Assembly of Large-Pore Silica Mesophases with Wormhole Framework Structures from α,ω-Diamine Porogens

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Large-pore mesoporous silicas with wormhole framework structures have been assembled through hydrogen-bonding pathways from sodium silicate or tetraethyl orthosilicate (TEOS) as the silica source and amine-terminated Jeffamine surfactants of the type $H_2NCH(CH_3)CH_2[OCH_2CH(CH_3)]_xNH_2$ as the structure-directing porogen. Depending on the molecular weight of the α,ω-diamine surfactant ($x \sim 33$ and 68 for Jeffamine D2000 and D4000, respectively) and the synthesis temperature (25−65 °C), the mean pore size distributions of the mesostructured silicas (denoted MSU-J) were centered between 4.9 and 14.3 nm, making these materials comparable to hexagonal SBA-15 mesostructures in average framework pore size. In addition to the BET surface areas of MSU-J silicas (408−1127 m^2/g) being comparable to those of SBA-15 (630−1040 m^2/g), MSU-J silicas exhibit larger pore volumes (1.37−2.29 cm^3/g) than SBA-15 silicas (0.56−1.23 cm^3/g) prepared in the absence of mesitylene. MSU-J wormhole mesostructures represent the largest pore sizes observed to date for a fully three-dimensional mesoporous framework assembled from a single micellar porogen. Only mesostructured micellar foam structures exhibit larger pore sizes, but the preparation of foam structures requires the use of more complex microemulsions or latex polymers as porogens.

Introduction

Supramolecular assembly pathways based on hydrogen-bonding interactions between electrically neutral amine surfactants and electrically neutral silica precursors typically afford mesostructures with wormhole framework motifs.[1] Compared to the highly ordered monolithic mesophases prepared through electrostatic templating pathways, wormhole mesostructures typically exhibit improved activity as heterogeneous catalysts for condensed phase reactions due to the three-dimensional pore network and an improved textural mesoporosity that minimize diffusion and facilitate access to reaction sites on the pore surfaces.[2−6] Neutral amine templating offers the additional advantage of facile recovery of surfactants by solvent extraction methods.[1,7−9] Also, the use of amine surfactant micelles as mesostructure-directing agents is not limited to silicate frameworks. Mesoporous forms of certain transition-metal oxides also have been prepared using amine surfactants.[7−9]

Despite the advantages of amine surfactants for the hydrogen-bonding assembly of highly accessible mesostructured silicas, the average framework pore sizes have been limited to the range 1.6−3.1 nm.[1] An expansion of framework pore sizes up to 4.5 nm can be achieved for some wormhole silicas through the incorporation of a cosolvent, such as 1,3,5-trimethylbenzene, in the hydrophobic interior region of the micelle.[10,11] Even greater mesopore accessibility and catalytic activity can be anticipated for these wormhole framework structures if the framework pore sizes can be expanded beyond these limiting values and into the >10 nm range.

We report herein a new group of large pore mesoporous silicas, denoted MSU-J, with three-dimensional wormhole framework structures prepared through hydrogen-bonding pathways. Our approach is based on the use of amine-terminated polypropylene oxide (PPO) Jeffamine surfactants of the type $H_2NCH(CH_3)CH_2[OCH_2CH(CH_3)]_xNH_2$ as the structure-directing porogen. We show that pore sizes and pore volumes up to 14.3 nm and 2.29 cm^3/g, respectively, can be achieved, depending on the synthesis conditions and the molecular weight of the surfactant. The resulting pore sizes and BET surface areas are comparable to those of SBA-15 silicas, but unlike SBA-15, the mesopores are three-dimensionally connected.

Experimental Section

Jeffamine D2000 and D4000 surfactants (abbreviated to D2000 and D4000, respectively) were obtained from Huntsman Corp. and used without further purification as structure-directing porogens. Commercially available sodium silicate (Aldrich, 27% SiO_2, 14%

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NaOH) solution and TEOS (Aldrich) were used as the silica precursors.

In a typical synthesis of MSU-J from sodium silicate, an amount of acid (HCl) equivalent to the formal hydroxide content of the sodium silicate precursor was added to an aqueous solution of the surfactant. The desired quantity of sodium silicate was added to the surfactant solution under vigorous stirring at ambient temperature, and the mixture with a pH of 8.0−8.5 was allowed to age in a heated water bath at the desired synthesis temperature for 20 h with stirring. The surfactant was then removed from the washed, air-dried solids by calcination at 600 °C for 4 h in air.

