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A versatile route to organically-modified silicas and porous silicas *via* the non-hydrolytic sol–gel process†

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The non-hydrolytic sol–gel route has been used to provide a versatile synthesis of organically-modified silicas (ormosils), *via* a rapid, facile reaction in the absence of any solvent. The ormosils are synthesised by reaction of silicon halides with alkoxides, where one or both of the reactants contains the organic substituent. The products are organic–inorganic hybrid nanocomposite materials, where the organic modification is an alkyl, aryl or vinyl group covalently bonded to silicon. The ormosils have low surface areas, but may be converted to high surface area, largely microporous silicas by thermal degradation of the organic component.

In recent years, much attention has focused on the novel combination of organic species with inorganic minerals and networks because of the exciting range of properties demonstrated by these hybrid materials and the potential they offer to mimic the vast array of structures on display in Nature.[1–6] Low temperature routes to inorganic oxides have attracted considerable interest, in part because of the opportunity provided for combining the oxides with thermally labile organic compounds. The oxides and their hybrids have a plethora of uses, including the development of next generation passive (*e.g.* semi-structural[7]) and active (*e.g.* electronic[8]) materials, catalysis and catalyst supports,[9] ceramics,[9,10] sensor applications[1,11,12] and active glasses.[1,13,14] The most common approach has involved the preparation of sol–gel hybrids, including the combination of inorganic oxides (particularly silica) with polymers[6,7,15] and the formation of organically-modified silica (ormosils) from alkylalkoxysilanes.[16–18] All of these methods use the well-established hydrolytic route to the oxide, involving the hydrolysis and condensation reactions of alkoxide (or other) precursors, usually in a solvent system carefully chosen to avoid the common problem of premature phase separation. In recent years, several groups such as that of Corriu[19–21] and ourselves[22,23] have reported the synthesis of inorganic oxides *via* a non-hydrolytic sol–gel route. This involves the reaction of a 'metal' halide with an oxygen donor, such as an alkoxide, an ether, an alcohol *etc.*, under non-aqueous conditions. This approach has a number of associated advantages, including:

(1) the potential to avoid the use of solvents, with their various drawbacks.
(2) reduction or elimination of residual silanol groups in the product resulting from the different mechanistic course of the reaction compared with the hydrolytic sol–gel route.

Although the non-hydrolytic route has been the subject of a number of studies aimed at assessing its merits as a route to inorganic oxides,[19–31] somewhat surprisingly, it has been overlooked for the synthesis of organic–inorganic hybrids until very recently. As early as 1956, Andrianov *et al.*[32] synthesised some alkyl- and aryl-modified silicates (and linear polyorganosiloxanes) by reacting various combinations of dimethyldichlorosilane, methylphenyldichlorosilane, phenyltrichlorosilane, phenyltriethoxysilane and phenylethyldiethoxysilane in the presence of iron(III) chloride or aluminium(III) chloride catalyst at 95–100 °C. Examination of the experimental data revealed these reactions to proceed *via* a heterofunctional stepwise polycondensation to form insoluble, branched organically-modified silicates, when di- and tri-functional precursor combinations were used. No further analyses were performed on these hybrids. The non-hydrolytic method has been extended to the formation of copolysiloxanes,[33] erbium doped methyl-modified silicates[34] and a poly(ferrocenylsilane) polymer.[35] Yuh *et al.*[34] showed that the non-hydrolytic sol–gel method is particularly useful in the preparation of luminescent gels. Conventional inorganic gels are notoriously inadequate matrices for trivalent, rare-earth luminescence because of hydroxyl quenching. Methyl-modified silicates with low hydroxyl contents were found to be critical in maintaining the luminescent properties of erbium in these hybrids.

Since our preliminary communication[36] on ormosil formation by the non-hydrolytic sol–gel process, Bourget *et al.*[37] have described the non-hydrolytic synthesis of methyl, vinyl, phenyl and octadecyl silsesquioxanes using alkoxysilanes and ethers as oxygen donors, and a range of metal chloride catalysts. Here we report in full the extension of our earlier work to a systematic study of the preparation of hybrid ormosils with a variety of organic groups, starting from organically modified precursors.[36] The mono- or di-substitution of alkyl groups of varying chain length (from methyl to decyl), aryl and vinyl moieties into a silica network is reported. The conversion of the hybrids to porous silicas *via* pyrolysis of the organic moieties is also described. Preliminary molecular models have been constructed to provide an indication of possible hybrid structures by comparison of predicted IR data with experimental results.

Experimental

Materials

Silicon(IV) chloride (Aldrich), tetraethyl orthosilicate [TEOS] (Lancaster), tetramethyl orthosilicate [TMOS] (Aldrich), methyltrimethoxysilane [MTMS] (Aldrich), methyltrichlorosilane [MTCS] (Aldrich), ethyltrimethoxysilane [ETMS] (Lancaster), ethyltrichlorosilane [ETCS] (Lancaster),

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†Electronic supplementary information available: synthetic details for all the systems studied. See http://www.rsc.org/suppdata/jm/a9/a908900d/

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phenyltrimethoxysilane [PTMS] (Lancaster), phenyltrichlorosilane [PTCS] (Aldrich), decyltrichlorosilane [DTCS] (Aldrich), hexyltrichlorosilane [HTCS] (Aldrich), vinyltrimethoxysilane [VTMS] (Aldrich), vinyltrichlorosilane [VTCS] (Aldrich) and iron(III) chloride (Aldrich) were all used as received. Diethyl ether (Fisons) was dried using sodium wire before use.

Safety note

Many of the precursors used in the non-hydrolytic sol–gel reaction are very reactive and require strict handling conditions. As a consequence, care should be taken when embarking on new experiments, particularly in the absence of a solvent. Air-sensitive liquid reactants are best introduced to the reaction system from a syringe *via* a septum.

Instrumentation

A Shimadzu Thermogravimetric Analyser-50 was used to determine sample mass loss over a temperature range of 25–490 °C. A heating rate of 20 K min^{-1} was applied under a nitrogen atmosphere (flow rate, 50 ml min^{-1}). For mass losses up to higher temperatures, a Perkin-Elmer TGA-7 interfaced with a Perkin-Elmer 7700 computer was used to measure sample mass loss over a temperature range of 40–-900 °C. A heating rate of 10 K min^{-1} was applied under a nitrogen atmosphere with a flow rate of 50 ml min^{-1}.

