

# Periodic mesoporous organosilicas, PMOs: fusion of organic and inorganic chemistry 'inside' the channel walls of hexagonal mesoporous silica

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Synthesis and characterization of new periodic mesoporous organosilicas, PMOs, containing benzene and thiophene groups 'within' the channel walls, is presented.

Since the first report of surfactant-templated mesoporous silica by Kresge *et al.*,<sup>1</sup> the area of periodic mesoporous materials has exploded. This is due to the promising properties and applications of materials with ordered arrangements of pores in a new length scale in chemistry, including size exclusion chemistry and chromatography, catalysis, sensors and host materials for polymers, organic and inorganic substances.<sup>2,3</sup>

Recently, a new class of materials, periodic mesoporous organosilicas (PMOs), have been reported.<sup>4-7</sup> These materials are unique compared to first generation periodic mesoporous silica materials since the channel walls contain both organic and inorganic substances. This marriage of organic chemistry with inorganic materials chemistry offers fascinating new possibilities and applications. Some important advantages of integrated organic-inorganic channel walls (smart channels) that were not possible with first generation materials include the following. (i) Organic moieties are homogeneously dispersed 'inside' the channel walls with a maximum loading of 100%, not achievable with organics 'hanging' in the channels with a maximum loading before collapse of 25%. (ii) Bridge bonded organics 'inside' the channel walls do not block the pores from chemistry. (iii) 'Soft' organics 'integrated within' the channel walls should impart interesting mechanical properties to the 'hard' inorganics not seen before. (iv) The organic precursors are easily varied to produce a wide range of materials with potentially interesting electronic, optical, charge-transport and magnetic properties.

The preparation of these materials involves the catalyzed hydrolysis of bis(trialkoxysilyl) organic precursors in the presence of a surfactant template. The presence of the organic moiety greatly influences the nature of the hydrolysis reaction and a number of new factors become important in the synthesis of these materials. Most notably, we were concerned with the stability of the Si-C bond under the hydrolysis conditions and the degree of order in the resulting product. Certain materials, such as the bis-silylated ethylene, methylene and ethane precursors show great stability to strongly acidic or basic conditions. This is confirmed by <sup>29</sup>Si NMR, which shows virtually no cleavage even under harsh conditions.<sup>7</sup> In more complicated bridging organic precursors, however, aqueous hydrolysis often results in significant cleavage, as well as a decrease in the degree of order in the material.

The synthesis of the precursors utilized bis-metallated organic intermediates, which reacted with chlorotriethoxysilane prepared from the partial alcoholysis of silicon tetrachloride.<sup>8</sup> Precursors that we synthesized include 1,4-bis(triethoxysilyl)benzene **1**,<sup>9</sup> 2,5-bis(triethoxysilyl)thiophene **2**,<sup>9</sup> 1,1'-bis(triethoxysilyl)ferrocene **3**,<sup>10,11</sup> bis(triethoxysilyl)bithiophene **4**,<sup>9</sup> and bis(triethoxysilyl)acetylene **5** (Fig. 1).<sup>12</sup> Thiophene and ferrocene PMOs may have interesting electrochemical applications. PMOs with unsaturated organic groups such as benzene offer the possibility of 'chemistry of the channels', or act as 'ligand channels' for metal complexes and organometallics in catalytic applications.

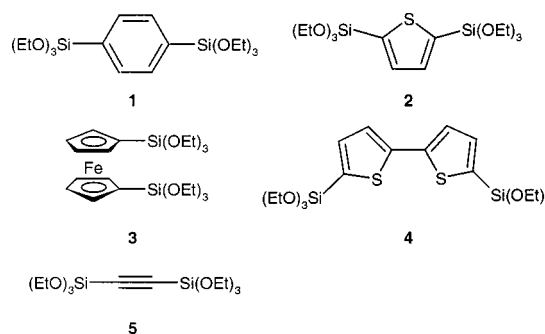


Fig. 1 Structures of the PMO precursors.

When the strongly basic conditions utilized for the synthesis of ethylene-bridged mesoporous silica<sup>4</sup> were applied to the benzene **1** and thiophene **2** precursors, white powders were obtained almost immediately [1.0 Si : 114 H<sub>2</sub>O : 15.0 NH<sub>3</sub> (aq) (35 wt%):0.12 CTABr]. The powders were aged at 80 °C for two days. <sup>29</sup>Si CP MAS NMR showed that almost all the organic moieties had been cleaved from the silica. When a similar experiment was performed under acidic conditions using the thiophene precursor, <sup>29</sup>Si CP MAS NMR showed characteristic signals attributed to Si(OSi)<sub>4</sub> (Q<sub>4</sub> δ -112), (HO)Si(OSi)<sub>3</sub> (Q<sub>3</sub> δ -103) and (HO)<sub>2</sub>Si(OSi)<sub>2</sub> (Q<sub>2</sub> δ -92), which clearly indicate that a proportion of the Si-C bonds had been cleaved, as well as signals which showed the presence of the organic moieties; CSi(OSi)<sub>3</sub> (T<sub>3</sub> δ -84), CSi(OSi)<sub>2</sub>(OH) (T<sub>2</sub> δ -76) and CSi(OSi)(OH)<sub>2</sub> (T<sub>1</sub> δ -66) [Fig. 2(a)]. <sup>13</sup>C CP MAS NMR showed that indeed the benzene and thiophene organic moieties were intact. The PXRD pattern showed very good structural order in the hexagonal phase. Most of the surfactant template could be removed by extracting into a MeOH-HCl mixture at room temp. for 2-3 days and the structural integrity of the material was maintained, as shown by PXRD and TEM studies.

