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Periodic mesoporous phenylenesilicas with ether or sulfide hinge groups—a new class of PMOs with ligand channels†

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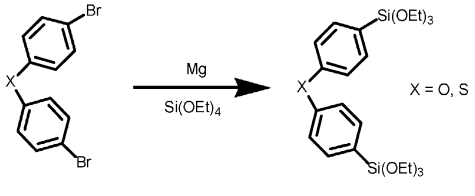
A new class of periodic mesoporous organosilicas (PMOs) with 4-phenyl ether and 4-phenyl sulfide bridge-bonded silsesquioxanes integrated into the pore walls to create ligand channels have been synthesized using inorganic salt-assisted self-assembly directed by a supramolecular polyoxyethylene (10) stearyl ether (Brij 76) template.

A new generation of nanoporous organic–inorganic hybrid materials with large surface areas and narrow pore size distributions ranging from 2 to 10 nm was discovered in 1999 and termed periodic mesoporous organosilicas (PMOs).[1] These materials were prepared by the hydrolysis and polycondensation of bridge-bonded ethane or ethene silsesquioxane precursors cast around a micellar surfactant template. Subsequent investigations extended the organic content to include the aromatic organic bridges thiophene, phenylene, and biphenylene in the organosilica matrix.[2] Self-assembly of phenylene bridge-bonded silsesquioxanes formed well-ordered materials in the presence of non-ionic oligomeric (Brij 56 and 76)[3] or polymeric (P123)[4] surfactant templates in aqueous acid. Addition of inorganic salts to a P123 aqueous HCl solution was shown to enhance the self-assembly process leading to improved structural order for an ethane-bridged PMO.[5] The 4-phenyl ether bridge was previously used to form a soluble ladder-like polyvinylsiloxane from 4,4′-bis(vinyldimethyloxysilyl)phenyl ether with a maximum of two siloxane bonds per silicon center.[6] We anticipated that the related bis-4-(triethoxysilyl)phenyl ether precursor containing six condensable Si–O units would yield a more robust and insoluble cross-linked structure suitable for incorporation of this organic bridge into a PMO framework. Similarly, a 4-phenyl sulfide PMO was prepared. Oxygen or sulfur atoms form hinge groups between two 4-phenyl silsesquioxane rings. Recently, a mercury adsorbing PMO was prepared by mixing a thioether bridged silsesquioxane with tetraethoxysilane as a network former. We expect comparable utility for our PMOs with ligand channels.[7]

Bridged silsesquioxane precursors were prepared *via* a Grignard type reaction, Scheme 1.‡ Resonances for the silicon atoms appeared as sharp singlets at −57.6 and −58.1 ppm for the 4-phenyl ether and 4-phenyl sulfide bridged precursors, respectively. PMOs were prepared through a cooperative self-assembly process using the non-ionic oligomeric polyoxyethylene(10) stearyl ether template [Brij 76 = $CH_3(CH_2)_{17}(OCH_2CH_2)_{10}OH$] as a structure-directing species. For a typical synthesis, H_2O (18.20 g, 1.01 mol), Brij 76 (0.39 g, 0.55 mmol) and HCl (1.29 g, 12 M, 13.1 mmol) were mixed at 60 °C for 1 hour in a closed polypropylene bottle, followed by adding NaCl (1.77 g, 30.3 mmol) and an additional 3 hours of stirring. The organosilica precursor $[O(C_6H_4Si(OEt)_3)_2]$ (1.00 g, 2.02 mmol) or $[S(C_6H_4Si(OEt)_3)_2]$ (1.03 g) was added and the reaction mixture stirred for 20 hours at 60 °C, followed by ageing under static conditions for 24 hours at 80 °C. The precipitate was filtered quickly before cooling yielding a microcrystalline white powder, which was washed with water and ethanol. Surfactant templates were removed by repeated extractions in acidified ethanol (1.5 g HCl in 100 g EtOH for 0.5 g PMO) at 50 °C for 12 hours. A compositional molar ratio of precursor : Brij-76 : HCl : NaCl : H_2O of 1 : 0.27 : 6.5 : 15 : 500 was used. Template-extracted PMOs were dried at 80 °C for 24 hours prior to the following material characterizations.