MSU-J molecular sieves also were prepared with TEOS used as a silica precursor in water/ethanol solvent mixture. The surfactant was dissolved in ethanol, and then the desired amount of water was added under stirring. TEOS was added to the surfactant solution. The molar composition of the reaction mixture was 1.0:0.125:220:17 TEOS:D2000:H_2O:EtOH. The assembly conditions were the same as those used in the preparation of MSU-J mesostructures made from sodium silicate.

X-ray diffraction (XRD) patterns were obtained on a Rigaku Rotaflex 200B diffractometer equipped with Cu K_α X-ray radiation and a curved crystal graphite monochromator operating at 45 kV and 100 mA. Transmission electron microscopy (TEM) images were taken on a JEOL JEM-100CX II microscope with a CeB_6 filament and an accelerating voltage of 120 kV. Sample grids of calcined mesoporous silicas were prepared via sonication of powdered sample in EtOH for 10 min and evaporating 2 drops of the suspension onto a carbon-coated, holey film supported on a 3 mm, 300 mesh copper grid.

Results and Discussion

Tetraethyl orthosilicate (TEOS) and alkylamine surfactants are known to be effective reagents for the supramolecular assembly of wormhole framework structures through hydrogen-bonding interactions between the amine headgroups of the micelles and the silanol groups of the TEOS hydrolysis products.[1,10,11] Sodium silicate also can be used for the preparation of silica mesophases through supramolecular hydrogen-bonding mechanisms, provided that the formal hydroxide ion content of the solution is balanced through the addition of an acid to achieve a reaction mixture at a near-neutral pH.[12] In the present work both reagents were used as the silica source for the amine-directed assembly of very large pore wormhole mesostructures.

To optimize the framework pore size of the mesostructured products, we selected two high molecular weight α,ω-diamine surfactants of the type $H_2NCH(CH_3)CH_2[OCH_2CH(CH_3)]_xNH_2$ as the structure-directing porogens. The derivatives with hydrophobic propylene oxide segments corresponding to $x \sim 33$ and 68 have approximate molecular weights of 2000 and 4000, respectively. Reflecting these average molecular weights, the surfactants are marketed under the trade names Jeffamine D2000 and Jeffamine D4000.

Numerous survey experiments indicated the optimum reaction stoichiometry for the assembly of MSU-J mesostructures from sodium silicate to be 1.0:0.83:0.125:0.83:230 SiO_2:NaOH:D2000 (or 0.062 for D4000):HCl:H_2O, as judged by N_2 adsorption isotherms and the corresponding textural properties of the assembly products. For TEOS as the silica precursor, the optimal reaction stoichiometry was 1.0:0.125:220:17 TEOS:D2000:H_2O:EtOH.

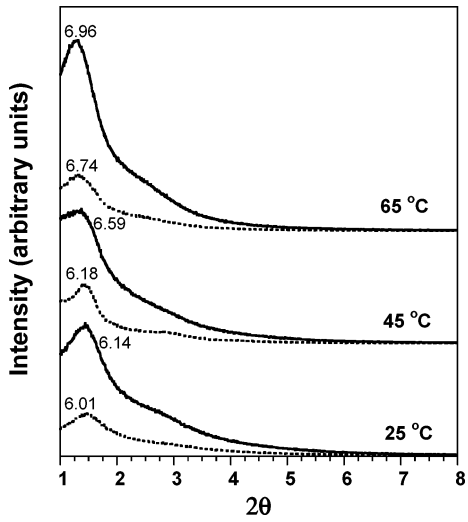

Figure 1. X-ray diffraction patterns of as-synthesized (·····) and calcined (—) MSU-J silica molecular sieves using D2000 as templating agents and sodium silicate as a silica source under neutral pH conditions at 25, 45, and 65 °C. The numbers are the pore−pore correlation distances in nanometer (nm) units.

