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Nonionic oligomeric polymer directed synthesis of highly ordered large pore periodic mesoporous organosilica

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Highly ordered large-pore organosilica with 2D hexagonal structure has been prepared reproducibly in high yield using nonionic oligomeric Brij 76 as the structure-directing agent at 50 °C.

Since the discovery of ordered M41S silica mesophases using a supramolecular self-assembly approach,[1] the field of mesoporous materials has undergone dramatic growth. Remarkable progress has been made in the areas of synthesis strategies, materials composition and potential applications. Among the most recent innovations in this field is undoubtedly the use of bridged silsesquioxane molecules as precursors for the synthesis of periodic mesoporous organosilicates (PMOs).[2–9] Unlike surface functionalized mesoporous silica, the organic moieties in PMOs are built directly in the walls of the channels. In addition to the unique features of periodic mesoporous materials such as their high surface area, tunable pore sizes and narrow pore size distributions, PMOs open a wide range of new and exciting opportunities for designing materials with controlled surface properties at the molecular level.[9] To date, PMOs with organic spacers R originating from methane, ethane, ethylene, acetylene, butene, benzene, toluene, xylene, dimethoxybenzene, thiophene, bithiophene and ferrocene have been achieved. Successful syntheses of PMOs have been reported to take place under basic, acidic or neutral conditions. Depending on the amphiphile templating material used and on the synthesis conditions, several PMO mesophases have been obtained. These include a cubic structure (*Pm*3*n*) akin to SBA-1,[2,6] 2D hexagonal structure (*p*6*mm*) similar to MCM-41[2–7] or SBA-15,[10,11] and a 3D hexagonal mesophase[2,6] whose space group is yet to be determined.

Whether prepared in the presence of long chain alkylammonium[9] or alkylamines,[12] or nonionic polymeric surfactants,[8] most of the obtained PMOs exhibited relatively small pores below 5 nm in diameter. There are, however, few reports on the synthesis of large pore PMOs. Fröba *et al.*[10] used neutral Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) triblock copolymer as structure-directing agent and 1,2-bis(trimethoxysilyl)ethane (BTME) as organosilica source under acidic conditions. Their material exhibited hexagonal symmetry akin to SBA-15 silica with large pores (6.5 nm) and high surface area (900 $m^2 g^{-1}$). Likewise, Burleigh *et al.*[13] used the same triblock copolymer in addition to trimethylbenzene micelle-swelling agent under acidic conditions in the presence of 1,2-bis(triethoxysilyl-)ethane (BTEE) to synthesize a series of PMOs with pore sizes ranging from 6 to 20 nm. Though the occurrence of large pore PMOs has been demonstrated in both cases, the obtained materials did not exhibit highly ordered porous structure. However, there are two reports on high quality large pore PMOs prepared in the presence of polymer surfactants as supramolecular templates. Using B50-6600 ($EO_{39}BO_{47}EO_{39}$) poly(butylenes oxide) containing triblock copolymer and BTEE under acidic conditions afforded a well-ordered organosilicate with large cagelike pores whose diameter was *ca.* 12 nm.[14] The structure of this material was similar to that of FDU-1 silica prepared under similar conditions using tetrethylorthosilicate instead of BTEE.[15] The other report dealing with highly ordered large pore organosilicate used a lyotropic liquid crystal Pluronic P123 triblock copolymer as template.[11] The pore sizes of the obtained PMOs were adjustable within the range of 5.8 to 7.7 nm.

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In our laboratory, we prepared numerous high quality mesoporous materials, including MCM-41,[16] and MCM-48[17] silica, as well as a series of PMOs.[6,7] This allowed us to use these materials as mesoporous model adsorbents to develop the first practical approach for calculation of pore size distributions,[18] now being widely used.[19] More recently, our materials were also used to establish empirical correlations between ^{129}Xe chemical shift and pore sizes.[20] In this communication, we provide a recipe for the synthesis of high quality, large pore ethanesilica in the presence of polyoxyethylene (10) stearyl ether oligomer $C_{18}H_{37}(OCH_2CH_2)_{10}OH$ (Brij 76).

