Synthesis of hybrid inorganic–organic mesoporous silica by co-condensation of siloxane and organosiloxane precursors

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Organically functionalized mesoporous silicas are prepared at room temperature by the co-condensation of tetraethoxysilane and organosiloxanes in the presence of surfactant templates; the resulting materials are the first examples of covalently linked, ordered, hybrid inorganic–organic networks.

Following the synthesis of the ordered mesoporous silica materials MCM-41 (hexagonal symmetry) and MCM-48 (cubic symmetry),[1] considerable attention has been focused on tailoring the chemical composition of these materials for applications in catalysis. Introduction of inorganic heteroatoms and attachment of metallocene derivatives *via* pendent Si–O–H groups (to form Si–O–metal linkages)[2] have been explored as routes to the preparation of catalytically active materials. A route to functionalized amorphous silica materials that has been widely investigated in sol–gel chemistry,[3] involves the co-condensation of siloxane and organosiloxane precursors to produce hybrid inorganic–organic networks. In these materials, an organic moiety is covalently linked, *via* a non-hydrolysable Si–C bond, to a siloxane species that is hydrolysed to form a silica polymer. Because formation of the silica walls in MCM-41 also occurs *via* siloxane hydrolysis and condensation, it seems feasible that co-condensation could be a viable synthetic approach to a wide range of functionalized hybrid materials with ordered mesopores. Examples of this new synthetic strategy using two different organosiloxanes are illustrated here.

MCM-41 type materials were synthesized at room temp. from mixtures containing varying molar ratios of phenyltriethoxysilane (PTES) or *n*-octyltriethoxysilane (OTES), along with tetraethoxysilane (TES) and the surfactant hexadecyltrimethylammonium bromide (C_{16}TMABr) (molar composition = 0.12 C_{16}TMABr : 0.50 NaOH : 1.0 total siloxane : 130 H_2O).† An acidic solvent extraction technique[4]‡ was used to remove the surfactant from the product to yield an ordered porous silica material.

Small-angle X-ray powder diffraction (XRD) (Table 1) indicates that a single phase is formed for materials containing up to either 20 mol% PTES or 10 mol% OTES in the initial synthesis composition. The observation of higher order peaks in the as-synthesized 10 and 20 mol% PTES samples confirms the presence of long-range hexagonal order, similar to that of the 100 mol% TES (MCM-41 control) material. The single peak present in the as-synthesized 10 mol% OTES sample is indicative of a disordered hexagonal phase.[5] Following surfactant extraction, the hexagonal order within the structures is preserved, although lattice contractions are observed for the 100 mol% TES, 10 mol% PTES, and 20 mol% PTES materials; surfactant extraction of the 10 mol% OTES sample appeared to disrupt the structure of the product. The greatest contraction is observed for the 20 mol% PTES sample, which suggests that flexibility of the silica walls is imparted by incorporation of organosiloxane moieties.

Nitrogen adsorption studies (Table 1) confirm that the surfactant-extracted 10 mol% PTES material is mesoporous, similar to the 100 mol% TES sample. The pore size of the 20 mol% PTES product, however, is close to the microporous (< 20 Å) regime, as suggested by the characteristic shape of the adsorption isotherm (data not shown).

Transmission electron microscopy (TEM) reveals a hexagonal system of lattice fringes as well as parallel fringes corresponding to the side-on view of the long pores. TEM evidence of the hexagonal structures is observed for the as-synthesized 100 mol% TES, 10 mol% PTES, 20 mol% PTES, and 10 mol% OTES samples. For samples synthesized at higher organosiloxane contents, however, hexagonal ordering is not apparent. TEM of the surfactant-extracted, 20 mol% PTES sample (Fig. 1) reveals a hexagonal array of approximately 15 Å pores, confirming that the silica mesostructure remains stable upon removal of the surfactant template.