To decrease the amount of cleavage of Si-C bonds in the benzene and thiophene PMOs, a decreased concentration of acid was used to catalyze the hydrolysis, as well as allowing the

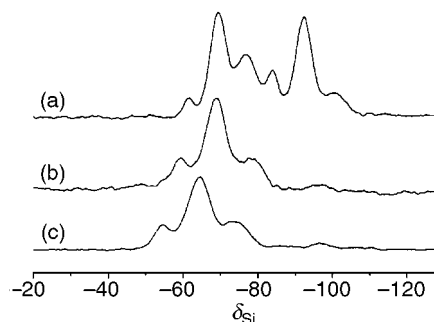
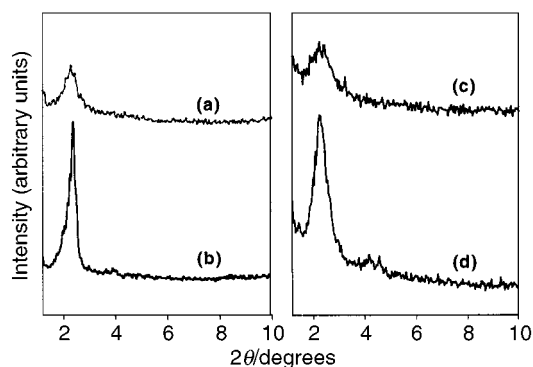


Fig. 2 <sup>29</sup>Si CP MAS NMR spectra of periodic organosilica materials. Thiophene bridged PMO prepared in (a) strong acid and (b) under the optimized procedure. (c) Benzene bridged PMO prepared under the optimized procedure.

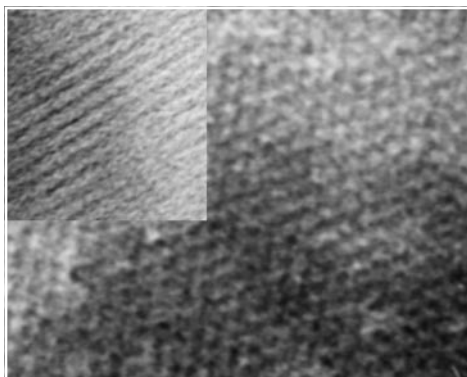


**Fig. 3** XRD of periodic mesoporous organosilica materials with a comparable degree of Si–C bond cleavage. Benzene bridged PMO prepared in (a) dilute acid and (b) under the optimized procedure. Thiophene bridged PMO prepared in (c) dilute acid and (d) under the optimized procedure.

powder to age at room temp. instead of 80 °C. NMR studies confirmed that under milder conditions, the amount of cleavage decreased. However, XRD indicated that the degree of order of the material was diminishing with decreased acid concentration [Fig. 3(a,c)]. This is presumably due to the decreased charge concentration on the silicate species. This reduces the coulombic attraction between surfactant and silicate species that contributes to the ‘surfactant templating’ mechanism.<sup>13</sup> Also, under very dilute acidic conditions, the yield of the powder product decreased considerably as did the degree of polymerization as observed by <sup>29</sup>Si NMR. This decreased yield may be due to the formation of low molecular weight soluble silicates.

To obtain a satisfactorily ordered PMO containing benzene or thiophene in an aqueous synthesis medium, a different approach to hydrolytic polycondensation needed to be considered. The following procedure for the bis-silylated thiophene PMO gives a satisfactory sample and is representative of the approach. Cetylpyridinium chloride (CPCl) followed by 2,5-bis(triethoxysilyl)thiophene was added to an acidic aqueous solution and stirred moderately at room temp. briefly. After the resulting mixture was neutralized with portionwise addition of solid NaHCO<sub>3</sub>, NH<sub>4</sub>F (0.1 mol%) was added and the slurry allowed to stand at room temp. for two days.<sup>14</sup> After filtering and washing with copious amounts of water, a white powder was obtained. The material thus obtained showed only a small amount of Si–C bond cleavage [Fig. 2(b,c)] and the XRD showed a good hexagonal mesoporous organosilica (100) reflection [Fig. 3(b,d)]. TEM also showed the presence of the expected crystalline mesoporosity (Fig. 4).<sup>15,16</sup> NMR did not show the presence of triethoxysilyl moieties, suggesting the hydrolysis is essentially complete.

