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Effects of Molecular Organic Additives on Formation and Properties of Organosilicate and Silica Xerogels Correlated to Structural Properties of the Additive

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This paper describes the effects of some polar organic additives on the sol−gel processing of organodisilicate and silica precursors. For a range of organic additives investigated, those for which molecular stacking is a feature of the crystal structure (type A) promote extensive fragmentation of organosilicate and silica xerogels into thin plates and small (~1 mm diameter) granules during the final drying stages. Two organic additives that do not exhibit such stacking (type B) were investigated, these did not promote such fragmentation, and the organic additive-treated monoliths were formed. Sol−gel mixtures investigated with type A organic additives include: 1,4-bis($(Cl_3SiCH_2)_2C_6H_4$ and organic additives *trans*-cinnamic acid (TCA), crotonic acid, or benzoic acid; 1,4-bis[$(n\text{-}BuO)_3SiCH_2)]_2C_6H_4$ and *m*-nitroaniline; 1,4-bis[$(EtO)_3Si]C_6H_4$ and [$(EtO)_4Si$] with *trans*-cinnamic acid. Sol−gel mixtures containing type B organic additives investigated were 1,4-bis$(Cl_3SiCH_2)_2C_6H_4$ and the organic additives phenol or pinacol; 1,4-bis[$(EtO)_3Si]C_6H_4$ or $(EtO)_4Si$ with PhOH. The additives may be removed by extraction of the xerogel materials with THF. The effects of tetrahydrofuran solutions of types A and B additives on monolithic additive-free organosilicate xerogels and silica gels is also reported. The materials have been variously studied by SEM(EDAX), XRD, ^{29}Si solid-state NMR, and ^{13}C solid-state NMR. The THF-extracted products were studied by nitrogen sorption porosimetry. BET measurements on THF extracted materials showed that type A additives generally gave low surface area materials while type B additives gave high surface area materials. ^{29}Si solid-state NMR and BET measurements revealed nonsystematic effects of TCA loading on local chemical structure and surface area, respectively.

Introduction

Over the past few years there has been a renaissance of the sol−gel area as researchers have come to realize its potential for the ready synthesis of advanced materials. Much of this work is concerned with the encapsulation of various organic and inorganic species into inorganic silica materials prepared from $Si(OEt)_4$ or related alkoxides often with a view to exploitation of specific catalytic[1a] or optical[1b] effects. The use of organosilicate precursors by themselves or in conjunction with orthosilicates is the current focus of much sol−gel work.[2−4] We have reported on the synthesis and characterization of a range of organosilicate xerogels derived through sol−gel processing of the bis(trichlorosilylmethyl)benzenes, $(Cl_3SiCH_2)_2Ar$ (Ar = aryl bridge).[5,6a] These materials are part of a growing family of inorganic−organic hybrid materials[2,3] but are unusual in being derived from chlorosilanes (alkoxysilanes are normally used for sol−gel processed silicas). For comparison, we have recently reported on materials derived from related bis((trialkoxysilyl)methyl)benzenes.[6b] We have begun to assess the potential of our materials as confinement matrixes for a range of organic and inorganic compounds. We report here on the effects on monolith formation, local chemical structure, and porosity after variable quantities of organic additive compounds, of type A for which molecular stacking is a common structural feature, e.g., *trans*-cinnamic acid,

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TCA, PhCH=CHCO$_2$H, were incorporated in sol–gel mixtures derived from 1,4-bis(trichlorosilylmethyl) benzene (1,4-bis(Cl$_3$SiCH$_2$)$_2$C$_6$H$_4$), 1,4-bis(triethoxysilyl)benzene (1,4-bis{(EtO)$_3$Si}$_2$C$_6$H$_4$),[7] and tetraethoxyorthosilicate (TEOS, Si(OEt)$_4$). We contrast this with effects of two organic additives type B investigated for which molecular stacking is not a structural feature. At relatively high loading levels type A additives induced fragmentation to dense thin plates (thickness ~10–50 μm) and granules during the final drying stages of the process for xerogel preparation while type B additives gave porous monoliths with no evidence of fragmentation. In addition tetrahydrofuran solutions of TCA (type A) induce fragmentation in suspended additive-free monolithic silica gel or organosilicate xerogel derived from 1,4-bis(Cl$_3$SiCH$_2$)$_2$C$_6$H$_4$ while solutions of phenol (type B) showed no such fragmentation effects.

