Tailoring the Framework and Textural Mesopores of HMS Molecular Sieves through an Electrically Neutral (S°I°) Assembly Pathway

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Water:ethanol solvent mixtures of differing polarity have been used to tailor the framework and textural mesopores of HMS molecular sieve silicas through an electrically neutral (S°I°) assembly pathway (S° = dodecyl- or tetradecylamine; I° = tetraethyl orthosilicate). Mesostructure assembly from a water-rich solvent mixture, water:ethanol = 90:10 (v/v), afforded wormhole-like framework structures with a complementary textural pore volume equal in magnitude to the framework pore volume. An ethanol-rich mixture, water:ethanol = 35:65 (v/v), also formed wormhole-like frameworks, but the textural porosity was less than 20% of the framework pore volume. HMS derivatives with high textural porosity were composed of mesoscale fundamental particles that aggregate into larger particles**.** In contrast, HMS mesostructures with low textural porosity were assembled into much larger aggregates of macroscale spheroid to disk-shaped fundamental particles. The differences in particle textures were attributed to differences in I° hydrolysis rates and S°I° nucleation and growth rates in the two solvent systems. The presence of mesitylene in the reaction mixtures resulted in an expansion of the framework pores under water-rich conditions. Pore contraction, however, was observed with mesitylene present under ethanol-rich conditions. This versatile structure-modifying property of mesitylene in S°I° assembly is explained by the solvent-dependent binding of the aromatic molecules to two structurally distinct and size-altering "dissolved" and "adsorbed" states at the centers and interfacial surfaces of the surfactant micelle, respectively. Thus, both the framework and the textural pores of HMS silica can be readily tailored to the needs of a particular materials application through S°I° assembly by a judicious choice of an appropriate solvent and an auxiliary structure modifier.

The discovery of Mobil MCM-41 mesoporous molecular sieves [1] has stimulated great interest in the surfactant-directed assembly of mesostructures by sol–gel methods. Thus far, three general assembly pathways have emerged. First, the electrostatic charge matching pathway between cationic or anionic surfactant micelles and charged inorganic precursors. Among these, the so-called S^+I^- and S^-I^+ pathways[2,3] represent the most commonly encountered electrostatic assembly pathways. Counterion-mediated $S^+X^-I^+$ and $S^-M^+I^-$ assembly processes, where surfactant and inorganic reagents are brought together at the micelle interface through triple ion interactions, represent extensions of the charge matching pathway.[3] The second pathway pairs neutral amine surfactants (S°) or nonionic polyoxyethylene surfactants (N°) with neutral inorganic precursors (I°) through hydrogen bonding at the S°I° or N°I° interface.[4–8] The third general assembly route to mesostructures exploits dative bond formation between donor groups on the surfactant and a metal acceptor centers in the inorganic precursor.[9]

The original synthesis of hexagonal MCM-41 silicas was accomplished through a S^+I^- assembly mechanism using quaternary ammonium ions as the surfactant and silicate anions as the inorganic precursor.[1] Related mesoporous structures, designated HMS silicas, have been obtained through S°I° assembly, wherein S° is an alkylamine and I° is a silicon alkoxide.[5] In general, surfactant removal from the neutral frameworks HMS silicas can be achieved by simple solvent extraction, whereas the displacement of the electrostatically bound surfactants from the anionic framework of as-synthesized MCM-41 requires proton exchange or destruction of the surfactant by combustion.[10] More importantly, there are significant structural differences between MCM-41 and HMS silicas. MCM-41 derivatives typically exhibit three or more X-ray diffraction lines indicative of long-range hexagonal channel packing. In

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contrast, HMS silicas show one or, at most, two broad X-ray peaks as a consequence of a small crystallite domain size and/or a much lower degree of channel packing order.

Although they are distinguishable with regard to structural ordering, MCM-41 and HMS molecular sieves both exhibit a sharp step in their nitrogen adsorption isotherms, corresponding to the presence of a regular mesoporous framework. Owing to the very small elementary particle size of many HMS derivatives, they can exhibit complementary textural mesopores, in addition to framework pores. The textural pore volumes for HMS can be up to 1.5 or more times as large as the framework pore volumes, whereas MCM-41 exhibits very little textural mesoporosity.[11] The textural mesopores are important because they greatly facilitate mass transport to the framework mesopores. For this reason the catalytic reactivity of HMS is usually superior to MCM-41, especially for conversions involving large substrates in a liquid reaction medium where reaction rates are diffusion limited.[12]

Another potential benefit of S°I° assembly is the possibility of conducting mesostructure synthesis in media of diverse polarity. Unlike their ionic counterparts, S° and I° reagents are generally soluble in a wide range of solvents. Thus, solvation effects on the rates of hydrolysis and assembly might be an effective means of controlling structure. One of the objectives of the present study was to examine the possibility of tailoring both the framework and textural mesopores of HMS silicas by controlling the polarity of the reaction medium in which the assembly process is carried out. Our approach makes use of two water: ethanol compositions to control polarity, one water-rich and the other ethanol-rich.

