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Non-ionic surfactant assembly of ordered, very large pore molecular sieve silicas from water soluble silicates

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Very large pore hexagonal and cellular foam-like molecular sieve silicas with well cross-linked framework walls (denoted MSU-H and MSU-F, respectively), have been prepared from soluble silicate precursors under neutral pH conditions.

The supramolecular assembly of periodically ordered mesoporous molecular sieves, such as hexagonal MCM-41, is normally accomplished through an electrostatically mediated pathway involving ionic surfactants assemblies (S^+ or S^-) and inorganic reagents (I^+ or I^-).[1,2] Electrostatic assembly also is involved in the preparation of exceptionally large pore mesostructured silicas such as hexagonal SBA-15 and mesostructured cellular foams (MCF) in the presence of non-ionic surfactants (N^0) derived from triblock co-polymers of propylene and ethylene oxides.[3] These materials are assembled under strongly acidic conditions to allow for counter ion mediated interactions of the type (N^0H^+)(X^-I^+), where X^- is the counter anion and I^+ is the protonated silicic acid derived from a silicon alkoxide reagent. Although the very large pore sizes (50 to 300 Å diameter) are attractive features for applications in large molecule reactions and separations, the high cost of silicon alkoxides and the strong acid reaction conditions, which can limit framework cross-linking and structural stability, are undesirable features of the preparative chemistry.

Mesoporous silica molecular sieves with wormhole framework structures, such as the MSU-X family of materials,[4] are also assembled from neutral surfactants and cost-intensive silicon alkoxides. In an effort to replace the costly alkoxides with sodium silicate, Guth and co-workers[5] reported the preparation of disordered mesostructures from sodium silicate solutions in the presence of a non-ionic surfactant. The complete removal of the surfactant by calcination at 600 °C, however, led to either the extensive restructuring of the silica framework or to the formation of a completely amorphous material. More recently, we achieved the high-yield synthesis of stable wormhole molecular sieve silicas from low-cost, water-soluble silicate precursors and non-ionic surfactants at near neutral pH.[6] In the present work we demonstrate that it is also possible to assemble from sodium silicate *highly ordered* mesoporous silica molecular sieves with very large framework pore structures analogous to both hexagonal SBA-15 and MCF, which we denote MSU-H and MSU-F, respectively.

In a typical synthesis the surfactant and an amount of acid equivalent to the hydroxide content of the sodium silicate solution (*e.g.* 27% SiO_2, 14% NaOH) were mixed at ambient temperature and then added to the sodium silicate to form a reactive silica in the presence of the structure directing surfactant. This allows for the assembly of the framework under neutral pH conditions. The assembly process for the preparation of a hexagonal mesostructure was carried out at molar ratios of $H_2O/Si = 230$ and $N^0/Si = 0.008–0.017$ and at a desired temperature for a period of 10–20 h. The surfactant was then removed from the washed, air-dried products either by solvent extraction with hot ethanol or by calcination in air at 600 °C.

Fig. 1 illustrates the powder X-ray diffraction patterns of as-synthesized and calcined (600 °C) forms of hexagonal MSU-H silica as prepared from Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) as the surfactant at a synthesis temperature of 60 °C. The as-synthesized and calcined products exhibit resolved *hkl* reflections consistent with two-dimensional hexagonal symmetry and unit cell dimensions of 130 and 119 Å, respectively. We may conclude that MSU-H mesostructures are isostructural with SBA-15. However, the two classes of as-made silicates are readily distinguishable on the basis of framework connectivity. The ^{29}Si NMR spectra of as-synthesized MSU-H (not shown) typically exhibit three resonances corresponding to the Q^2 (93 ppm), Q^3 (100 ppm) and Q^4 (109 ppm) connectivities of the SiO_4 tetrahedra. The ratio of fully condensed (Q^4) silica sites to incompletely condensed Q^3 and Q^2 sites is 4.5, considerably higher than the value of 1.28 reported[3a] for conventional SBA-15. The neutral pH conditions of the present assembly pathway allow for a much higher degree of framework crosslinking, presumably, because there is little or no charge present on the silica framework walls under these conditions.

Further evidence for the hexagonal mesostructure of MSU-H silica is provided by the transmission electron micrograph (TEM) images shown in Fig. 2. In comparison to conventional SBA-15, which has a particle size in the micron range, MSU-H shows smaller particle sizes in the range 300–500 nm [Fig. 2(a)]. Fig. 2(b) unmistakably shows the highly ordered hexagonal arrays of mesopores and equidistant parallel lines related to the hexagonal repeat between tubules. Also evident are the small hexagonal domain sizes within the small particles.

Fig. 3 illustrates the N_2 adsorption–desorption isotherms and BJH pore size distribution plot (insert) calculated from the adsorption branch of the N_2 isotherms for calcined MSU-H. A typical, type IV adsorption isotherm with an irreversible H1 hysteresis loop is observed as expected for a large pore material.[7] The step-like uptake of N_2 in the range 0.7–0.9 P/P_0 corresponds to capillary condensation within framework pores with a BJH diameter of 98 Å. The pore volume is 1.24 cm^3 g^{-1}, the BET surface area is 625 m^2 g^{-1} for this calcined MSU-H.