The synthesis was carried out as follows: 4.0 g of Brij 76 was dissolved in 20 g of water and 80 g of 2 M HCl solution under vigorous stirring in a thermostated oven at 50 °C. Then, 7.49 g of BTEE was added to the homogeneous solution at the same temperature, while the stirring continued for 20 h. The solid product obtained was separated by filtration, washed and air-dried at room temperature. The surfactant was removed by extraction using 1 g of as-synthesized organosilica into 150 ml 98% ethanol and 2 g of concentrated HCl (36.5%) at 50 °C under stirring for 5 h. The synthesis was reproducible, and its yield was typically 90%. The weight loss during extraction was approximately 70%. The product was characterized by X-ray diffraction, nitrogen adsorption, solid state NMR and transmission electron microscopy.[18]

The powder XRD patterns for as-synthesized and solvent extracted materials are presented in Fig. 1. The as-synthesized

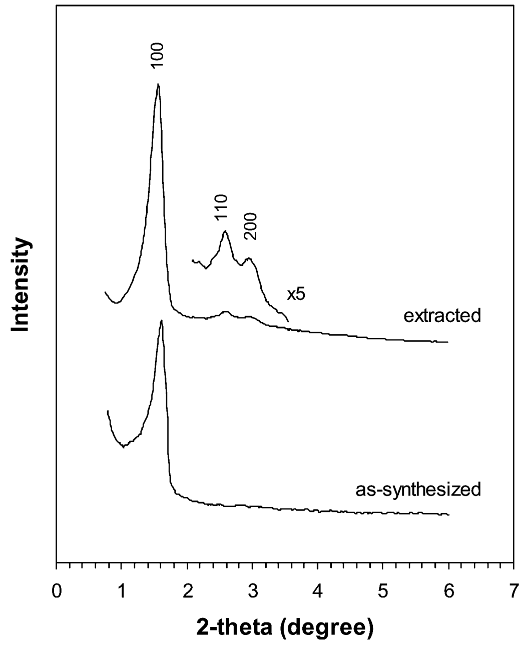

Fig. 1 Powder X-ray diffraction patterns for mesoporous ethanesilica prepared in the presence of Brij 76.

sample exhibited a strong peak at $2\theta = ca.$ 1.6° (d spacing of 54.5 Å) whose intensity increased significantly upon surfactant extraction. In addition, two well-resolved peaks developed at 2θ values between 2 and 3.5°, which were attributed to the (110) and (200) planes for 2D hexagonal mesostructure.

Typical TEM images shown in Fig. 2 provided direct evidence of the occurrence of 2D hexagonal structure. The material showed extended areas with the same high pore structure periodicity as displayed in Fig. 2. Analysis of high-resolution images such as in Fig. 2b led to an estimated pore size of 5.5 nm and a pore wall thickness of *ca.* 1.2 nm.

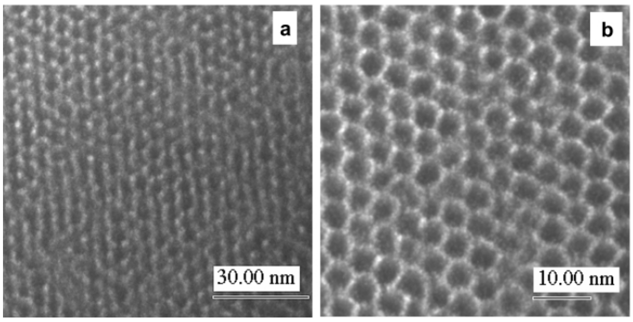

Fig. 2 TEM images under different magnifications for the current ethanesilica sample.