We also have investigated the role of mesitylene as an auxiliary structure-directing agent in both solvent systems. By using solvation effects to shift the equilibrium between structurally distinct binding states of mesitylene in the surfactant micelles,[13−15] we are able to effect an expansion or contraction of the framework pore structure of HMS. The ability to control both framework and textural mesoporosity can be of great value in designing HMS materials as catalysts, adsorbents and sensor materials.

Experimental Section

HMS molecular sieves were prepared by S°I° assembly pathways in water:ethanol solvent mixtures of differing composition and polarity. In both reaction media tetraethyl orthosilicate (TEOS) served as the neutral silica precursor and dodecylamine and tetradecylamine were the neutral structure director. In a typical synthesis the surfactant was dissolved in ethanol, and then the desired amount of water was added under vigorous stirring to obtain a homogeneous solution. TEOS was added to the surfactant solution and the mixture was allowed to react under stirring at ambient temperature for about 20 h. The reactions were carried out in an open beaker in a well ventilated hood to allow for some evaporation of solvent and concentration of the solid reaction products. When mesitylene was used as an auxiliary structure director, it was added to the surfactant solution and stirred for 15 min before the addition of TEOS. All of the HMS reaction products were filtered and dried in air. Although the surfactant can be readily removed from HMS mesostructures by solvent extraction, there was no need to recover the surfactant from the small quantities of products formed in the present work. Consequently, the as-synthesized products were directly calcined at 650 °C in air for 4 h to simutaneously remove the surfactant and dehydroxylate the framework.

For the purposes of probing the effect of solvent polarity on textural porosity, it was desirable to form HMS silicas from water-rich and ethanol-rich solutions with equivalent framework porosities. To achieve equivalent framework pore structures, we used reagent concentrations in the ethanol-rich system that were twice the concentrations for the water-rich medium. For HMS assembly in the relatively low-polarity ethanol-rich reaction medium, where water:ethanol volume ratio was 35:65, the molar composition of the reaction mixture was 1.0 TEOS:0.25 surfactant:18 EtOH:34 H_2O. For assembly in a relatively high polarity, water-rich solvent mixture, namely, 90:10 (v/v) water: ethanol, the molar composition was 1.0 TEOS:0.25 surfactant:10 EtOH:130 H_2O.

Powder X-ray diffraction patterns were measured using Cu Kα radiation ($\lambda = 1.542$ Å) and a Rigaku Rotaflex diffractometer equipped with a rotating anode operated at 45 kV and 100 mA. The scattering and receiving slits were 1/6 deg and 0.3 deg, respectively.

N_2 adsorption and desorption isotherms at −196 °C were obtained on a Coulter Omnisorp 360CX sorptometer operated under continuous adsorption mode. Pore size distributions were calculated from the N_2 adsorption branch using the Horvath−Kawazoe model.[16]

Transmission electron microscopy (TEM) studies were carried out on a JEOL 100CX instrument using an electron beam generated by a CeB_6 filament and an acceleration voltage of 120 kV. The resolution of the instrument was about 6 Å, as estimated by indirect measurement of the spherical aberration constant[17] under medium-high magnification (i.e., 100 000×). Therefore, it was possible to resolve pores above about 30 Å. The specimens were prepared by dipping a carbon-coated copper grid into a suspension (0.1 wt %) of mesoporous material in ethanol that was pre-sonicated for 10 min. Attempts to use thin-sectioned specimens were abandoned, because thin sectioning caused damage and loss of texture-pore information.

Results

Two versions of HMS silicas were prepared through S°I° assembly at ambient temperature in reaction media that differed in solvent polarity. In one reaction system the mesostructures were formed from a “water-rich” solution of 90:10 (v/v) water:ethanol. The other reaction medium was a less polar “ethanol-rich” solution of 35:65 (v/v) water:ethanol. Two S° surfactants, namely, dodecylamine and tetradecylamine, were used as structure directors. The reaction stoichiometries were the same for both the water-rich and the ethanol-rich reaction systems (S°/I° = 0.25). When mesitylene (Mes) was present as an auxiliary structure director, the Mes/S° molar ratio was 1.0 or 4.5.

Figures 1 and 2 provide N_2 adsorption−desorption isotherms for the HMS silicas obtained from dodecylamine and tetradecylamine as structure directors, respectively. The adsorption properties of the mesostructures assembled from the two surfactants under the

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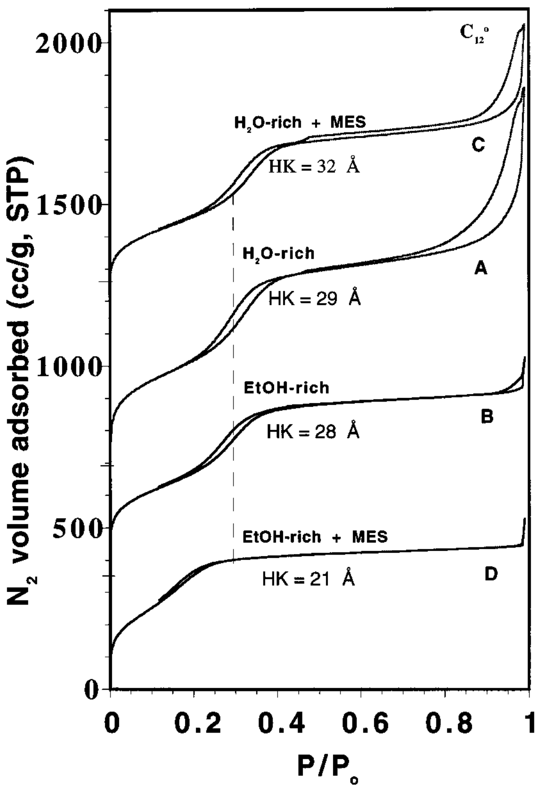