A TA Instruments modulated temperature dynamic scanning calorimeter, MDSC 292010, was used to determine thermal transitions over a temperature range of -70 to 350 °C. Samples were contained in hermetically sealed aluminium pans and heated at a rate of 2 K min^{-1} with an amplitude of ± 1 °C under a nitrogen purge with a flow rate of 40 ml min^{-1}.

All calcinations were carried out in a Lenton UAF 16/21 furnace The sample was contained in a mullite tube during heating at 700 °C.

A Philips PW1830 X-Ray Diffractometer was used to determine sample morphology. Samples were ground into fine powders before being scanned with Cu-Kα radiation at 40 kV, 40 mA from 15–90° 2θ, with a step size of 0.02° and a count time per step of 7 s.

Small angle X-ray scattering (SAXS) analyses were carried out on an Area X-ray Imaging System with a Hilton Brooks generator operating at 40 kV. The Cu-Kα wavelength was selected using a monochromator crystal and 0.5 mm collimators were used to define a narrow beam. Samples were sandwiched between two Kapton sheets to produce samples of *ca.* 500 μm in thickness and mounted in the beam. The area detector was moved *ca.* 0–300 mm from the sample. All the samples analysed were isotropic and so the scattering vector was computed by taking an equatorial intensity profile of the scattered intensity. The maximum was computed by fitting a Gaussian curve to the profile.

Surface morphology and evidence of any microporosity in the samples were evaluated using a Philips 505 Scanning Electron Microscope with an accelerating voltage of 25 kV for both the secondary electron imaging (SEI) and the energy dispersive X-ray (EDX) analyses. Prior to mounting, the specimens were carbon coated to prevent charging under the electron beam. EDX spectra were acquired from a number of areas to determine the elemental composition of the sample.

Elemental analyses were carried out on a Leeman Laboratories Inc. CE 440 Elemental Analyser.

Infrared (IR) spectra were recorded on a Perkin-Elmer 1750 FT-IR Spectrophotometer interfaced with a Perkin-Elmer computer. Samples were ground and prepared for diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). IR spectra were measured on undiluted samples, with potassium bromide used as a reference. Absorbances in the resultant reflectance spectra are given in Kubelka–Munk units. Abbreviations used to describe peaks are as follows: vs = very strong; s = strong; m = medium; w = weak; vw = very weak; b = broad; sp = sharp and sh = shoulder.

Solid-state ^{29}Si and ^{13}C cross polarised (CP) and directly polarised (DP) nuclear magnetic resonance (NMR) spectroscopy was undertaken at the University of Durham, at ambient temperature on a Varian UNITY*plus* spectrometer. Spectra were recorded against an external TMS standard with magic angle spinning (MAS) at a spinning rate of 4300 Hz and an angle of 54.7°. The CP spectra were obtained as single contact experiments with a contact time of 3 ms and a relaxation delay of 2.0 s (700 repetitions). An acquisition time of 9.6 ms was used. Tetrafunctional silicon sites were labelled with the conventional Q^n notation where Q refers to tetrafunctional SiO_4 units and n to the number of bridging oxygen atoms surrounding the central silicon atom. Trifunctional silicon sites were labelled with the conventional T^n notation where T refers to the trifunctional silicon environment and n to the number of bridging oxygen atoms surrounding the central silicon atom.[38]

Surface area analysis was performed on a Coulter SA 3100 instrument and obtained from nitrogen (99.99% purity) adsorption measurements at -196 °C. Prior to the analysis, samples were outgassed *in vacuo* for 10 h at 110 °C. Total surface areas (S_t) were calculated using the Brunauer, Emmett and Teller (BET) method. Specific surface areas (S_{BET}) were calculated by dividing S_t by the sample weight. Total pore volumes (V_p) were measured at a relative pressure of 0.9907.

Mercury porosimetry analyses were performed by Quantachrome Ltd. Samples were outgassed *in vacuo* at room temperature for 30 min before intrusion. Intrusion and extrusion mercury contact angles of 140.00° were used with a moving point average of 51 (scan mode). The operating equation for this technique is the Washburn equation, which assumes cylindrical pore shapes.

For both techniques the % porosity (ϕ) and average pore diameter (D) were calculated using:

$$\phi = \frac{V_p}{V_p + 0.455} \times 100$$

$$D = \frac{4V_p}{S_t} \times 900$$

Computer simulations were carried out on Cerius^2 software, which is a molecular modelling system supplied by Molecular Simulations Inc. Hexylsilanol models were assembled to form structures with increasing degrees of condensation. Energy minimisation was performed to produce the preferred structures. IR spectra were simulated using the MOPAC module (part of the MSI Cerius^2 software package).

Synthesis of organically-modified silicas

The ormosils were generally synthesised using the method described previously[22] for the synthesis of unmodified inorganic oxides. In contrast to many previous non-hydrolytic sol–gel studies using sealed tubes, here an open system is used, with reactions performed under flowing nitrogen. Three types of ormosil were synthesised (see Results and discussion) and a representative example of each method is given below.

Synthesis of singly-modified ormosils. Selected experiments are summarised in Table 1. Full details of all systems studied are given in the supplementary information.

