Pore Size Modification of Mesoporous HMS Molecular Sieve Silicas with Wormhole Framework Structures

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Wormhole HMS silica molecular sieves with average framework pore sizes in the range 2.9 to 4.1 nm were assembled from 4:1 molar mixtures of TEOS as the inorganic precursor (I^o) and dodecylamine as the structure-directing surfactant (S°) in 63:27 (v/v) water/ethanol. Increasing the assembly temperature from 25 °C to 65 °C resulted in an increase in the Horvath–Kawazoe pore size (from 2.9 to 4.1 nm). Also, the ratio of fully cross-linked (Q^4) to incompletely cross-linked (Q^3) SiO_4 sites (Q^4/Q^3) increased more than 2-fold from 1.96 to 4.26 with little or no change in the framework wall thickness (~1.0 nm). Analogous results were obtained for HMS mesostructures assembled at an I^o/S° ratio of 10. Postsynthesis remodeling of as-made HMS mesostructures through digestion in hot distilled water resulted in comparable expansions in the framework pore sizes. The pore expansion process, whether achieved through an increase in the direct assembly temperature or through postsynthesis remodeling in distilled water, is consistent with a mechanism based on temperature-dependent changes in the polarity of the $S^\circ I^o$ interface and concomitant changes in the surfactant packing parameter and self-swelling of the structure-directing micelle.

Introduction

The supramolecular assembly of mesoporous molecular sieves can be achieved through various types of interactions at the micelle–solution interface. Electrostatic charge matching,[1-3] H-bonding,[4,5] and dative bonding interactions[6] between the organic structure director and the inorganic precursor have all been successfully utilized in the formation of mesostructured materials. The original work of the Mobil group on the electrostatic assembly of hexagonal MCM-41 silicas[1] has shown that the pore size of the framework could be mediated by controlling the size of the structure-directing surfactant or by incorporating an auxiliary organic solvent as a cosurfactant to swell the micelles. Further studies[7-10] have shown that increases in the

assembly temperature or digestion time can also be used to increase the framework pore size. Increases in the assembly temperature can lead to decomposition of the quaternary ammonium ion surfactants[7,10] through either reaction with OH^- to yield neutral amines or by Hoffman degradation to yield alkenes. Both long-chain amines and alkenes are efficient swelling agents and can act as auxiliary surfactants in increasing framework pore sizes. In addition, ex situ postsynthesis hydrothermal treatment methods[11] have been used to expand the pore sizes of electrostatically preassembled mesostructures by an analogous mechanism.

Relatively little work has been reported, however, for the pore size mediation of mesostructures assembled through H-bonding interactions between electrically neutral surfactants and inorganic precursors. Assembly pathways based on H bonding are generally designated either $S^\circ I^o$ or $N^o I^o$, where I^o is the inorganic precursor (typically an alkoxide) and S° or N^o is the surfactant (typically an amine or a nonionic PEO-based surfactant, respectively). These pathways normally afford mesostructures with wormholelike framework structures. HMS[4] and MSU-X[5] silicas assembled from electrically neutral amines and nonionic di- and triblock surfactants, respectively, are examples of wormhole framework mesostructures. As expected, pore size control can be achieved for both HMS and MSU-X materials through the use of a family of surfactants with different hydro-

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phobic chain lengths.[4,12] In the case of MSU-X silicas,[13] controlled pore size expansions up to 2.4 nm can also be achieved using a single PEO surfactant simply by increasing the assembly temperature over the range 25–65 °C. Additionally, the pore sizes of MSU-X materials can be expanded through ex situ postsynthesis thermal treatments.[14,15] These pore expansion processes arise due to temperature-dependent changes in the conformation of the surfactant and, hence, in the amphiphilic character and size of the surfactant.

Reliable methods for the pore size mediation of a HMS mesostructure assembled from a single amine surfactant, however, are generally lacking. The use of an auxiliary organic solvent as a cosurfactant, such as 1,3,5-trimethylbenzene (TMB), can lead to either an increase or a decrease in the framework pore diameter, depending on whether the cosolvent resides in the hydrophobic interior or the hydrophilic palisade region of the micelle.[16] Incorporating ethanol as a cosolvent has been found to decrease HMS pore diameters[17] because this cosolvent binds primarily at the palisade region of the micelle and decreases the surfactant packing parameter. A high concentration of ethanol (>50 vol %) also promotes the undesirable nucleation of large monolithic particles that limit framework accessibility.[18] It has been noted qualitatively[11] that the pore size of HMS could be enlarged through an ex situ hydrothermal treatment of the predried, as-made mesostructure in H_2O at 100 °C. Subsequent results[15] indicate that postsynthesis hydrothermal treatment causes a significant decrease in the X-ray diffraction intensity and a broadening of the N_2 adsorption step, suggesting an accompanying loss in the integrity of the wormhole framework structure.