Figure 1. N_2 adsorption–desorption isotherms for HMS silicas assembled at ambient temperatures from dodecylamine and TEOS: Curves A and B are for derivatives obtained from a water-rich (water: ethanol = 90:20 (v/v)) and ethanol-rich solution (water: ethanol = 35:65 (v/v)); curves C and D are for derivatives prepared from the same water-rich and ethanol-rich solutions, but in the presence of mesitylene (Mes/S° = of 1.0). The HK values are the Horvath–Kawazoe pore diameters.

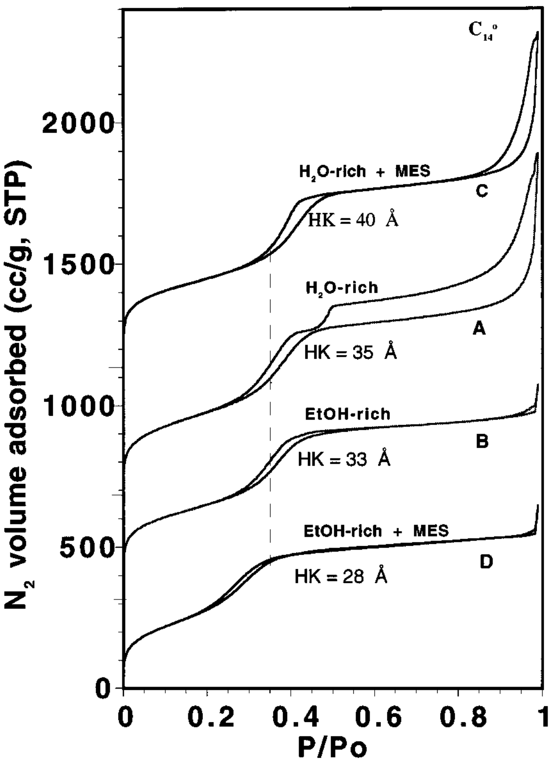

Figure 2. N_2 adsorption–desorption isotherms for HMS silicas prepared from tetradecylamine and TEOS in water-rich and ethanol-rich solution. The labeling of the isotherms is the same as in Figure 1.

same reaction conditions are qualitatively equivalent. As can be seen from the isotherms labeled A and B in both figures, the structures obtained from the water-rich and ethanol-rich solutions give stepped-shaped isotherms at $P/P_0 < 0.4$. The positions of the steps correspond to Horvath–Kawazoe pore sizes of 28–29 Å ($S° = C_{12}H_{25}NH_2$) and 33–35 Å ($S° = C_{14}H_{29}NH_2$).

Although the mesostructures obtained from the water-rich and ethanol-rich media have equivalent frameworks, the textural mesoporosity, as evidenced by the N_2 adsorption/desorption in the region $P/P_0 > 0.4$, depends dramatically on the polarity of the medium used for assembly. A textural pore volume even larger than the framework pore volume can be obtained from the water-rich system, whereas the ethanol-rich medium generates a mesostructure with little or no textural pores. As will be seen from TEM images presented below, the high textural mesoporosity for the water-rich system is associated with the presence of extremely small fundamental particles.

We consider next the effect of mesitylene on the framework pore structure and textural mesoporosity of HMS silicas assembled from water-rich and ethanol-rich solutions. The structure mediating properties of mesitylene is manifested in the adsorption–desorption curves labeled C and D in Figures 1 and 2. The presence of mesitylene at Mes/S° = 1 in the water-rich systems causes the adsorption step to be significantly shifted to higher relative pressure. The shift in the step position corresponds to a 3–5 Å *increase* in HK pore size. In the ethanol-rich medium, however, the presence of mesitylene results in a shift of the step position to lower relative pressures, corresponding to a 5–7 Å *decrease* in HK pore diameter.

Although mesitylene can substantially expand or contract the framework pores depending on the polarity of the reaction medium, it does not alter the key role of the solvent in regulating the textural porosity. As will be shown below, mesitylene actually increases the textural mesoporosity under water-rich assembly conditions, but it has only a minor influence on the extremely low textural pore volume of HMS when assembled under ethanol-rich conditions.

To further probe the influence of mesitylene on the framework pores assembled from a water-rich environment, we repeated HMS assembly in 90:10 (v/v) water:ethanol at a much higher Mes/S° ratio of 4.5. As shown by the N_2 isotherms in Figures 3, the adsorption step due to framework pore filling is further shifted to higher relative pressure as a consequence of a HK pore size (38 Å) that is 9 Å larger than the value obtained in the absence of mesitylene. The insert to Figure 3 shows the half-width of the HK pore distribution to be ~10 Å, a value typical of HMS materials. On the basis of the hysteresis loop at higher relative pressure, it appears that the textural pore volume is substantially increased by ~50% from ~550 mL STP/g in the absence of mesitylene to ~850 mL STP/g by the presence of mesitylene.