Hexyl-modified silica was formed by reacting HTCS with TEOS. HTCS (5.62 g; 26 mmol) and TEOS (4.00 g; 19 mmol) were mixed together with iron(III) chloride catalyst (0.071 g; 0.73%) under nitrogen. The material gelled within 1–2 days at 35 °C to produce a waxy, yellow solid containing a colourless liquid. This was subjected to Soxhlet extraction in air using

Table 1 Synthesis of selected ormosils^a

Chloride (equiv.)	Oxygen donor (equiv.)	Gel time (approx.)	Temp./ °C	Yield (%)	TG anal., wt. loss (25–900 °C)/%	Calc. organic content (wt.%)	Elemental analysis (CH wt.%)
$SiCl_4$ (1.0)	$Si(OEt)_4$ (1.0)	20 min	90	117	23	—	—
$MeSiCl_3$ (1.0)	$Si(OEt)_4{}^b$ (0.75)	20 min	90	102	29	14	17
$EtSiCl_3$ (1.0)	$Si(OEt)_4$ (0.75)	30 min	90	99	20	23	22
$Me(CH_2)_5SiCl_3$ (1.0)	$Si(OEt)_4$ (0.75)	60 min	90	85	42	47	47
$Me(CH_2)_9SiCl_3$ (1.0)	$Si(OEt)_4{}^b$ (0.75)	<3 h	90	92	56	59	57
$PhSiCl_3$ (1.0)	$Si(OEt)_4{}^c$ (0.75)	2 h	90	90	37	44	35
$H_2C{=}CHSiCl_3$ (1.0)	$Si(OEt)_4{}^d$ (0.75)	<4 days	25	109	18	22	21
$MeSiCl_3$ (1.0)	$MeSi(OMe)_3$ (1.0)	40 min	90	89	15	22	19
$EtSiCl_3$ (1.0)	$EtSi(OMe)_3$ (1.0)	10 min	90	97	26	36	32
$PhSiCl_3$ (1.0)	$PhSi(OMe)_3{}^c$ (1.0)	<6 h	90	95	51	60	56
$H_2C{=}CHSiCl_3$ (1.0)	$PhSi(OMe)_3$ (1.0)	<40 min	85	98	47	50	49
$H_2C{=}CHSiCl_3$ (1.0)	$Si(OMe)_4$ (1.0)	1 min	85	83	12	26	16
$SiCl_4$ (1.0)	$EtSi(OMe)_3{}^b$ (1.0)	35 min	90	78	21	17	23

^{a}Reactions used an iron(III) chloride catalyst loading of 0.8 wt.%, unless otherwise stated. ^{b}0.7 wt.% of iron(III) chloride catalyst. ^{c}0.9 wt.% of iron(III) chloride catalyst. ^{d}1.0 wt.% of iron(III) chloride catalyst.

diethyl ether for three days and the product then dried in air at 80 °C for 48 h, yielding a white, semi-transparent waxy material (3.92 g; 84%). Elemental analysis gave: C, 39.9; H, 8.1%. (Calculated: C, 39.5, H, 7.2%). The organic content calculated from the elemental analysis is 48.0%, in good agreement with the theoretical value of 46.7%. Thermogravimetric (TG) analysis in nitrogen at a heating rate of 10 K min^{-1} from 40 to 900 °C showed a weight loss of 47%, in excellent agreement with the theoretical organic content. The diffuse reflectance IR spectrum showed C–H stretching vibrations at 2860–2970 cm^{-1}, an Si–CH_2 deformation band at 1400–1420 cm^{-1} and various Si–O–Si vibrations between 480 and 1210 cm^{-1}. Note that this type of product is variously described as hexyl-modified silica, hexyl-substituted silica or polyhexylsilicate.

Synthesis of silsesquioxanes ('doubly-modified ormosils'). Selected experiments are summarised in Table 1. Full details of all systems studied are given in the supplementary information.

Dimethylsilsesquioxane was synthesised by reacting equimolar amounts of MTMS (3.65 g; 27 mmol) and MTCS (4.00 g; 27 mmol) in the presence of iron(III) chloride (0.059 g; 0.78%) for 45 min at 90 °C. Soxhlet extraction with diethyl ether in air for 3 days, followed by drying at 80 °C for 24 h in air yielded a ginger brown translucent solid (3.18 g; 89%). TG analysis gave a weight loss of 15.3% (theoretical organic content 22.4%). IR ν_{max}/cm^{-1}: 2970(m), 1411(m), 1288(vs, sp), 1217(s), 1205(s), 1000(m), 797(m), 530(w) and 451(w).

Synthesis of ormosils with residual alkoxy or chloro functionality. Selected experiments are summarised in Table 1. Full details of all systems studied are given in the supplementary information.

Equimolar amounts of silicon(IV) chloride (4.52 g; 27 mmol) and ETMS (4.00 g; 27 mmol) were stirred together with iron(III) chloride (0.062 g; 0.73%) for 35 min at 90 °C. Soxhlet extraction with diethyl ether in air for 3 days, followed by drying at 80 °C for 24 h in air yielded a shiny grey solid (3.51 g; 78%). TG analysis gave a weight loss of 21.0% (theoretical organic content 17%). IR ν_{max}/cm^{-1}: 3700–3100(w, b), 2868(s, sp), 2884(m, sp), 1630(w), 1464(m, sp), 1416(m, sp), 1375(w), 1268(vs, sp), 1222(vs, sp), 1100(m, sh), 1080(m), 960(w), 800(m, b), 720(m, sp), 498(m) and 460(m).

Results and discussion

Ormosil synthesis

The non-hydrolytic sol–gel route has been used for the synthesis of a range of organically-modified silicas. Although a range of inorganic oxides can be synthesised by the non-hydrolytic method, silica hybrids are particularly accessible by this route since the necessary precursors (alkylalkoxysilanes and alkylchlorosilanes) are in many cases commercially available and relatively easily handled. Synthesis of hybrids of other metal oxides such as alumina suffers from the serious drawback that the metal–alkyl bonds are highly reactive, perhaps even leading to pyrophoric behaviour in the presursor. The silica hybrids synthesised in this study are represented by the five general equations shown below:

