Synthesis and characterization of ordered organo–silica–surfactant mesophases with functionalized MCM-41-type architecture

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Ordered organo–silica–surfactant mesophases containing covalently linked functionalized moieties are prepared with MCM-41-type architectures by template-directed co-condensation of tetraethoxysilane and organotrialkoxysilanes $(RO)_3Si–R'$ [R = Me, Et; R′ = $(CH_2)_3SH$, $(CH_2)_3NH_2$, $(CH_2)_3OCH_2CH(O)CH_2$, $(CH_2)_3\overline{NCHNCH_2C}H_2$ or CH_2CHCH_2].

The synthesis of ordered mesoporous silica materials, MCM-41 (hexagonal symmetry) and MCM-48 (cubic symmetry), and related transition-metal oxide analogues, is a burgeoning field of materials chemistry (for recent reviews see refs. 1–4). Tailoring of these materials for specific applications requires both structural and compositional control. This can be achieved by chemical modification of the reaction constituents or *via* post-synthesis activation of the mesostructured product. In a recent paper,[5] we described a new route to the synthesis of MCM-41-type hybrid mesophases containing covalently linked phenyl or *n*-octyl groups. The basis of this approach was to couple the use of supramolecular surfactant templates with co-condensation reactions involving siloxane (tetraethoxysilane, TEOS) and organosiloxane precursors. TEOS was used as the primary silica source and as a reagent for the formation of fully saturated Q^4 linkages which are required to maintain structural integrity in the organo–silica–surfactant mesophase. Here we extend this approach to the direct synthesis of more complex organo–MCM-41-type materials containing covalently linked chemically reactive groups. We show that organosiloxanes containing thiol, amine, epoxide, imidazole or allyl functionalities can be incorporated into ordered hybrid mesophases by cooperative assembly of silicate and organosilicate species at the cationic headgroups of rod-like surfactant micelles.

Organo–silica–surfactant mesophases with MCM-41-type architectures were synthesized at room temp. from alkaline mixtures containing varying molar ratios of TEOS and a functionalized organotrialkoxysilane in the presence of the surfactant, hexadecyltrimethylammonium bromide (C_{16}TMABr) (molar composition = 0.12 C_{16}TMABr : 0.50 NaOH : 1.0 total siloxane : 130 H_2O).† The following functionalized organotrialkoxysilanes $(RO)_3Si–R'$ were used; 3-sulfanylpropyltrimethoxysilane [TTMS, R′ = $(CH_2)_3SH$], 3-aminopropyltriethoxysilane [ATES, R′ = $(CH_2)_3NH_2$], 3-(2,3-epoxypropoxy)propyltrimethoxysilane [EPTMS, R′ = $(CH_2)_3OCH_2CH\overline{(O)CH_2}$], 3-imidazoletriethoxysilane [IMTES, R′ = $(CH_2)_3\overline{NCHNCH_2C}H_2$], allyltrimethoxysilane (ALTMS, R′ = CH_2CHCH_2). Experiments with ATES and IMTES were repeated using a neutral surfactant, *n*-dodecylamine.[6] In each case, an acidic solvent extraction technique[7] was used to prepare functionalized mesoporous silicas by removal of the surfactant from the as-synthesized materials.

Small-angle X-ray powder diffraction (XRD) (Table 1) and transmission electron microscopy (Fig. 1) indicated that the as-synthesized materials were single phases with mesoscopic order. Samples were generally prepared with 20 mol% of the functionalized organotrialkoxysilane in the initial synthesis composition and gave a series of higher-order XRD peaks which were indexed to organo–silica–surfactant hexagonal mesophases with unit-cell parameters between 40 and 45 Å ($a = 2d_{100}/\sqrt{3}$). Materials prepared using C_{16}TMABr were more ordered than those synthesized in the presence of *n*-dodecylamine. Removal of the surfactant by acid extraction gave ordered organo-functionalized mesoporous silicas for the materials derivatized with amino and thiol moieties (Table 1). In each case, contractions in the lattice parameter and loss of the higher order reflections were observed. For the EPTMS, ALTMS and IMTES samples, surfactant extraction appeared to significantly disrupt the ordered mesostructure of the as-synthesized material.