To verify that the textural pores do indeed arise from interparticle voids and not from a large pore component of the framework, the HMS silica assembled from $S° = C_{12}H_{25}NH_2$ at 90:10 (v/v) H_2O:ethanol and Mes/S° = 4.5 was calcined at 1000 °C to collapse the framework pores. The N_2 adsorption/desorption isotherms are given by

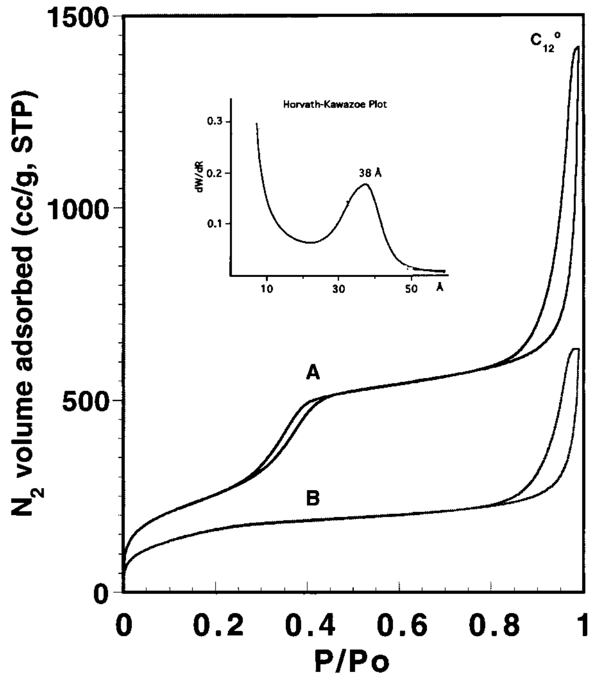

Figure 3. N_2 adsorption−desorption isotherms for a HMS silica prepared from dodecylamine in water-rich solution in the presence of mesitylene (Mes/S = 4.5): (A) after calcination at 650 °C with retention of framework and textural mesopores and (B) after calcination at 1000 °C with collapse of framework pores but with retention of textural pores. Insert: Horvath−Kawazoe pore size distribution after calcination at 650 °C.

curve B of Figure 3. Note that the framework pores indeed have collapsed, as signified by the loss of the pore filling step, but a substantial fraction (>50%) of the textural porosity is retained. Thus, the textural porosity cannot be a consequence of framework structure.

The TEM images shown in Figure 4 provide insights into the framework structure and textural mesoporosity associated with HMS materials assembled from water- and ethanol-rich media. Regular framework pores are readily observed, regardless of solvent system used to prepare the products. It is quite clear that the pores originate from the space initially occupied by uniform supramolecular assemblies of surfactant, but there is no apparent long-range order to the pore arrangement. Instead, the pore-packing motif is more wormhole-like, perhaps, even sponge-like, in character.

The most important distinguishing feature between the water- and ethanol-rich reaction products is the particle texture. As shown in Figure 4a, the water-rich reaction mixture yields irregularly shaped mesoscale fundamental particles. These fundamental particles aggregate into larger particles. The coastline-like silhouette of the aggregates, which persists over length scales differing by at least an order of magnitude, are suggestive of a fractal texture. Textural mesopores comparable in size to the mesoscale fundamental particles are clearly evident. In contrast, the ethanol-rich medium forms spheroid to disklike fundamental particles that are typically 100 nm or larger in size (see Figure 4b). These macroscale fundamental particles are linked into larger aggregates with a beads-on-a-string texture. The interparticle voids are much larger, typically in the macropore range (>50 nm). Figure 4c,d provides higher resolution images of the wormhole to

