Template-directed synthesis of bi-functionalized organo-MCM-41 and phenyl-MCM-48 silica mesophases

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Template-directed co-condensation was used to synthesize organo-functionalized MCM-41 silica hexagonal mesophases containing binary combinations of covalently linked phenyl and amino, thiol or allyl moieties; similar methods were used to prepare a phenyl-functionalized organo-MCM-48 silica with cubic structure.

The direct synthesis of ordered MCM-41 silica mesophases containing covalently coupled organic moieties has been recently reported.[1–5] These materials could have important uses in optical applications,[5] catalysis,[6,7] metal-ion extraction[8] and adsorption processes.[9] Here we extend the method of template-directed co-condensation to the synthesis of MCM-41 structures containing two distinct types of covalently linked organic functionalities. We show that allyl, thiol or amine moieties can be incorporated along with phenyl residues into the hexagonally ordered mesophase. In addition, we report the direct synthesis of an organo-MCM-48 cubic mesophase with covalently linked phenyl functionalities by adaptation of a previously reported method involving hydrothermal phase transformation.[10]

Bifunctionalized organosilica–surfactant mesophases with hexagonal MCM-41-type structure were synthesized at room temperature and pressure from alkaline solutions of hexadecyl-trimethylammonium bromide (CTAB) containing varying molar ratios of tetraethoxysilane (TEOS), phenyltriethoxysilane (PTES), and another organotrialkoxysilane [$(RO)_3Si–R'$, R′ = CH_2CHCH_2 (allyltrimethoxysilane, ATMS), $(CH_2)_3NH_2$ (3-aminopropyltriethoxysilane, APTES) or $(CH_2)_3SH$ (3-mer-captopropyltriethoxysilane, MPTES). The molar composition of a typical synthesis was: 0.12 CTAB : 0.50 NaOH : 1.0 total siloxane : 130 H_2O.‡ Acidic extraction of the surfactant from the as-synthesized products was used to prepare the corresponding organo-functionalized mesoporous silica materials.

Transmission electron microscopy (TEM) [Fig. 1(a)] and small-angle X-ray powder diffraction (SAXRD) indicated that well ordered hybrid mesophases were formed when the total amount of organotrialkoxysilanes in the synthesis mixture was *ca.* 20 mol% or less. Under these conditions, it was possible to covalently link two organic functionalities into the ordered silica framework without disruption of the long range meso-scopic order established by self-assembly of the surfactant template. For example, materials perpared from 10 mol% of PTES and 10 mol% of ATMS, MPTES or APTES, showed four reflections that were assigned to the (100), (110), (200) and (210) reflections of hexagonally ordered MCM-type structures with unit cell parameters between 4.4 and 4.6 nm.§ The *d* spacings were similar to those reported for non-functionalized MCM-41, as well as ordered organosilica mesophases prepared from co-condensation of TEOS and a single organotrialk-oxysilane.[1,3] Bifunctionalized mesoporous derivatives, prepared by surfactant extraction, were generally less ordered than the as-synthesized products, except for materials prepared from PTES and APTES which showed four diffraction peaks.§ In each case, significant contractions in the unit cell length to values below 4 nm were observed.BET data gave a surface area of 1220 $m^2\,g^{-1}$ and pore diameter of *ca.* 3.5 nm for a surfactant-

extracted material prepared from 5 mol% of phenyl- and 5 mol% amino-trialkoxysilanes.

MCM-41 type materials prepared from 20 mol% PTES and 20 mol% ATMS showed evidence for extensive structural disorder (broad reflections at *d* = 3.61 and 1.87 nm) and lattice contraction (*a* = 4.17 nm) in the as-synthesized materials, presumably due to the decreasing number of fully condensed Si (Q^4) centres associated with the higher levels of organosiloxane linkages. Surfactant extraction gave only a single, broad ill defined peak, indicative of collapse of the partially ordered channel structure in these hybrid materials.