$$RSiCl_3 + 0.75Si(OR')_4 \rightarrow [RSi_{1.75}O_3]_n + 3R'Cl \qquad (1)$$

$$0.75SiCl_4 + RSi(OR')_3 \rightarrow [RSi_{1.75}O_3]_n + 3R'Cl \qquad (2)$$

$$RSiCl_3 + RSi(OR')_3 \rightarrow [R_2Si_2O_3]_n + 3R'Cl \qquad (3)$$

$$RSiCl_3 + Si(OR')_4 \rightarrow [RSi_2O_3\text{–}OR']_n + 3R'Cl \qquad (4)$$

$$SiCl_4 + RSi(OR')_3 \rightarrow [RSi_2O_3\text{–}Cl]_n + 3R'Cl \qquad (5)$$

These are class II hybrids according to the classification of Judeinstein and Sanchez.[39] The use of a single organically-modified precursor (eqn. 1 and 2) leads to an ormosil with only one type of organic modifying group. Not every silicon atom is substituted by an R group. The organic groups can be alkyl (groups of varying length from methyl to decyl have been used), vinyl or aryl (Table 1). If both precursors are organically-modified (eqn. 3), the resulting hybrid is formally a silsesquioxane. Every silicon atom is substituted by an R group and these groups can all be the same, or the hybrid can contain two different types of organic modification (Table 1). Eqn. 4 and 5 show the cases where only one precursor is organically-modified, but equimolar stoichiometry is used in the reaction. The product therefore theoretically contains one residual alkoxy group or chlorine atom for every two silicon atoms. This might be useful for further chemical modification of the products. If this is required, caution must be exercised in the choice of solvent for Soxhlet extraction since oxygen donor solvents could react with residual Si–Cl groups and exchange reactions with alkoxy groups could also occur. High yields of the ormosils are obtained in all cases—yields are calculated based on the theoretical empirical formula of the product. In some cases, 'yields' above 100% are probably a result of incomplete reaction as indicated by the presence of Q^3 and/or T^2 (and other) species (see below) and perhaps some residual washing solvent. Experimental conditions were not optimised in most cases. Elemental analysis values were generally in good agreement with the calculated organic contents (Table 1 and supplementary information).

In the hydrolytic synthesis of structurally similar ormosils in an aqueous acidic medium, it was found that phase separation limited synthesis of octyl-substituted silica to molar ratios of octyltriethoxysilane : TMOS of well below 1 : 1.[40] This incompatibility problem does not arise for longer alkyl chains using the non-hydrolytic sol–gel process and this represents an advantage of this method over the hydrolytic route.

The non-hydrolytic route produces a volatile by-product, in this case an alkyl (methyl or ethyl) chloride, which is gaseous under ambient conditions and is assumed to be removed in the nitrogen flow during the reaction. Any traces of residual by-product and unreacted starting materials are easily separated from the product by Soxhlet extraction using diethyl ether or ethanol as the solvent. There is also a possibility that residual silicon chloride species may be converted to silicon-oxide moieties by reaction with the oxygen-donating extraction solvent, although this was not confirmed in the present work. Residual Si–Cl groups might also be converted to alkoxysilanes with ethanol.

Kinetic features of the reactions

Gelation occurs from within a few minutes to several hours at temperatures of 90 °C using iron(III) chloride as catalyst, the actual gel time being a function of the type of organic modification (Table 1). When the organic groups are very small, the results show that the reduction in functionality caused by the organic substituent on the silicon atom(s) has a minimal effect on the reaction kinetics compared to the unmodified silica reaction. This is presumably due to the reduced functionality being counterbalanced by the electron-donating capacity of the alkyl groups, which increases the stability of the transition state(s), the effect being particularly marked in the case of vinyl-modified systems, where use of vinyltrichlorosilane in place of silicon(IV) chloride can reduce the gel time by an order of magnitude (Table 1). As the size of the organic moiety is progressively increased, steric hindrance makes nucleophilic attack at the silicon atom more difficult. Together with the reduced functionality, this causes a reduction in the reaction rate; however, gel-times rarely exceed 4 h at 90 °C, showing that the non-hydrolytic approach provides a rapid route to hybrid materials. Even in the case of the highly sterically hindered phenylsilsesquioxane, the gel-time is only 6 h at 90 °C. Similar effects of steric hindrance and reduced functionality on gel time have been observed for the mechanistically different hydrolytic sol–gel synthesis of analogous ormosils.[40]

Mechanistic and structural features of the reactions

Solid-state ^{13}C and ^{29}Si NMR results support the formation of the expected structures. ^{13}C CP-MAS NMR spectra show the relevant carbon resonances. ^{29}Si CP-MAS NMR spectra show the presence of a mixture of T (mono-substituted silica) and, except in the case of the silsesquioxanes, Q (unmodified silica) species. The absence of T^0 and Q^0 species in the majority of the samples indicates that although the polymerisations do not proceed to completion in most cases, no monomer is left unreacted. Fully condensed T^3 and Q^4 species are usually abundant, together with some T^2 and Q^3 species, except in the case of the longer chain alkyl substitutions . Here, no T^3 species are formed in the case of hexyl- and decyl-substitution. Only T^1, T^2, Q^3 and Q^4 species are observed for the hexyl- and decyl-modified silicas, presumably due to steric factors restricting access to silicon reaction centres and hence reducing the extent of condensation reaction. This effect is particularly marked at the substituted silicon atoms where condensation is more incomplete than at TEOS-derived silicon centres. Q^3, T^2 and related species can also be observed in the ^{13}C spectra of many of the hybrids where, for example, resonances are seen at *ca.* 18 and 60 ppm for the CH_3 and CH_2O carbon atoms respectively of residual ethoxysilane groups. The effects are exemplified by deconvoluted solid-state ^{29}Si DP-MAS NMR spectroscopy of the disubstituted vinylphenylsilsesquioxane (Fig. 1), which reveals the presence of characteristic resonances for T^0, T^1, T^2 and T^3 species, confirming the importance of steric factors in the reaction. Optimisation of reaction conditions may increase the degree of condensation in some of these cases.

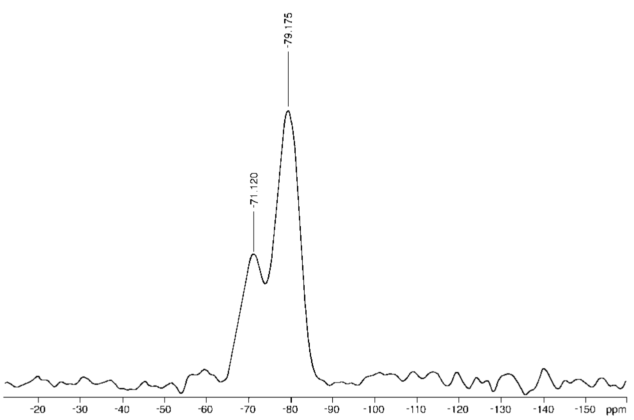

Fig. 1 ^{29}Si DP-MAS NMR spectrum of vinylphenylsilsesquioxane.