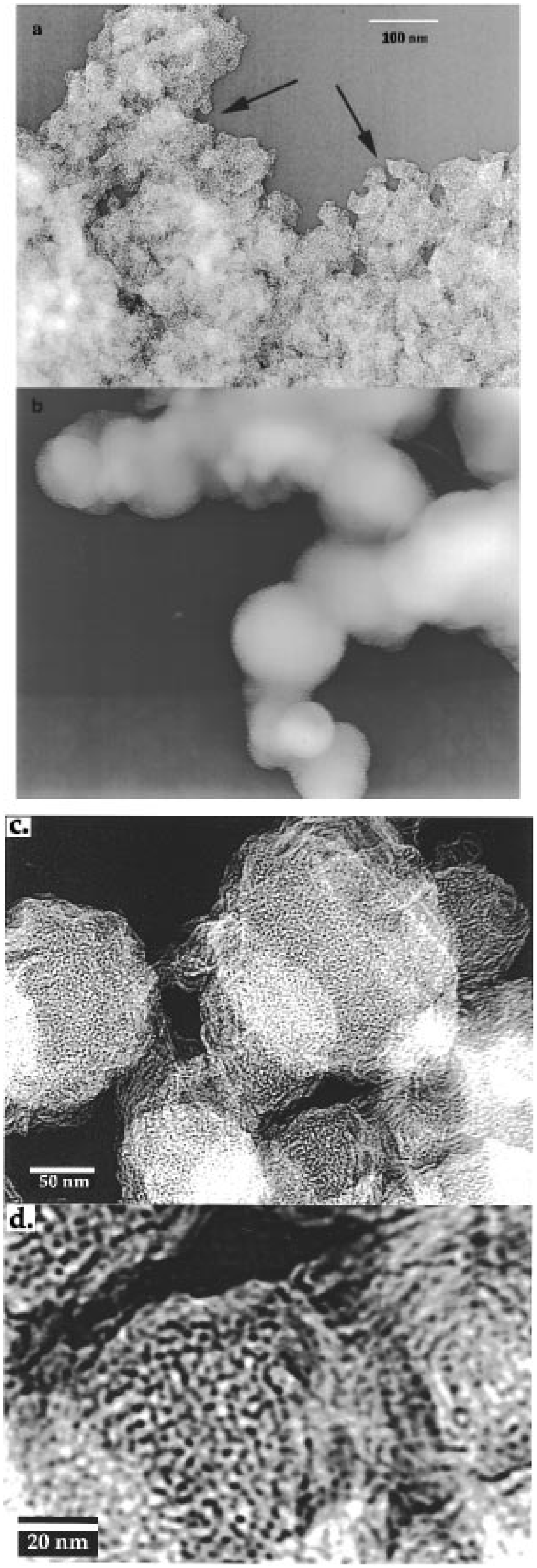

Figure 4. TEM images of calcined (650 °C) HMS molecular sieve silicas assembled from dodecylamine: a, mesoscale fundamental particles obtained from water-rich solution; b, the spheroid fundamental particles and macroscale beads-on-a-string texture obtained from ethanol-rich solution; c and d, wormhole-like framework pores obtained from water-rich solution.

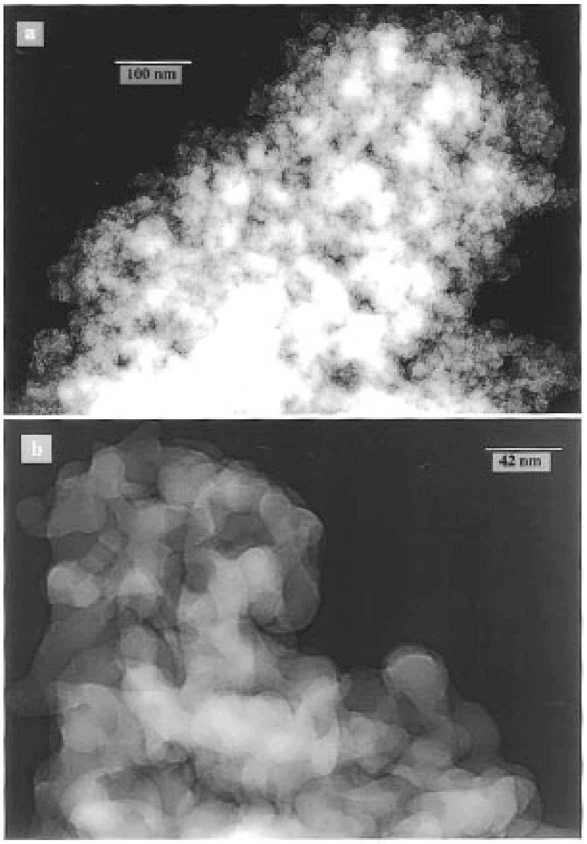

Figure 5. TEM images of HMS silica prepared from dodecylamine in water-rich solution in the presence of mesitylene (Mes/S = 4.5) and calcined at 1000 °C to collapse the framework pore structure: (a) low magnification image showing the retention of the textural mesopores and, (b) high magnification image showing the absence of framework pores.

sponge-like framework structure obtained from water-rich solution.

Figure 5 provides TEM images for a HMS derivative assembled from water-rich solution in the presence of a relatively high concentration of mesitylene (Mes/S° = 4.5) but calcined at 1000 °C to collapse the framework mesopore structure. Image (a), obtained at low magnification, shows the retention of the textural pores. Image (b), obtained at higher magnification, shows that the framework mesopores indeed have been destroyed by thermal treatment. This result, which is consistent with the N_2 adsorption results described earlier (*cf.*, Figure 3), further identifies the interparticle voids as being the origin of the textural mesopores.

Figure 6 provides the X-ray powder diffraction patterns for HMS derivatives assembled from $C_{12}H_{25}NH_2$ as the structure director. Structures formed from $C_{14}H_{29}NH_2$ showed qualitatively equivalent diffraction features. The patterns all contain a strong, relatively broad reflection at 2.0−3.0° 2θ and a very weak broad shoulder in the region near 5.0° 2θ. The qualitative form of the patterns is not affected by the water- or ethanol-rich polarity of the assembly medium or by the presence of mesitylene. However, the positions of the intense reflection and the weak broad shoulder are dependent by the polarity of the reaction medium and by the presence of mesitylene.