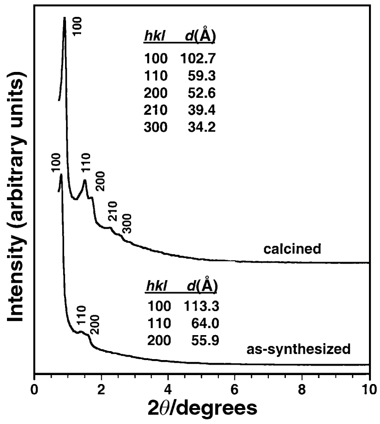

Fig. 1 XRD patterns of as-synthesized and calcined (600 °C) forms of a MSU-H silica molecular sieve assembled from sodium silicate and Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) under neutral pH conditions at 60 °C.

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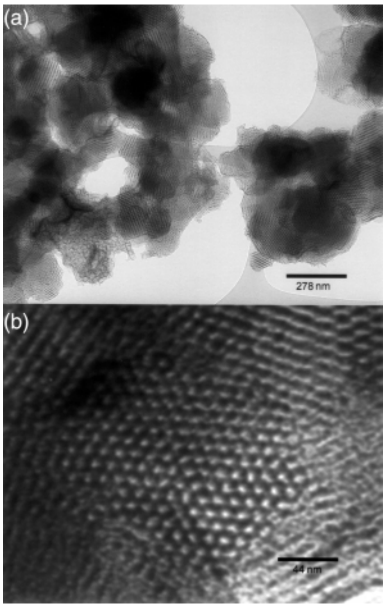

Fig. 2 TEM images of the calcined MSU-H silica: (a) low and (b) high magnification.

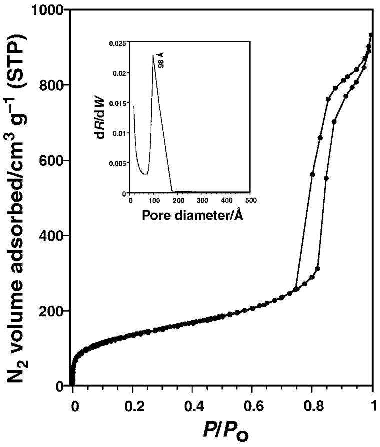

Fig. 3 N_2 adsorption–desorption isotherms for the calcined MSU-H silica molecular sieve. The insert provides the BJH pore size distribution calculated from the adsorption branch of the N_2 isotherm.

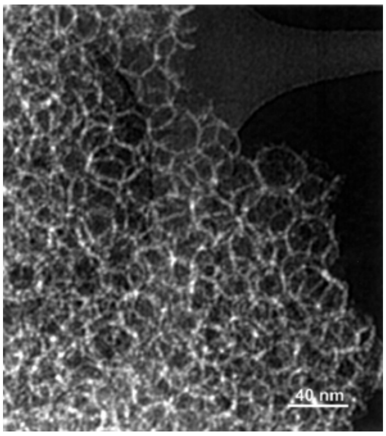

Fig. 4 TEM image of the calcined MSU-F silica formed from sodium silicate, TMB and Pluronic P123 under neutral pH conditions at 60 °C.

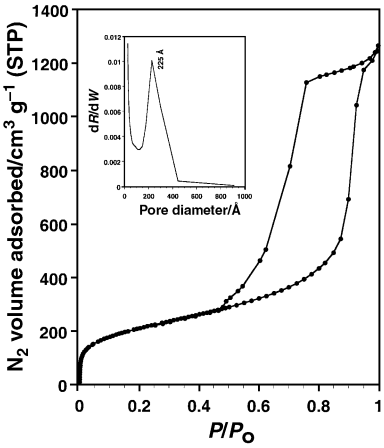

Fig. 5 N_2 adsorption–desorption isotherms for the calcined MSU-F silica. The insert provides the BJH pore size distribution calculated from the adsorption branch of the N_2 isotherm.

MSU-H silicas with (100) X-ray spacings in the range 99–108 Å and pore sizes between 82 and 110 Å have been synthesized with Pluronic P123 surfactant simply by varying the N^0/silica ratio or the synthesis temperature. More significantly, the addition of 1,3,5-trimethylbenzene (TMB) to expand the pore size of MSU-H leads instead to mesostructured cellular foams (denoted MSU-F) that are composed of large, uniform spherical cells, as shown in Fig. 4. This material has an average pore size of 225 Å, a BET surface area of 759 $m^2\ g^{-1}$, and a mesopore volume of 1.87 $cm^3\ g^{-1}$, very much like conventional MCF silicas[3b] formed from acidic TEOS mixtures in the presence of P123 and TMB (Fig. 5). The formation of a TMB/P123 microemulsion and the assembly of silica around the microemulsion droplets explain the phase transition from MSU-H to MSU-F.

The same chemistry described above for the preparation of MSU-H and MSU-F also applies to other non-ionic polyethylene oxide surfactants. For instance, molecular sieve silicas with two-dimensional hexagonal symmetry and BJH pore sizes of 32–53 Å, BET surface areas of 492–745 $m^2\ g^{-1}$ and pore volumes of 0.31–0.70 $cm^3\ g^{-1}$ were assembled from water-soluble silicate precursors using Brij 76 as the non-ionic surfactant at temperatures in the range 25–60 °C. Thus, the new assembly pathway reported here is general, as well as being especially suitable for the assembly of stable analogs of silica mesostructures with the largest of known framework pore sizes. The generality of the assembly pathway, together with the use of low-cost sodium silicate as the silica source, are attractive features for use in the commercial production of mesostructured silicas with framework pore sizes over the entire range from 20 to > 225 Å.

Note added in proof: The synthesis of SBA mesostructures from sodium metasilicate and non-ionic block copolymers as structure directing agents under strong acid conditions has recently been reported: J. M. Kim and G. D. Stucky, *Chem. Commun.*, 2000, 1159.

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