[10] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134999 and -135000. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[14] Preliminary experiments have shown that (*E*)-1-alkoxybutadienes and (*E*,*E*)-1-alkoxy-2-methylpenta-1,3-dienes can be combined with enoxysilanes **3**, **9**, and others, and with carbon electrophiles different from MeI.

Metamorphic Channels in Periodic Mesoporous Methylenesilica[**]

Tewodros Asefa, Mark J. MacLachlan,
Hiltrud Grondey, Neil Coombs, and Geoffrey A. Ozin[*]

Since the discovery of mesoporous silica, MCM-41, in 1992,[1, 2] the synthesis of mesoporous inorganic materials using supramolecular organic templates continues to draw a great deal of attention due to the potential application of these materials in catalysis,[3] nanoelectronics,[4] separation science,[5] and environmental remediation.[6] The composition of mesoporous materials span a variety of inorganic compounds, including a range of oxides,[7, 8] Pt metal,[9] phosphates,[10] CdS,[11] and M/Ge_4S_{10},[12] but, until very recently,[13–16] none have included organic moieties as a structural component of the framework.

A vast number of organic, inorganic, organometallic, and polymeric species have been included inside the periodic hexagonal channels of MCM-41.[17] In particular, many species have been anchored or grafted to the channel wall of the silica by synthesis or postsynthesis treatment with $RSi(OR')_3$ compounds.[17, 18] These organic groups, which protrude into the channels, have potential for many useful transformations, catalysis, separations, and other interesting chemistry.

We and others have recently reported an interesting class of materials possessing organic groups fused "within" the mesoporous frameworks.[13–16] These novel organic–inorganic hybrid materials, denoted periodic mesoporous organosilicas (PMOs), are prepared through the surfactant-templated condensation of bifunctional organosiloxane precursors, $(R'O)_3SiRSi(OR')_3$.[19] This new approach extends the realm of mesoporous materials to "chemistry of the channel walls" rather than limiting it to "chemistry of the void space". In contrast to mesoporous materials that have terminally bonded organic groups dangling into the channels, PMOs offer a unique opportunity to affect the chemistry of the framework through organic transformations. The physical and chemical properties of these materials may be modified with suitable choice of organic and organometallic groups (R) inside the channel wall of the PMO. Examples of PMOs containing ethane, ethene, acetylene, ferrocene, thiophene, and benzene inside the framework have been reported.[13–16] Here we report the discovery of thermally robust periodic mesoporous methylenesilica and demonstrate a unique thermal transformation in which bridging methylene groups "inside the channel walls" convert into terminally bound methyl groups residing "within the channel spaces".

Methylene-bridged PMOs are also an interesting class of materials from the point of view of fundamental theory and applications. As the simplest organic group, methylene is a useful moiety to study for sophisticated ab initio calculations.[20, 21] Methylene is also useful for the preparation of silicon carbides and oxycarbides.[22, 23] Since methylene is isoelectronic with oxygen, periodic mesoporous methylenesilica is a useful analogue for structural, mechanical, and electronic comparison with the widely studied periodic mesoporous silica. Moreover, periodic mesoporous methylenesilica may be useful as a precursor for additional chemical modifications.

To prepare hexagonal mesoporous methylenesilica, we used a procedure similar to that of other PMOs.[13, 14] With a surfactant as the template, samples were synthesized with different proportions of methylene groups (Scheme 1). For this, a mixture of two precursors was used: bis(triethoxysilyl)methane (**1**), containing the bridging methylene groups, and tetraethoxysilane (**2**). The cationic cetyltrimethylammonium surfactant template was then removed from the samples by solvent extraction with methanol/hydrochloric acid.

The mesoporous methylenesilica materials were investigated by powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM) before and after solvent extrac-

$$(EtO)_3Si\text{-}CH_2\text{-}Si(OEt)_3 \quad + \quad Si(OEt)_4 \quad \xrightarrow[H_2O\,/\,OH^-]{\text{surfactant}} \quad \text{surfactant-templated methylenesilica}$$

1	**2**	
100%	0%	**3**
50%	50%	**4**
25%	75%	**5**

Scheme 1. Synthesis of the hexagonal mesoporous methylenesilica. The ratio of **1** and **2** corresponds to the molar contribution of Si from each reagent (i.e., **5** was prepared from BTM **1** and TEOS **2** in a molar ratio of 1:6; see the Experimental Section).