No Q species are detected in any silsesquioxane spectra, confirming that no Si–C bonds are broken as a result of the non-hydrolytic sol–gel reaction. This result contrasts with a recent report where it was shown that metal halide catalysed cleavage of phenyl–silicon bonds occurs during non-hydrolytic synthesis of phenylsilsesquioxane.[37] In our case, ^{29}Si NMR spectroscopy shows only peaks at −78.2 (59%; $PhSi(OSi)_3$), −69.8 (38%; $PhSi(OMe)(OSi)_2$) and −60.0 ppm (3%; possibly $PhSiCl(OSi)_2$). Evidence for the presence of Q sites is negligible, as indicated by the absence of peaks below −90 ppm. Since the C–Si bond cleavage also involves reaction of the alkyl halide by-product,[37] the absence of this reaction in our case may be a consequence of the use of an ‘open’ system, as opposed to the sealed tubes used by the other workers. The use of sealed tubes may be disadvantageous in promoting side reactions by trapping the alkyl halide.

Similarly, no evidence of C–Si bond cleavage is observed in the case of vinyl-substituted silicas. Another potential side reaction which can occur in this case is electrophilic addition of RCl across the double bond. This could occur by reaction with the alkyl halide by-product, or by initial attack of a carbenium ion, R^+, which is a possible intermediate in the non-hydrolytic reaction.[19] Spectroscopic analysis suggests that any side reaction is insignificant. The double bond vibrations are clearly visible in the IR spectrum at 1610, 1000 and 960 cm^{-1}, while the ^{13}C CP-MAS NMR spectrum (Fig. 2) shows intense vinyl carbon resonances at 130.4 and 137.0 ppm. No other resonances indicative of the possible by-products are observed in this case. The existence of the Si–C bond is confirmed by an IR absorption at *ca.* 1400 cm^{-1} and a large peak in the ^{29}Si DP-MAS NMR spectrum at −79.8 ppm consistent with the

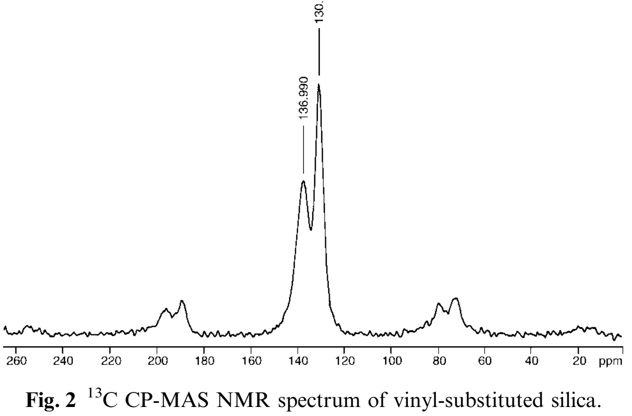

Fig. 2 ^{13}C CP-MAS NMR spectrum of vinyl-substituted silica.

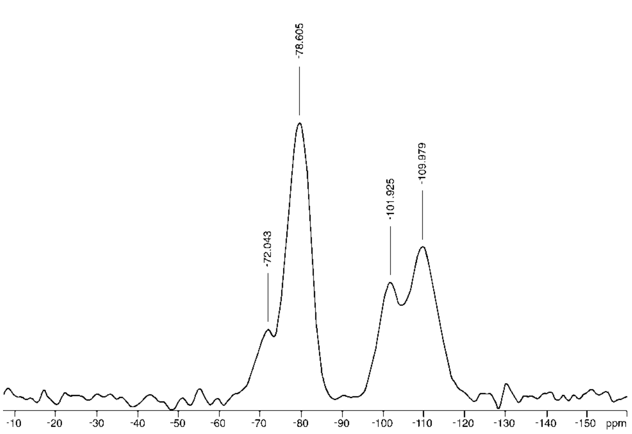

Fig. 3 ^{29}Si DP-MAS NMR spectrum of vinyl-substituted silica.

presence of the T^3 species (Fig. 3).[38] Peaks due to T^2 [$RSi(OSi)_2(OR)$] (-71.2 ppm), Q^3 and Q^4 species are also observed. These results are consistent with those of Bourget *et al.* for vinylsilsesquioxane.[37]

IR spectra of all hybrids showed formation of Si–O–Si bonds and retention of Si–C bonds following the non-hydrolytic reaction. For example, a methyl-substituted hybrid (Fig. 4) produces sharp, intense absorptions at *ca.* 1288 cm^{-1}, characteristic of symmetric methyl deformations in the $Si–CH_3$ groups. The accompanying CH_3 rocking and Si–C stretching bands observed at *ca.* 800 cm^{-1} confirm the presence of methyl-substituted silicon atoms. The formation of Si–O–Si bonds is supported by absorptions at 483 (symmetric bending), 950 (flexion) and 1180 cm^{-1} (asymmetric stretching).[41–47] Following the initial hybrid synthesis, no specific care was taken to exclude moisture during subsequent handling of the products and so the presence of silanol species might be expected. The absorptions assigned to organic groups and any hydroxy groups formed by Si–Cl hydrolysis are often broad and/or overlap those assigned to siloxane vibrations.[10,17,41–47] Considering only the region above 3000 cm^{-1}, it can be seen that OH absorptions are present in the case of methyl-substituted silica (Fig. 4), but are less apparent in the case of the more hydrophobic hexyl system (Fig. 5), where water ingress is likely to be more difficult.

Computer simulations using Cerius^2 software (Molecular Simulations Inc.) were carried out in conjunction with the experimental work. An assembly of hexyl silanol molecules was found to be able to form laminar structures, as shown in Fig. 6a; however, as the reaction to a network silica structure developed, the area per silicon atom in the bonded network was found to be insufficient for the organic segments with a greater cross-sectional area to pack into a planar structure. This means that local domains of organosilica tended to form, with the organic segments radiating out from the silica network

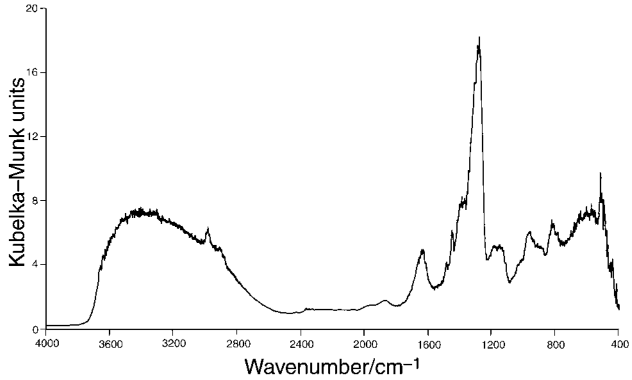

Fig. 4 IR spectrum of methyl-substituted silica (absorbance in Kubelka–Munk units).