HMS silicas, particularly those with a spongelike particle texture for improved framework access,[18] have found promising applications as heterogeneous catalysts[19,20] and as supports for the immobilization of reagents.[21] A simple method for tailoring the framework pore size of HMS materials in the presence of a single amine surfactant could make them even more attractive for such applications. Accordingly, in the present work we have examined the effect of assembly conditions and postsynthesis modification methods on the pore size characteristics, framework cross-linking, and particle texture of HMS silicas assembled though a H-bonding $S°I°$ pathway using dodecylamine as the surfactant $(S°)$

and tetraethyl orthosilicate (TEOS) as the inorganic precursor $(I°)$.

Experimental Section

Direct Assembly of HMS Silicas. Dodecylamine (DDA, 4.9 mmol) was dissolved in 5 mL of ethanol, and 45 mL of H_2O was then added to afford a 90:10 (v/v) H_2O/EtOH solution of the surfactant. The surfactant solution was heated to the desired reaction temperature, and tetraethyl orthosilicate (TEOS, 19.6 or 49 mmol) was added to give a reaction mixture with an $I°/S°$ ratio of 4 or 10, respectively. For the reaction mixture containing 19.6 mmol TEOS, an additional 7 mL of EtOH was added to account for the difference in ethanol released upon TEOS hydrolysis between the two mixtures. The reaction flask was sealed and shaken at 220 rpm in a heated water bath at the desired synthesis temperature for 20 h. The synthesis temperatures were varied from 25 to 85 °C in 10-deg increments. The resulting white precipitates were filtered out, washed with copious amounts of H_2O, and allowed to air-dry at room temperature for 24 h. The surfactant was removed by calcination in air at 600 °C for 4 h. The final composition of the assembly medium was 63:27 (v/v) water/ethanol, and the reaction stoichiometries were as follows:

$$4 \ (10):1:41.5 \ (17.5):510 \ \text{TEOS/DDA/EtOH/H}_2\text{O}$$

Postsynthesis Remodeling of HMS Silicas. As-made HMS wormhole silica molecular sieves were subjected to a postsynthesis modification treatment to remodel the framework pore topology. In one series of experiments, an as-made product was first assembled at 25 °C and a reaction stoichiometry $I°/S° = 4.0$, recovered from the mother liquor, washed with two 150 − mL portions of H_2O, and then remodeled by heating at 65 °C for 1–5 days in distilled H_2O. The remodeled products were filtered out, washed with copious amounts of H_2O, and allowed to air-dry at room temperature for 24 h. The surfactant was then removed by calcination in air at 600 °C for 4 h.

In a second experiment, an as-made HMS silica with a spherical particle morphology was assembled at an $I°/S°$ ratio of 8.0 and then examined by TEM before and after framework remodeling in distilled water. To prepare the as-made product, DDA (3.4 mmol) was dissolved in 10 mL of ethanol, and then 90 mL of H_2O was added to afford a 90:10 (v/v) H_2O/EtOH solution of the surfactant. TEOS (27.6 mmol) was added to the surfactant solution, and the flask was sealed and shaken at 220 rpm in a H_2O bath at 25 °C for 20 h. The final composition of the reaction medium was 85:15 (v/v) water/ethanol, and the reaction stoichiometry is as follows:

$$8:1:50.4:1471 \ \text{TEOS/DDA/EtOH/H}_2\text{O}$$

After 20 h of reaction time the product was washed with two 150-mL portions of H_2O and then heated in 60 mL of distilled water at 65 °C for 4 days. The product was then filtered, washed with H_2O, and allowed to air-dry at room temperature for 24 h. The surfactant was removed by calcination in air at 600 °C for 4 h.