^{13}C CP MAS NMR of the as-synthesized materials confirms qualitatively that the organosiloxanes are incorporated into the ordered silica mesostructures. In all samples, resonances are observed for the surfactant molecules (δ 14.5, 23.0, 27.0, 30.5, 32.5, 54.0 and 67.0). For PTES-containing samples, the additional resonances (δ 127.5, 128.0 and 135.0) correspond to

Table 1 Characterization of mesostructured silica materials (AS = as synthesized; SE = surfactant extracted)

		XRD *d* Spacings/A				Nitrogen adsorption	
		(100)	(110)	(200)	(210)	Pore size /Å[a]	BET surface area /m^2 g^{-1}
100 mol%	AS	39.5	23.2	20.1	15.2	—	—
TES	SE	38.8	22.4	19.6	15.0	30	1520
10 mol%	AS	37.6	21.5	18.6	14.0	—	—
PTES	SE	33.1	19.3	16.7	—	24	1386
20 mol%	AS	36.1	20.5	19.3	13.5	—	—
PTES	SE	31.4	—	—	—	18	1060
10 mol%	AS	37.3	—	—	—	—	—
OTES	SE	—[b]	—	—	—	—[b]	—[b]

[a] From Horvath-Kawazoe analysis of adsorption isotherms. [b] Data not available due to apparent sample instability to surfactant extraction.

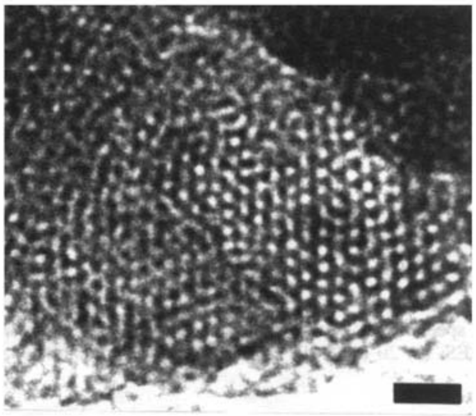

Fig. 1 TEM micrograph of surfactant-extracted, 20 mol% PTES sample. Scale bar = 100 Å.

phenyl carbon atoms. For OTES-containing samples, one resonance for the organosiloxane moiety (δ 34.5) is distinguished from the surfactant resonances.

^{29}Si MAS NMR of the as-synthesized materials indicates quantitatively the extent of organosiloxane incorporation into the mesostructured silica materials. Distinct resonances are 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). Organosiloxane incorporation increases with increasing mol% in the synthesis composition, although the relationship is not directly proportional. For the 10 mol% PTES, 20 mol% PTES, and 10 mol% OTES samples, the relative amounts of ($Q^4 + T^3$), ($Q^3 + T^2$), and ($Q^2 + T^1$) species are essentially constant and are equal to the respective Q^4, Q^3, and Q^2 content of the 100 mol% TES sample. This observation suggests that the organosiloxane species are distributed uniformly throughout the silica network. It also implies that there is likely an upper limit (final molar content < 40 mol%) to the extent of organosiloxane incorporation into hybrid mesostructured materials, since the presence of some Q^4 is necessary to form stable silica materials of this type.

Table 2 ^{29}Si MAS NMR data from as-synthesized mesostructured silica materials

	δ (relative peak area)					
	T^1	T^2	T^3	Q^2	Q^3	Q^4
100 mol% TES	—	—	—	−89.7 (6.4)	−99.2 (52.6)	−109.2 (41.0)
10 mol% PTES	−62.4 (1.4)	−71.3 (8.1)	−80.0 (10.0)	−89.5 (6.4)	−99.0 (43.1)	−109.0 (31.0)
20 mol% PTES	—	−72.0 (10.6)	−80.5 (21.3)	−89.6 (6.5)	−98.8 (42.1)	−108.4 (19.5)
10 mol% OTES	—	−58.1 (5.6)	−67.0 (14.6)	−89.7 (6.4)	−99.0 (42.5)	−108.9 (30.9)