Powder X-ray diffraction (PXRD) patterns for the template extracted materials reveal an intense low-angle Bragg reflection at 47 Å indicating ordered mesostructured materials (Fig. 1). The 4-phenyl sulfide bridged material displays a weaker diffraction pattern and is presumably less well-ordered than the oxygen bridged analogue. Less efficient packing of the organic units in the channel walls is attributed to steric effects and restricted rotation about the sulfur hinge group. Transmission electron microscopy (TEM) images reveal the porous channel structure of both PMOs with pore diameters of 2–3 nm and a channel wall thickness of approximately 3 nm (Fig. 2). The combination of a single low-angle XRD diffraction peak and the analysis of SEM and TEM images suggests a ‘wormhole’ type mesoporous structure.

Connectivity of the synthesized PMO materials was confirmed by solid-state ^{13}C and ^{29}Si cross-polarization magic angle spinning (CP-MAS) NMR measurements (Fig. 3). Resonances for the silicon environments are centered between −60 to −80 ppm, which correspond to T-type silica moieties [T_n = $RSi(OSi)_n(OH)_{3-n}$] covalently bonded to an sp^2 aromatic carbon atom. No signals for SiO_4 species were observed indicating that all the silicon atoms in the material remain covalently bonded to a carbon atom of the framework and Si–C bond cleavage was insignificant. In the ^{13}C



Scheme 1

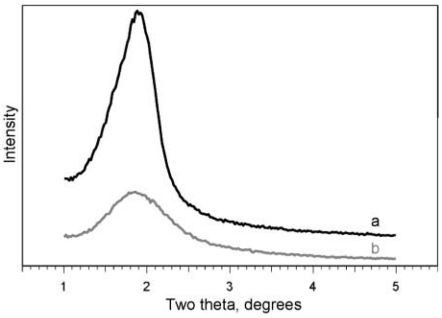


Fig. 1 PXRD patterns of the template-extracted PMOs (a) 4-phenyl ether (b) 4-phenyl sulfide bridged PMO.

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† Electronic supplementary information (ESI) available: experimental details, ^{29}Si solution NMR of the precursors, ^{13}C CP/MAS-NMR spectra of 4-phenyl ether PMO and 4-phenyl sulfide PMO and thermogravimetric analysis plots of the template extracted PMOs under nitrogen. See http://www.rsc.org/suppdata/cc/b4/b410397a/

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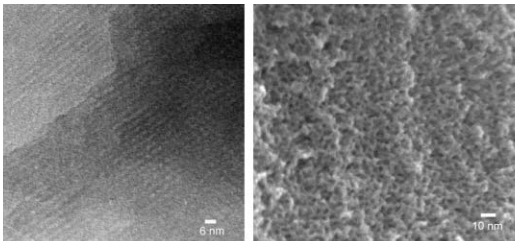

Fig. 2 TEM and SEM images of the 4-phenyl ether bridged PMO.

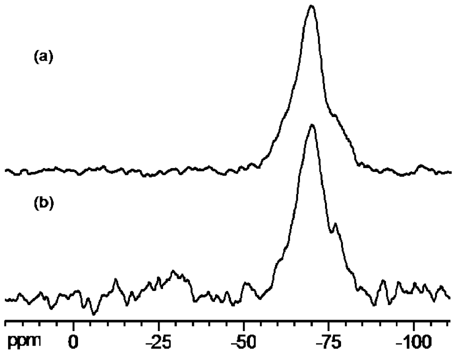

Fig. 3 ^{29}Si CP-MAS NMR of PMOs (a) 4-phenyl ether (b) 4-phenyl sulfide.

CP-MAS NMR spectrum, chemical shifts for aromatic carbon atoms appear between 115 and 160 ppm. Resonances at 16 and 58 ppm are due to the conversion of uncondensed silanol groups to ethoxysilane units during the acidified ethanol extractions.

Nitrogen adsorption isotherms for the PMOs are presented in Fig. 4. A low-pressure type-IV isotherm was observed with a sharp increase in adsorption between $P/P_o = 0.10$–0.25, confirming capillary condensation diagnostic of a mesoporous structure. Pore sizes were evaluated using density functional theory (DFT), and shows the materials are supermicroporous with pore diameters between 2–3 nm. The corresponding BET (Brunauer–Emmett–Teller) surface areas were 637 m^2 g^{-1} and 432 m^2 g^{-1} for the 4-phenyl ether and 4-phenyl sulfide PMOs, respectively.