Physical Measurements. Wide-angle powder X-ray diffraction (XRD) patterns were obtained using a Rigaku Rotaflex diffractometer with Cu Kα radiation ($\lambda = 0.154$ nm). Counts were accumulated every 0.02 deg (2θ) at a scan speed of 1° (2θ)/min.

N_2 adsorption−desorption isotherms were obtained at −196 °C on a Micromeritics ASAP 2010 sorptometer using static adsorption procedures. Samples were outgassed at 150 °C and 10^{-6} Torr for a minimum of 12 h prior to analysis. BET surface areas were calculated from the linear part of the BET plot according to IUPAC[22] recommendations. Pore size distribution

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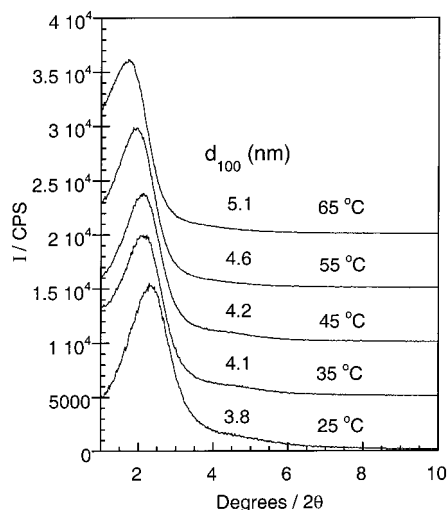
Figure 1. Powder X-ray diffraction patterns of calcined HMS silicas assembled from dodecylamine (S°) as the structure-directing surfactant and TEOS as the inorganic precursor (I°) at temperatures in the range 25–65 °C and a reaction stoichiometry I°/S° = 4.0.

was estimated from the adsorption branch of the isotherm by the method of Horvath and Kawazoe.[23]

TEM images were obtained on a JEOL 100CX microscope with a CeB$_6$ filament and an accelerating voltage of 120 KV, a beam diameter of approximately 5 μm, and an objective lens aperture of 20 μm. Sample grids are prepared via sonication of powdered sample in EtOH for 20 min and evaporating 1 drop of the suspension onto a carbon-coated, holey film supported on a 3 mm, 300 mesh copper grid.

^{29}Si MAS NMR spectrums were recorded on a Varian 400 VRX solid-state NMR spectrometer at 79.5 MHz under single-pulse mode with a 7-mm zirconia rotor, a spinning frequency of 4 kHz, pulse width of 8.5 μs, and a pulse delay of 800 s. The chemical shifts where externally referenced to talc (−98.1 ppm relative to tetramethylsilane).

Results

Assembly of HMS Framework Structures. The S°I° assembly of HMS molecular sieve silicas with wormhole framework structures was accomplished using dodecylamine (abbreviated DDA) as the structure-directing surfactant, S°, and tetraethyl orthosilicate (TEOS) as the inorganic precursor, I°. The effect of the assembly temperature over the range 25–85 °C was assessed at two silica to surfactant reaction ratios, namely I°/S° = 4.0 and 10.

Figure 1 provides the X-ray powder diffraction patterns for the calcined HMS derivatives formed at different assembly temperatures and an I°/S° stoichiometry of 4.0. Each sample exhibited a single low angle reflection indicative of the average pore–pore correlation distance. As the synthesis temperature increased, the pore–pore correlation distance systematically increased from a low of 3.8 nm at 25 °C to a maximum value of 5.1 nm at 65 °C. An analogous increase in the pore–pore correlation distance with increasing assembly temperature was also observed for a reaction stoichiometry of I°/S° = 10. Samples assembled at 75 and 85 °C, however, gave diffraction patterns (not shown) with greatly reduced XRD intensity. The loss of a well-expressed pore–pore correlation peak indicated