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[*] Prof. G. A. Ozin, T. Asefa, Dr. M. J. MacLachlan, Dr. H. Grondey, Dr. N. Coombs
Materials Chemistry Research Group, Department of Chemistry
University of Toronto
Toronto, Ontario M5S 3H6 (Canada)
Fax: (+1)416-971-2011
E-mail: gozin@alchemy.chem.utoronto.ca

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tion. The surfactant-free material was also investigated by gas adsorption. Figure 1 shows PXRD patterns of as-synthesized and solvent-extracted materials and a representative TEM image of as-synthesized **3**. The presence of (100), (110), and (200) peaks in the diffraction patterns is characteristic of well-ordered, hexagonal mesoporous materials. Moreover, the PXRD peak intensities decreased as the relative amount of the methylene precursor used increased. This is consistent with the decreased electron contrast expected between the wall and the channel with the incorporation of methylene species inside the silica framework. After solvent extraction, the materials showed an enhanced intensity diffraction pattern (Figure 1 A). The TEM investigation of the PMOs confirmed that they were well organized and have the hexagonal structure (Figure 1 B). The N_2 adsorption isotherm of the materials showed a type IV isotherm with little hysteresis revealing the mesoporosity of the materials with a Brunauer–Emmett–Teller (BET) surface area over 900 $m^2 g^{-1}$, a total pore volume of 0.72 $cm^3 g^{-1}$, and an average pore diameter of 31 Å, which in conjunction with the unit cell dimension of 46 Å estimated from PXRD and TEM provide a wall thickness of 15 Å.

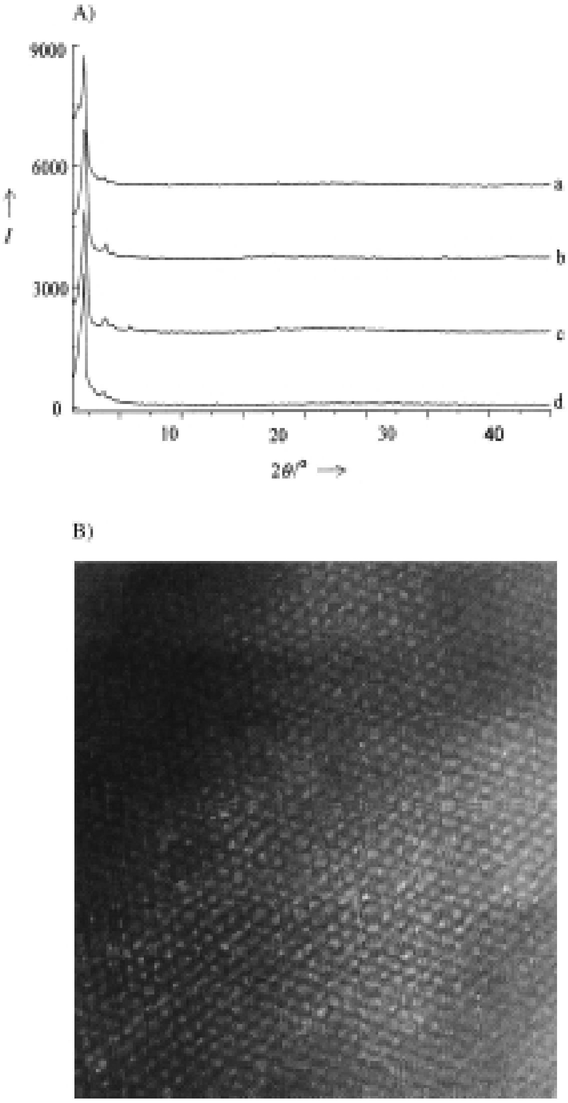


Figure 1. A) PXRD patterns for as-synthesized samples of **3** (a), **4** (b), and **5** (c), and solvent-extracted **3** (d). B) TEM image of as-synthesized **3**.

