaptopropyl, phenyl, butyl, and propyl moieties show for all incorporation values the retention of very high surface areas (>900 m^2/g) and pore volumes (>0.30 $cm^3\ g^{-1}$) (Figure 3b−e, Table 2). Unlike the Oct−HMS-C8 series, no systematic decrease in surface area and pore volume as a function of chain loading is noted in these compounds. This is due to the relatively small size of the incorporated functional groups that do not significantly block the framework pore channels. The pore sizes for these materials, on the other hand, are found to systematically decrease with increasing incorporation of each moiety (Figure 4b−e). These observations demonstrate the ability of the direct addition approach (Scheme 1, pathway B) for the controlled loading of small-chain functional groups within the pore channel of HMS-C8 silica, allowing the formation of compounds in which both chemical function and structural properties can be simultaneously and accurately tuned.

In the case of the framework-disordered, ethyl-incorporated HMS-C8 compounds, the isotherms show much lower surface areas and pore volumes in compari-

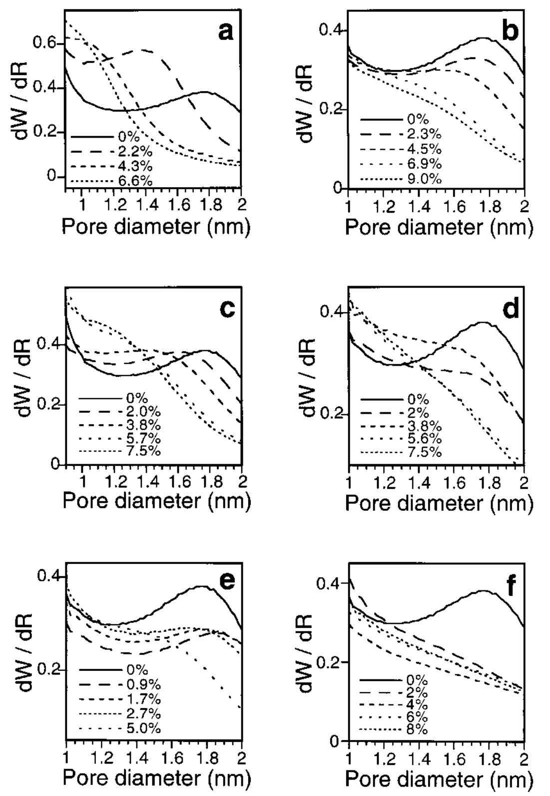


Figure 4. Pore size distributions for octylamine-assembled HMS-C8 silica derivatives functionalized with (a) OctTEOS, (b) MPTMS, (c) PhTEOS, (d) BuTMS, (e) PrTMS, and (f) EtTEOS. The distributions were calculated from the N_2 adsorption isotherm data using the Horvath–Kawazoe model[25] (d*W*/d*R* is the derivative of the normalized adsorbate (nitrogen) volume adsorbed with respect to the pore diameter of the adsorbent).

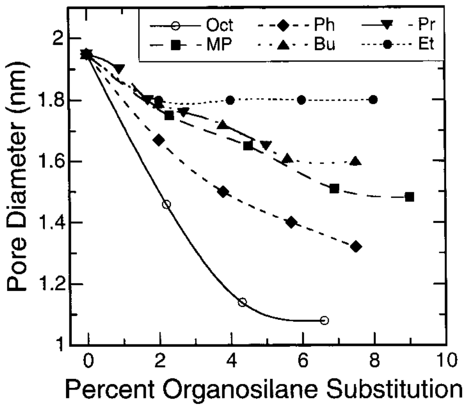


Figure 5. Effect of organosilane substitution on the pore diameter of octylamine-assembled functionalized HMS-C8 derivatives.