Incorporation of the covalently linked organic groups was confirmed by ^{29}Si solid-state CP NMR spectroscopy which showed distinct resonances for siloxane [$Q^n = Si(OSi)_n$-$(OH)_{4-n}$, n = 2–4] and organosiloxane [$T^m = RSi(OSi)_m$-$(OH)_{3-m}$, m = 1–3] environments (graphical abstract). The integrated signal due to the latter approximately doubled when
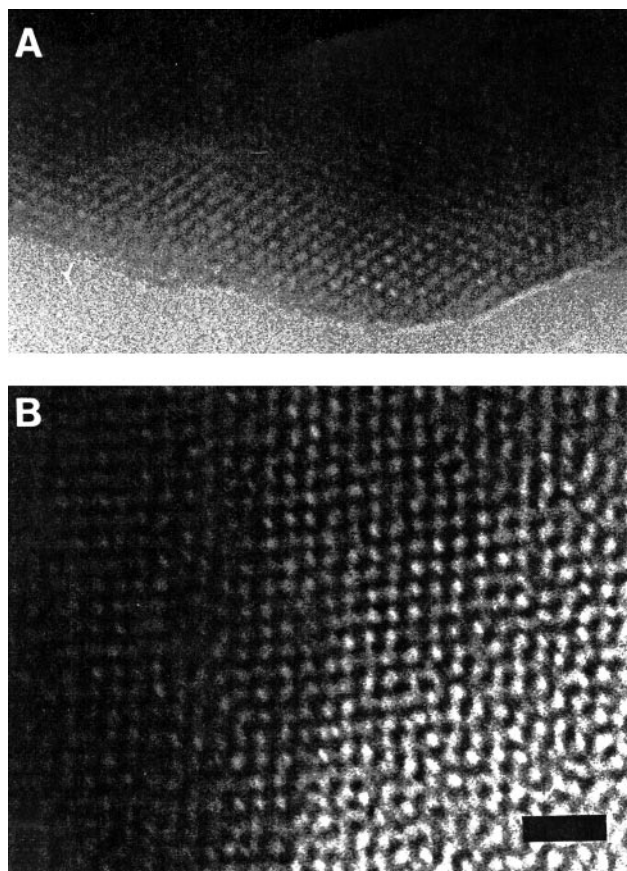

Fig. 1 TEM micrographs of (A) as-synthesized bi-functionalized phenyl-amino-MCM-41 mesophase (10 mol% PTES/10 mol% APTES) showing hexagonally ordered channel structure, (B) phenyl-functionalized MCM-48 mesophase (10 mol% PTES) showing cubic structure viewed down the <110> zone. Scale bar (both micrographs) = 10 nm.
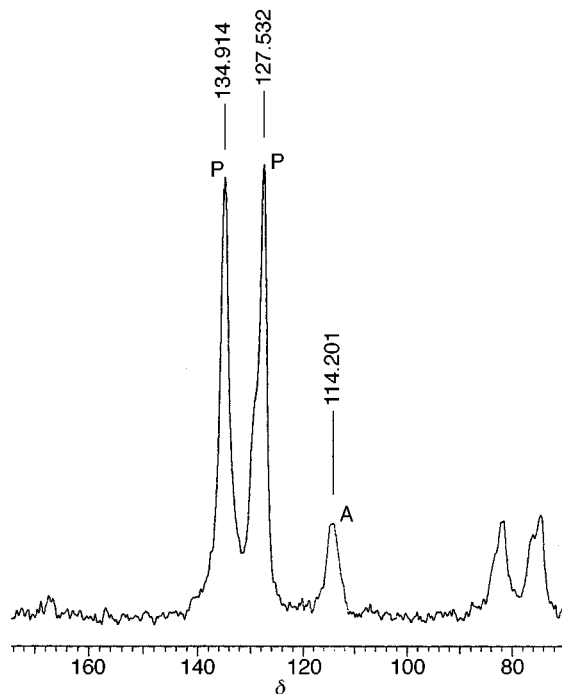
Fig. 2 ¹³C CP MAS NMR spectrum for a bifunctionalized organo-MCM-41 mesophase showing resonances for intact phenyl (P) and allyl (A) moieties.

the total amount of organoalkoxysilanes in the synthesis mixture was increased from 20 to 40%. In most cases, the Q^3 and T^2 linkages were predominant, indicating that the organosilica mesophases contained significant amounts of uncondensed Si–OH centres. The bifunctional nature of the materials was confirmed by ¹³C CP MAS NMR studies which showed intact phenyl moieties along with unmodified allyl, amine or thiol groups (Fig. 2).¶ This was consistent with FTIR spectra of the surfactant-extracted materials which showed characteristic absorption bands for the covalently-linked organic residues.‖