Fourier transform micro-Raman spectroscopy (FT-MRS) and solid-state cross-polarization magic angle spinning nuclear magnetic resonance spectroscopy (^{13}C CP-MAS and ^{29}Si MAS NMR) confirmed that the methylene groups survive hydrolysis, condensation and solvent-extraction conditions, and afterwards retain their integrity inside the channel walls of the PMO. The Raman spectrum of **3** showed the ν(C–Si) bond stretching mode at 860 cm^{-1}, which remains unchanged after solvent extraction. The intensity of this peak, when compared with other resonances, increased with the relative amount of bis(triethoxysilyl)methane **1** (BTM) used in the synthesis. The ^{13}C CP-MAS NMR spectrum also indicates the presence of methylene groups in the materials. A broad resonance at $\delta \approx 0$ corresponds to the Si-CH_2-Si carbon atoms, whose relative intensity with respect to the surfactant increases with the relative amount of **1** used in the synthesis. The peak is broad, consistent with methylene groups present in a variety of microenvironments inside a rigid methylene-silica framework. These data show that the methylene groups are incorporated into the materials and that the Si–C bond remained intact under the synthesis conditions. The latter was also confirmed by ^{29}Si MAS NMR spectroscopy, in which only T sites (T_x, $RSi(OSi)_x(OH)_{3-x}$) and no Q sites (Q_x, $Si(OSi)_x(OH)_{4-x}$) were observed in sample **3**. Furthermore, ^{29}Si MAS NMR spectroscopy confirmed that the Si–C bond is stable to solvent extraction.

The thermal properties of the materials were studied using a combination of thermogravimetric analysis (TGA) under N_2 and solid-state NMR spectroscopy. The TGA of **3** shows a weight loss at 35–80 °C corresponding to the evolution of adsorbed water and a weight loss at 150–300 °C corresponding to the removal of surfactant. Unlike periodic mesoporous ethylenesilica we previously prepared,[13] the periodic mesoporous methylenesilicas **3**–**5** showed little weight loss above 300 °C, indicating the stability of the methylene spacers at higher temperatures. ^{13}C CP-MAS NMR spectroscopy of samples **3** and **4** treated at 400 °C for 4 h in air showed a peak at $\delta \approx -3$ corresponding to hydrocarbons attached to silicon and a small peak at $\delta \approx 53$ attributed to a trace of surfactant. Figure 2 A shows the ^{13}C CP-MAS NMR spectra of **4** after treatment at different temperatures. After thermal treatment at 500 °C for 4 h, all surfactant peaks had disappeared and only the peak at $\delta \approx -3$ remained. This peak appeared even after the same sample was treated in air at 550 and 600 °C for 4 h. The ^{29}Si MAS/CP-MAS NMR spectra of the same samples showed the presence of T sites after treatment at 400, 550, and 600 °C (Figure 2 B). Pyrolysis mass spectrometry of a sample of **3** (with surfactant completely removed by thermal treatment in air for 7 h at 400 °C) showed fragments consistent with the elimination of small organic and organosiloxane molecules at 550 °C, which could be satisfactorily associated with the thermal decomposition of methylenesilica.

These results indicated that the materials still contained stable organic groups attached to silicon atoms when treated thermally in air at temperatures as high as 600 °C. There was, however, a continuous conversion of framework T sites into Q

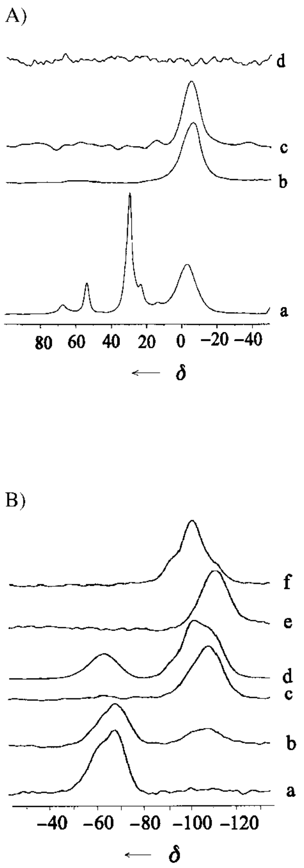


Figure 2. A) ^{13}C CP-MAS NMR spectra of as-synthesized **4** (a) and **4** thermally treated in air to 400 (b), 550 (c), and 700 °C (d). B) ^{29}Si MAS spectra of as-synthesized **4** (a) and **4** thermally treated in air to 400 (b), 550 (c) and 700 °C (e); CP-MAS NMR spectra of **4** thermally treated in air to 550 (d) and 700 °C (f). Thermal treatment was performed sequentially for the same sample in air for 4 h at each temperature.