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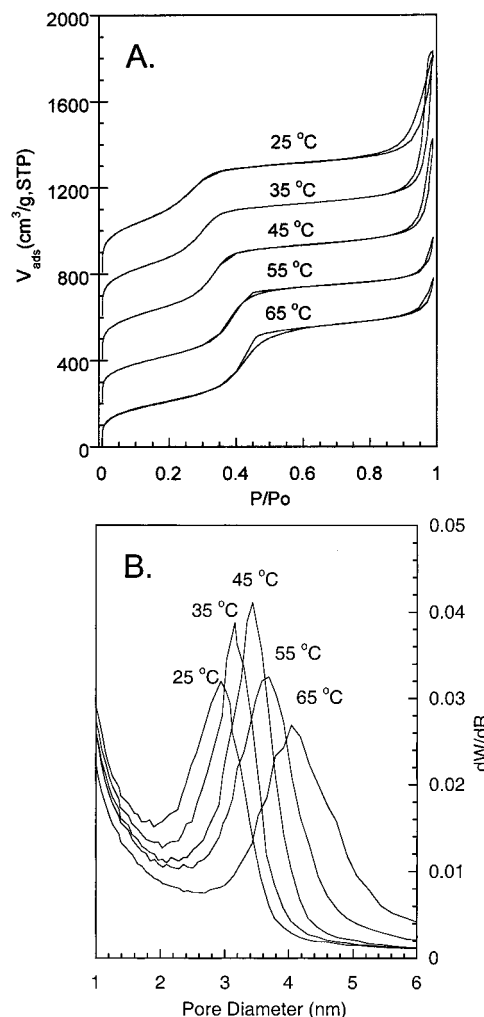
Figure 2. (A) N$_2$ adsorption–desorption isotherms and (B) Horvath and Kawazoe pore size distribution plots for calcined HMS silicas assembled at temperatures in the range 25–65 °C and a reaction stoichiometry I°/S° = 4.0. The isotherms are offset vertically by 200 cm^3 g^{-1} STP for clarity.

that the wormhole framework structure is largely lost at these higher assembly temperatures due to thermal motions that severely disorder H-bonding interactions at the micelle–solution interface.

Figure 2, parts A and B, show the N$_2$ adsorptions isotherms and Horvath and Kawazoe (HK) pore size distributions, respectively, for calcined HMS silicas assembled over the temperature range 25–65 °C and I°/S° = 4.0. The samples exhibit type IV isotherms (Figure 2A) as expected for mesoporous silica. Filling of the framework-confined mesopores occurred at P/P_0 = 0.2–0.5. The shift to higher relative pressures indicates an increase in framework pore size with increasing assembly temperature. Additionally, each sample displayed a significant uptake of N$_2$ at high relative pressures (P/P_0 > 0.90), a signature of a high degree of textural porosity.[18]

As can be seen from the Horvath–Kawazoe plots in Figure 2B, the pore size increased systematically with increasing temperature from 2.9 nm at 25 °C to a 4.1 nm at 65 °C, a 41% increase. At 45 °C, the pore size distribution was narrowest, indicating an optimum temperature for HMS assembly with DDA. It is noteworthy that the maximum HK pore diameter achieved

Table 1. Structural Properties of Calcined HMS Molecular Sieves Prepared by S^oI^o Assembly[a]

assembly temp, °C	I^o/S^o (mol/mol)	d-spacing (nm)	HK pore diameter (nm)	wall thickness[b] (nm)	surf area (m²/g)	framework pore vol (cm³ g⁻¹)
25	4.0	3.8	2.9	0.9	1121	0.78
35	4.0	4.1	3.2	0.9	1025	0.80
45	4.0	4.2	3.4	0.8	938	0.81
55	4.0	4.6	3.7	0.9	888	0.82
65	4.0	5.1	4.1	1.0	780	0.75
25	10	3.7	2.3	1.4	1069	0.44
35	10	4.0	2.3	1.7	747	0.43
45	10	4.0	2.6	1.4	697	0.42
55	10	4.6	3.0	1.6	666	0.39
65	10	5.0	3.2	1.8	644	0.31

[a] All mesostructures were prepared from TEOS as the inorganic precursor (I^o) and dodecylamine as the structure-directing surfactant (S^o) and calcined at 600 °C. [b] Wall thickness was calculated by subtracting the HK pore diameter from the XRD d spacing. The framework pore volume was obtained from the volume of N_2 adsorbed in pores less than 5.0 nm in diameter.
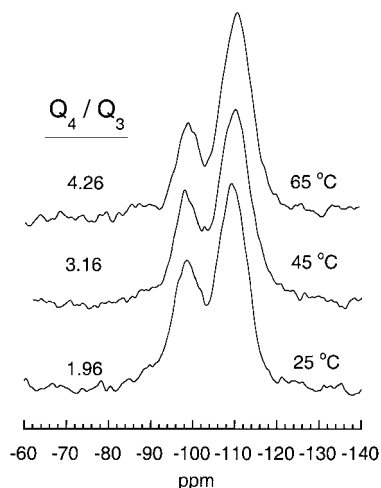
Figure 3. ²⁹Si MAS NMR spectra of calcined HMS silicas assembled at 25−65 °C and a reaction stoichiometry I^o/S^o = 4.0. Resonances near −98 and −110 ppm are assigned to Q^3 and Q^4 silica environments, respectively.