Results and Discussion

Synthesis. To incorporate organic additives in organosilicate gels, precursor sol–gel solutions in tetrahydrofuran, THF, containing both the organic additives and the organosilicate precursors

1,4-bis(Cl$_3$SiCH$_2$)$_2$C$_6$H$_4$ or 1,4-bis[(EtO)$_3$Si]C$_6$H$_4$ were first prepared. The hydrolysis process was initiated by addition of water, and the resultant mixtures were vigorously stirred to clear sols. Gelation occurred within 24 h in all cases, and after a further 24 h of aging under a static nitrogen atmosphere slow drying under ambient conditions was initiated through two pinholes ~1 mm in diameter. After 5 days the whole sample surface was exposed and after a further 3 weeks the materials were analyzed.

Organic additives were also incorporated in silica gels derived from (EtO)$_4$Si using a modification of a reported method for the additive-free material (see Experimental Section).[8] The xerogel materials derived from precursors 1,4-bis(Cl$_3$SiCH$_2$)$_2$C$_6$H$_4$, 1,4-bis[(EtO$_3$)Si]C$_6$H$_4$, or (EtO)$_4$Si will subsequently be prefixed by the labels X1, X2, and X3. The organic additive-treated gels are subsequently abbreviated, e.g., X1 containing *trans*-cinnamic acid as X1TCA. A more detailed account of the general procedures is in the Experimental Section, and a key to materials prepared is given in Table 1. Only those organic additives that gave transparent homogeneously dispersed sols are discussed. This was not possible in the case of 1,4-bis(Cl$_3$SiCH$_2$)$_2$C$_6$H$_4$ with *m*-nitroaniline, *m*-(O$_2$N)C$_6$H$_4$NH$_2$, and therefore the silicate precursor 1,4-bis{(*n*-BuO)$_3$SiCH$_2$)}$_2$C$_6$H$_4$ was used instead in this case. Type A organic additives (with molecular stacking as shown by crystal packing) employed in this work were *trans*-cinnamic acid (TCA, PhCH=CHCO$_2$H),[9] benzoic acid (PhCO$_2$H),[10] *p*-chlorobenzoic acid, crotonic acid (MeCH=CHCO$_2$H),[11] and *m*-nitroaniline (*m*-O$_2$NC$_6$H$_4$NH$_2$);[12] type B additives used were phenol (PhOH),[13] and pinacol (HO(CH$_3$)$_2$-C$_2$(CH$_3$)$_2$OH).[14] With the exception of *m*-nitroaniline all of these were used in experiments with 1,4-bis(Cl$_3$SiCH$_2$)$_2$C$_6$H$_4$. Experiments with 1,4-bis[(EtO$_3$)Si]$_2$C$_6$H$_4$ and (EtO)$_4$Si involved TCA and PhOH only.

Table 1. Organic Additive Effects on Organosilicate Gels

xerogel[a]	(A/P)[b]	additive effect[c]
X1	no additive	no fragmentation observed
X1TCA1	0.13 and 0.25	no fragmentation observed
X1TCA2	0.50	fragmentation within 12 h
X1TCA3	1.00	fragmentation within 12 h
X1TCA4	2.00	fragmentation within 12 h
X1BA	1.00	fragmentation within 12 h
X1ClBA	0.50	fragmentation within 12 h
X1ClBA1	1.00	fragmentation within 12 h
X1crotonic	1.00	fragmentation within 5 days
X1PhOH	1.00	no fragmentation observed
X1PhOH1	2.00	no fragmentation observed
X1pinacol	0.50	no fragmentation observed
X2TCA	1.00	fragmentation within 12 h
X3TCA	0.24 and 0.46	fragmentation within 12 h
X3PhOH	0.23 and 0.46	no fragmentation observed

[a] X1 derived from *p*-(Cl$_3$SiCH$_2$)$_2$C$_6$H$_4$; X2 derived from 1,4-bis[(EtO)$_3$Si]C$_6$H$_4$; X3 derived from TEOS, TCA = *trans*-cinnamic acid; BA = benzoic acid; ClBA = *p*-chlorobenzoic acid; PhOH = phenol. [b] Mass of additive/mass of silicate precursor. [c] From point at which the whole surface area of the gel sample was exposed to air until fragmentation began.