Organosilica–surfactant mesophases were also synthesized at 100 °C from alkaline solutions of hexadecyltrimethylammonium chloride (CTACl) containing varying molar ratios of TEOS and PTES, APTES, MPTES or ATMS; typically the molar composition was: 0.64 CTACl:0.25 NaOH:1.0 total siloxane:62 H_2O.** Under these conditions, which utilise lower surfactant concentrations than are normally required for MCM-48 synthesis, the cubic mesophase is formed by an ethanol-induced phase transformation of a MCM-41 precursor.[10] SAXRD data for a functionalized silica mesophase prepared from 10 mol% PTES gave four reflection peaks at d = 3.93, 3.52, 2.15 (broad) and 1.79 nm that were indexed to the (211), (220), (400)/(420) and (431) reflections, respectively, of a cubic $Ia3d$ mesophase with unit cell length of 9.62 nm. TEM images confirmed the formation of an ordered MCM-48-type material [Fig. 1(b)] and ¹³C CP NMR showed resonances (δ 127.5, 135.0) corresponding to the covalently linked phenyl moieties. FTIR peaks at 702 and 3000–3100 cm⁻¹ also confirmed the presence of the phenyl functionality. SAXRD profiles of the surfactant extracted, phenyl-functionalized MCM-48 silica showed three main reflections (d = 3.93, 2.10, 1.49 nm) which were indexed to the (100), (110) and (210) peaks of a hexagonally ordered organo-mesoporous material. The apparent structural collapse of the cubic material in the absence of the surfactant was consistent with TEM images which showed a marked decrease in the amount of cubic pore order in the sample. BET analysis gave a surface area of 1040 m² g⁻¹ for the surfactant extracted product.

Analogous samples functionalized with amino, thiol or allyl groups gave only broad XRD peaks, with no evidence of an ordered organo-MCM-48 (or MCM-41) mesophase. ¹³C CP NMR and FTIR data on these samples indicated that the organic

groups were not incorporated to any significant extent into the silica materials. This suggests that APTES, MPTES and ATMS did not undergo significant condensation, or that the functional groups are labile under the reaction conditions, or both. In particular, the elevated temperature of the synthesis method is likely to increase the rate of formation of the Q^n centres at the expense of the T^m linkages.

Our results suggest that bifunctionalization of the MCM-41 mesostructure could provide a general route to multi-component inorganic–organic hybrids and their (partially) ordered mesoporous derivatives. Such materials extend the complexity of self-organized inorganic matter and should be useful in processes requiring controlled confinement, for example where the channel reactivity needs to be coupled with the hydrophobic/hydrophilic balance of the localized environment. Because the 3-D channel network of MCM-48 is less susceptible to pore blockage compared with the linear channel structure of MCM-41, organoMCM-48 materials could have specific technological advantages. However, significant advances are required to improve the structural stability of these organized materials.

Notes and references

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‡ In a typical preparation (mol% PTES:ATMS:TEOS = 10:10:80), 1.6 g CTAB was dissolved in a solution of 70.2 g of distilled deionized H_2O containing 20 g of 1.0 M NaOH, 0.59 g ATMS and 0.87 g PTES added, and the mixture stirred vigorously for 5 min; 5.99 g TEOS was then added and the mixture stirred for 24 h at room temp. The white precipitate was filtered, washed with distilled deionized H_2O, and dried for 10 h at 100 °C *in vacuo*. Acid extraction was performed by stirring a suspension of the solid product (0.99 g dm⁻³) in 1.0 mol dm⁻³ HCl in EtOH under reflux at 75 °C for 24 h. The extracted material was then filtered, washed with ethanol and dried in a vacuum oven at 100 °C for 10 h.

§ SAXRD d spacings/nm [hkl = (100), (110), (200) and (210), unless specified]: MCM-41 materials (10 mol% per functionality); PTES-ATMS, as-synthesized, 3.83, 2.20, 1.92, 1.52, a = 4.42; surfactant-extracted, 3.26 (100), a = 3.64. PTES-MPTES, as-synthesized, 3.86, 2.20, 1.91, 1.44, a = 4.45; surfactant-extracted, 3.07 (100), a = 3.54. PTES-APTES, as-synthesized, 4.03, 2.29, 1.99, 1.49, a = 4.65; surfactant-extracted, 3.17 (100), 2.11 (200), a = 3.66.

¶ ¹³C CP MAS NMR data (δ): phenyl, 127, 129, 130, 134; allyl, 114, 135; thiol, 23.0, 41.4; amino, 16.8, 44.8.

‖ FTIR data (cm⁻¹): phenyl, 668, 702, 1430, 3000–3100; allyl, 800, 1420; thiol, 2550–2590 (weak); amino, 3400, 1620–1650.

** For MCM-48 functionalized with 10 mol% PTES, 0.67 g of solid NaOH was dissolved in 17 g of distilled deionized H_2O and 6.50 g of TEOS and 0.63 g PTES added under vigorous stirring, and the solution left for 5 min 27.8 g of CTACl solution was added and the mixture left to stir for 15 min, then poured into a stoppered PTFE bottle, and heated without stirring at 100 °C for 72 h. After cooling to room temperature, the solid product was recovered by filtration, washed with distilled, deionized H_2O, and dried for 10 h at 100 °C *in vacuo*. Surfactant extracted materials were prepared as for the MCM-41 samples.

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