Table 1 summarizes the basal spacings, HK pore sizes, N_2 BET surface areas (S_{BET}), total liquid pore volumes (V_t), liquid framework pore volumes (V_{fr}), the ratio of textural to framework pore volumes (V_{tx}/V_{fr}), and the bulk densities for our HMS materials. The basal spacings represented by the strong diffraction line are correlated with the HK pore sizes, even though the framework lacks regular long-range order. The BET surface areas are in the range 900−1464 m^2/g. The incorporation of mesitylene into the synthesis of HMS from a water-rich medium increases the HK pores size and decreases the surface area of the mesostructure. Conversely, mesitylene *decreases* the pore sizes and increases the surface areas of HMS assembled from ethanol-rich solution.

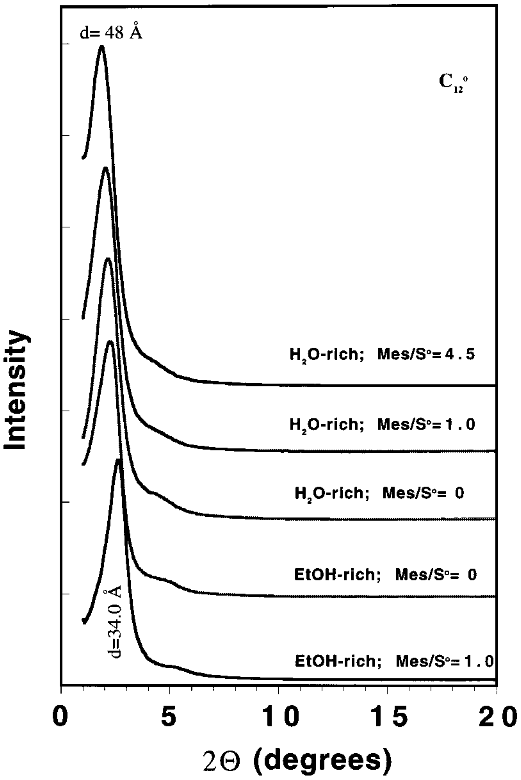

Figure 6. X-ray powder diffraction pattern of calcined (650 °C) HMS silicas assembled from dodecylamine amine in water-rich and ethanol-rich solution with or without mesitylene as an auxiliary structure director.

It is especially noteworthy from the results in Table 1 that the total pore volumes are much larger for HMS derived from a water-rich medium (~1.3−1.7 cm^3/g) than an ethanol-rich medium (~0.5−0.7 cm^3/g). Yet, the framework pore volumes are confined to the approximate range 0.5−0.7 cm^3/g. The difference between the total and framework pore volumes is expressed as the textural pore volume, V_{tx}. For HMS assembled from a water-rich medium, the textual pore volume which can be up to 1.6 times as large as the framework volume, depending on the amount of mesitylene used as a structure modifier. In contrast, the textural pore volume for HMS obtained from an ethanol-rich medium is equivalent to only a small fraction (6−18%) of the framework volume. Finally, the differences in total pore volumes is manifested in the bulk densities, which are substantially lower for HMS derived from a water-rich medium (0.16−0.35 g/cm^3) than an ethanol-rich medium (0.53−0.67 g/cm^3).

Discussion

The results of the present work demonstrate several important advantages of S°I° assembly for the prepara-

Table 1. Physical Parameters for Calcined (650 °C) HMS Molecular Sieve Silicas Prepared by S°I°Assembly in H_2O-Rich and EtOH-Rich Medium

S°	reaction medium[a]	d (Å)	H−K pore (Å)	S_{BET} (m^2/g)	V_t cm^3/g	V_{fr} cm^3/g	V_{tx}/V_{fr}	d_{bulk} g/cm^3
$C_{12}H_{25}NH_2$	H_2O-rich; Mes/S° = 0	41.7	29	1035	1.30	0.62	1.10	0.33
	H_2O-rich; Mes/S° =1.0	43.3	32	993	1.37	0.65	1.11	0.21
	H_2O−rich; Mes/S° =4.5	48.0	38	957	1.63	0.63	1.59	0.16
	EtOH-rich; Mes/S° = 0	39.4	28	1070	0.66	0.56	0.18	0.53
	EtOH-rich; Mes/S° = 1.0	34.0	21	1464	0.51	0.48	0.06	0.67
$C_{14}H_{29}NH_2$	H_2O−rich; Mes/S° = 0	44.2	34	1035	1.28	0.65	0.97	0.35
	H_2O−rich; Mes/S° = 1.0	50.2	40	927	1.30	0.67	0.94	0.20
	H_2O−rich; Mes/S° = 4.5	55.2	45	900	1.67	0.67	1.49	0.16
	EtOH-rich; Mes/S° = 0	49.1	33	936	0.69	0.61	0.13	0.57
	EtOH-rich; Mes/S° = 1.0	38.7	28	1117	0.62	0.57	0.09	0.65

[a] The compositions of H_2O-rich and EtOH-rich solutions were 90:10 and 35:65 (v/v) for H_2O:EtOH, respectively.

tion of mesoporous metal oxide molecular sieves. In the case of HMS silicas we have shown through N_2 adsorption studies that the textural mesoporosity, which greatly facilitates access to the framework mesopores, can be controlled by a judicious choice of solvent (cf., Figures 1 and 2). A water-rich solvent, such as 90:10 (v/v) water:ethanol, promotes the formation of mesopore fundamental particles sizes. TEM images show that the interparticle voids responsible for the textural mesoporosity are on a length scale comparable to the fundamental particles (cf., Figure 4a). Conversely, a solvent of lower polarity, namely, 35:65 (v/v) water:ethanol, minimizes the textural porosity by forming much larger fundamental particles (cf., Figure 4b). There is no doubt that the textural mesoporosity for HMS assembled in 90:10 (v/v) water:ethanol arises from interparticle pores. The retention of a well-expressed hysteresis loop in the N_2 adsorption/desorption isotherm show the retention of textural pores even after the framework pores have been collapsed by calcination at 1000 °C (cf., Figure 3). Thus, the textural porosity can be tailored to a particular materials application by simply controlling the polarity of the solvent for supramolecular assembly.

