A non-hydrolytic route to organically-modified silica

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A versatile route to organic–inorganic hybrid nanocomposite materials is described, where organically modified silicon halides and alkoxides are reacted together in a solvent-free non-hydrolytic sol–gel process.

The combination of organic species and inorganic minerals and networks has attracted much interest in recent years for a number of reasons,[1–4] including the development of next generation passive (*e.g.* semi-structural[5]) and active (*e.g.* electronic[6]) materials. Much work has focused on the preparation of sol–gel hybrids, such as the combination of inorganic oxides (particularly silica) with polymers[4,5,7] and the organic modification of silica ('Ormosils') starting from alkylalkoxysilanes.[8–10] All of these methods use the well established hydrolytic route to the oxide. In recent years, the group of Corriu[11–13] and others including ourselves[14,15] have reported the synthesis of inorganic oxides *via* a non-hydrolytic sol–gel route which involves the reaction of a 'metal' halide with an oxygen donor such as an alkoxide, an ether, an alcohol, *etc.* One advantage of this approach is that it can avoid the use of solvents and their associated drawbacks. In addition, residual silanol groups in the product should be substantially reduced because of the different mechanism involved. The method has been extended to the formation of copolysiloxanes[16] and erbium doped methyl-modified silicates.[17] To the best of our knowledge, there have been no reports to date of the extension of this method to the preparation of hybrid Ormosils with a variety of organic groups.

Here, we describe the synthesis of organic–inorganic hybrids using the non-hydrolytic sol–gel method starting from organically modified precursors. Silica hybrids are particularly accessible by this route since the necessary precursors such as alkylalkoxysilanes and alkylchlorosilanes are in many cases commercially available. Related hybrids such as those based on alumina suffer from the serious drawback of the high, sometimes pyrophoric, reactivity of the metal–alkyl bonds. The silica hybrids are represented by the general equations shown below:

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

$$\mathrm{RSiCl_3 + RSi(OR')_3 \rightarrow [R_2Si_2O_3]_\mathit{n} + 3R'Cl} \qquad (2)$$

The use of a single organically-modified precursor [eqn. (1)] leads to an Ormosil with only one type of organic modifying group. If both precursors are organically modified [eqn. (2)], the resulting hybrid can contain two different types of organic modification. The organic groups can be alkyl (groups of varying length from methyl to decyl have been used), vinyl or aryl. In a typical experiment, the hexyl-modified silica was formed by reacting hexyltrichlorosilane (5.62 g, 26 mmol) with tetraethylorthosilicate (TEOS) (4.00 g, 19 mmol) in the presence of iron(III) chloride catalyst (0.071 g, 0.73%) under nitrogen. The material gelled within 1–2 days at 35 °C. The resulting solid (containing a colourless liquid) was subjected to Soxhlet extraction using diethyl ether for three days, yielding a white, semi-transparent waxy product (3.92 g, 84%). Elemental analysis gave: C, 39.9; H, 8.1 (Calc. 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 $\mathrm{SiCH_2}$ deformation band at 1400–1420 cm^{-1} and various Si–O–Si vibrations between 480 and 1210 cm^{-1}. Preliminary BET surface area analysis gave values well below 1 m^2 g^{-1} for the total surface area, but isotherms are complex and are the subject of further work.

Gelation could normally be accomplished at temperatures of 90 °C or below using iron(III) chloride as catalyst.[14] Gel times at 90 °C typically range from a few minutes to several hours depending on the nature of the organic modification. For long alkyl chains and phenyl groups, gel times were longer for the organically-modified systems than for pure silica because of the combined effects of reduction of the concentration of reacting groups and steric hindrance by the bulky organic groups. The presence of short alkyl chains such as methyl and ethyl in the halide precursor had little effect on gel times, the effect of reduced functionality presumably being counterbalanced by the electron-donating capacity of the alkyl groups increasing the reactivity of the silicon halide. This effect is particularly marked in the case of vinyl-modified systems, where use of vinyltrichlorosilane in place of silicon(IV) chloride could reduce the gel times by an order of magnitude. The non-hydrolytic approach therefore provides a rapid route to the Ormosils.

The non-hydrolytic route produces a volatile by-product, in this case an alkyl, aryl or vinyl chloride, hence the liquid produced in the above experiment. The by-product and any unreacted starting materials are easily separated from the product by Soxhlet extraction. In the case of vinyl-substituted silica, and perhaps also the aryl-substituted materials, a possible side reaction is electrophilic attack of '$\mathrm{R^+}$' (a possible intermediate in the non-hydrolytic reaction[11]) on the double bond leading in the vinyl case to addition of RCl across the double bond. IR and solid state ^{13}C CPMAS NMR spectroscopy show the presence of unreacted vinyl group and suggest 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 NMR spectrum (Fig. 1) shows intense vinyl carbon resonances at δ 130.4 and 137.0. The existence of an Si–C bond is indicated by an IR absorption at *ca.* 1400 cm^{-1} and a large peak in the ^{29}Si CPMAS NMR spectrum at δ −79.8

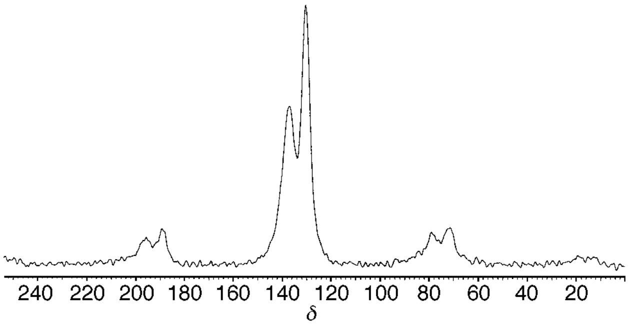

Fig. 1 ^{13}C NMR spectrum of vinyl-substituted silica.

consistent with the presence of the T^3 species.[18] Peaks due to T^2 [$R–Si(OSi)_2(OR)$] (δ −71.2), Q^3 and Q^4 species are also present as expected.

In general, TG analysis to 900 °C showed weight losses in good agreement with the theoretical organic content of the hybrids since all organic material is expected to volatilise by this temperature. The physical nature of the hybrids varies according to the type of organic modification with short alkyl chains leading to solid Ormosils, while those containing longer alkyl chains (C_8–C_{10}) are rubbery in appearance. DSC, however, shows no obvious glass transitions from −70 to 200 °C.

Molecular modelling using the Cerius^2 software package (Molecular Simulations Inc.) suggests that hybrids such as hexyl-modified silica could form a layered structure, but we have no experimental evidence to support this prediction. Future work is planned using extended X-ray absorption fine structure (EXAFS) to attempt to clarify this. None of the hybrids shows any evidence for crystallinity or other structural ordering by X-ray diffraction (XRD). Potential packing problems in the system may inhibit formation of an ordered structure. The synthesis of the hexyl-modified silica was carried out at a lower temperature and a longer reaction time than usual to try to facilitate ordering of the organic and inorganic components of the hybrid; however, XRD provides no evidence for such ordering.

Surface area analysis of these hybrids is complex. BET nitrogen adsorption isotherms and mercury porosimetry suggest the hybrids have low surface area, but further work is in progress to characterise these materials more fully.

Current work is aimed at characterising the properties of these hybrids more fully and assessing their use as precursors to new microporous silicas. Preliminary results show that removal of the organic component at elevated temperatures can lead to microporous silicas with surface areas above 150 m^2 g^{-1}.

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