Thiol-Functionalized Silica with Mesocellular Foam and Hybrid Mesocellular Foam−Wormhole Structures

Jainisha Shah and Thomas J. Pinnavaia*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

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Among the various mesostructured forms of silica that have been discovered over the past decade,[1,2] those with cubic, wormhole, or mesocellular foam framework structures provide pore networks in which the mesoporosity is maintained in three dimensions. Mesocellular foams offer 3D mesopore systems in the range 16−42 nm,[3,4] substantially larger than the pore sizes of any other mesostructure. Organofunctional derivatives of mesocellular foams show promise as supports for protein separations and enzyme immobilization.[5,6] Until now, the organo-functionalization of mesocellular foams has been achieved only through post-synthesis grafting reactions with silane coupling agents. In the present report we show that the preparation of an organofunctional silica with a mesocellular foam structure can be greatly simplified through direct supramolecular assembly chemistry. More significantly, we show that the same supramolecular chemistry provides a unique hybrid mesocellular foam−wormhole framework structure, particularly at high loadings of the organofunctional group in the framework.

Mesocellular foam silica normally is prepared in the presence of a "oil in water" microemulsion as the structure director.[7,8] In the present work, survey experiments showed that it was not possible to form homogeneous aqueous microemulsions in water from sodium silicate as the silica source, mercaptopropyltriethoxysilane (MPTS) as the organo siloxane, $(EO)_{20}(PO)_{70}(EO)_{20}$ (Pluronic P123) as the surfactant, and 1,3,5-trimethylbenzene (TMB) as the cosurfactant. The inability to form homogeneous aqueous emulsions was traced to the rapid precipitation of silica with little or no incorporation of organosilyl groups in the framework as judged by ^{29}Si NMR. To achieve homogeneous mixing of the framework reagents in microemulsion droplets, we formed the desired microemulsions in formamide, a solvent that has been previously used to form titania foam structures.[9,10] In this way we were able to prepare a series of thiol-functional silicate compositions with the anhydrous formula $(SiO_2)_{1-x}(LSiO_{1.5})_x$, where L is a mercaptopropyl and $x = 0-0.65$.

In a typical synthesis of a $(SiO_2)_{1-x}(LSiO_{1.5})_x$ composition, the P123 surfactant and the TMB cosurfactant were dissolved in a solution of concentrated acetic acid in formamide. The acid content of the solution equaled the formal sodium hydroxide content of the sodium silicate reagent (27% SiO_2, 14% NaOH). An appropriate mole fraction of the MPTS organosilane corresponding to $x = 0.00-0.65$ was then added to the stirred formamide solution. An aqueous sodium silicate solution then was added to the formamide solution. The resulting mixture was aged first at 25 °C and then at 100 °C for 24 h periods at each temperature. The overall molar composition of the reaction mixture was $1-x$:x:$0.8(1-x)$:0.0165:$0.80(1-x)$:20:0.60:134+$7.3(1-x)$ SiO_2:organosilane:NaOH:P123 surfactant:acetic acid:formamide:TMB:water. Surfactant removal was accomplished by refluxing the products three times in ethanol.

Figure 1 provides the nitrogen adsorption−desorption isotherms for representative thiol-functionalized $(SiO_2)_{1-x}(LSiO_{1.5})_x$ compositions with $x = 0.10$, 0.20, and 0.50. The compositions with $x = 0.10$ and 0.20 mimic the behavior of the pristine silica ($x = 0.00$) and exhibits a predominant H1 hysteresis loop that is characteristic of an open mesoporous cellular foam structure. In such structures the struts defining the mesoporous cells are smaller than the window size, allowing the window size to approach the cell size.[3] At high levels of thiol functionalization ($x = 0.30-0.50$), the hysteresis loop adopts a H2 shape, as illustrated in Figure 1 for the composition with $x = 0.50$. Little or no nitrogen adsorption was observed for $x = 0.65$, indicating the nearly complete absence of mesoporosity at very high levels of thiol functionalization.

Table 1 provides the surface areas and pore volumes for the thiol-functionalized $(SiO_2)_{1-x}(LSiO_{1.5})_x$ compositions over the entire composition range $x = 0.00-0.65$. Note that the surface areas and pore volumes of the thiol-containing compositions with open cell structures (i.e., $x = 0.10$ and 0.20) are substantially larger than the compositions with thiol contents corresponding to $x = 0.30$, 0.40, and 0.50. As will be explained below, the origin of these textural differences arise from differences in framework structure, as revealed by TEM images.

