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Non-ionic surfactant assembly of wormhole silica molecular sieves from water soluble silicates

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Thermally stable mesoporous silica molecular sieves with wormhole framework structures, previously obtainable only from silicon alkoxides, have been prepared from low cost soluble silicate precursors in the presence of non-ionic surfactants as structure directors.

Mesoporous molecular sieve silicas with wormhole framework structures (*e.g.* MSU-X,[1,2] and HMS[3]) are generally more active heterogeneous catalysts in comparison to their ordered hexagonal analogs (*e.g.* MCM-41,[4] SBA-3[5] and SBA-15[6]). The enhanced reactivity has been attributed, in part, to a pore network that is connected in three dimensions, allowing the guest molecules to more readily access reactive centers that have been designed into the framework surfaces.[7–10] All of the wormhole framework structures reported to date have been prepared through supramolecular S^oI^o[3] and N^oI^o[1,2] assembly pathways wherein I^o is an electrically neutral silica precursor (typically, tetraethylorthosilicate, TEOS), S^o is a neutral amine surfactant, and N^o is a neutral di- or tri-block surfactant containing polar polyethylene oxide (PEO) segments. One disadvantage of these pathways, as with other assembly pathways based on TEOS, is the high cost of the hydrolyzable silicon alkoxide precursor. Greater use of wormhole framework structures as heterogeneous catalysts may be anticipated if a more efficient approach to either S^oI^o or N^oI^o assemblies could be devised based on the use of low cost soluble silicate precursors, without sacrificing the intrinsically desirable processing advantages of these pathways (*e.g.* facile removal and recycling of the surfactant).

Recently, Guth and coworkers reported the preparation of disordered silica mesostructures by precipitation from sodium silicate solutions over a broad range of pH in the presence of Triton-X 100, an N^o surfactant.[11] The retention of a mesostructure was observed up to a calcination temperature of 480 °C, but the complete removal of the surfactant at 600 °C led either to the extensive restructuring of the silica framework, as indicated by the loss of mesoporosity or the formation of a completely amorphous material. In contrast, MSU-X mesostructures are structurally stable to calcination temperatures in excess of 800 °C. The present work demonstrates that mesoporous molecular sieve silicas equivalent in structure and thermal stability to MSU-X silicas (denoted MSU-X′) can in fact be prepared from soluble silicate precursors under the appropriate assembly conditions.

Our approach, like that of Guth and coworkers, uses a sodium silicate as the silica source and an N^o surfactant as the structure director, but our methodology results in thermally stable wormhole structures. 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, Aldrich) are first mixed at ambient temperature and then added to the sodium silicate solution to form reactive silica in the presence of the surfactant. This allows the assembly of the framework structure at near-neutral pH and avoids the need for readjusting the pH once the reactive silica has been formed. The assembly process is carried out at a molar ratio SiO_2/surfactant in the range 13–7.0 and at a temperature in the range 25–60 °C for a period of 10–20 h. The surfactant is then removed from the washed and 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 MSU-X′ silicas prepared at three different temperatures using Brij 56 [$C_{16}H_{33}(EO)_{10}H$] as the structure-directing surfactant. Each product exhibits an intense reflection at low 2θ corresponding to a pore–pore correlation distance of *ca.* 63 Å with a broad shoulder in the 2θ range 2–3. These patterns are typical of disordered wormhole-like pore structures and are similar to those of MSU-X silicas assembled from the same surfactant, but with TEOS as the silica precursor. After calcination at 600 °C, the intensities of the pore–pore correlation peaks are substantially greater than the as-synthesized samples due to the removal of the contrast-matching surfactant. This result is consistent with the retention of the framework pore structure upon complete removal of the surfactant from the framework.

Further evidence for the wormhole framework pore structure of MSU-X′ silicas is provided by the typical transmission electron micrograph (TEM) image shown in Fig. 2. This micrograph clearly exhibits disordered wormhole-like pores similar to MSU-X materials. Fig. 3 illustrates the N_2 adsorption–desorption isotherms and Horvath–Kawazoe pore size distributions (inset) for the calcined MSU-X′ products assembled at 25, 45 and 60 °C. The sample assembled at 25 °C exhibits the smallest pore size (32 Å) in the series, and the largest HK pore diameter (50 Å) is observed for the 60 °C sample. The increase in framework pore size with increasing assembly temperature is a characteristic feature of an N^oI^o assembly pathway.[2] The desorption hysteresis observed for the product prepared at 60 °C is indicative of the necking of the interconnected wormhole pore structure. In addition, the pore

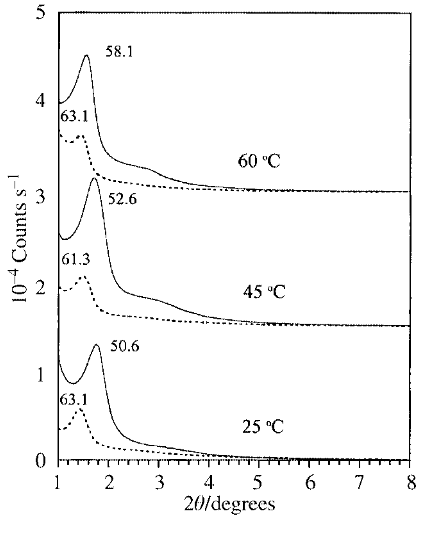

Fig. 1 XRD patterns of MSU-X′ silica molecular sieves formed from sodium silicate and Brij 56 under neutral pH conditions at 25, 45 and 60 °C, respectively. Dashed and solid curves are for the as-synthesized and calcined products, respectively. The numbers adjacent to each diffraction peak are the pore–pore correlation distances in angstrom (Å) units.