for these materials (4.1 nm) is greater than the d_{001} spacing found for the lipid bilayer phase that DDA forms in a water−alcohol solution (3.6 nm). The trend to larger framework pores with increasing assembly temperature also was observed for HMS wormhole silicas assembled at I^o/S^o = 10.

²⁹Si MAS NMR spectra of the as-made HMS derivatives assembled at I^o/S^o = 4.0 (Figure 3) show that increasing the assembly temperature increases the fraction of fully cross-linked Q^4, $Si(OSi)_4$, tetrahedra (∼110 ppm) in comparison to the Q^3, $HOSi(OSi)_3$, sites (∼98 ppm). The Q^4/Q^3 ratio increased from a value of 1.96 at 25 °C to 4.26 at 65 °C, corresponding to 66% and 81% of all SiO_4 sites being fully cross-linked, respectively. The NMR spectra for the calcined versions of the samples assembled at 25 and 65 °C were virtually indistinguishable (not shown), indicating that the extent of framework cross-linking achieved upon calcination was independent of the degree of cross-linking in the initial as-made mesostructures. For both calcined samples, the peak centered at near 110 ppm broadened significantly due to the formation of a range of Q^4 sites. Although this broadening made quantitative analysis of the Si siting difficult, the retention of some Q^3 sites in the calcined derivatives was clearly indicated by a shoulder at 98 ppm.

Table 1 summarizes the effect of assembly temperature on the structural properties of the HMS silicas

assembled at I^o/S^o ratios of 4.0 and 10 and temperatures in the range 25−65 °C. Clearly, the X-ray correlation distances and framework pore diameters increase with assembly temperature for both reaction stoichiometries (I^o/S^o = 4.0 or 10). Subtraction of the HK pore size from the observed pore−pore correlation distance shows that the pore wall thickness is essentially independent of the assembly temperature, though the wall thickness is substantially larger for the mesostructures assembled at I^o/S^o = 10 (1.6 ± 0.2 nm) than at I^o/S^o = 4.0 (0.9 ± 0.1 nm). The thicker framework walls are associated with lower specific BET surface areas, pore volumes, and framework pore diameters, as expected. Also, the BET surface areas show the expected decrease with increasing pore diameter increases at constant pore volume.

Postsynthesis Remodeling of As-Made HMS Wormhole Frameworks. To more fully explore the possibility of remodeling the framework pore size of an as-made HMS through postsynthesis treatment,[11,15] a mesostructure was assembled at 25 °C (I^o/S^o = 4.0), washed free of mother liquor, and then digested in distilled water at 65 °C for 1−5 days. In this procedure it was important that the initial as-made mesostructure was washed free of the original mother liquor prior to being remodeled in distilled water. A significant loss of pore structure occurred if the as-made mesostructure was allowed to digest in the ethanol-containing mother liquor. It appears that the presence of ethanol in the mother liquor increased the solubility of the pore-filling surfactant at elevated temperatures and this compromised the integrity of the remodeled mesostructure.

As in the case of HMS derivatives formed by direct assembly, the XRD patterns and N_2 adsorption/desorption isotherms for the remodeled mesostructures were consistent with the retention of the mesoporous wormhole framework and spongelike particle morphology. The relevant structural parameters for the calcined products are provided in Table 2. A substantial increase in pore−pore correlation distance (d spacing) from 3.8 to 4.6 nm was realized after only 1 day of digestion, followed by a more gradual increase to 5.3 nm after 5 days. Also, an overall pore expansion of 1.5 nm was achieved, somewhat larger than the 1.2 nm expansion afforded through direct assembly at 65 °C due to the lack of ethanol in the digestion liquor.[17]

The remodeling of the above HMS mesostructure in distilled water at 65 °C was further manifested by an increase in the framework cross-linking. The Q^4/Q^3