Figure 1 illustrates X-ray diffraction (XRD) patterns of as-synthesized and calcined MSU-J silicas prepared from the sodium silicate and D2000 surfactant at temperatures of 25, 45, and 65 °C. Each sample exhibits an intense and relatively broad reflection in the 2θ range 1−1.5° with a weak, broad shoulder appearing at 2−3°. The absence of multiple *hkl* reflections indicates that the framework pore system is lacking in long-range order, but the well-expressed low-angle reflection is consistent with the average correlation distance between pores in a wormhole framework structure. Relatively broad XRD reflections (not shown) also were observed for MSU-J silicas synthesized from TEOS and D2000 at 60 °C and from sodium silicate and D4000 at 45 and 65 °C. In case of MSU-J silicas with pores > 8 nm, no XRD reflections could be detected at a 2θ angle higher than 1° due to the detection limit of our wide-angle X-ray diffractometer.

The presence of a wormhole framework structure for each of the mesostructured products was verified by TEM images, examples of which are shown in Figure 2. Although we were not able to observe a low-angle XRD peak for mesostructures with a pore size > 8 nm, the pore structures shown in the TEM images of this product (Figure 2c,d) confirm the wormhole structure and the relatively regular porosity.

N_2 adsorption−desorption isotherms and Barrett−Joyner−Halenda (BJH) framework pore-size distributions (inset) for calcined MSU-J phases synthesized from TEOS are presented in Figure 3. Filling of the framework-confined mesopores occurred at $P/P_o = 0.5-0.9$. As seen from the BJH plots, the pore size increases from 4.9 at 25 °C to 11.9 nm at 60 °C. The TEM images of the calcined MSU-J mesostructures assembled from TEOS and D2000 at 45 and 60 °C in (see Figure 2, parts b and c, respectively) reveal pore sizes consistent with those obtained from the pore-size distributions calculated on the adsorption branches of the nitrogen adsorption isotherms.

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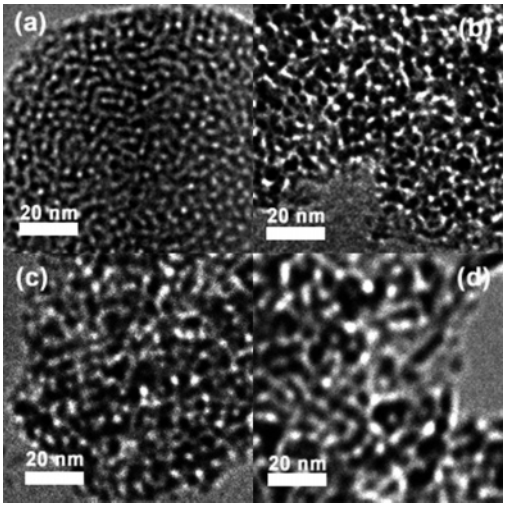

Figure 2. TEM images of calcined MSU-J silicas synthesized with the Jeffamine surfactants and the silica sources: (a) D2000 and sodium silicate at 25 °C, (b) D2000 and TEOS at 45 °C, (c) D2000 and TEOS at 60 °C, and (d) D4000 and sodium silicate at 65 °C. Average pore sizes are 5.3, 7.5, 11.9, and 14.3 nm for a, b, c, and d, respectively.