The relationship between fundamental particle size and solvent polarity most likely is determined by the relative rates of I° hydrolysis and supramolecular assembly in the reaction medium. A water-rich medium leads to rapid nucleation of the mesostructure. For assembly in 90:10 (v/v) water:ethanol, a solid product is formed virtually within minutes of mixing the reagents at ambient temperature. This leads to rapid nucleation and the formation of irregularly shaped fundamental particles. The fundamental particles further aggregate into a self-similar agglomerates (cf., Figures 4a). However, in the lower polarity 35:65 (v/v) water:ethanol solvent, I° hydrolysis and mesostructure assembly is relatively slow, requiring several hours at ambient temperature for the onset of product formation. The slower nucleation and growth of the mesostructure results in spheroid to disk-shaped fundamental particles 100 nm or larger in size. These fundamental particles interpenetrate to form even larger aggregates with interparticle voids beyond the mesopore range (cf., Figure 4b).

The role of mesitylene as an auxiliary structure director is highly dependent on the polarity of the medium in which mesostructure assembly is carried out. As shown by the results in Table 1 for HMS assembly in the water-rich medium, mesitylene enlarges the framework pores and increases the textural mesoporosity. This latter result is consistent with the effect of mesitylene on the pore size of MCM-41 prepared by S^+I^- assembly.[1] On the other hand, for assembly in the ethanol-rich medium, mesitylene *reduces* the framework pore size and decreases still further the already low textural pore volume.

The role of mesitylene on the framework pore structure is intriguing. Mesitylene is known to bind to surfactant micelles in at least two binding states, namely, in a "dissolved" state at the hydrophobic center of the micelle, and in an "adsorbed" state at the hydrophilic micelle/solvent interface.[13−15] It is reasonable to expect the equilibrium between these structurally distinct states to depend on the polarity of the solvent in which the surfactant micelles are formed. In accordance with the structurally distinct binding states of mesitylene in surfactant micelles, we propose the mechanism illustrated in Figure 7 for the expansion or contraction of the framework pores by mesitylene during HMS assembly. In water-rich solvent, in which the solubility of mesitylene is low, the "dissolved" binding state should be favored over the adsorbed state. In this case the size of the micelle will be increased and this will be manifested as an enlarged pore in the mesostructure. But in the lower polarity ethanol-rich solvent, the solubility of mesitylene in the medium will be increased and this will favor binding at the "adsorption" site. Hydrogen bonding between the p-electrons of the aromatic and water dipoles associated with the polar headgroups at the micelle−solvent interface is believed to stabilize the adsorbed state of mesitylene.[13] Binding of mesitylene at the micelle surface increases the size of the effective polar headgroup. The increase in headgroup size leads to a decrease in the radius of curvature and to a reduction in micelle size, so that van der Waals interactions between the surfactant chains are retained at the micelle center. Consequently, a framework with a smaller pore size is formed in the assembled mesostructure.

In our earlier studies of HMS assembly in 50:50 (v/v) water:ethanol we noted that certain alkylamine surfactants (e.g., dodecylamine) gave derivatives with high textural mesoporosity, whereas others afforded relatively low textural pore volumes (e.g., tetradecylamine).[18] It is now apparent that the degree of textural mesoporosity is quite sensitive to both the solvent polarity and the nature of the S° surfactant. The results of the present work show that dodecylamine and tetradecylamine afford high textural mesoporosity when the solvent is highly polar, as in 90:10 (v/v) water: ethanol (cf., Figures 1 and 2).

