A new nonionic surfactant pathway to mesoporous molecular sieve silicas with long range framework order

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Received (in Oxford, UK) 16th June 1999, Accepted 2nd August 1999

Mesoporous molecular sieve silicas with ordered structures are formed from tetraethylorthosilicate (I^0) in a new reaction pathway based on nonionic $R(EO)_nH$ surfactants (N^0) and denoted (N^0M^{n+})I^0, wherein electrostatic forces are introduced into the assembly process through –$(EO)_nH$ complexation of small metal cations (M^{n+} = Li^+, Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+}).

The long-range structures of mesoporous molecular sieve silicas and other metal oxides are determined in part by the pathways used to assemble the polymerizable inorganic reagent at the surface of the structure-directing supramolecular micelle.[1] Assembly pathways that utilize electrostatic charge matching between ionic surfactants (S^+ or S^-) and inorganic reagents (I^+ or I^-) typically afford hexagonal, cubic or lamellar structures that minimize the electrostatic energy.[2,3] In contrast, coulombic forces are absent in pathways that exclusively utilize H bonding interactions between electrically neutral surfactants (S^0) and inorganic reagents (I^0).[4] Consequently, S^0I^0 pathways and related N^0I^0 pathways based on non-ionic polyethylene oxide surfactants,[5] afford disordered framework structures with wormhole-like channel motifs.[6]

Electrically neutral assembly pathways offer several attractive features for the preparation of mesoporous molecular sieve silicas.[4,5] For instance, assembly can be carried-out at near-neutral pH and relatively low reaction temperatures (20–65 °C). Also, recovery of the surfactant by simple solvent extraction can be achieved without sacrificing the surface areas and pore size fidelity obtained through charge matching pathways. In addition to these processing advantages, the pore branching and, especially, the complementary textural porosity associated with wormhole frameworks, can improve catalytic reactivity by facilitating access to reactive sites in the framework.[7] Nevertheless, long range order is desirable for certain electronic and photonic applications where structural periodicity can be important.[8]

In the present work we describe the synthesis of ordered silica mesostructures without sacrificing the processing advantages of neutral surfactant assembly. Our approach is based on a new pathway, denoted (N^0M^{n+})I^0, in which hydrogen bonds are formed between a cationic metal complex form of a nonionic (N^0) polyethylene oxide surfactant of the type $R(EO)_nH$ and the electrically neutral inorganic precursor (I^0). The complexation of small M^{n+} cations by the EO groups of N^0 brings the assembly process under electrostatic control and forms ordered mesostructures in much the same way as the recently reported acid-mediated $N^0(H^+X^-)I^+$ pathway,[9] except that strong acid conditions are avoided.

As shown by the representative X-ray powder diffraction pattern in Fig. 1A, one-dimensional hexagonal mesostructures were formed upon hydrolysis of tetraethylorthosilicate (TEOS) at 25–65 °C in the presence of Brij 56 [$C_{16}H_{33}(EO)_{10}H$], Triton X-100[$C_8H_{17}(C_6H_4)(EO)_{10}H$], and Tergitol 15-S-12 and the chloride salts of Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} as structure modifiers at a reaction stoichiometry of $H_2O/Si = 85$, $N^0/Si = 0.04–0.07$ and $M^{2+}/N^0 = 0.5–2.0$. All of these structure-modifying cations are known to form complexes with polymeric EO units.[10] For each modifier, a hexagonal mesostructure was indicated by the presence of at least three XRD lines that could be indexed as 100, 110 and 200 reflections (*cf.*, Fig. 1A). Consequently, these one-dimensional hexagonal framework structures are analogous to MCM-41[2] and SBA-3 silicas[3] in long range order. In the absence of the metal ion salts, only wormhole structures with a single broad diffraction line were formed.

