Templating of Mesoporous Molecular Sieves by Nonionic Polyethylene Oxide Surfactants

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Mesoporous silica molecular sieves have been prepared by the hydrolysis of tetraethylorthosilicate in the presence of low-cost, nontoxic, and biodegradable polyethylene oxide (PEO) surfactants, which act as the structure-directing (templating) agents. This nonionic, surfactant–neutral, inorganic-precursor templating pathway to mesostructures uses hydrogen bonding interactions between the hydrophilic surfaces of flexible rod- or worm-like micelles and $Si(OC_2H_5)_{4-x}(OH)_x$ hydrolysis products to assemble an inorganic oxide framework. Disordered channel structures with uniform diameters ranging from 2.0 to 5.8 nanometers have been obtained by varying the size and structure of the surfactant molecules. Metal-substituted silica and pure alumina mesostructures have also been prepared by the hydrolysis of the corresponding alkoxides in the presence of PEO surfactants. These results suggest that nonionic templating may provide a general pathway for the preparation of mesoporous oxides.

The discovery by Mobil researchers (*1*) of the M41S family of mesoporous molecular sieves with pore sizes from 1.5 to 10 nm has stimulated interest in the potential use of these materials as catalysts for large molecule transformations (*2*) and as hosts for supramolecular assembly (*3*). Mesostructure syntheses rely on surfactant micelles or liquid-crystal arrays of micelles as structure-directing agents (templates) for the assembly and subsequent polymerization of inorganic precursors at the surfactant-solution interface (*4*). Electrostatic charge-matching between long-chain quaternary ammonium cation surfactants (S^+) and anionic inorganic precursors (I^-) is especially effective in generating mesostructures with hexagonal, cubic, or lamellar symmetry (*1*). Schüth, Stucky, and co-workers (*5*) have extended the electrostatic templating concept to include a charge-reversed S^-I^+ pathway between anionic surfactants, such as sulfonates, phosphonates, and carboxylates, and cationic precursors. They also demonstrated counterion-mediated $S^+X^-I^+$ (X^- = halide) and $S^-M^+I^-$ (M^+ = alkali metal ion) pathways.

Tanev and Pinnavaia recently demonstrated (*6*) that the assembly of hexagonal mesoporous metal oxides also can be achieved by hydrogen bonding between neutral amine surfactants (S^0) and neutral inorganic precursors (I^0). Relative to electrostatic templating pathways, S^0I^0 templating offers the practical advantage of facile template recovery by noncorrosive solvent extraction or evaporation methods. Because of weaker repulsive interactions between neutral metal oxide precursors at the surfactant-solution interface than between charged precursors, the S^0I^0 pathway also tends to afford structures with thicker framework walls for improved stability (*6*) and smaller elementary particle sizes for added textural mesoporosity. Perhaps the most chemically significant advantage of S^0I^0 templating, however, is that it allows the synthesis of mesostructures that are not readily accessible by electrostatic templating. For instance, it is possible to prepare nonlamellar aluminum oxide mesostructures by S^0I^0 templating with octyl- or dodecylamine used as the surfactant and aluminum alkoxides used as the inorganic precursor. Analogous structures are not known to form by electrostatic templating.

Despite the attractive benefits of mesostructure templating by neutral amines, these surfactants still share some of the same drawbacks as quaternary ammonium surfactants. In particular, neutral alkyl amines are costly and toxic and consequently are not ideally suited to the large-scale synthesis and processing of mesostructures. A need therefore exists to develop new, low-cost, and environmentally compatible neutral templating pathways to mesoporous molecular sieves. We now demonstrate that nonionic polyethylene oxide (PEO) surfactants, which are relatively inexpensive and biodegradable (*7*), are exceptionally promising neutral templating agents. These surfactants form spherical to flexible rod- or worm-like micelles at critical concentrations approximately one-hundredth of those necessary for ionic surfactants (*7*). At higher concentrations, the micelles undergo cubic, hexagonal, or lamellar liquid-crystal phase formation (*8*, *9*). At the cloud point temperature, the hydrogen bonding interactions between the solvent water and the hydrophilic ethylene oxide (EO) units are disrupted, and the surfactant undergoes a phase transition with separation of the surfactant from solution (*9*, *10*). These features of PEO surfactant chemistry offer new opportunities for mesostructure synthesis and template recovery.