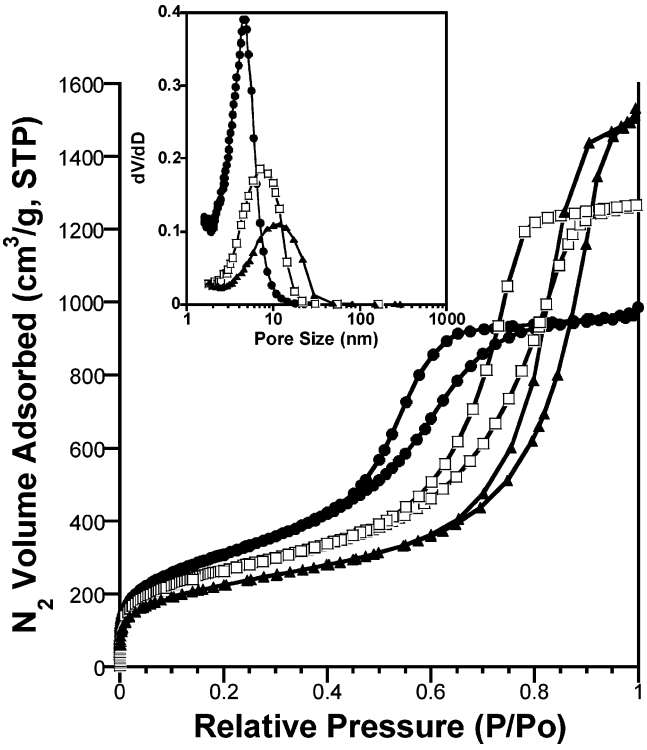

Figure 3. N_2 adsorption−desorption isotherms of MSU-J silica molecular sieves assembled from TEOS in the presence of D2000 as a structure director at different synthesis temperatures and calcined at 600 °C for 4 h. The insert provides BJH framework pore-size distributions determined from the adsorption branches of the N_2 isotherms (●, □, and ▲ for 25, 45, and 60 °C, respectively).

As shown by the nitrogen isotherms and pore-size distributions in Figure 4, the pore volumes and pore sizes of MSU-J materials assembled from sodium silicate and D2000 surfactant are less sensitive to the assembly temperature in comparison to the mesostructures assembled from TEOS. The silicate oligomers generated from these two precursors are presumed to differ in molecular weight and in the extent of cross linking. Also, differences in the ionic strengths of the sodium silicate and TEOS reaction mixtures are likely to contribute to differences in pore sizes of the

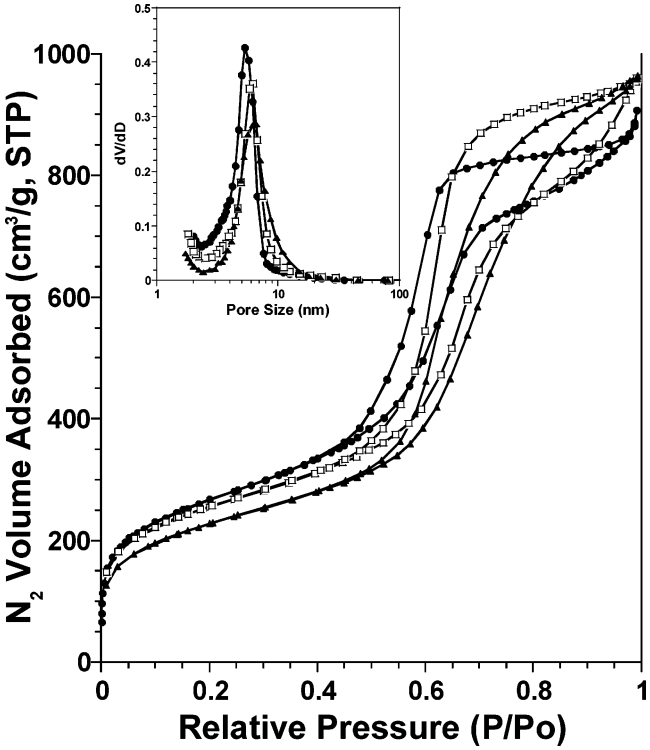

Figure 4. N_2 adsorption−desorption isotherms of MSU-J silica molecular sieves assembled from sodium silicate in the presence of D2000 as a structure director at different synthesis temperatures and calcined at 600 °C for 4 h. The insert provides BJH framework pore-size distributions determined from the adsorption branches of the N_2 isotherms (●, □, and ▲ for 25, 45, and 65 °C, respectively).

resulting mesostructures. These differences in precursor structure are manifested in differences in the temperature dependence of the framework pore sizes, as well as the pore−pore correlation distance.

As expected on the basis of polypropylene oxide chain length, the pore sizes of mesostructures assembled from D4000 are larger than those assemble from D2000 at the same synthesis temperature. Table 1 provides the BET surface areas and pore volumes of calcined MSU-J wormhole mesostructures. The pore diameter expands with increasing synthesis temperature over the range 25−65 °C from 5.3 to 6.7 nm with sodium silicate as the silica source. The use of TEOS as the silica source results in even larger average pore sizes of 7.5 and11.9 nm at assembly temperatures of 45 and 60 °C, respectively. The increases are accompanied by expected decreases in the BET surface areas. The largest average pore size (14.3 nm) is observed for the mesostructure assembled at 60 °C from D4000 and sodium silicate.