Effects of Organic Additives on Sol–Gel Processed Organosilicate and Silica Gels. The effects of various additives on the sol–gel reaction process to silica gels has been the subject of many recent reports. For example, drying control chemical additives (DCCAs) such as formamide, *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, and ethylene glycol featured in attempts to control gelation time and monolith cracking.[15] Varying the concentration of formamide in sol–gel mixtures was shown to have pronounced effects on gel particle morphology.[16] The modification of pore structure by additives (ranging from DCCAs,[15,16] water-soluble polymers,[17] surfactants,[18] inorganic salts[18]) is widely discussed.

This particular study started from some initial observations when *trans*-cinnamic acid was used as additive in conjunction with 1,4-bis(trichlorosilylmethyl)-benzene (1,4-bis(Cl$_3$SiCH$_2$)$_2$C$_6$H$_4$). Extensive fragmentation of the additive-treated gel into thin plates (thickness ~10–50 μm) was observed during the final drying of hard transparent glassy monolith to the xerogel stage. This occurred for additive to precursor, mass ratios (A/P) $\geq$0.5 but not when A/P = $\leq$0.25. For the higher additive loading the composition of the plate-type materials formed varied according to the drying process employed. For gel samples X1TCA4 (see Table 1) allowed to dry very slowly, initially through a small pinhole over a period of several days to give a hard transparent monolith, the thin plates formed after the

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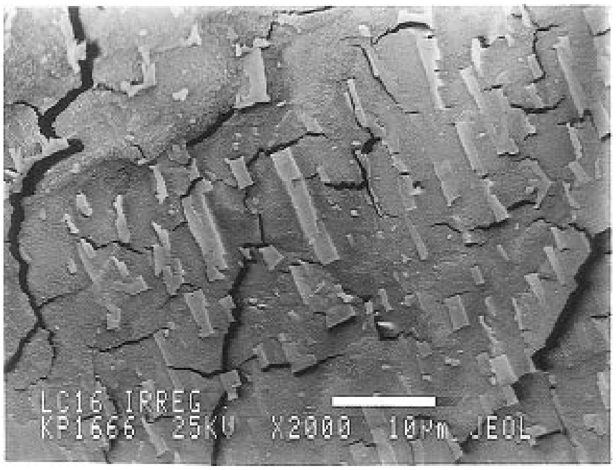

Figure 1. SEM of a single plate from X1TCA4 showing ordered embedded TCA crystallites. Bar = 10 μm.

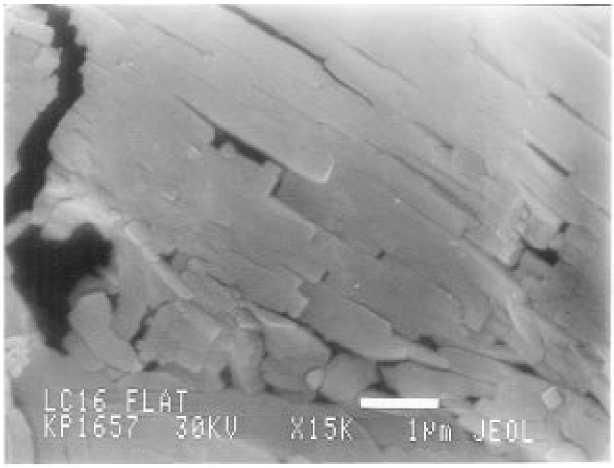

Figure 2. SEM of a single plate from X1TCA4 showing ordered crystalline TCA domain. Bar = 1 μm.