The extent of organotrialkoxysilane incorporation into the mesostructured materials, and the local structure of the organosilica walls were determined by ^{29}Si MAS NMR of the as-synthesized and post-synthesized materials. Distinct resonances were observed for the 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) units (Table 2). The data indicate that increasing amounts of the organo-functionalized moieties are condensed into the wall structures with increasing mol% in the synthesis composition, but that the yield of incorporation was often low (Table 2). The relative amounts of ($Q^4 + T^3$), ($Q^3 + T^2$) and ($Q^2 + T^1$) species were essentially constant and equal to the respective Q^4, Q^3 and Q^2 contents of a sample prepared from 100 mol% TEOS sample (data not shown), suggesting that the organosiloxane species are distributed uniformly throughout the silica network.

The nature of the organic functional groups incorporated into the ordered mesostructured silica framework was investigated by ^{13}C CP MAS NMR. The data qualitatively indicated that functional groups such as amine, imidazole, allyl and thiol could be incorporated without significant modification after surfactant extraction (NMR data: ATES, δ 10.0, 21.3, 43.0; ALTES, δ 19.8, 115.3, 131.7; IMTES, δ 9.0, 20.0, 37.1, 45.6, 50.4, 159.3; TTMS, δ 11.2, 23.0, 41.4). In contrast, the epoxide moiety underwent a ring-opening reaction during the synthesis procedure. Under the highly alkaline conditions employed, the epoxide ring was transformed into a diol terminal group

Table 1 XRD data for organo–silica–surfactant mesophases

Sample	XRD *d*-spacings/Å (100)	(110)	(200)	(210)
ATES 20%	38.7	22.5	19.9	15.2
ATES[a] 20%	36.8	19.2	—	—
	35.7[b]	18.9[b]	—	—
EPTMS 20%	36.0	19.8	—	—
IMTES 20%	37.4	21.5	18.8	13.7
IMTES[a] 20%	35.1	—	—	—
TTMS 20%	35.1	20.0	17.9	—
	31.0[b]	—	—	—
ALTMS 10%	37.9	21.7	18.5	14.0
ALTMS 20%	34.7	—	—	—
ALTMS 40%	36.5	—	—	—

[a] Samples prepared using *n*-dodecylamine surfactant. [b] Data from surfactant-extracted samples.

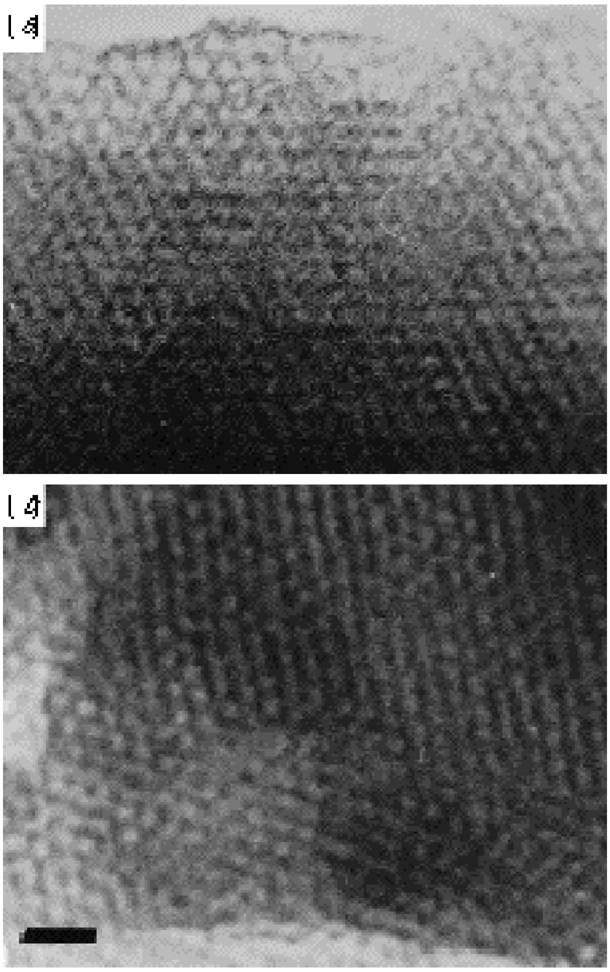

Fig. 1 TEM micrographs of functionalized organo–silica–surfactant ordered mesophases containing covalently linked (*a*) amino and (*b*) thiol moieties; scale bar = 8 nm in both micrographs

(indicated by the broadening of the two resonances at δ 67 and 73 in the NMR spectrum of the as-synthesised material). The presence of hydrochloric acid in the surfactant extraction procedure led to further reaction and substitution of the beta hydroxyl group by chloride (NMR data: δ 46.8, 64.2).