We have prepared nonionic, templated structures (designated MSU-*X*, where *X* denotes specific materials templated by a particular family of PEO-based surfactants; see Table 1) by hydrolysis of tetraethylorthosilicate (TEOS) in the presence of different nonionic PEO surfactants (N^0). The Tergitol 15-S-*n* (Union Carbide, Danbury, Connecticut) series of alkyl-PEO alcohols of the type $C_{11-15}H_{23-31}$-

Table 1. Physicochemical properties of MSU silicas and an MSU alumina prepared by N^0I^0 templating. The d_{100} x-ray reflections are quoted for materials calcined in air at 873 K. Framework-confined mesopore sizes were determined by HK analysis (*11*) of N_2 adsorption isotherms, and surface areas were determined by the BET method (*18*).

Material designation	Surfactant	Template concentration (mol liter^{-1})	Abbreviated formulae*	d_{100} (nm)	HK pore diameter (nm)	BET surface area (m^2 g^{-1})
MSU-1 silica	T15-S-9†	0.1	$C_{11-15}(EO)_9$	5.2	2.5	1010
	T15-S-12	0.1	$C_{11-15}(EO)_{12}$	4.1	3.1	1005
	T15-S-15	0.1	$C_{11-15}(EO)_{15}$	5.4	2.6	640
	T15-S-20	0.1	$C_{11-15}(EO)_{20}$	7.8	4.8	605
	T15-S-30	0.1	$C_{11-15}(EO)_{30}$	7.9	4.5	525
MSU-2 silica	TX-114‡	0.023	$C_8Ph(EO)_8$	6.1	2.0	780
	TX-100	0.027	$C_8Ph(EO)_{10}$	6.2	3.5	715
	RC760§	0.001	$C_{12}Ph(EO)_{18}$	4.3	2.1	800
MSU-3 silica	P64L‖	0.054	$(PEO)_{13}(PPO)_{30}(PEO)_{13}$	6.1	5.8	1190
Ti-MSU-1 silica¶	Ti(5%)-NTS T15-S-12	0.08	$C_{11-15}(EO)_{12}$	4.9	3.0	950
Zr-MSU-1 silica¶	Zr(5%)-NTS T1 5-S-12	0.08	$C_{11-15}(EO)_{12}$	4.9	2.8	940
MSU-3 alumina#	P64L	0.012	$(PEO)_{13}(PPO)_{30}(PEO)_{13}$	6.3	4.8	420

*C = alkyl, Ph = phenyl. †Tergitol. ‡Triton-X. §Igepal. ‖Pluronic. ¶Transition metal content is 5 mol%. #Calcined at 773 K for 6 hours in air.

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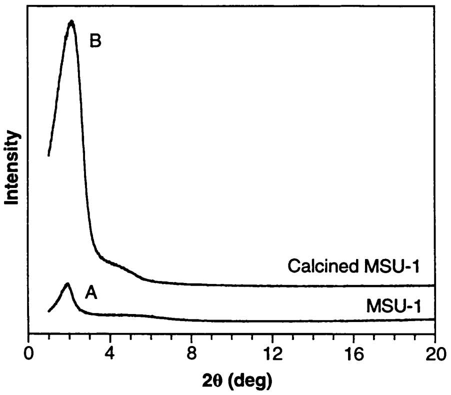

Fig. 1. Powder XRD patterns of (curve A) as-synthesized Tergitol 15-S-12 templated MSU-1 silica and (curve B) MSU-1 silica calcined at 873 K in air for 4 hours. Patterns were obtained with a Rigaku Rotaflex diffractometer equipped with a rotating anode and Cu-Kα radiation (wavelength λ = 0.15418 nm).