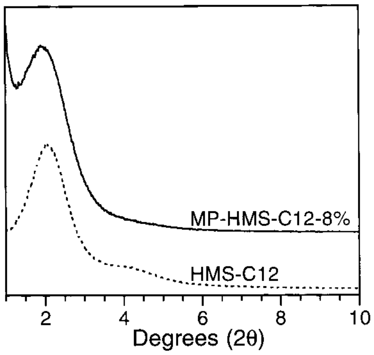


Figure 6. Powder X-ray diffraction patterns for dodecylamine-assembled HMS-C12 (dashed line) and its mercaptopropyl-incorporated derivative (MP–HMS-C12-8%, solid line).

son to the other functionalized HMS derivatives (Figure 3f, Table 2). Moreover, the pore size distributions were very broad, exhibiting only a very weak peak at 1.8 nm for each Et–HMS-C8 material (Figure 4f, Table 2). These results are consistent with the formation of a distorted pore network with very little uniformity in pore channel structure.

Figure 5 shows the variation in pore size as a function of the organosilane loading for all of the studies samples. These relationships clearly demonstrate the accurate pore size control that was achieved by the stoichiometric control of organosilane loading in a direct synthesis approach to functionalized mesostructured silica. As would be expected, the larger incorporated groups (such as octylsilane and phenyl) are shown to diminish the pore sizes to a greater extent than do the smaller groups. In most cases, there is an apparent leveling of the minimum pore diameter when organosilane loadings exceed about 6%. This finding is consistent the maximum loading amount of functional groups measured by NMR and elemental analysis (5.3–5.7%), beyond which relatively little incorporation of organic groups is possible because the pore channel walls have accommodated the maximum amount of functional groups possible, resulting in total mesostructure surface coverage.

Incorporation of Functional Groups in Larger Pore Structures. As in the case of HMS-C8, the XRD patterns of the larger pore HMS-C12 silica assembled using dodecylamine as structure-directing agent (Figure 6) were typical of a wormhole motif pore structure, featuring a dominant d_{100} peak corresponding to a lattice spacing of 4.2 nm and a broad low-intensity peak at higher 2θ value.[6–8] Similar to the results obtained for functionalized derivatives of HMS-C8, the XRD pattern of mercaptopropyl-incorporated HMS-C12 (MP–HMS-C12-8.0%) featured a d_{100} peak corresponding to the same spacing as that of HMS-C12 (4.2 nm). The disappearance of the higher order peak in the organically functionalized derivative may be attributed to increased framework disorder resulting from the organosilane incorporation.

As in the case of the functionalized HMS-C8 compounds, ^{29}Si MAS NMR shows the appearance of the mercaptopropylsilyl signal at −69 ppm in the MP–HMS-C12-8% spectrum (Figure 7c), along with a slight decrease in the intensity of the Q^3 signal with respect to the HMS-C12 spectrum (Figure 7a). By comparison to HMS-C12 functionalized with mercaptopropylsilane moieties by postsynthesis grafting, wherein the organosilane signal appears at −57 ppm (Figure 7b), the mercaptopropyl signal resulting from the direct addition pathway appears at significantly higher field (−69 ppm). This indicates that complete cross-linking of the organosiloxane units has occurred as a result of incorporation into the pore walls of the mesostructure. The −57 ppm signal observed for the grafted mercaptopropyl groups, on the other hand, indicates that the mercaptopropylsilyl moieties are not completely cross-linked to the framework but rather become anchored to Si–OH groups on the pore walls of HMS-C12. The relative

