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Periodic mesoporous organosilica from micellar oligomer template solution†

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Periodic mesoporous organosilica (PMO) with two-dimensional hexagonal symmetry was synthesised using a bridged silsesquioxane $(CH_3O)_3Si\text{-}CH_2\text{-}CH_2\text{-}Si(CH_3O)_3$ as precursor and polyoxyethylene non-ionic surfactant (Brij-56) as template. The hybrid material was characterised by X-ray diffraction, N_2 adsorption, TEM, and solid-state ^{29}Si MAS NMR spectroscopy.

Recently, a new class of mesoporous silica materials integrating organic moieties within their framework was reported.[1–3] These novel materials designated as periodic mesoporous organosilicas (PMOs) were synthesised *via* surfactant templating using organosilane precursors with two trialkoxysilyl groups bridged by an organic group. PMOs are foreseen to have many remarkable properties related to the possibility of tailoring their framework properties between those of ceramics and organic materials. Several synthesis strategies were proposed for the preparation of such materials. What began with alkyltrimethylammonium cationic surfactants of different chain lengths under basic conditions[1–4] was extended to other amphiphilic species such as block copolymers, poly(oxyethylene) alkyl ethers and primary amine surfactants under acidic or neutral conditions.[5–10] Among the non-ionic surfactant family, triblock copolymers such as PEO-PPO-PEO pluronic P123 or F127[5–9] as well as PEO-PLGA-PEO[7] were used under acidic conditions and yielded materials with large pores (up to 10 nm) and rather poor structural ordering. Furthermore, syntheses under neutral conditions in the presence of short chain alkylamines or slightly acidic conditions in the presence of alkylphenylpolyethylene oxide surfactants provided materials in the super-microporous domain.[10]

In the present work, we report the synthesis of a highly ordered PMO in the presence of a non-ionic oligomeric alkylethylene oxide surfactant with the nominal chemical structure $CH_3(CH_2)_{15}(OCH_2CH_2)_{10}OH$ commercially designated as Brij-56. Such surfactant presents the advantages to be inexpensive, biodegradable and nontoxic, and to have excellent interfacial stabilization properties.[11] Furthermore, this class of surfactant was already used in the synthesis of all-silica mesoporous materials in both lyotropic liquid crystal and micellar solutions.[12]

The PMO was thus synthesised from 1,2-bis(trimethoxysilyl)ethane (BTME) precursor and Brij-56 surfactant. The synthesis gel mass composition (g) was: BTME, 0.84; Brij-56, 0.5; HCl/H_2O, (500 ml). In a typical synthesis, Brij-56 (0.5 g) was heated until melting at 35 °C, then dissolved in BTME (0.84 g). To this mixture was added 500 mL of HCl (0.5 N) and the stirring was continued for 3 h. The clear suspension was then transferred to a polyethylene bottle and heated at 60 °C for one week under static conditions. The obtained white precipitate was separated by filtration, washed thoroughly with deionised water and dried at room temperature. The surfactant was removed by solvent extraction with anhydrous ethanol in a Soxhlet apparatus for 24 h.

XRD spectra were obtained on a Philips X-ray diffractometer (PW 1010 generator and PW 1050 computer-assisted goniometer) using nickel-filtered CuK_α (λ = 1.5406 Å) radiation. Adsorption measurements were performed using a Coulter Omnisorp 100 gas analyzer. Transmission electron micrographs (TEM) were obtained using a JEOL 200 CX microscope operated at 80 kV. Solid-state ^{29}Si MAS NMR spectra were recorded at room temperature on a Bruker ASX 300 spectrometer. Tetramethylsilane (TMS) was used as an external reference. Thermogravimetric analyses were performed with a Perkin Elmer 7 series thermal analysis system from ambient temperature to 800 °C at a heating rate of 5 °C min^{-1} under nitrogen atmosphere.

The powder XRD pattern of solvent-extracted sample depicted in Fig. 1 showed the occurrence of three reflection peaks at 2θ values between 1.2 and 3.5°. The three peaks were indexed to (100), (110) and (200) diffractions of a hexagonal symmetry (*p6mm*) with lattice *d* spacings of 58.8, 33.6 and 29.5 Å, respectively. The corresponding unit cell parameter a_0 was 67.9 Å. The well-resolved XRD data attest that a highly ordered hexagonal structure was obtained.

Nitrogen adsorption analysis displayed a type IV isotherm with a slight hysteresis loop and extremely sharp adsorption and desorption steps between relative pressures at 0.4 and 0.5, respectively (Fig. 2). The BET surface area evaluated from adsorption data at relative pressures from 0.05 to 0.3 was 1190 $m^2\ g^{-1}$, while the pore volume reached 1.32 $cm^3\ g^{-1}$. As depicted in Fig. 2 (inset), the BJH pore size distribution centered at 4.5 nm was very narrow, indicating an excellent textural uniformity of the organosilica material. The PMO wall thickness evaluated from diffraction (a_0) and adsorption data (pore size) was 23 Å, which represents at least twofold that of the PMO materials synthesised in the presence of cationic surfactants[13,14] and more than 30% above that of ethane-silicas synthesised using Pluronic P123 surfactant.[8]

Moreover, as shown in Fig. 3, TEM analysis confirmed the high periodicity of the material with a clear hexagonal (2-D P6*mm*) arrangement of uniform pores of *ca.* 5 nm.