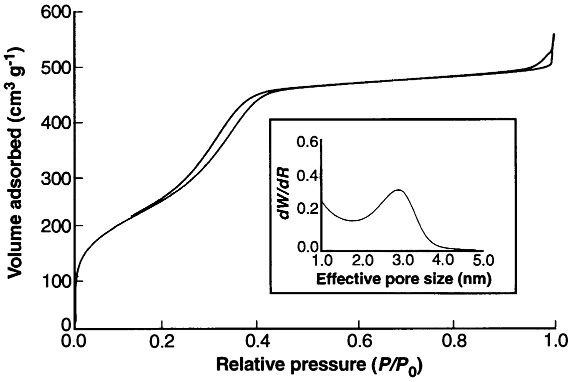

Fig. 2. Nitrogen adsorption and desorption isotherms for calcined MSU-1 silica. The volume of N_2 sorbed is expressed at standard temperature and pressure; P/P_0 is the partial pressure of N_2 in equilibrium with the sample at 77 K. (**Inset**) Corresponding Horvath-Kawazoe pore size distribution determined from the N_2 adsorption isotherm; dW/dR is the derivative of the normalized N_2 pore volume adsorbed with respect to the diameter of the adsorbent. Before analysis, the samples were evacuated at 423 K and 10^{-6} torr for 16 hours. The N_2 isotherms were obtained on a Coulter Omnisorp 360CX Sorptometer under continuous adsorption conditions.

$O(CH_2CH_2O)_nH$, in which the hydrophobic alkyl group consists of between 11 and 15 carbon units and the hydrophilic head group contains *n* EO units, illustrates the effectiveness of the N^0I^0 templating strategy. We added, at once, TEOS under moderate stirring to 0.1 mol liter^{-1} Tergitol 15-S-*n* solutions with *n* values in the range 9 to 30 to form solutions with final TEOS:surfactant:H_2O molar ratios of 10:1:560.

The TEOS, which is immiscible in water alone, dissolved readily in the template solutions. White solids formed within reaction times of 2 to 5 min, whereas little or no TEOS hydrolysis was observed over several hours under the same reaction conditions in the absence of the surfactant. The precipitated products were allowed to age under moderate stirring for 12 to 16 hours, filtered, air-dried at room temperature, and finally calcined in air at 2 K min^{-1} to 873 K for 4 hours to remove the template. The template could also be extracted from the as-synthesized, air-dried products by washing with ethanol, but calcination was the method used to remove the template from all of the materials reported in the present study.

Powder x-ray diffraction (XRD) patterns of the as-synthesized and calcined MSU-1 silica products prepared in the presence of Tergitol 15-S-12 are shown in Fig. 1. The pattern for the as-synthesized product contains a broad diffraction peak centered at 4.6 nm and a broad shoulder at ~1.5 nm. Analogous diffraction patterns have been observed for hexagonal mesostructures prepared both by electrostatic and by neutral templating pathways (*4*, *6*). The broadening of higher order reflections is now acknowledged to arise from a lack of long-range crystallographic order or finite size effects. Upon removal of the template by calcination, the basal spacing decreases to 4.1 nm and the scattering intensity increases substantially, suggesting that the calcination process may promote siloxane cross-linking and thereby improve the ordering of the oxide framework.

The N_2 adsorption-desorption isotherm and the Horvath-Kawazoe (HK) pore size distribution (*11*) for MSU-1 silica are presented in Fig. 2. A well-defined step occurs in the adsorption curve between partial pressures P/P_0 of 0.2 to 0.4, which is indicative of the filling of framework-confined mesopores (*12*) with an average HK pore size of 3.0 nm. The fidelity of the pore distribution, as indicated by the ~0.9 nm width at half height, is only slightly less than that observed for mesoporous silicas prepared by S^+I^- templating (*1*) from alkylammonium ions (0.5 nm) or by S^0I^0 templating (*6*) from neutral amines (0.7 nm). In contrast to mesostructures templated by neutral amines (*6*), however, none of the derivatives formed from Tergitol or any of the other nonionic PEO-based surfactants used in this study (see below) exhibited substantial N_2 adsorption-desorption hysteresis at high partial pressures due to interparticle capillary condensation (compare with Fig. 2). The lack of textural mesoporosity indicates that the elementary particle size of the MSU-1 silica is orders of magnitude larger than the framework-confined mesopores and that the broad lines observed in the XRD patterns arise from disorder in the assembly of the surfactant-templated channels rather than from the effects of finite particle sizes.