The temperature dependence of MSU-J pore sizes is related to a decrease in H-bonding at the silica−surfactant interface with increasing temperature. As the framework cross-linking is enhanced through further condensation of silanol groups at higher temperature, the polarity of the interface is decreased.[11] Consequently, the loss of hydrogen-bonding structure between the surfactant and silica aggregates at the I°S° interface will decrease the effective headgroup area (a_0) and increase the surfactant packing parameter ($g = V/(la_0)$, where V is the volume of the surfactant molecule and l is the surfactant length.). The resulting decrease in micelle curvature results in an increase in the

Table 1. Textural Properties of Calcined MSU-J Silicas with Wormhole Framework Structures

silica source	surfactant	synth temp (°C)	S_{BET} (m^2/g)	*d* (nm)	BJH pore size (nm)	wall thickness (nm)[d]	pore volume (cm^3/g)
SS[a]	D2000	25	947	6.1 (6.0)[b]	5.3	0.8	1.41
SS	D2000	45	899	6.6 (6.2)	6.0	0.6	1.49
SS	D2000	65	805	7.0 (6.7)	6.6	0.4	1.49
TEOS	D2000	25	1127	6.6 (6.0)	4.9	1.7	1.53
TEOS	D2000	45	962	8.2 (7.2)	7.5	0.7	1.96
TEOS	D2000	60	798	*c*	11.9		2.29
SS	D4000	45	756	*c*	8.0		1.56
SS	D4000	65	408	*c*	14.3		1.37

[a] SS = sodium silicate. [b] The *d* values in parentheses are for as-synthesized MSU-J mesostructures. [c] XRD reflections were not resolved for these samples. [d] The wall thickness was determined by subtracting the BJH pore size from the pore−pore correlation distance.

pore size. The maximum chain lengths of D2000 and D4000 are approximately 12 and 25 nm, respectively, when the propylene oxide units of the structure-directing agents are placed in a "stretched" all-trans conformation, as indicated by reverse Monte Carlo simulation.[13] The more likely conformations of the PPO chains include kinks that allow for hairpin configurations in the structure-directing micelles. In accord with this expectation, the largest pore sizes observed for MSU-J silicas are smaller than would be predicted by the maximum surfactant chain lengths.

The pore-size maxima for hexagonal MCM-41[14] and SBA-15[15,16] mesostructures has been widely examined and characterized. In the case of MCM-41 electrostatically assembled from quaternary ammonium ion surfactants, the framework pore sizes can be increased from values in the 3−4 nm range up to values approaching ~7 nm by increasing the assembly temperature over the range 100−150 °C.[17] Also, SBA-15 silicas prepared under strongly acidic conditions in the presence of a triblock copolymer (Pluronic 123) exhibit pore sizes of 4.7−10.6 nm, depending on reaction and post-synthesis reaction conditions.[18,19] Thus, the average pore sizes observed for the wormhole framework structures in the present work span the values found for large-pore MCM-41 and SBA-15. Only mesostructured micellar foam structures exhibit larger pore sizes. However, foam structures require the use of much more complex microemulsions[18,19] and latex polymers[20] as porogens. Also, the BET surface areas of MSU-J silicas (408−1127 m^2/g) are comparable to those of SBA-15 (630−1040 m^2/g). Moreover, MSU-J silicas have larger framework pore volumes (1.37−2.29 cm^3/g) in comparison to SBA-15 materials (0.56−1.23 cm^3/g).

In addition to spanning the pore sizes characteristic of large-pore MCM-41 and SBA-15, the mesostructures reported herein add a new dimensionality to the family of large pore mesostructures. Being wormhole frameworks, the mesopores in MSU-J materials are fully three-dimensional, which can be an advantage over the one-dimensional pore system of MCM-41, particularly in facilitating access to the framework walls under diffusion-controlled conditions. SBA-15 formally has a three-dimensional pore system, but the mesopores are one-dimensional and linked primarily through micropores. Secondary mesopores that link the primary mesopores can be formed in some SBA-15 derivatives, but the secondary mesopores represent less than 6% of the total pore volume.[21] Because MCM-41 and SBA-15 are assembled through electrostatic assembly pathways, the pore-size distributions for these mesostructures are typically narrower than the distributions for wormhole framework structures assembled through hydrogen-bonding pathways. The broader pore-size distributions for MSU-J silicas, however, do not represent a substantial disadvantage for most catalytic or adsorption applications, save perhaps for separations of macromolecules on the basis of size.

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