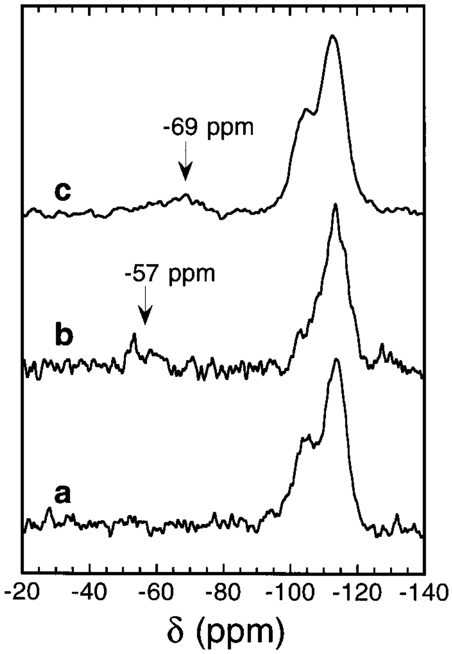


Figure 7. ^{29}Si MAS NMR spectra for dodecylamine-assembled (a) HMS-C12 silica, (b) HMS-C12 grafted with MPTMS,[11] and (c) mercaptopropylsilane-incorporated HMS-C12 (MP−HMS-C12−8%).

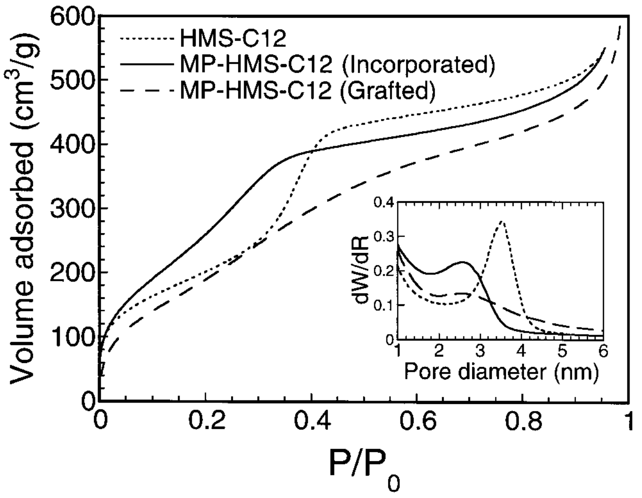


Figure 8. Nitrogen adsorption isotherms for dodecylamine-assembled HMS-C12 (dotted line), HMS-C12 grafted with mercaptopropyltrimethoxysilane (dashed line),[11] and mercaptopropylsilane-incorporated HMS-C12 (MP−HMS-C12-8%) (solid line). P/P_0 is the relative pressure, where P is the equilibrium pressure of the adsorbate and P_0 its saturation pressure at the adsorbent. Inset: pore size distributions based on the Horvath−Kawazoe model[25] (dW/dR is the derivative of the normalized adsorbate (nitrogen) volume adsorbed with respect to the pore diameter of the adsorbent).

Table 4. Physicochemical Data of Mercaptopropylsilane-Functionalized HMS-C12 Derivatives

sample	surf. area ($m^2\ g^{-1}$)	pore vol ($cm^3\ g^{-1}$)	pore size (nm)	thiol group content (mmol g^{-1})
HMS-C12	854	0.66	3.5	0
MP−HMS-C12-8.0 (incorporated)	891	0.60	2.6	1.2
MP−HMS-C12 (grafted)[11]	722	0.56	2.7	1.5

integrated intensities of the ^{29}Si NMR organosilane signal (Table 3) showed that 8.0% of the total Si in the sample is present in the form of mercaptopropylsilane, representing the complete incorporation of all of the MPTMS in the reaction mixture. This indicates that the maximum organosilane incorporation threshold in HMS-C12 hydrid materials is greater than that of functionalized HMS-C8 derivatives, in which a maximum loading of only 5.7% was observed. This discrepancy can be explained by the decrease in curvature for the larger pore HMS-C12 structure, which can allow, on the grounds of reduced steric repulsion, the packing of a greater number of organic moieties on the pore wall surface.