sites, as shown by the increase in intensity of signals for Q sites at the expense of those for T sites as the treatment temperature increased from 400 to 700 °C. Complete conversion occurred between 600 and 700 °C as there were no observable T sites for the sample treated at 700 °C, as shown by the ^{29}Si CP-MAS NMR spectrum. The mesoscale periodicity of the materials, however, was maintained after each of the thermal treatment steps with a concomitant decrease in d spacing from about 40 to 35 Å after pyrolysis at 700 °C for 4 h.

As the quantity of Q sites increased at the expense of T sites, we were curious about the nature of the organic species present in the thermally treated materials. Due to the breadth of the peak and similarity in chemical shift for Si-CH$_2$-Si and Si-CH$_3$, a challenge remained to assign the broad peak observed at $\delta \approx -3$ in the ^{13}C CP-MAS NMR spectra to methylene and/or methyl groups. For this, we applied a nonquaternary suppression (NQS) pulse sequence to the ^{13}C CP-MAS NMR spectrum for the selective observation of methyl groups. As a control, an NQS experiment performed on the as-synthesized sample **4** did not show a methylene peak near $\delta = 0$, but showed only resonances for the surfactant carbon atoms. With the same parameters, the ^{13}C CP-MAS NQS NMR spectrum of the pyrolyzed sample **4** showed a peak at $\delta = -6$, which was unequivocally assigned to methyl carbon atoms attached to silicon (Figure 3) since the methylene carbon atoms are not observable under these conditions. The normal ^{13}C CP-MAS NMR spectra of the same pyrolyzed sample **4** displayed a relatively broader peak from $\delta = -3$ to -6, showing that both methyl and methylene groups are present in the sample. These results demonstrate that an interesting transformation began at around 400 °C. Cleavage of one Si–CH$_2$ bond of bridging methylene groups upon addition of residual silanol groups or water in air yielded methyl groups terminally bonded to the silicon, (Scheme 2). This is the first observation of a chemical transformation from a bridging organic group bonded inside the framework of a mesoporous material to a terminally bound organic suspended within the channel space.[24] To prove that the methyl groups originated from the bridging methylene spacers inside the channel walls and not from the surfactant imbibed within the channel void space, we pyrolysed an as-synthesized mesoporous silica (MCM-41) sample under the same conditions—the product did not show any trace of methyl or methylene groups.

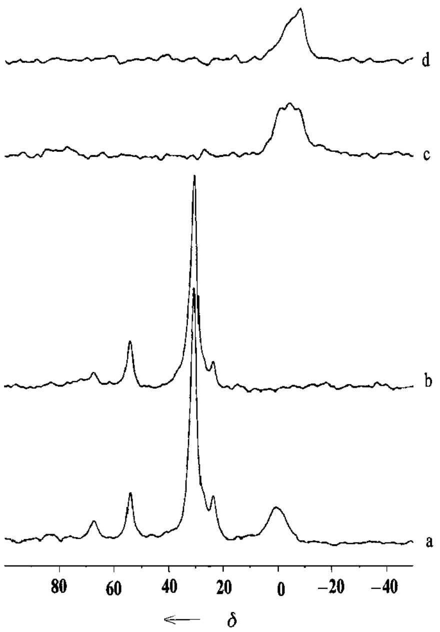
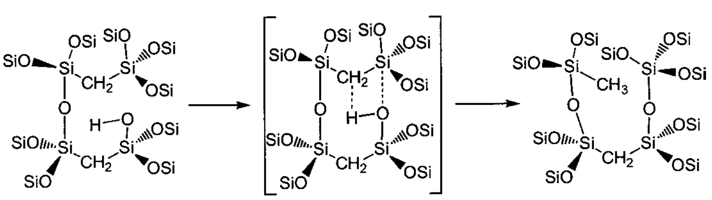


Figure 3. ^{13}C CP-MAS NMR (a) and ^{13}C NQS CP-MAS NMR (b) spectra of **4** before being thermally treated in air and ^{13}C CP-MAS NMR (c) and ^{13}C NQS CP-MAS NMR (d) after thermal treatment in air for 4 h at 550 °C.