The other precursors proved to be more challenging. For example, the bis(triethoxysilyl)ferrocene precursor **3** showed partial cleavage of the Si–C bond and a lower degree of order.



**Fig. 4** TEM of hexagonal mesoporous benzene silica. Images perpendicular and parallel (inset) to the channel axis confirm the hexagonal structure of the PMO. Extensive TEM lattice imaging studies of large areas of the sample show that the PMO phase always dominates over any amorphous organosilicate xerogel phase.

NMR studies showed that a significant amount of ferrocene remained intact in the silica framework, and thus shows promise for further study. The acetylene precursor **4** had a particularly labile Si–C bond and was difficult to control under aqueous conditions. The attempt to place the bithiophene moiety **5** within the walls of the channels resulted in a material with poorer order.

The preparation of various hybrid ‘organic–inorganic’ walled periodic mesoporous silicas is currently being optimized.

PMOs with organic functionality ‘inside’ the channel walls are a new class of materials with much promise for a wide variety of applications. PMOs are distinct from organosilica xerogels that have been previously reported. Organosilica xerogels have a ‘random distribution of polydispersed mesopores’. This is to be contrasted with PMOs that have ‘crystalline mesoporosity’ and ‘Angstrom precise pore dimensions’, both considered necessary prerequisites for size selective applications.

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## Notes and references

- C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
- K. Moller and T. Bein, *Chem. Mater.*, 1998, **10**, 2950.
- G. A. Ozin, E. Chomski, D. Khushalani and M. J. MacLachlan, *Curr. Opin. Colloid Interface Sci.*, 1998, **3**, 181.
- T. Asefa, M. J. MacLachlan, N. Coombs and G. A. Ozin, *Nature*, 1999, submitted.
- S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna and O. Terasaki, *J. Am. Chem. Soc.*, 1999, **121**, 9611.
- B. J. Melde, B. T. Holland, C. F. Blanford and A. Stein, *Chem. Mater.*, 1999, **11**, 3302.
- Ö. Dag, C. Yoshina-Ishii, T. Asefa, M. J. MacLachlan, H. Grondey and G. A. Ozin, *Adv. Mater.*, 1999, submitted.
- D. F. Peppard, W. G. Brown and W. C. Johnson, *J. Am. Chem. Soc.*, 1946, **68**, 70.
- R. J. P. Corriu, J. J. E. Moreau, P. Thepot and M. W. C. Man, *Chem. Mater.*, 1992, **4**, 1217.
- G. Cerveau, C. Chuit, E. Colomer, R. J. P. Corriu and C. Reyé, *Organometallics*, 1990, **9**, 2415.
- M. S. Wrighton, M. C. Palazzotto, A. B. Bocarsly, J. M. Bolts, A. B. Fischer and L. Nadjo, *J. Am. Chem. Soc.*, 1978, **100**, 7264.
- R. J. P. Corriu, J. J. E. Moreau, P. Thepot, M. W. C. Man, C. Chorro, J.-P. Lère-Porte and J.-L. Sauvajol, *Chem. Mater.*, 1994, **6**, 640.
- For a recent review, see: J. Y. Ying, C. P. Mehnert and M. S. Wong, *Angew. Chem., Int. Ed.*, 1999, **38**, 56.
- The following procedure for the synthesis of mesoporous benzenesilica is representative: bis(triethoxysilyl)benzene (0.96 g, 2.4 mmol) was added to a homogeneous solution of water (4.88 g, 0.27 mol), HCl (36%, 0.81 g, 8.1 mmol), and CPCl (0.11 g, 0.3 mmol) at ca. 32 °C, and the solution was stirred moderately for 15 min. The resulting mixture was neutralized with portionwise addition of NaHCO<sub>3</sub> prior to adding NH<sub>4</sub>F (0.1 mg, 2.7 μmol) and aging at room temp. for two days. The powder was filtered and washed with copious amounts of water.
- The possibility that a mixture of amorphous organosilica and periodic mesoporous organosilica resulting from hydrolytic cleavage of the Si–C bond could give rise to the observed XRD and NMR was addressed by examining large areas of the powder by TEM. The results of an extensive TEM study show that the PMO phase dominates over any amorphous organosilicate xerogel phase. Therefore the PMOs are responsible for both the solid state NMR and XRD data reported here. Polarisation optical microscopy and micro-Raman spectroscopy confirm this proposal and show bridge bonded organics homogeneously dispersed throughout the PMO.<sup>7</sup>
- Surfactant-free mesoporous benzenesilica shows a Type IV nitrogen adsorption isotherm at 77 K. Calculated BET surface area = 1365 m<sup>2</sup> g<sup>-1</sup>, pore volume = 0.67 cm<sup>3</sup> g<sup>-1</sup>, pore diameter = 2 nm, which together with XRD–TEM  $d_{100}$  = 3.8–3.2 nm provides a channel wall thickness ≈ 2 nm.