The importance of the functionalization pathway is further elucidated by comparing the N_2 adsorption isotherms for both grafted and framework-incorporated MP−HMS-C12 compounds (Figure 8). As shown in Table 4, the former (grafted) compound shows (with respect to the parent HMS-C12 mesostructure) a significant drop in both surface area (viz., from 854 to 722 m^2/g) and pore volume (viz, from 0.66 to 0.56 cm^3/g), whereas the latter (incorporated) compound shows no significant change in surface area (891 m^2/g) and only a small reduction in pore volume (0.60 cm^3/g). The incorporation of the siloxane group of the mercaptopropylsilane moiety within the HMS silica framework results in a mesostructured material whose surface characteristics are not significantly affected by the organic substituents, resulting in no detectable differences in measured surface area and pore volume with respect to pristine HMS silica. On the other hand, the grafting of mercaptopropyl groups on a preformed HMS silica framework results in a more significant depression of surface properties, because a larger amount of anchored moieties have been included within the pore channel space (Table 4).[11] Another point worthy of notice is the apparent retention of a significant amount of surface hydroxyl groups on the surface of the incorporated MP−HMS-C12 mesostructure. This property may prove useful, for instance, in the preparation of *multifunctional* mesostructured materials, where the subsequent grafting of different chemical species on the surface Si−OH sites may be possible.

The pore diameter of the mercaptopropyl-incorporated HMS-C12 derivative (2.6 nm, Figure 8) is virtually identical to that of the mercaptopropyl-grafted compound (2.7 nm, Figure 8). The pore size distribution, however, is much broader for grafted MP−HMS-C12 than for the incorporated material. Direct incorporation thus results in a more even distribution of functional groups within the pore channels of the mesostructure. Postsynthesis grafting, on the other hand, causes some distortion in the pore morphology because of the random position of the anchored mercaptopropylsilyl moieties on the HMS-C12 surface.

Conclusions

Neutral amine surfactant assembly is a most convenient synthesis methodology, allowing the one-step preparation of functionalized mesostructured materials in which both organic loading and pore dimensions can be accurately tuned by reagent stoichiometry control.

Unlike electrostatic S^+I^-, S^-I^+, or $S^+X^-I^+$ mesostructure formation mechanisms, the S^0I^0 templating mechanism involved in the formation of HMS silica mesoporous molecular sieves allows the complete removal and recovery of neutral amine assembly surfactants from the mesostructures by ethanol extraction. In addition, the resulting materials retain a very large surface silanol concentration suitable for the anchoring of functional groups by postsynthesis grafting.

The two approaches used for the direct synthesis of hybrid inorganic−organic compounds (*template substitution* (pathway A) and *direct addition* (pathway B)) were found to produce functional mesostructured compounds that had the same crystallographic structure as the parent (unfunctionalized) HMS silica, but in which the pore diameters varied as a function of the amount of organosilane incorporated in the structures. In the case of the octylamine-assembled materials, the control of pore dimensions was evident only at organosilane loadings of 6% and lower, above which the functional group coverage on the mesostructure surface was maximized.

The one-step synthesis of mercaptopropyl-functionalized mesostructures produced materials with the same pore dimensions as that of similar materials prepared by postsynthesis grafting. Unlike the grafting approach, however, materials functionalized by direct incorporation retained considerably higher surface areas and pore volumes. Moreover, the comparatively narrow pore size distributions observed in the functionalized mesostructures prepared by direct incorporation denote greater uniformity in the functional group distribution inside the pore channels, thereby avoiding local clustering of the organic moieties and curtailing necking of the pore channels. ^{29}Si NMR evidence suggests a greater degree of cross-linking between the organosilane moieties and the HMS silica framework. These aforementioned observations support the incorporation mechanism proposed in this study, whereby the siloxane “anchoring” group (viz., $-\mathrm{Si(OR)_3}$) of the organosilane molecules becomes *internally* embedded within the framework walls of the mesostructure, as opposed to being *externally* linked to the pore channels via condensation on surface Si−OH sites.

The results presented in this work represent the first systematic study of the parameters involved in the functionalization of mesoporous silica molecular sieves by a one-step synthetic process. The accurate structure and function control that was demonstrated by this research is expected to be of seminal importance for the design of novel advanced materials with implication in the fields of adsorption and catalysis, in particular, where size selectivity is of concern.

Acknowledgment. L.M. is grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support. T.J.P. acknowledges the partial support of this research through NSF-CRG Grants CHE-9633789 and 9903706.

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