The PMOs were examined by thermogravimetric analysis (TGA) and showed thermal stability to over 500 °C under both air and nitrogen atmospheres (Fig. 5). The 4-phenyl ether bridged PMO showed greater thermal stability than the 4-phenyl sulfide bridged analogue by about 20 °C. The thermal stability of these PMOs is similar to other rigid *para*-phenylene and biphenylene bridged PMOs.[2]

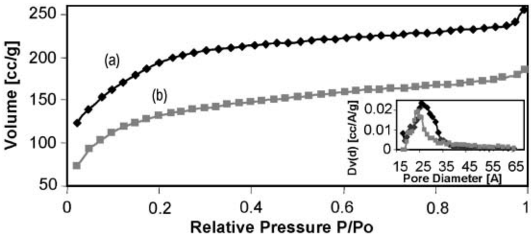

Fig. 4 Nitrogen adsorption isotherms and pore size distribution curves: (a) 4-phenyl ether (b) 4-phenyl sulfide.

In summary, PMOs containing phenylene bridged silsesquioxanes with ether or sulfide hinge groups were synthesized by a non-ionic template-based self-assembly strategy. Inorganic salts were used to assist the interaction between silicate species and the hydrophilic headgroups of non-ionic oligomeric surfactants and thereby improve the mesostructural order of the materials. This new class of PMOs with "ligand channels" might prove to be environmentally useful for sequestering toxic heavy metals and organic pollutants from waste water, lakes, and rivers and serve as a support for heterogeneous catalysts.

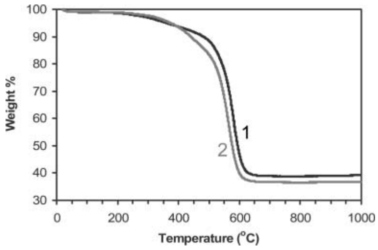

Fig. 5 TGA plots of the template-extracted PMOs under an air atmosphere (1 = 4-phenyl ether, 2 = 4-phenyl sulfide bridged PMO).

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Notes and references

‡ *Bis-4-(triethoxysilyl)phenyl ether.* 4-Bromophenyl ether (25.0 g, 76.2 mmoles) was dissolved in THF (250 mL) and added dropwise to a mixture of iodine activated Mg (7.41 g, 0.30 moles), TEOS (170 mL, 0.76 moles) and THF (250 mL) at 60 °C and stirred for 48 hours. Volatile solvents were removed, the yellow residue washed with hexanes (3 × 100 mL), filtered to remove magnesium salts, and the hexanes removed under vacuum. Vacuum distillation yielded the product as a colorless liquid (180 °C, 0.050 mmHg). Yield: 11.1 g, 29%. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.29 (t, 18H, $\mathrm{SiOCH_2}\mathit{CH_3}$, $^3J = 7.0$ Hz), 3.91 (q, 12H, $\mathrm{SiO}\mathit{CH_2}\mathrm{CH_3}$, $^3J = 7.0$ Hz), 7.06 (d, 4H, OArH), 7.69 (d, 4H, ArH). ^{13}C (75.48 MHz, CDCl$_3$) δ 18.40 ($\mathrm{SiOCH_2}\mathit{CH_3}$), 58.92 ($\mathrm{SiO}\mathit{CH_2}\mathrm{CH_3}$), 118.63 (ArH), 125.69 (ipso-CSi), 136.80 (ArH), 158.92 (ipso-CO). ^{29}Si (79.42 MHz, CDCl$_3$) δ −57.55. EI-MS, *m*/*z*: 494.215; calcd for $C_{24}H_{38}O_7Si_2$: 494.214. *Bis-4-(triethoxysilyl)-phenyl sulfide.* Prepared similarly using 4-bromophenyl sulfide (185 °C, 0.050 mmHg). ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.27 (t, 18H, $\mathrm{SiOCH_2}\mathit{CH_3}$, $^3J = 7.0$ Hz), 3.90 (q, 12H, $\mathrm{SiO}\mathit{CH_2}\mathrm{CH_3}$, $^3J = 7.0$ Hz), 7.37 (d, 4H, SArH), 7.63 (d, 4H, ArH). ^{13}C (75.48 MHz, CDCl$_3$) δ 18.39 ($\mathrm{SiOCH_2}\mathit{CH_3}$), 58.96 ($\mathrm{SiO}\mathit{CH_2}\mathrm{CH_3}$), 129.94 (ipso-CSi), 130.31 (ArH), 135.72 (ArH), 138.13 (ipso-CS). ^{29}Si (79.42 MHz, CDCl$_3$) δ −58.11. EI-MS, *m*/*z*: 510.193; calcd for $C_{24}H_{38}O_6SSi_2$: 510.193.

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