The incorporation of lithium chloride into the reaction mixtures also yielded hexagonal mesostructures. Interestingly, however, metals such as Fe^{3+}, Cr^{3+} and Rh^{3+} afforded only wormhole structures. The inability of these latter cations to induce long range electrostatic order presumably is related to their formation of polynuclear oxocations[11] under near neutral conditions of pH and the inability of these large ions to form stable complexes with the $(EO)_n$ segment of the N^0 surfactant.

Decreasing the divalent metal ion concentration in the reaction mixture to M^{2+}/N^0 values in the range 0.10–0.20 results in an ordered structure different from the one-dimensional hexagonal frameworks described above. Fig. 2 provides a representative TEM image and an electron diffraction pattern for this new structure in comparison with the hexagonal framework formed by (N^0M^+)I^0 assembly. The deviation from a hexagonal structure most likely is associated with a change in the surfactant packing parameter upon decreasing the average charge on the surfactant head group through metal ion complexation. Similar TEM images and electron diffraction patterns have been reported for electrostatically assembled cage–like frameworks with 3D hexagonal symmetry,[12] as well as for cubic and faulted 3D hexagonal–cubic structures.[13] The X-ray powder diffraction patterns of the products formed at lower M^{2+}/N^0 values contain only a single, well-resolved line (*cf.*, Fig. 1B), which precludes a definitive structural assignment. Nevertheless, the TEM and electron diffraction properties

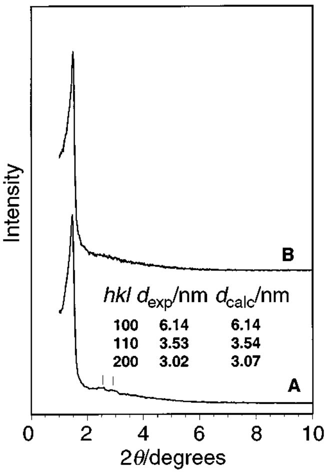

Fig. 1 XRD patterns of silica molecular sieves formed through (N^0M^{n+})I^0 assembly at 45 °C: (A) the product assembled at a Co^{2+}/Brij 56 ratio of 0.50; (B) the product formed at a Co^{2+}/Brij 56 ratio of 0.12. The N^0/Si ratio was 0.04 in both cases and the samples were calcined at 600 °C. Analogous patterns were obtained for solvent-extracted products.

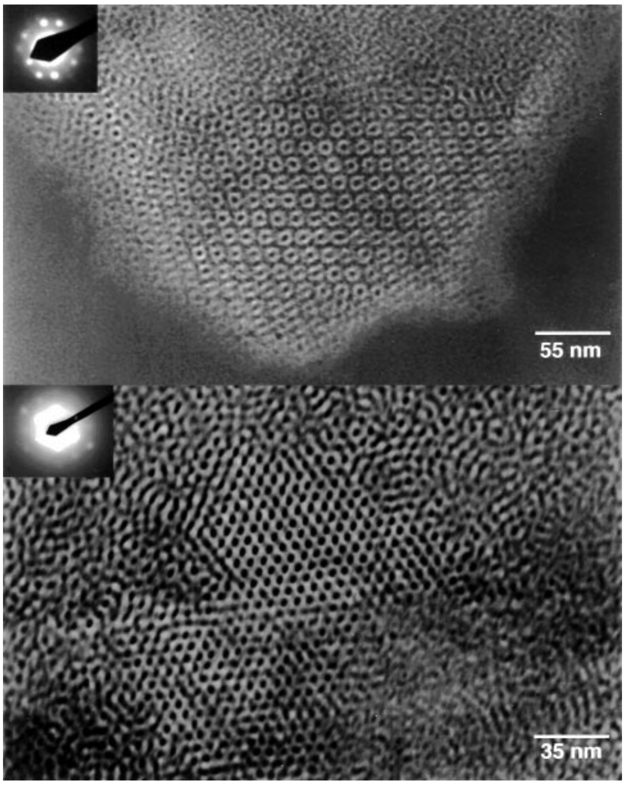

Fig. 2 TEM images and electron diffraction patterns (insets) of the silica mesostructures assembled at Co^{2+}/Brij 56 ratios of 0.50 (lower image) and 0.12 (upper image).

closely resemble the faulted 3D hexagonal–cubic structures recently observed for silica films on glass,[12] and we tentatively favor this type of 3D faulted structure.