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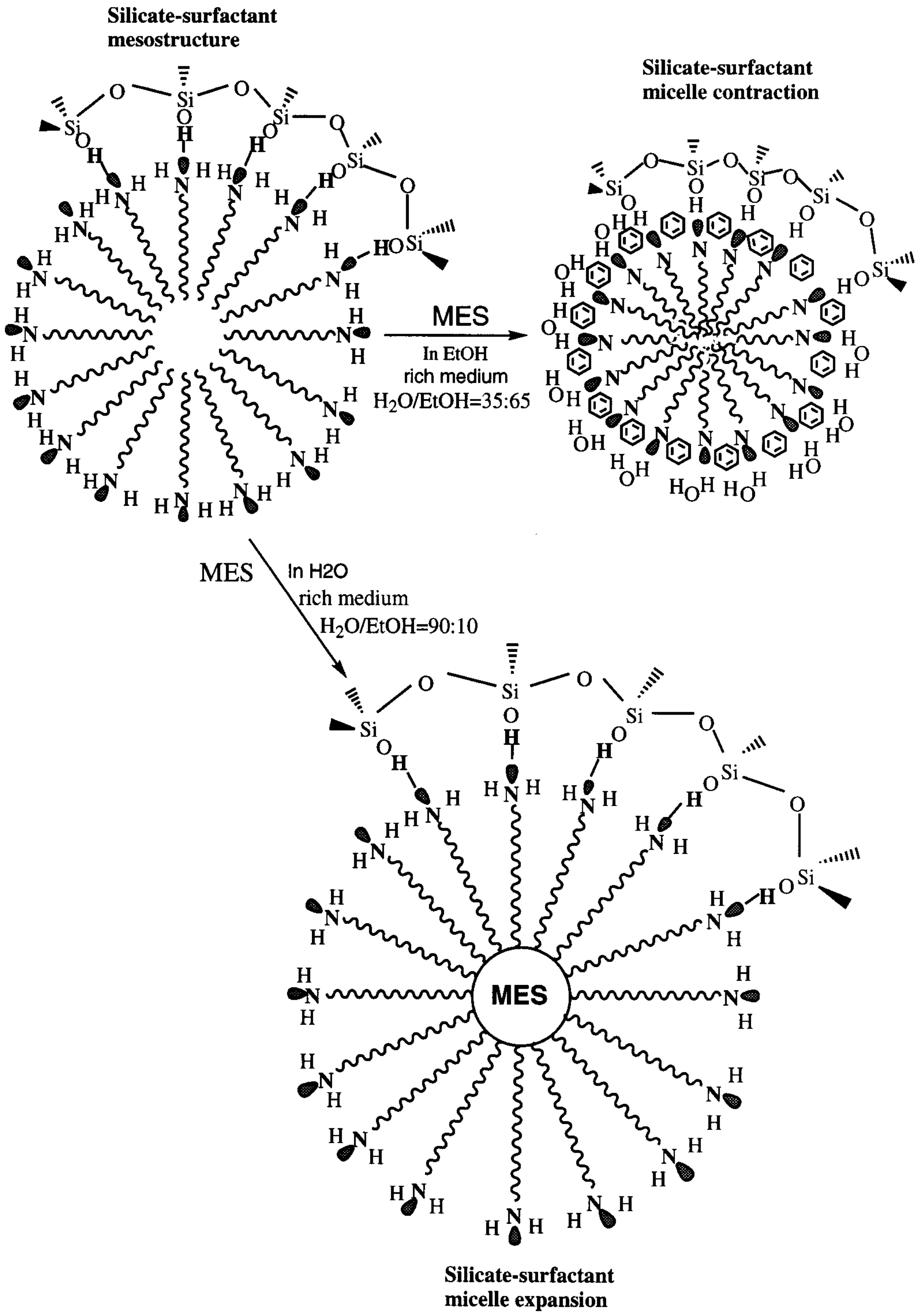

Figure 7. Schematic representation of the structure-directing effects of mesitylene on HMS assembly. In the water-rich media, the mesitylene "dissolves" in the hydrophobic central core of the micelle leading to pore expansion. In the ethanol-rich environment, mesitylene preferentially "adsorbs"to interfacial headgroups, thus increasing effective headgroup size and subsequently decreasing the pore size.

We have previously described as-synthesized HMS materials as neutral framework analogues of hexagonal MCM-41.[5] Evidence for the hexagonal ordering of channels was obtained from selected area electron diffraction.[4] The X-ray powder diffraction patterns were attributed to a very small scattering domain size. It is clear from the results of the present study, however, that the broad diffraction lines characteristic of HMS materials are not due exclusively to a small scattering domain size. The patterns obtained for the fine grained HMS particles are indistinguishable from those obtained for the much larger spheroid to disklike fundamental particles (cf., Figure 6). Consequently, framework disorder, in addition to small scattering domain sizes, plays an important role in broadening the diffraction lines. On the basis of the TEM images obtained in the present work (cf., Figures 4 and 5), we find no evidence for hexagonal long range channel packing order. Even "disordered" hexagonal channel packing, which has been previously documented for MCM-41 prepared by S^+I^- assembly, [19] appears to be difficult to

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achieve by S°I° assembly. Additional work is progress to better describe the reaction conditions that determine the assembly of hexagonal vs wormhole or sponge-like HMS framework structures.

Wormhole motifs have been observed for silica and alumina mesostructures obtained by N^oI^o assembly, where N° is a polyoxyethylene surfactant.[6−8] Also, sponge-like framework structures have been described for mesoporous silicas obtained by electrostatic S^+I^- assembly in the presence of a structure disrupter (e.g., ethylenediaminetetraacetate).[20] Distinguishing between wormhole and sponge-like pore structures is not a straightforward matter. “Wormholes” imply channel structures with nearly uniform diameters, whereas “sponges” imply substantially reticulated structures. On the basis of the relatively narrow HK pore size distributions observed in the present work and the presence of channel-like voids in the TEM images, we prefer describing HMS materials as wormhole frameworks. Future work will require more incisive quantitative descriptions based in part on the X-ray and neutron scattering properties of these and other highly disordered framework structures.

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