Table 1 Physicochemical properties of mesoporous silica (MSU-X′) prepared using sodium silicate and non-ionic surfactants

Surfactant	Synthesis temperature/°C	Pore–pore distance/Å As-synth.	Calcined[a]	BET surface area/m^2 g^{-1}	Pore size/Å	Wall thickness[b]/Å	Pore volume/cm^3 g^{-1}
Brij 56	25	63.1	50.6	602	32	25	0.36
Brij 56	45	61.3	52.6	769	37	16	0.57
Brij 56	60	63.1	58.1	849	50	8	0.90
Brij 35	60	59.7	52.5	853	33	20	0.65
Brij 58	60	66.9	58.1	821	43	15	0.80
Brij 78	60	69.0	61.4	851	48	13	0.83
Tergital (15-S-15)	60	59.7	53.2	979	40	13	0.86
Tween 20	60	58.9	52.9	883	42	11	0.84
Tween 40	60	65.9	58.9	753	49	10	0.80
Tween 60	60	66.9	58.9	773	48	11	0.75
Tween 80	60	71.2	65.0	867	51	14	0.89

[a] Calcined at 600 °C for 4 h in air. [b] The wall thickness was calculated by subtracting the HK pore diameter from the correlation distance.

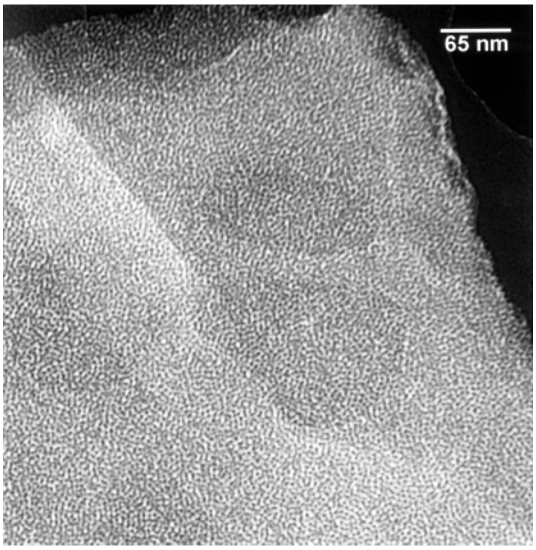

Fig. 2 TEM image of wormhole pore structure of the calcined MSU-X′ sample prepared from sodium silicate and Brij 56 under neutral pH conditions at 60 °C.

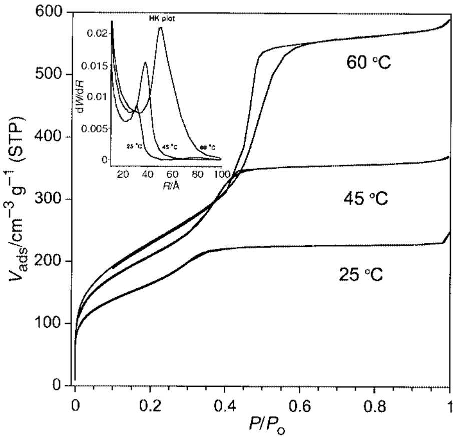

Fig. 3 N_2 adsorption–desorption isotherms for the calcined MSU-X′ silica molecular sieves formed from sodium silicate and Brij 56 under neutral pH conditions at 25, 45 and 60 °C, respectively. The insert provides the Horvath–Kawazoe pore size distributions.

wall thickness, as obtained from the difference between the pore–pore correlation distance and the HK pore size, decreases with increasing assembly temperature (Table 1). This latter behavior, which is related to the increase in the hydrophobic character of the PEO block as the surfactant approaches the cloud point, also is a characteristic feature of N^{o}I^o assembly.[2] Because Na$^+$ ions are present in the assembly process, there may also be an electrostatic contribution to framework formation through complexation of Na$^+$ by the N^o surfactant. However, electrostatically controlled [N^{o}M$^+$]I^o assembly processes tend to form ordered hexagonal or cubic framework structures, not wormhole frameworks.[12]

Wormhole silica molecular sieves can also be assembled from water-soluble silicate precursors using N^o surfactants other than Brij 56. Table 1 summarizes the textural properties of wormhole silica assembled from sodium silicate and other Brij surfactants, a Tergitol $[C_{11-15}H_{23-31}(EO)_{15}H]$ surfactant, and several alkyl-PEO/furan Tween X surfactants (X = 20, 40, 60 and 80). Table 1 shows that each of these surfactants form mesostructures with 33–51 Å pore sizes, and surface areas and pore volumes comparable to MSU-X silicas prepared from TEOS. TEM analysis of each product conformed the wormhole pore structure.

The successful assembly of thermally stable mesoporous silica molecular sieve silicas with wormhole frameworks from soluble silicate precursors suggests that it may be possible to substitute soluble silicate precursors for the assembly of many other silica mesostructures that heretofore have been assembled exclusively from silicon alkoxide precursors. Future studies will focus on the assembly of other members of the MSU family of mesostructures, as well as SBA mesostructures obtained through an electrostatic N^o(H$^+$X$^-$)I$^+$ assembly pathway.[6]

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