Scheme 2. Schematic representation of the cleavage of one Si–CH$_2$ bond to a bridging methylene group, leading to methyl groups terminally bonded to silicon.

Although the formation of methyl from methylene groups upon thermal treatment in air was probed with the NQS experiment, quantification of the methyl and methylene moieties was not possible with this CP experiment. It is noteworthy that the pyrolysis of periodic mesoporous methylenesilica under Ar resulted in a similar transformation of the methylene spacers, the organic moieties again being stable up to 700 °C. However, other pyrolysis products, such as aromatic species, were also observed in the sample under these conditions. The arenes most likely originated from the methylene/methyl groups, as they appeared in the ^{13}C CP-MAS NMR spectra ($\delta = 128$) only above temperatures at which the surfactant was thermally decomposed.

In conclusion, we have prepared a new PMO material, periodic mesoporous methylenesilica, with bridging methylene spacers incorporated "inside" the walls of the hexagonally close packed channels. This new material shows enhanced chemical and thermal stability relative to other PMOs prepared to date. We have also described the first example of "channel metamorphosis" of a PMO; in this case, the chemical transformation occurs from organosilica channels containing bridging organic moieties to ones having terminally bonded organic groups located in the mesopores.

Experimental Section

3–**5**: A base-catalyzed surfactant-templating sol–gel technique was employed using NH_4OH (14.18 g, 0.122 mol) as base, cetyltrimethylammonium bromide (CTAB; 0.672 g, 0.00184 mol), H_2O (26.73 g, 1.485 mol), and **1** and **2** as silica sources (molar ratio $Si:CTAB:NH_4OH:H_2O = 1.00:0.12:15.0:114$). These reagents were combined and stirred for 30 min to form a homogeneous solution. To that solution, Si (0.015 mol) from a mixture of BTM **1** and tetraethoxysilane (TEOS) **2** (100 % BTM for **3**, 50 % BTM for **4**, and 25 % BTM for **5**) was slowly added. BTM (Gelest, used without further purification) was considered to provide twice as many moles of Si as moles of TEOS in the above composition (i.e., the sample of 50 % BTM (**4**) was prepared from 1.32 g of BTM (3.86 mmol) and 1.61 g of TEOS (7.72 mmol)). The resulting solution was stirred for 30 min and then aged at 80 °C for 4 d. After filtration and washing, the product was dried under ambient conditions. Yields: **3**: 1.40 g, **4**: 1.19 g, **5**: 1.36 g. To prepare the solvent-extracted materials, a sample of **3**–**5** (0.5 g) was stirred in a solution of 10 M HCl (12 g) and methanol (70 g) for 24 h at 40 °C. The product was filtered, washed with methanol, and dried under ambient conditions. Yield: **3**: 0.32 g.

The PXRD, TEM, TGA, and pyrolysis mass spectrometry investigations were carried out as reported previously.[12c] The N_2 adsorption and desorption measurements were conducted at 77 K with a Quantachrome Autosorb 1 instrument by immersing the sample in liquid nitrogen. The FT micro-Raman spectra were obtained on a S.A. LabRam confocal Raman microscope. The signal collected was transmitted through a fiber optic cable into a single grating spectrometer equipped with a 1024 × 256 element CCD. Raman spectra were collected by manually placing the probe tip, with micron spatial resolution, near the desired point of the sample on a glass slide. Identical Raman spectra were obtained over the entire area of the sample, confirming the homogeneous distribution of methylene groups in the material. The ^{13}C (100.6 MHz) and ^{29}Si (79.5 MHz) solid-state NMR spectra were obtained with a Bruker DSX400 spectrometer. Experimental conditions: ^{13}C CP-MAS NMR: 6.5 kHz spin rate, 2.5 ms contact time, 3 s recycle delay, 20000 scans; ^{29}Si MAS NMR: 6.5 kHz spin rate, 100 s recycle delay, 800 scans; ^{13}C NQS CP-MAS NMR: 6.5 kHz spin rate, 30 s recycle delay, 30000 scans.

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