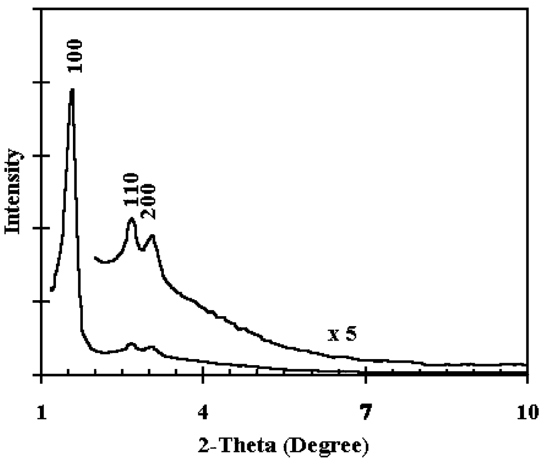

Fig. 1 Powder X-ray diffraction pattern.

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† Electronic supplementary information (ESI): available: TG/DTG data. See http://www.rsc.org/suppdata/cc/b2/b207134g/

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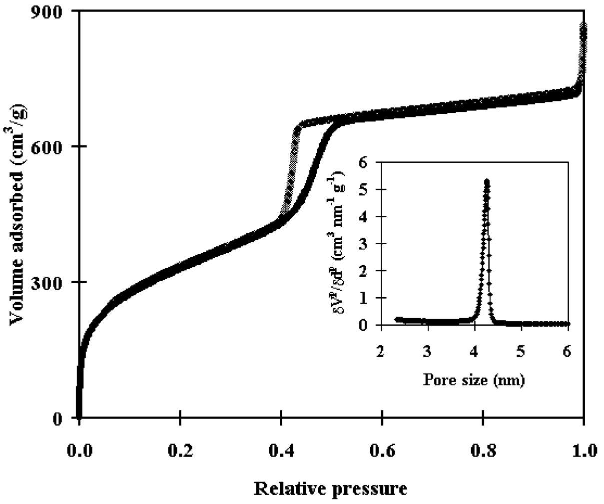

Fig. 2 Nitrogen adsorption–desorption isotherm and pore size distribution (inset).

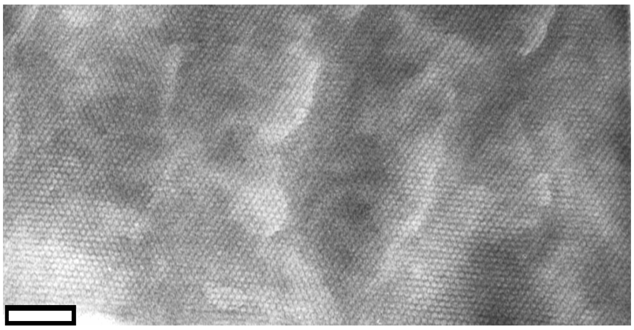

Fig. 3 Representative transmission electron micrograph. The white scale bar corresponds to 50 nm.

Solid state ^{29}Si NMR of the solvent-extracted material showed two signals at −56 and −63 ppm assigned to T^2 [$RSi(OSi)_2OH$] and T^3 [$RSi(OSi)_3$] resonances, respectively (Fig. 4). No signals from Q^n [$Si(OSi)_n(OH)_{4-n}$] species were registered, indicating that all silicon atoms were covalently bound to carbon atoms as previously reported for ethane-silica materials synthesised in the presence of cationic surfactants.[1–4] Moreover, these data indicate clearly the hydrolytic stability of the Si–C bonds under the acidic synthesis conditions used herein.

Thermogravimetric analysis performed on as-synthesised organosilica under nitrogen indicated a pronounced weight loss (*ca.* 45%) in the temperature interval [200–400 °C] corresponding to the thermal decomposition of the oligomeric occluded template and a moderate weight loss (*ca.* 5%) within [400–700 °C] attributed to the decomposition of the ethane bridging groups. The solvent-extracted sample exhibited only a moderate weight loss (*ca.* 5%) in the temperature range [400–700 °C], thus indicating the high thermal stability of the organosilica material (Supplementary Fig. 1A–B†).

In summary, this is the first mesoporous ethane-silica material with hexagonal symmetry synthesised in the presence of a micellar solution of non-ionic Brij-56 surfactant. The well-resolved XRD peaks, the sharp nitrogen condensation step and the narrow pore size distribution demonstrate the excellent quality in terms of framework periodicity of the synthesised ethane-silica. The new synthesis procedure involving the use of Brij-56 under mild acidic conditions yields therefore high quality PMO materials with unprecedented pore wall thickness. The present PMOs having high surface area, substantial pore volume and pore wall thickness show remarkable thermal stability (up to 400 °C) which makes them excellent candidates for catalysis and adsorption applications.

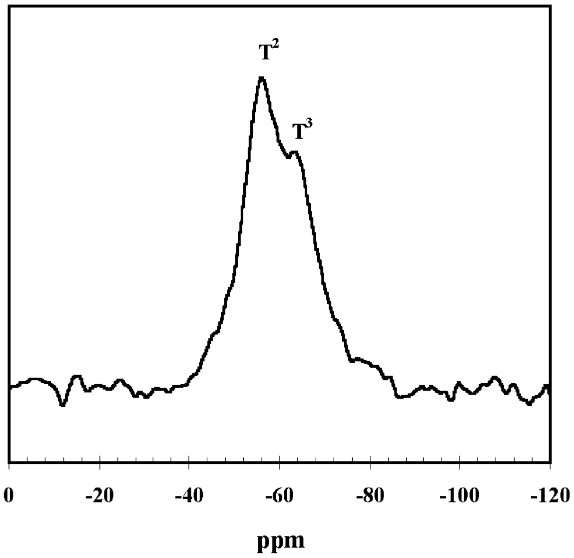

Fig. 4 Representative ^{29}Si MAS NMR data for solvent-extracted sample.

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