The inserts to Figure 1 illustrate the broad cell size distributions obtained from the nitrogen adsorption isotherms. The cells diameters extend beyond 20 nm and up to 100 nm, regardless of the level of thiol functionalization over the composition range $x = 0-0.50$. However, only the

* To whom correspondence should be addressed. E-mail: pinnavaia@chemistry.msu.edu.

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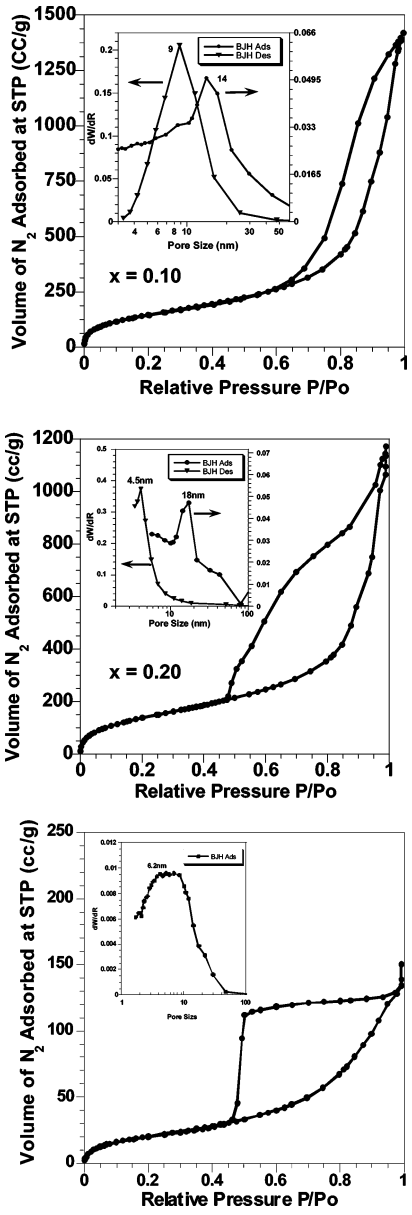

Figure 1. N_2 adsorption−desorption isotherms for $(SiO_2)_{1-x}(LSiO_{1.5})_x$ compositions with L = mercaptopropyl. The inserts provide the BJH window and/or cell size distributions.

Table 1. Textural Properties of $(SiO_2)_{1-x}(LSiO_{1.5})$ Compositions, L = Mercaptopropyl

x	surface area (m^2/g)	pore volume (cm^3/g)
0.00	285	0.90
0.10	545	1.97
0.20	520	1.55
0.30	281	0.67
0.40	202	0.46
0.50	77	0.19
0.65	13	0.04

compositions with well-expressed mesocellular foam structures provided H1 isotherms suitable for the determination of window sizes, Thus, the compositions with $x = 0.00$, 0.10, and 0.20 exhibited window size distributions with maxima at 18, 9.0, and 4.5 nm, respectively. These values are in general agreement with the window sizes normally observed for mesocellular foam structures.[11]

It was not possible to obtain the window size distributions from the desorption isotherms for the $(SiO_2)_{1-x}(LSiO_{1.5})_x$ compositions with $x = 0.30-0.50$. As noted above, all of these latter compositions exhibit a H2 hysteresis loop that abruptly closes at a partial pressure near 0.45. This behavior most likely is a consequence of the meniscus instability of the pore liquid and not indicative of window size. All that can be said of the average window diameter for the $x = 0.30$, 0.40, and 0.50 compositions on the basis of the nitrogen adsorption data is that it is larger than 3 nm.