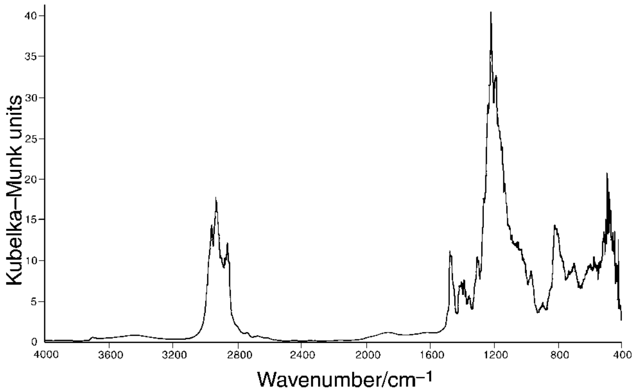

Fig. 5 IR spectrum of hexyl-substituted silica (absorbance in Kubelka–Munk units).

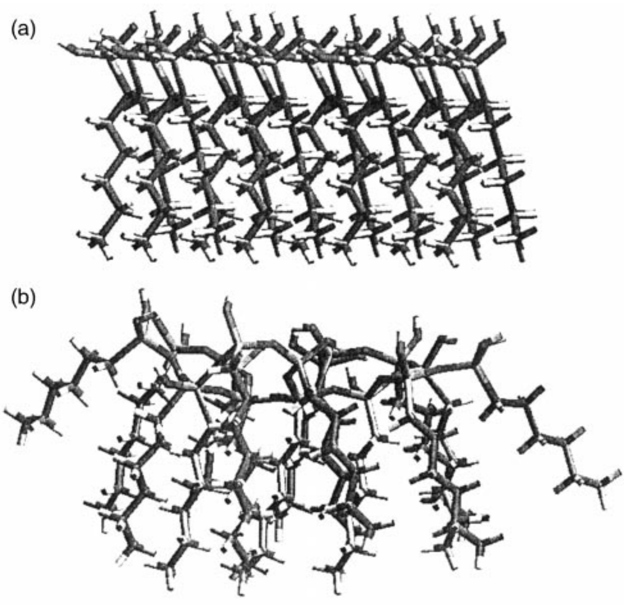

Fig. 6 Molecular simulation (Cerius^2) of the structure of hexylsilsesquioxane showing (a) initial laminar structure and (b) structure formed later in the reaction.

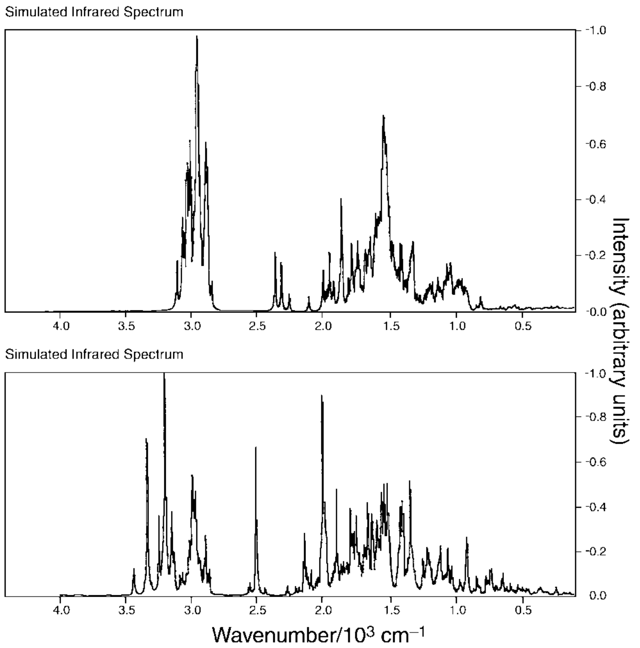

Fig. 7 Simulated IR spectra of planar (bottom) and caged (top) structures of hexylsilsesquioxane.

(Fig. 6b), leading ultimately to a silsesquioxane cage structure. IR spectra were simulated using the MOPAC module. Fig. 7 shows the predicted IR spectra for planar and caged structures of hexylsilsesquioxane. The general pattern of the spectrum for the caged structure compares reasonably well to the experimental data shown for the hexyl-modified silica (Fig. 5) and even the methyl-modified silica (Fig. 4), suggesting that caged structures may be formed *via* this route; however, further work would be needed to confirm this suggestion.

Physical and thermal properties of hybrids

Many of the hybrid materials have the same physical appearance as the unmodified silicas, *i.e.* brittle and glassy, with some of the hybrids showing transparency or translucency. In these last cases, the optical properties are indicative of a sub-micron phase morphology and perhaps the formation of true nanocomposites (assuming that serendipitous refractive index matching of the phases does not occur). Physical properties are only affected when longer alkyl chains, *e.g.* hexyl and decyl groups, were incorporated into the silica network and organic contents reached above 47 wt.%. In these cases, the hybrids were rubbery, suggesting the formation of organic domains with sub-ambient glass transition temperature.

No conclusive information on thermal transitions could be obtained using modulated temperature dynamic scanning calorimetry (MDSC). The reversible heat flow curves show no obvious glass transitions between −70 and 350 °C, despite the rubbery nature of some of the hybrids. A broad endothermic peak seen in the non-reversible heat flow curve at *ca.* 80 °C, possibly due to evaporation of solvent (used to wash the gels), obscures any transitions that might otherwise be visible.