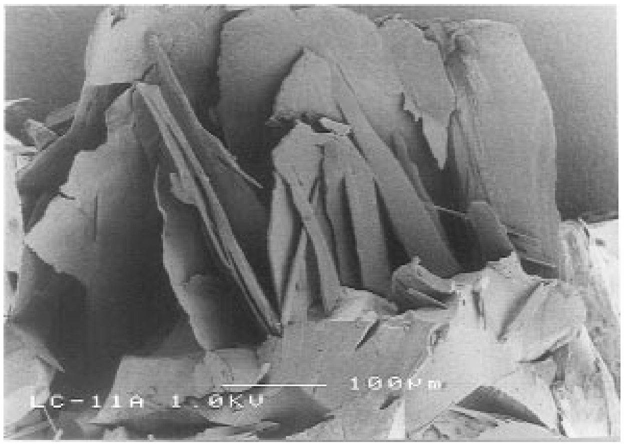

Figure 3. SEM of bulk material X1TCA3 showing plate-type fragmentation. Bar = 100 μm.

whole sample was exposed to air were found to consist of amorphous silicate layers with ordered crystallites of *trans*-cinnamic acid embedded in these layers (SEM Figure 1). Several plates examined had similar surface features. Gel samples of X1TCA4 which were dried rapidly by exposing the whole surface of the wet gel sample to air gave plates which were similar to those described above and also plates of pure *trans*-cinnamic acid (SEM Figure 2). In this case we have some complete phase separation of TCA. The composition of the plates thus depends on the drying process with slow drying restricting the potential for complete phase separation. In both cases some residual glassy particles were also obtained. The surface morphology of the glassy particles was typical of the amorphous additive-free xerogel. The plate-type appearance of the bulk of the xerogel sample which underwent fragmentation is illustrated by the SEM of X1TCA3 shown in Figure 3. A single plate-type layer from X1TCA4 (SEM in Figure 1) was examined by powder diffraction. While the XRD pattern of this material (Figure 4) shows that there are significant amorphous regions, some peaks are present that are coincident with those of *trans*-cinnamic acid (TCA). Analysis of the peak pattern suggests that crystal growth has occurred preferentially along the [010] direction consistent with the rodlike appearance of the crystallites. Soxhlet extraction of the XTCA materials with THF showed the TCA completely available.

The tendency of carboxylic acids to form stacked structural arrangements is well documented.[9] The natural crystal habit for *trans*-cinnamic acid is plate-type, and it appeared as though plate-type morphology was imposed on the xerogel by the *trans*-cinnamic acid additive where the alignment of the *trans*-cinnamic crystallites within the gel-facilitated cleavage. To test the generality of this observation, we investigated a range of other organic additives. Similar fragmentation effects were seen with other type A carboxylic acids, e.g., benzoic acid (X1BA) and *p*-chlorobenzoic acid (X1ClBA, SEM Figure 5); A/P = 1 in each case. In the case of X1ClBA materials plate-type layers with amorphous flat-surface features but distinctly crystalline edges (SEM Figure 5) are formed. The flat surfaces contained varying quantities of Si:Cl (EDAX) in different regions.

Where crotonic acid, $CH_3CH{=}CHCO_2H$, was used as additive the drying stages of the process were accompanied by fragmentation into small glassy granules. *m*-Nitroaniline was employed as an additive to test the effect of a non-carboxylic acid type A additive, and once again fragmentation to layers during air-drying resulted (SEM Figure 6).

In contrast to type A additives, type B could be incorporated at high A/P levels with no fragmentation of the resultant additive-containing monolithic xerogels (see Table 1). Thus transparent monoliths were obtained from gel mixtures containing phenol (A/P = 1 and 2) and pinacol (A/P = 0.5). We have also investigated effects of additives TCA and PhOH on X2 materials derived from 1,4-bis[$(EtO)_3Si]C_6H_4$ and X3 materials derived from TEOS, $Si(OEt)_4$. With *trans*-cinnamic acid we see behavior similar to that observed for the X1TCA series, that is, extensive fragmentation to layers for X2TCA where A/P = 1 and to granules for X3TCA where A/P = 0.24 or 0.46. In contrast no fragmentation was observed with phenol as additive in sol−gel mixtures employing TEOS where A/P = 0.23 or 0.46, and transparent monolithic xerogels were obtained.