Evidence for disordered, hexagonal-like packing of channels in MSU-1 mesostructures is provided by the transmission electron micrograph (TEM) image presented in Fig. 3 for MSU-1 templated with Tergitol 15-S-20, a material that also exhibits a one-line XRD pattern with d_{100} = 7.8 nm. The micrograph shows that the particle contains a large number of channels. The cylindrical- to hexagonal-shaped channels are regular in diameter, although they lack long-range packing order. Defects in channel assembly also have been observed for hexagonal-like M41-S silicates formed under reaction conditions in which silicate anions bind electrostatically to segregated rod-shaped micelles of quaternary ammonium ions that subsequently aggregate into a mesostructure (*13*). An analogous assembly mechanism most likely operates for templating by nonionic PEO micelles, except that the micelles formed in the presence of $Si(OC_2H_5)_{4-x}(OH)_x$ precursors are more worm-like than rod-like (*14–16*) and the precursors bind to the flexible micelles by hydrogen bonding. Although the flexibility of the micelles contributes to channel packing defects, such defects do not adversely affect pore uniformity. The framework-confined mesoporosity of these materials, which is determined by the diameter of the tem-

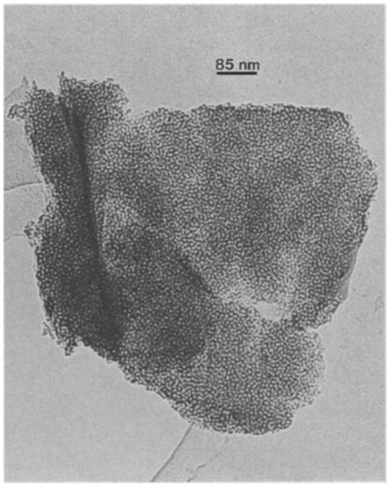

Fig. 3. Representative TEM of calcined MSU-1 silica obtained on a JEOL 100 CX microscope with an accelerating voltage of 120 kV and an objective lens aperture of 20 μm. We prepared the sample by allowing an ethanol suspension of the finely divided silica to evaporate on a Cu grid coated with a holey C film.

plating micelles, remains relatively regular and comparable in uniformity to the channels formed by electrostatic templating mechanisms.

To obtain further insights into the mechanism of MSU-X mesostructure formation, we carried out dynamic light-scattering studies for dilute aqueous solutions of Igepal RC-760 (Rhône Poulenc, Cranbury, New Jersey), an alkyl-aryl PEO surfactant with the formula $CH_3(CH_2)_{11}C_6H_4O(CH_2CH_2O)_{18}H$. At low concentrations ($\approx$0.01 mol liter^{-1}) this surfactant forms spherical micelles. Owing to a low rate of MSU-X formation, TEOS can be dissolved in the surfactant solution without the formation of a precipitate. The addition of a small amount of TEOS to the surfactant solution increases the mean micelle diameter from an initial value of $\approx$6.5 nm to $\approx$7.8 nm, but then the micelle size remains nearly constant up to a TEOS:surfactant molar ratio of 6:1 (Fig. 4). The abrupt increase in hydrodynamic diameter suggests that TEOS has a limited solubility in the inner hyrophobic core of the micelles. Moreover, the lack of a further increase in micelle size with increasing TEOS:surfactant ratio indicates that most of the TEOS in the homogeneous solution is accommodated between EO segments at the outer hydrophilic shell of the micelle. Thus, interfacial interactions between the surfactant EO groups, bound water, and TEOS may explain why precursor hydrolysis is much more rapid under nonionic templating conditions than in the absence of surfactant at the same reaction pH ($\approx$6). The assembly of silica precursors at the outer surface of segregated PEO micelles appears be an important aspect of N^{0}I^0 mesostructure templating. A study (*17*) of TEOS hydrolysis in the presence of an alkylphenyl PEO surfactant under conditions in which most of the surfactant was preassembled in lamellar liquid-crystal form yielded a silica gel containing encapsulated surfactant rather than a templated silica mesostructure.