Table 2. Structural Properties of HMS Mesostructures Remodeled through Postsynthesis Treatment at 65 °C[a]

reacn time (days)	d-spacing (nm)	HK pore size (nm)	wall thickness (nm)	surf area (m²/g)	framework pore vol (cm³ g⁻¹)
0	3.8	2.9	1.0	1121	0.78
1	4.6	3.7	0.9	747	0.64
2	4.9	4.1	0.8	697	0.67
3	5.1	4.1	1.0	666	0.65
5	5.3	4.4	0.9	644	0.64

[a] The initial as-made mesostructure (reaction time = 0 days) was assembled from TEOS and DDA at 25 °C and a reaction stoichiometry $I^o/S^o = 4.0$.

cross-linking parameter prior to calcination increased from an initial value of 1.96 to a value of 4.1 after 5 days of digestion at 65 °C. Although previously reported postsynthesis treatments of as-made HMS silicas at 100 °C resulted in the loss of pore uniformity and the partial collapse of the mesostructure,[15] remodeling at 65 °C substantially improved both the framework pore size and framework cross-linking. Apparently, the thermal disorder at 100 °C disrupted the hydrogen bonding interactions at the micelle interface and caused structural collapse. At 65 °C, the hydrogen-bonding interactions were sufficient to retain the wormhole structure and allow remodeling of the framework walls and the expansion of the pore size.

We also investigated the framework remodeling of a HMS mesostructure assembled at 25 °C and a reaction stoichiometry $I^o/S° = 8.0$. At this reaction stoichiometry, the wormhole framework prevailed, but the particles were monolithic and spherical in comparison to the fractal or spongelike particles[18] obtained at $I^o/S° = 4.0$. Digesting the as-made mesostructure in distilled water at 65 °C for 4 days increased the pore−pore correlation distance from 4.1 to ∼7.1 nm. As shown by the nitrogen isotherms and pore size distribution curves in Figure 4, this increase in correlation distance was accompanied by an increase in the framework pore size from 2.5 to 4.4 nm. In addition, the Q^4/Q^3 cross-linking parameter increased from 1.77 to 3.87 upon remodeling.

The TEM images of this remodeled sample provided insight into the remodeling mechanism. As seen in Figure 5A, the initial as-made mesostructure consists of submicrometer, spherical monolithic particles. Though the spheres are not uniform in size, they are clearly independent particles and discriminate in shape. The framework mesopores are wormholelike throughout each particle (Figure 5B). There appears to be some spatial orientation of the pores within the particles, as suggested by the concentric rings within the spherical particles (Figure 5A). The remodeled mesostructure, however, clearly shows Ostwald ripening of the amorphous silica as the spheres became intergrown (Figure 5C,D).

Discussion

In the absence of TEOS, dodecylamine forms a lipidlike bilayer phase in a water−alcohol solution at ambient temperature as evidenced by a lamellar X-ray diffraction pattern corresponding to a basal spacing d_{001} = 3.6 nm. The lamellar surfactant structure is consistent with a small amine headgroup area (a_o) and a surfactant packing parameter,[24] $g = V/(la_o)$, near 1.0.

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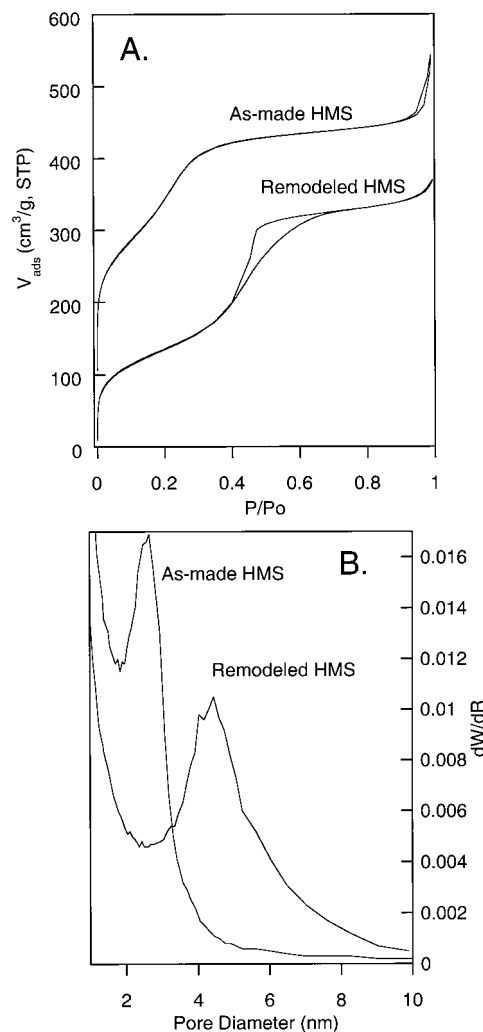
Figure 4. (A) N_2 adsorption−desorption isotherms and (B) Horvath and Kawazoe pore size distribution plots for a HMS mesostructure prepared by direct assembly (25 °C, $I^o/S° = 8.0$) and for the corresponding mesostructure remodeled by digestion in distilled water (65 °C, 4 days).