The N^0 surfactant is easily removed from the ordered mesostructures by ethanol extraction or by calcination. Moreover, the solvent-extracted products are free of both framework metal ions and the structure-mediating metal salt. These observations are consistent with our proposed $(N^0M^{n+})I^0$ pathway, wherein hydrogen bonds are formed between the uncomplexed EO oxygen atoms of the cationic (N^0M^{n+}) complex and the silanol protons of the hydrolyzed I^0 precursor. Charge balance at the surfactant–silica interface is achieved through ion pairing with the counter anions of the metal salt. However, the anion does not play a direct structure-directing role, because the same structures are obtained regardless of the type of anion (chloride, nitrate, or acetate) used in the assembly process.

Fig. 3 shows N_2 adsorption–desorption isotherms for representative mesostructures formed in the presence of Brij 56 and Co^{2+} as the structure modifier. Pore necking in the 3D faulted structure, as suggested by the cage-like pore structure of the upper TEM image of Fig. 2, is verified by the hysteresis loop associated with the filling and emptying of the framework void space. Little or no hysteresis is observed for the one-dimensional hexagonal structure, as expected. The BET surface areas, pore volumes, and Horvath–Kawazoe pore diameters for the 3D faulted structure are 1103 $m^2\ g^{-1}$, 1.06 $cm^3\ g^{-1}$ and 6.0 nm, respectively. The corresponding values for the hexagonal mesostructures are 937 $m^2\ g^{-1}$, 0.68 $cm^3\ g^{-1}$ and 4.3 nm. These textural parameters are comparable to those for mesoporous silica molecular sieves obtained through conventional electrostatic assembly pathways. Future studies will examine the framework crosslinking and hydrothermal stability of these ordered silicas in comparison to silicas formed through other electrostatic pathways.

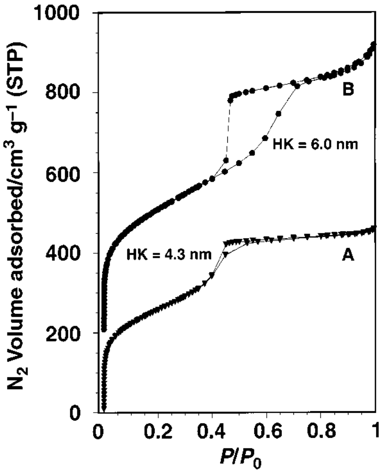

Fig. 3 N_2 adsorption–desorption isotherms for the silica mesostructures assembled at Co^{2+}/Brij 56 ratios of 0.50 (lower isotherm) and 0.12 (upper isotherm). The upper isotherm is offset by 200 $cm^3\ g^{-1}$ for clarity.

In conclusion, we have shown that long range structural order can be introduced through complex formation of the N^0 surfactant with small metal ions at M^{n+}/N^0 ratios in the range 0.1–2.0 and near-neutral pH. In comparison, acid mediated pathways that use comparable amounts of protons rather than complexable metal ions have been shown previously to yield only wormhole structures.[14] In order to assemble ordered silica frameworks through acid mediation of EO–based nonionic surfactants, much higher H^+/N^0 ratios, typically in the range 30–600, are needed to introduce structural order.[9] The new $(N^0M^{n+})I^0$ pathway reported here offers a promising alternative approach for introducing electrostatic forces and long range structural order into the assembly process while avoiding the need for high acid concentrations. It also avoids the need for high surfactant concentrations and liquid crystal templating (casting) as a means of generating ordered frameworks.[15]

The support of this work by NSF-CRG grants CHE-9633798 and −9903706 is gratefully acknowledged.

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Communication 9/04803K