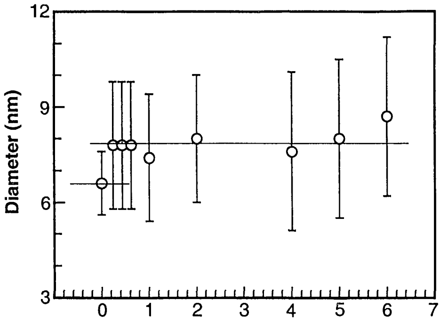

Fig. 4. Relation between the hydrodynamic diameter of spherical micelles of the PEO surfactant Igepal RC-760 in water (0.01 mol liter^{-1}) and the TEOS:surfactant molar ratio, as determined by dynamic light scattering. The circles indicate the mean micelle diameters, and the vertical bars indicate the widths of the micelle size distributions. Scattering analyses were performed on a PSS NICOMP 370 computing autocorrelator. Scattered light from an argon ion laser was collected from one coherence area at 90° and imaged onto the slit of an EMI 9789 photomultiplier.

In addition to Tergitol 15-S-*n* and Igepal RC-760, two other types of nonionic PEO derivatives, namely, Pluronic (BASF, Wyandotte, Michigan) and Triton-X surfactants (Union Carbide, Danbury, Connecticut), were effective templating agents for mesostructure syntheses. Pluronic surfactants are PEO-polypropylene oxide (PPO) block copolymers in which the PPO linkages act as the hydrophobic segments. These surfactants exhibit concentration- and temperature-dependent structural transitions from monomers through spherical, cubic, hexagonal, and lamellar phases (*15*). Pluronic 64L, the representative PEO-PPO block copolymer used in the present work, has the abbreviated structural formula $(PEO)_{13}$-$(PPO)_{30}(PEO)_{13}$. Triton-X surfactants have structures given as $(CH_3)_3CCH_2CH(CH_3)$-$C_6H_4O(CH_2CH_2O)_xH$, where $x = 8$ (TX-114) or 10 (TX-100).

Table 1 summarizes the basal spacings, HK pore sizes, and Brunauer-Emmett-Teller (BET) surface areas (*18*) for calcined MSU-X silicas prepared from representative Tergitol, Igepal, Pluronic, and Triton-X templating agents. All of the products in Table 1 exhibit single-line powder XRD patterns indicative of hexagonal-like channel structure with d_{100} in the range of 4.1 to 7.9 nm, adsorption-desorption isotherms containing a well-defined step indicative of framework-confined mesoporosity, HK pore sizes in the range from 2.0 to 5.8 nm, and BET surface areas between 525 and 1190 m^2 g^{-1}. These structural features are in accord with those reported previously for silica mesostructures prepared by both neutral and electrostatic templating routes. Among the materials listed in Table 1, those templated by Triton-X surfactants show broader d_{100} XRD lines, and hence lower crystallographic order, than the materials prepared with Tergitol, Igepal, or Pluronic surfactants. In general, the Tergitol-templated mesostructures have basal spacings and pore sizes that increase with increasing size of the surfactant, but the relation between pore size and surfactant size is not monotonic.

The templating of mesostructures by nonionic PEO surfactants is not limited to silica. A large number of metallic elements form alkoxides that readily hydrolyze to the corresponding metal oxides or hydroxides. As suggested by earlier studies of mesostructure synthesis using amine surfactants (*6*), one of the great advantages of neutral surfactant templating is the ability to prepare mesoporous metal oxides (such as alumina) that are not accessible by electrostatic templating routes. Exceptional synthetic versatility also is offered by N^{0}I^0 templating routes. For instance, we have prepared nonionic templated mesostructures of alumina-, titania-, and zirconia-substituted silica and also pure alumina, titania, tin oxide, and zirconia by hydrolysis of the corresponding alkoxides in the presence of a variety of nonionic PEO-based surfactants as the templating agents. The physicochemical properties of MSU-3 alumina templated by Pluronic 64L after calcination at 773 K are exhibited in Table 1. Thus, nonionic PEO surfactants promise to provide new families of mesoporous metal oxide molecular sieves complementary to those obtained with primary amine and quaternary ammonium ion surfactants but without the limitations imposed by the high cost and toxicity of amine-based templates.

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