Upon the addition of TEOS to the surfactant solution, a wormholelike HMS mesostructure is formed via $I^oS°$ assembly. The transformation from a lamellar to a wormhole structure arises due to H-bonding interactions between the amine headgroup and the silica precursors formed through TEOS hydrolysis increasing the surface curvature of the surfactant micelle.

In the present work we have shown that one can substantially mediate the pore size, framework wall thickness, and framework cross-linking of HMS molecular sieve silica simply by controlling the assembly temperature and reaction stoichiometry. In general, increasing the assembly temperature from 25 to 65 °C increases the framework pore size by about 40% (from
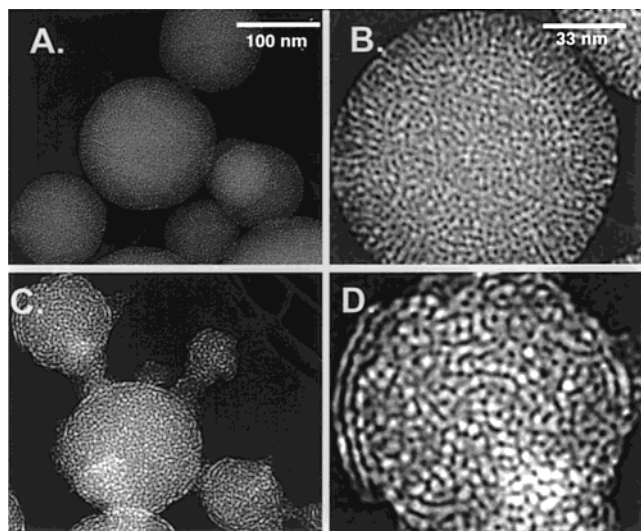
Figure 5. TEM images of HMS particles: (A, B) spherical particles prepared by direct assembly (25 °C, $I^o/S° = 8.0$); (C, D) the corresponding mesostructure showing evidence for Ostwald ripening after being remodeled by postsynthesis treatment in distilled water at 65 °C for 4 days. Scale bars correspond to 100 nm in images A and C and to 33 nm for images B and D.

2.8 to 4.1 nm at $I^o/S° = 4.0$ and from 2.3 to 3.2 nm at $I^o/S° = 10$) when the solvent composition is maintained at a water:ethanol ratio of 63:27 (v/v). Above ∼65 °C, however, thermal disorder begins to disrupt mesostructure formation, and there is no benefit to further increasing the assembly temperature.

For HMS assembly temperatures in the range 25 to 65 °C, where the wormhole structure is well-expressed, the framework cross-linking improves substantially with increasing temperature. For example, the fraction of totally cross-linked Q^4 sites increases from 66% to 81% as the assembly temperature is increased from 25 °C to 65 °C. As indicated by similarities in ^{29}Si MAS NMR spectra, the calcination of HMS silicas at 600 °C tends to level the Q^4/Q^3 values, regardless of the initial framework cross-linking achieved under assembly conditions. It is especially notable, however, that the calcined versions of samples assembled at 65 °C are stable to boiling water at 100 °C for 6 h, whereas the calcined form of HMS assembled at 25 °C experiences structural collapse under these conditions, as judged by XRD. That is, an as-made HMS mesostructure with an initially high Q^4/Q^3 cross-linking value exhibits better hydrothermal stability upon calcination than a calcined HMS with an initially low Q^4/Q^3 value. This difference in structural stability occurs even though the Q^4/Q^3 values for the final calcined derivatives may be quite similar. This suggests that the overall Q^4/Q^3 value is not a reliable predictor of structural stability. Other factors, such as the siloxane ring strain induced upon silanol condensation, may also influence framework stability.