Weight losses by TG analysis are normally in good agreement with the calculated organic contents and elemental analysis values (Table 1 and supplementary information). Fig. 8 shows thermograms for hexyl- and vinyl-modified silicas, which shows the hexyl material to be thermally stable up to at least 250 °C. The vinyl hybrid shows only a small weight loss to beyond 400 °C, which may be due to entrapped solvent or some residual reaction. The main weight loss occurs rapidly beyond *ca.* 500 °C, suggesting that the Si-vinyl groups are stable up to this temperature. Polymerisation of the vinyl groups may contribute to the apparent stability. It was difficult to establish the thermal stability of all the hybrids synthesised since many of the thermograms are complex, perhaps because of incomplete condensation in the products. In general, the TG analysis results are similar to those found by Bourget *et al.*[37] For comparison, methyl- and phenyl-substituted[48] and bridged[49–52] polyorganosilicates formed using the hydrolytic route have been found to be thermally stable to *ca.* 500 °C.

Hybrid morphology

The SEM micrographs highlight porosity and surface fractures, consistent with the brittleness of these materials. None of the SEM micrographs provide evidence for any specific morphology in the hybrids. EDX shows the presence of silicon, oxygen, iron and chlorine in most of the hybrids studied. Carbon present comes from both the sample and the conducting coating. None of the hybrids show any evidence for crystallinity or other structural ordering by X-ray diffraction (XRD) or SAXS. Further XRD and SAXS work, together with extended X-ray absorption fine structure (EXAFS) and structure simulations are planned to provide further evidence for the hybrid structures.

Hybrid porosity

Problems were experienced when using the BET method to obtain surface area data. Many of the sorption isotherms obtained for both the inorganic and hybrid materials show high errors in the correlation coefficients, produce erratic desorption curves and have extremely long equilibration times. This is attributed to the very low surface areas of the hybrid products leading to problems in accurately measuring the void volume. A few reliable surface area results obtained using nitrogen sorption are reported in Table 2, along with data obtained from mercury porosimetry. The isotherm exhibited by phenyl-modified silica is shown in Fig. 9. In general, although the validity of the precise numbers quoted may be disputed, the results from both nitrogen adsorption and mercury porosimetry show that the (mostly mono-substituted) hybrids display low surface areas of between 0.05 and 12 $m^2 g^{-1}$ coupled with low pore volumes and % porosities. The values are similar to those obtained for the unmodified silica (prepared by the non-hydrolytic route), with the exception of ethyl-modified silica and ethylphenylsilsesquioxane, which show low surface areas but higher % porosities and pore volumes. This perhaps arises because of the larger average pore sizes ($D = 132$ and 58 nm respectively) in these cases, although the reasons for the differences are not clear. Although low surface areas and porosities are commonly found in the products of the present study, other work has shown that this is not a general feature of the non-hydrolytic sol–gel process.[53]

Like unmodified silica, all the hybrids display type II isotherms indicative of non-porous surfaces or materials with pore diameters larger than micropores, *i.e.* ⩾2 nm (Fig. 9). The calculated average pore diameters and the absence of any micropores (where V_{mp} data could be acquired) are in agreement with this conclusion, showing pore sizes in the mesoporous range of 17–35 nm diameter. Again, the results for ethyl-modified silica and ethylphenylsilsesquioxane deviate from the other hybrids analysed with average pore diameters in the macropore range; however, the results still show type II isotherms. These results contrast with those for silicas prepared by the hydrolytic sol–gel route using acid catalysis, where type I

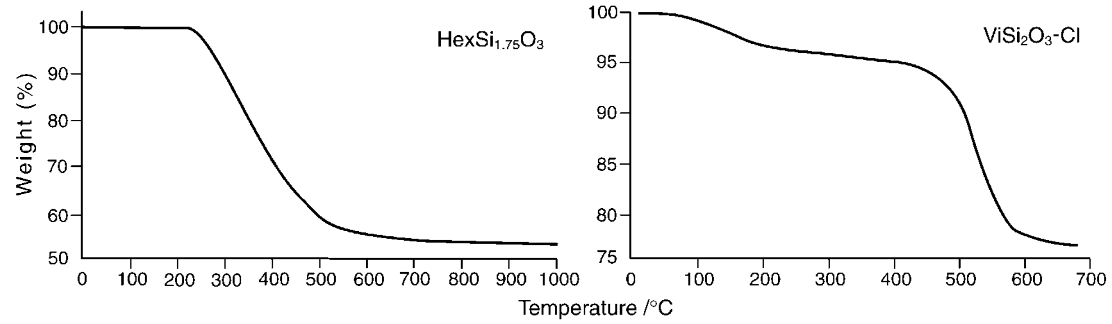

Fig. 8 TG thermograms for hexyl- and vinyl-modified silicas.

Table 2 Surface area analyses of mono-substituted silicas and silsesquioxanes

Product	$S_{BET}{}^a$ /m^2 g^{-1}	$V_p{}^b$ /cm^3 g^{-1}	$V_{mp}{}^c$ /cm^3 g^{-1}	$V_m{}^d$ /cm^3 g^{-1}	ϕ, % porosity	D^e /nm	Isotherm type	Method used
SiO_2	4.88	0.0039	—	—	0.8	2.9	II	BET
	5.00	0.047			9.3	33.6	II	Hg porosimetry
$MeSi_{1.75}O_3$	5.33	0.052	—	—	10.3	35.1	II	Hg porosimetry
$EtSi_{1.75}O_3$	2.82	0.103	—	—	18.5	132	II	Hg porosimetry
$Me(CH_2)_5Si_{1.75}O_3$	0.05	—	0.0000	0.0125	—	—	II	BET
$PhSi_{1.75}O_3$	0.24	0.001	0.0000	0.0544	0.2	16.7	II	BET
$EtPhSi_2O_3$	12.36	0.201	—	—	30.6	58.5	II	Hg porosimetry

$^a S_{BET}$ = BET total surface area. $^b V_p$ = total pore volume. $^c V_{mp}$ = micropore volume. $^d V_m$ = monolayer volume. $^e D$ = average pore diameter.

