

Synthesis of Phenylene Bridged Mesoporous Silsesquioxanes with Spherical Morphology in Ammonia Solution

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The morphologically controlled synthesis for monodispersed spherical phenylene bridged mesoporous silsesquioxanes with relative mesoporous regularity using ammonia as catalyst and the dilute surfactants solution is reported.

The research interest in organically functionalized mesoporous silicas has been intensified recently focusing on the potential utility of materials in diverse fields, such as electric and optoelectronic devices, chemical and biochemical sensors, nanofluidic system, membranes, and catalyst.¹⁻⁴ The scope of the materials utilization is already recognized on the ability of their efficient functionalization with variety of spatially arranged organic moieties in designed hybrid mesoporous silsesquioxanes.^{3,4} The particle morphology control is also an important factor to facilitate the mass transport properties of these hybrid mesoporous silsesquioxanes. The nanosize properties are quite different for the materials with different morphology, depending on their size, shape, and packing density. In most widely studied modified Stöber process, the desired particle morphological shapes were usually controlled by optimization of molar concentration of reactants, the pH control, the basic medium as catalyst and the utilization of co-solvents.⁵ Apart from the mesoporous MCM-type silica, the morphological control in the ethane-bridged mesoporous organosilica produces cubic, spherical, flower-like, worm type, and others as widely reported in the literature.^{1,6} The previously reported periodic mesoporous benzene-silica with crystal like pore-walls, derived from phenylene-bridged organosilane precursor [(C₂H₅O)₃Si-C₆H₄-Si(OC₂H₅)₃] in NaOH solution and C₁₈TMACl surfactant, showed the clear hexagonal symmetry.^{4a} The particle morphology showed the plate-like particles (0.5–30 μm in side length and 1 μm thickness), composed of needle like single crystals aligned perpendicular to the plate surface. However, the mesoporous benzene-silicas with large pore derived from the triblock copolymer surfactant were without structural periodicity and showed specific straight rod-like morphology.^{7a} Further, the mesoporous benzene-silica prepared using the biodegradable oligomeric polymer surfactants (brij 56 and brij 76) showed some extent of architectural controls without structural periodicity and exhibit flat or twisted cluster type (2–4 μm in size) mixed morphology.^{7b}

Herein, we describe a design strategy for the monodispersed spheres of phenylene-bridged mesoporous silsesquioxanes in basic medium. We employed the ammonia solution instead of aqueous NaOH solution along with the dilute surfactant conditions to obtain the spherical mesoporous benzene-silica in this study. Effect of the different synthesis approach on the spherical morphology is also summarized. In a typical synthesis procedure, the monomer precursor 1,4-bis(triethoxysilyl)benzene (2 g) was subjected to ammonium hydroxide (28% aq NH₃ solu-

tion; 5 g) catalyzed condensation reaction in the presence of dilute ethanolic octadecyltrimethylammonium chloride surfactant solution (C₁₈TMACl, 0.3 g; H₂O, 8 g; and C₂H₅OH, 6.2 g) under vigorous stirring at ambient temperature for 3 h. The materials were also prepared using the C₁₆TMACl, C₁₄TMACl, and C₁₂TMACl surfactants. The surfactant was removed by acid extraction at 50 °C for 6 h using 3 vol % HCl/C₂H₅OH solution.

The X-ray diffraction patterns of the surfactant free materials derived using different surfactants confirm the mesopore structure (Figure 1). The materials are relatively less in mesoporous regularity compared to previously reported benzene-silica mesoporous materials. The *d* spacing increased with an increase in the alkyl chain length of the surfactant. The *d* spacings were 39.0, 35.5, 31.6, and 31.3 Å for the materials derived from C₁₈, C₁₆, C₁₄, and C₁₂ surfactants. In addition to lower angle diffraction peak, an additional broad peak (*d* spacing = ca. 8–9 Å) display at medium scattering angle revealed the rather disordered molecular scale periodicity exist in the pore wall, which consist of the benzene-silica composites.^{4a}

The corresponding nitrogen adsorption-desorption isotherms were the intermediate of type IV and type I and confirmed the mesobehavior of the materials. The BET specific surface areas were in the range 900–1000 m²·g⁻¹ depending on the alkyl chain length of the surfactant. The DFT pore size distributions revealed that pore sizes were in the range of 1.8 to 2.0 nm for the materials. ²⁹Si and ¹³C MAS NMR measurements provide the valuable information about the degree of condensation and the intact nature of Si–C and Si–O bonds, which confirm the presence of covalently bonded network consist of O_{1.5}Si–C₆H₄–SiO_{1.5} units in the materials.^{4,7}

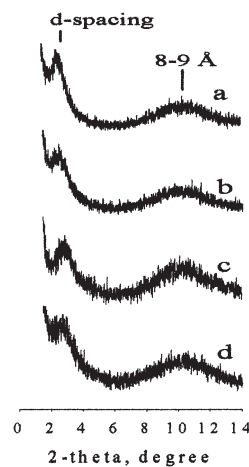


Figure 1. X-ray diffraction patterns of benzene-silica mesoporous silsesquioxanes of spherical morphology derived from a) C₁₈TMACl, b) C₁₆TMACl, c) C₁₄TMACl, and d) C₁₂TMACl surfactants.