Increasing the $I^o/S°$ reaction stoichiometry for HMS assembly adds more silica to the framework walls, resulting in an increase in average wall thickness from 0.9 ± 0.1 nm at $I^o/S° = 4.0$ to 1.6 ± 0.2 nm at $I^o/S° = 10$. The 2.5-fold increase in silica-to-surfactant ratio, however, also is accompanied by a decrease in framework pore size (cf., Table 1). The increases in framework

wall thickness with increasing reaction stoichiometry, as well as the increases in framework pore size and framework cross-linking with increasing assembly temperature, are consistent with an electrically neutral $I^o/S°$ assembly pathway based on H-bonding interactions at the surfactant micelle−silica interface. The absence of charge matching requirements between the surfactant and the silica framework places no constraints on the Q^4/Q^3 siting of SiO_4 tetrahedra and this allows more silica to be condensed into the framework walls under the influence of mass action.

The mechanism leading to an increase in framework pore size with increasing assembly temperature is related to changes in the polarity of the $I^oS°$ interface and, consequently, a decrease in H-bonding at the interface. As the assembly temperature is increased, the framework cross-linking is enhanced through further condensation of silanol groups, leading to a reduction in the framework polarity. The degree of H-bonding, along with the hydration of the amine headgroup, decreases as the polarity of the interface decreases. This leads to an increase in the surfactant packing parameter (g) with decreasing effective headgroup area (a_o) and, therefore, to an increase in the framework pore diameter as the interfacial curvature decreases. The maximum pore diameter attained in these materials (4.4 nm) is significantly larger than twice the surfactant molecule length of approximately 1.6 nm. There is, therefore, the likelihood that the decreasing degree of H-bonding between the silicate wall and the surfactant molecules at elevated temperatures results in a fraction of the surfactant molecules migrating to the micelle core. The hydrophobic nature of the non-H-bonded alkylamine causes the molecule to penetrate the core and expand the micelle analogous to electrostatic pore expansion mechanisms.[10]

The pore expansion process is, consequently, a combination of the decreasing interfacial curvature due to an increasing average surfactant packing parameter coupled with the alkylamine swelling of the micelle with increasing temperature.

Although pore expansion in HMS may involve micelle swelling, it is initiated through a fundamentally different event. For MCM-41 and related electrostatically assembled mesostructures, increases in the assembly temperature does not fundamentally alter the framework charge. Instead, partial degradation of the quaternary ammonium ion surfactants leads to the formation of neutral amines and alkenes that act as auxiliary surfactants and increase the framework pore size by expanding the micelle.[7−11]

In the case of MSU-X mesostructures, the temperature-dependent pore expansion is attributable to changes in the conformation of the PEO segment of the nonionic surfactant and, hence, to an increase size of the surfactant.[14,15] For HMS silicas, however, it is the decrease in H-bonding interactions between the silica and the surfactant that initiates an increase in the micelle diameter and the expansion of framework pores.

An analogous pore expansion mechanism based on temperature-dependent changes in the polarity of the $I^oS°$ interface accounts for the framework remodeling that occurs upon postsynthesis treatment of as-made HMS mesostructures in hot distilled water. The sub-

stantial increase in framework pore size (cf., Table 2) and enhancement in Q^4/Q^3 cross-linking that occurs upon postsynthesis treatment at 65 °C is almost certainly a consequence of the reduction in interfacial H-bonding and polarity at the remodeling temperature. As the interface becomes less polar, the surfactant packing parameter becomes larger, the surfactant becomes partitioned between the micelle interface and the micelle core, and the increase in micelle size is reflected in the framework pore size.

The transport of silica in the remodeling process occurs through dissolution and reprecipitation, as evidenced by the Ostwald ripening of the mesostructured particles under remodeling conditions (cf., Figure 5). Localized dissolution of the silica matrix during thermal treatment is most likely to occur in regions of high surface curvature such as at the intersections of pores within the wormhole network.[25] The presence of the basic amine at these intersections promotes this localized dissolution of the silica. H-bonding controls the reprecipitation and re-forming of the silica at the micelle interface, resulting in an expansion of the pore diameter.

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