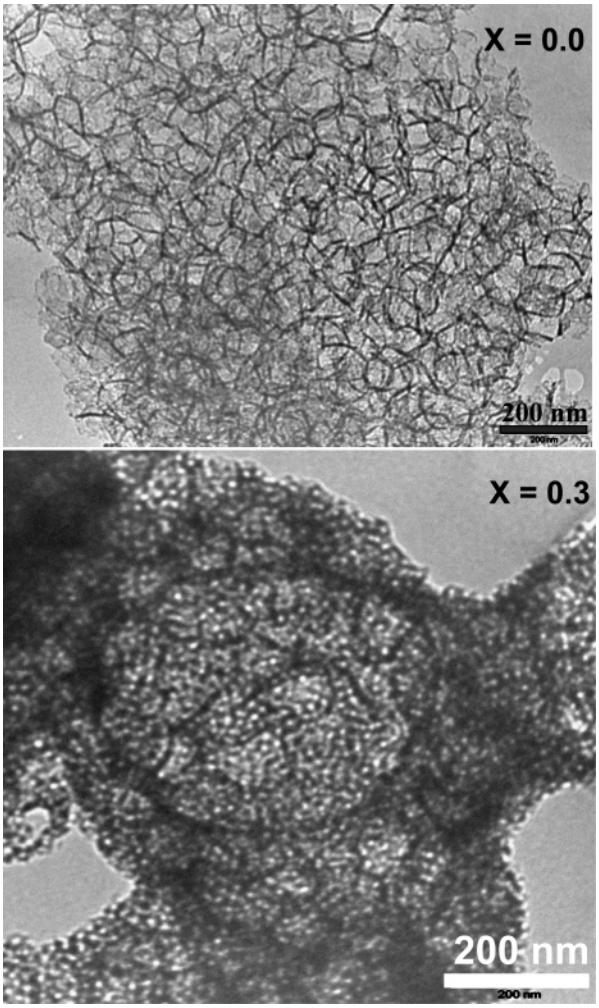

Figure 2. TEM images for representative $(SiO_2)_{1-x}(LSiO_{1.5})_x$ compositions (L = mercaptopropyl) with an open mesocellular foam structure ($x = 0.0$) and a hybrid mesocellular foam−wormhole structure ($x = 0.30$).

The differences in the textural properties of thiol-functionalized $(SiO_2)_{1-x}(LSiO_{1.5})_x$ compositions over the range $x = 0.00-0.50$ are explained by differences in framework structure. TEM images for two representative compositions, namely, with $x = 0.00$ and 0.30, are shown in Figure 2. At $x = 0.00$ an open mesocellular foam structure is clearly present, whereas at $x = 0.30$ a new structure is formed. The new structure retains the thin strut characteristics of an open mesocellular framework, but the windows between the struts are filled by a wormhole structure. That is, the structure at $x = 0.30$ is a hybrid that combines the structural elements of a foam and a wormhole framework. The open window foam structure predominates up to a thiol loading of $x =$

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0.20, but the filling of the foam windows by the wormhole structure occurs over the composition range $x = 0.30-0.50$. Although the hybrid structure is present even at $x = 0.65$, at this level of functionalization the pores of the wormhole structure filling the windows of the foam structure are blocked by the organo groups, leading to the near-total loss of surface area and pore volume.

The retention of cellular struts over the entire composition range $x = 0.0-0.65$ indicates that microemulsion templating is responsible for the formation of an underlying foam framework structure. In addition to stabilizing a microemulsion for templating the underlying foam structure, the surfactant serves the additional function of directing the wormhole framework structure that span the foam windows when $x \geq 0.30$. The dual role of the surfactant is dependent on the organosilane composition of the reaction mixture. Future studies are needed to determine whether the mesocellular foam and wormhole elements of structure represented in the hybrids form cooperatively or sequentially.

At least 85% of the organosilane initially present in the reaction mixture is incorporated into the framework structure of the assembled products, as judged by ^{29}Si NMR spectroscopy. Figure 3 shows the ^{29}Si MAS NMR spectra for representative compositions. Resonances assigned to fully cross-linked T^3 $LSiO_3$ units and Q^4 SiO_4 units dominate the spectra, indicating the presence of a well-cross-linked structure.

In summary, using formamide as a reaction medium, we have demonstrated for the first time the direct supramolecular assembly of organofunctional $(SiO_2)_{1-x}(LSiO_{1.5})_x$ compositions (L = mercaptopropyl) with an open mesocellular framework structure ($x \leq 0.20$), as well as a new hybrid framework structure formed by bridging the windows of an open mesocellular foam structure with a secondary wormhole framework structure ($x = 0.30-0.50$). The hybrid foam−wormhole structure has not been observed previously for any mesoporous composition.

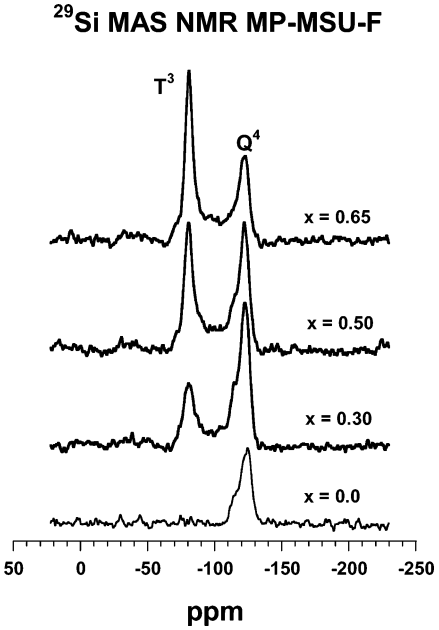

Figure 3. ^{29}Si MAS NMR spectra for thiol-functionalized $(SiO_2)_{1-x}(LSiO_{1.5})_x$ compositions.

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