Scanning electron micrographs (Figure 2) reveal that all mesoporous benzene-silicas derived from the different cationic surfactants of varied alkyl chain have the homogeneous spherical morphology. The size of the spherical particles was almost the same for the range of surfactants used in this study. The particles were similar in shape and 0.6–1.0 μm in size with an average diameter of 0.8 μm . However, the size homogeneity was increased with decrease in the alkyl chain length of the surfactant.

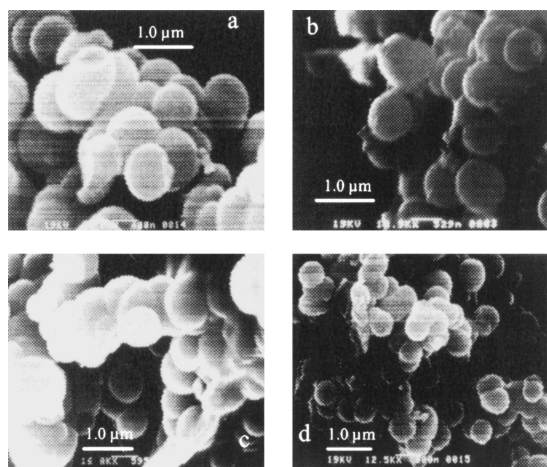


Figure 2. Scanning electron micrographs of benzene-silica mesoporous silsesquioxanes derived from a) $\text{C}_{18}\text{TMACl}$, b) $\text{C}_{16}\text{TMACl}$, c) $\text{C}_{14}\text{TMACl}$, and d) $\text{C}_{12}\text{TMACl}$ surfactants.

Further, the growth of the spherical particles was monitored by collecting the aliquots of the precipitate formed after 30 min, 1, and 3 h of stirring during the synthesis. Initially until 1 h, no specific morphology was observed (Figures 3a and 3b). The particles were irregular in shape and size (0.2–0.3 μm). However, the spherical morphology was evident after 3 h of reaction (Figure 3c) and final product could be obtained with homogeneous spherical morphology after 4 h of synthesis (Figure 3d). These results indicate that smaller particle formed in the initial stage of reaction eventually undergo the aggregation during the condensation reaction and form the relatively bigger spherical particles.

Interestingly, spherical morphology was not evident in the mesoporous benzene-silica prepared with NaOH (3N) aqueous solution instead of ammonia solution. This suggests that very mild basicity is required to control the condensation reaction of phenylene-bridged precursor for tuning the morphology to spherical particles. Also, the spherical particles were not formed with higher surfactant concentration (1.3 to 4.5 folds), suggesting that at higher surfactant to silica ratio the particles grow large enough even at the initial stage and exclude from the solution by the rapid progress in condensation reaction. Since the rate of condensation is independent from the type of surfactants, therefore the hydrophobic property of particle plays an important role for the growth of spherical particles. This also explains why the $\text{C}_{12}\text{TMACl}$ -derived materials have a better homogeneity, where lower hydrophobicity of $\text{C}_{12}\text{TMACl}$ surfactant is involved. Thus, these combined results indicate that formation of spherical particles could be achieved only when the condensation reaction was proceed very slowly regulating by strength of reaction medium and hydrophobic nature of the reactant mixtures. Besides

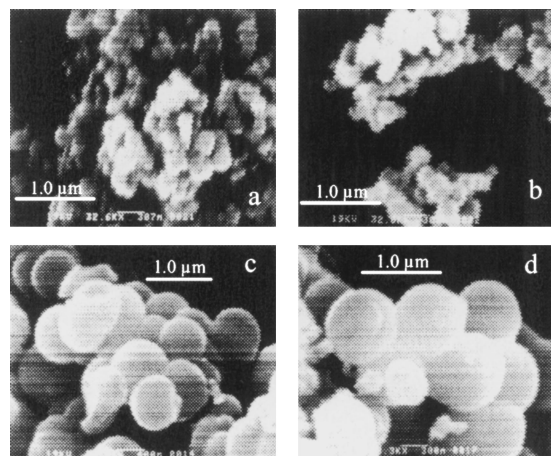


Figure 3. SEM micrographs of the evolution of spherical morphology for benzene-silica mesoporous silsesquioxanes derived from $\text{C}_{18}\text{TMACl}$ surfactants. a) after 30 min, b) after 60 min, c) after 3 h and d) after 4 h of synthesis.

the formation of spherical morphology it is also important to understand the possible symmetry of these mesoporous materials. We do not have the evident answer yet.

In conclusion, this morphologically controlled synthesis favors the dilute ethanolic surfactants solution, mild basicity and very slow condensation reaction where the fundamental aspects of monodispersed spherical particle formation is the simultaneous generation, followed by propagation and subsequent termination of each and every particle under constant rate of condensation. These mesoporous materials with spherical morphology and the hybrid composition of hydrophilic silica and hydrophobic phenylene group could find the potential application in chromatographic separation materials, absorbent and catalysis.

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