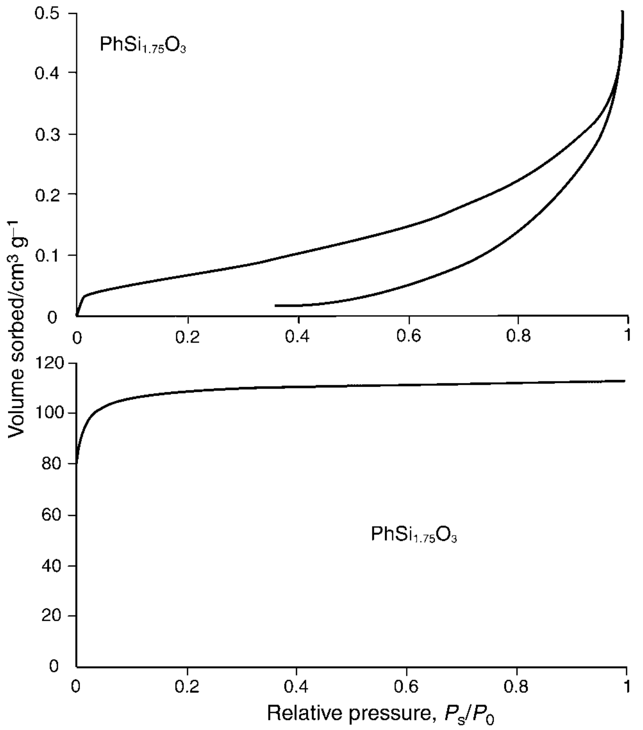

Fig. 9 Nitrogen adsorption–desorption isotherms for phenyl-modified silica before (top) and after calcination (bottom).

isotherms are normally obtained.[10] Regardless of the presence and size of the organic groups attached to the silica network, the surface area results are relatively similar in terms of low surface areas and the type of isotherm obtained.

Calcination of hybrids

Preliminary investigations have been undertaken of calcination of the hybrids at 700 °C. This temperature is high enough to remove the covalently bound organic groups, as confirmed by elemental analysis, but considered low enough to avoid inducing significant structural changes in the silica network, thereby allowing possible templating effects to be detected. Previous work has shown that much higher temperatures are required to induce major structural reorganisation, such as crystallisation, of non-hydrolytic sol–gel silica.[23] Calcination of polyvinyl-, polyphenyl- and polydecylsilicates, as well as mixed silsesquioxanes, normally leads to products exhibiting a type I isotherm (Fig. 9). In addition, surface areas, pore volumes, micropore volumes and porosities are generally larger than those measured for the ormosils, while the average pore diameters are much smaller (Table 3). This is easily seen in the example of polyphenylsilicate. After thermal treatment, the surface area increases dramatically from 0.24 to 397 m^2 g^{-1} and the pore volume increases from 0.001 to 0.159 cm^3 g^{-1}, with 94% of this volume being microporous. The porosity of this material is increased by a factor of 130 (to 26%) upon calcination and the average pore diameter reduced from 16.7 to 1.4 nm. Porosities up to 34% with surface areas close to 500 m^2 g^{-1} have been achieved, with the products showing a high degree of microporosity (>80%). It can be seen from Table 3 that formation of high surface area microporous silicas does not always result from thermal treatment of the hybrids. The silsesquioxanes containing methyl groups form very low surface area silicas on calcination, but it is not clear yet whether this effect is dependent on the size of the organic group.

The calcination process removes any covalently bound organics, freeing up space within the silica network. It is suggested that the presence of the organic groups may prevent initial collapse of the pore network, thus maintaining the presence of micropores, at least in some cases. The failure to form microporous products in other cases may be a size effect, the smaller organic groups being insufficient to prevent collapse of the pores. A much more detailed study would be needed to confirm this hypothesis and this will be the subject of future work.

Conclusions

The non-hydrolytic sol–gel route to inorganic oxides has been extended to the synthesis of a series of organically-modified silicas. The reactions generally proceed rapidly at moderate temperatures in the absence of a solvent and the presence of a catalyst [iron(III) chloride]. Using this method, silicas containing one type of organic group or two different types of organic group or a residual reactive group such as alkoxy or chloro are

Table 3 Surface area analyses of calcined silica hybrids

Product	Calcination conditions	$S_{BET}{}^a$ /m^2 g^{-1}	$V_p{}^b$ /cm^3 g^{-1}	$V_{mp}{}^c$ /cm^3 g^{-1}	$V_m{}^d$ /cm^3 g^{-1}	ϕ, % porosity	D^e /nm	Isotherm type	Method used
$H_2C{=}CHSi_{1.75}O_3$	700 °C for 5 h	119	0.052	—	0.0239	10.2	1.6	I	BET
$PhSi_{1.75}O_3$	700 °C for 2 h	373	0.175	0.148	85.6	27.8	1.7	I	BET
$PhSi_{1.75}O_3$	700 °C for 48 h	397	0.159	0.150	91.2	25.9	1.4	I	BET
$Me(CH_2)_9Si_{1.75}O_3$	700 °C for 5 h	186	0.086	0.083	42.6	15.9	1.7	I	BET
$Me_2Si_2O_3$	700 °C for 2 h	0.77	0.002	—	0.177	0.4	9.3	II	BET
$Me_2Si_2O_3$	700 °C for 48 h	0.38	—	—	0.0873	—	—	—	BET
$(Me(CH_2)_9)MeSi_2O_3$	700 °C for 5 h	0.37	0.002	0.0000	0.0848	0.4	21.6	II	BET
$(Me(CH_2)_9)PhSi_2O_3$	700 °C for 2 h	494	0.233	0.196	114	33.9	1.9	I	BET
$(Me(CH_2)_9)PhSi_2O_3$	700 °C for 48 h	467	0.189	0.156	107	29.3	1.5	I	BET

$^a S_{BET}$ = BET total surface area. $^b V_p$ = total pore volume. $^c V_{mp}$ = micropore volume. $^d V_m$ = monolayer volume. $^e D$ = average pore diameter.

all accessible. Analytical data generally support the formation of amorphous ormosils when the organic group is alkyl, phenyl or vinyl. Possible side reactions in the presence of vinyl and phenyl groups are shown to be negligible.

The ormosils prepared in this study are relatively low surface area, low porosity (with some exceptions) materials. Thermal treatment of the hybrids to remove the organic moiety can lead to formation of high surface area silicas with a high degree of microporosity. The nature of the final silica product appears to be dependent on the size of the organic group present in the ormosil.

The non-hydrolytic sol–gel route thus offers a versatile and simple approach to organically-modified silicas, which can act as precursors to largely microporous silicas with high surface areas.

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