Our results indicate that functionalized organotrialkoxysilanes can be covalently linked into ordered silica mesophases by co-condensation reactions in the presence of surfactant templates. Several different functional groups have been incorporated, suggesting that with appropriate modifications in the synthesis protocol, a wide range of ordered hybrid inorganic–organic frameworks could be prepared by this approach. A vinyl-functionalized MCM-41 has been reported recently.[8] The chemical reactivity of some of these materials is currently under investigation.

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Table 2 ^{29}Si NMR data for organo–silica–surfactant mesophases

	δ_{Si} [relative peak area]					
Sample	T^2	T^3	Q^2	Q^3	Q^4	% Organic incorporation
ATES[a]	−58.2	−66.6	−90.9	−100.6	−110.2	11
20 mol%	[3.1]	[7.9]	[5.8]	[37.2]	[45.9]	
ATES	−56.0	−65.9	−91.3	−100.8	−110.0	13
20 mol%	[3.5]	[9.1]	[7.7]	[41.2]	[38.5]	
EPTMS	−55.7	−64.2	−91.9	−100.7	−109.4	14
20 mol%	[2.9]	[11.4]	[5.6]	[37.9]	[43.2]	
EPTMS	−56.9	−64.8	−92.1	−100.6	−108.9	27
50 mol%	[7.7]	[19.2]	[4.4]	[30.8]	[37.9]	
IMTES[a]	−57.6	−66.5	−91.0	−100.5	−109.4	11
20 mol%	[2.1]	[8.7]	[6.4]	[37.5]	[45.2]	
IMTES	−56.9	−66.8	−91.8	−101.2	−109.9	4
20 mol%	[0.7]	[3.1]	[5.2]	[40.3]	[50.7]	
TTMS	−57.2	−65.4	−91.2	−100.5	−108.9	20
20 mol%	[2.6]	[17.2]	[7.9]	[34.6]	[37.7]	
ALTMS	−61.6	−70.9	−90.1	−99.0	−108.6	11
10 mol%	[1.8]	[9.2]	[9.2]	[45.5]	[34.3]	
ALTMS	−60.9	−69.7	−91.7	−100.6	−109.4	25
20 mol%	[6.2]	[18.5]	[3.9]	[32.5]	[38.9]	
ALTMS	−60.5	−70.6	−90.7	−100.7	−109.1	38
40 mol%	[4.2]	[34.1]	[5.1]	[25.6]	[31.0]	

[a] Samples prepared using *n*-dodecylamine surfactant.

Footnotes and References

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† In a typical preparation (20 mol% EPTMS), 0.40 g of C_{16}TMABr (Aldrich) was dissolved in 5.00 g of 1.0 mol dm^{-3} NaOH and 17.55 g of distilled, deionized H_2O. 1.51 g of TEOS (Aldrich) and 0.43 g of EPTMS were added and the solution was stirred for 24 h at room temp. The solid product was filtered, washed with H_2O and dried for 10 h at 100 °C *in vacuo*. ATES, EPTMS, IMTES and TTMS were obtained from Aldrich and ALTMS was obtained from Apollo Sci. Ltd. All compounds were used as received. Extraction of the surfactant was performed by stirring a suspension of the solid product (0.99 g dm^{-3}) in 1.0 mol dm^{-3} HCl in EtOH at 75 °C for 24 h. The extracted material was filtered, washed with EtOH and dried for 10 h at 100 °C *in vacuo*. Extraction of the *n*-dodecylamine surfactant was carried out by stirring a suspension of the solid product (0.99 g dm^{-3}) in EtOH at 75 °C for 24 h. The extracted material was filtered, washed with EtOH and dried for 10 h at 100 °C *in vacuo*.

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