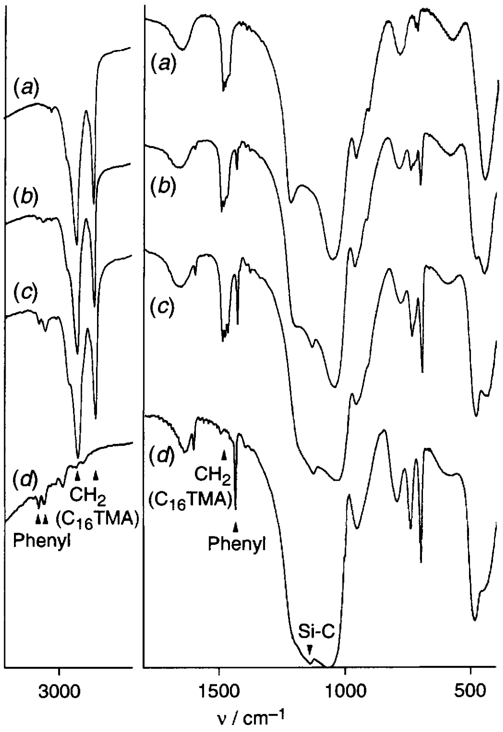

Fig. 2 IR spectra of as-synthesized materials: (*a*) 100 mol% TES; (*b*) 10 mol% PTES; (*c*) 20 mol% PTES and (*d*) surfactant-extracted, 20 mol% PTES

IR spectroscopy also indicates qualitatively that the amount of organosiloxane incorporated into the silica framework is related to the composition of the synthesis mixture. The appearance of an additional peak at 1140 cm^{-1} in the Si–O–Si stretching region (1000–1200 cm^{-1}) indicates the presence of Si–C bonds in the as-synthesized PTES-containing (Fig. 2) and OTES-containing (data not shown) hybrid mesostructured materials. IR vibrations indicative of the specific organic functionalities, which increase in intensity with increasing mol% organosiloxane, and of the surfactant species are also observed. The organosiloxane peaks are still present in the IR spectra of the surfactant-extracted samples, confirming that the organic moieties are linked covalently to the mesoporous silica framework.

The results suggest that co-condensation of siloxanes and organosiloxanes in the presence of surfactant templates could provide a general route to the synthesis of organically functionalized, uniformly porous, ordered silica materials with a range of potential applications. Many other organosiloxanes could be used, although compounds that are very hydrophobic or for which hydrolysis is slow may be sequestered in the hydrophobic portion of the micelles. The synthesis of hybrid mesoporous silica materials with controlled functionality and hydrophobicity could open up new avenues for organometallic chemistry, catalysis, and organic and inorganic host–guest chemistry.

Previous attempts to fill the channels of pure-silica MCM-41 materials have yielded low loadings of the guest species, perhaps due to the absence of specific interactions between host and guest. The use of organically functionalized, porous, ordered silicas with tunable binding sites may alleviate this problem. Studies involving the synthesis and reactivity of organometallic complexes of the phenyl-substituted mesoporous silica material are currently in progress.

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Footnotes

† In a typical preparation (20 mol% PTES), 0.334 g of C$_{16}$TMABr (Aldrich) was dissolved in 3.980 g of 1.0 mol dm^{-3} NaOH and 14.096 g of distilled, deionized H$_2$O. 1.273 g of TES (Aldrich) and 0.367 g of PTES (Aldrich) were added and the solution was stirred for 48 h at room temp. The solid product was filtered, washed with H$_2$O and dried for 10 h at 100 °C *in vacuo*. OTES was obtained from Fluka. All compounds were used as received.

‡ Surfactant extraction was performed by stirring a suspension of the solid product (3.3 g dm^{-3}) in 1.0 mol dm^{-3} HCl in EtOH at 75 °C for 24 h.[4] The extracted material was filtered, washed with EtOH and dried for 10 h at 100 °C *in vacuo*.

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