The nitrogen adsorption isotherm and the corresponding pore size distribution for the solvent extracted material are presented in Fig. 3. The adsorption isotherm is of Type IV with the characteristic condensation and evaporation steps indicating that the material is endowed with mesopores with a narrow size distribution. The occurrence of a hysteresis loop is consistent with an average pore size above 4 nm.[16] The pore size distribution shown in Fig. 3 exhibited a FWHM of only 0.8 nm. Consistent with TEM observations, the maximum of the PSD corresponded to a pore size w_{KJS} of 5.5 nm. The pore wall thickness b calculated based on XRD and adsorption data using the equation: $b = 2d_{100}/(3)^{1/2} - w_{KJS}$ was equal to 1.0 nm. This value is comparable to that derived from TEM images. Another indication that the obtained material was of high quality stems from the calculated pore size w based on the following formula, $w = cd[\rho V/(1+\rho V)]^{1/2}$, which was derived from the infinite structure of uniform cylindrical pores of diameter w arranged into a hexagonal pattern with a (100) interplanar spacing d.[21] Here ρ is the framework density of the material, V is the primary mesopore volume, and c is constant equal to 1.213 for cylindrical pores. Using $\rho = 1.52$ g cm^{-3},[22] a pore size $w = 5.3$ nm was calculated. This value, being very close to those calculated above using nitrogen adsorption and TEM data, lends further support as to the high quality of the current material. In addition, this material exhibited a high surface area of 1024 m^2 g^{-1}, and a particularly large pore volume of 1.01 cm^3 g^{-1}.

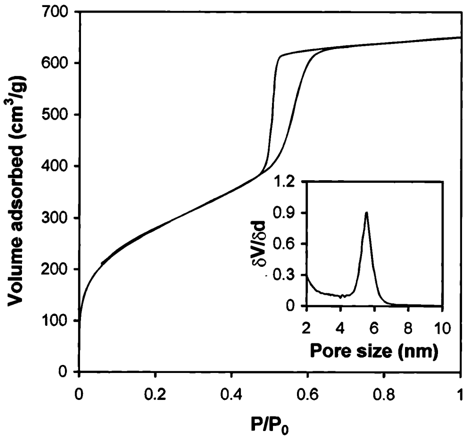

Fig. 3 Nitrogen adsorption isotherm and pore size distribution curve.

^{13}C CP MAS NMR data for the solvent extracted sample showed the occurrence of a large peak at *ca.* 5.5 ppm, attributed to CH_2–CH_2 groups connected to Si. Small peaks assigned to residual CH_3–CH_2–O– groups appeared at *ca.* 59 ppm and 17.2 ppm. These data clearly indicate that the Si–C bonds were preserved under the conditions of synthesis and extraction. Consistent with this conclusion, ^{29}Si MAS NMR spectra showed no Q^n, *i.e.* $Si(OSi)_n(OH)_{4-n}$ species. Two main signals corresponding to partially hydrolyzed silicon $C(OH)\mathbf{Si}(OSi)_2$ and fully condensed silicon $C\mathbf{Si}(OSi)_3$ appeared at −56.7 and at −64.4 ppm, respectively. A much smaller peak at −47.3 ppm was attributed to $C(OH)_2\mathbf{Si}(OSi)$.

In summary, this communication provides a reproducible recipe for the synthesis of highly ordered large-pore organosilica with a 2D hexagonal array of channels using nonionic oligomeric Brij 76 as the structure-directing agent at 50 °C.

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18 X-ray powder diffraction (XRD) patterns were collected on a Scintag X_2 Advanced Diffraction System using Cu Kα radiation. Nitrogen adsorption experiments were performed at 77 K using a Coulter Omnisorp 100 gas analyzer after lengthy degassing at room temperature. The specific surface area, S_{BET}, was determined from the linear part of the BET plot ($P/P_0 = 0.05$–0.15). The pore size distribution (PSD) was calculated from the adsorption branch using the KJS method (M. Kruk, M. Jaroniec and A. Sayari, *Langmuir*, 1997, **13,** 6267). Transmission electron micrographs (TEM) were obtained using a Philips CM20 instrument operated at 200 kV. ^{13}C and ^{29}Si MAS NMR spectra were collected at room temperature on a Bruker AMX300 instrument in a magnetic field of 7.04 T (the resonance frequencies were 75.46 and 59.6 MHz, respectively), using a 5 mm MAS probe from DOTY Scientific.
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