It is noteworthy that fragmentation to layers of thin plates was observed only when both type A organic additives and the silicate precursor possessed aryl substituent groups. When this was not the case fragmentation to granules occurred as for TEOS and TCA and 1,4-bis$(Cl_3SiCH_2)_2C_6H_4$ with crotonic acid.

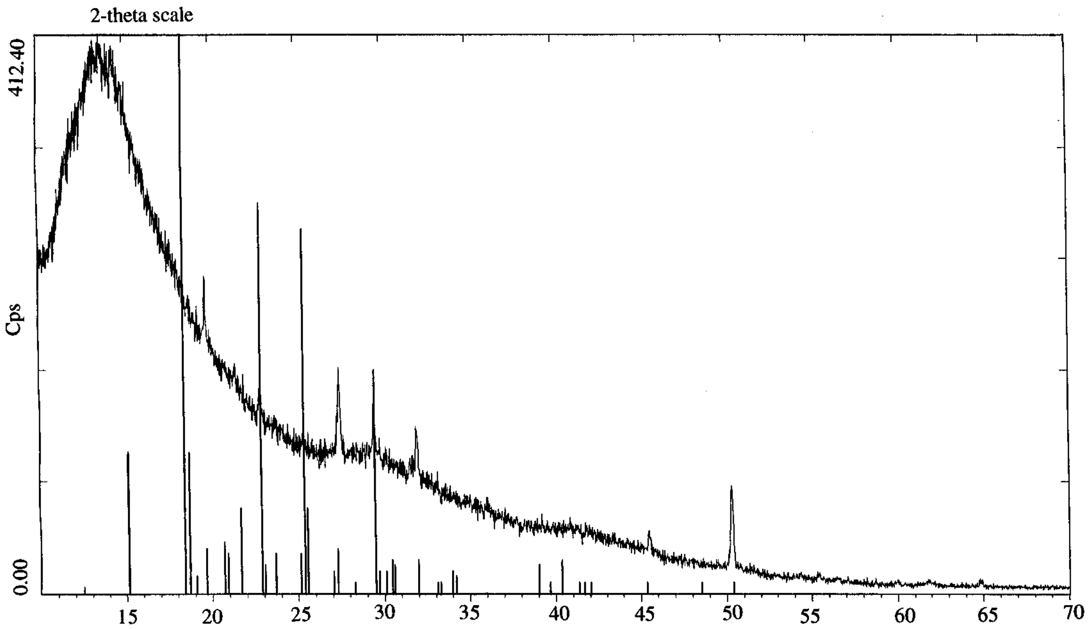

Figure 4. X-ray powder pattern of a single plate from X1TCA4 overlayed with measured pattern for TCA.

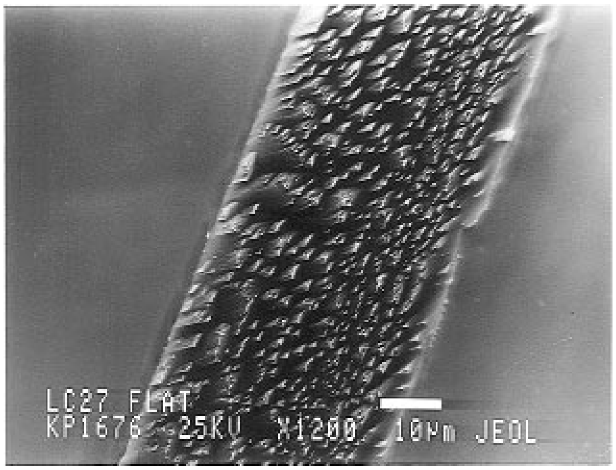

Figure 5. SEM of edge of a single plate from X1ClBA showing fractured edge and stacked ClBA crystallites. Bar = 10 μm.

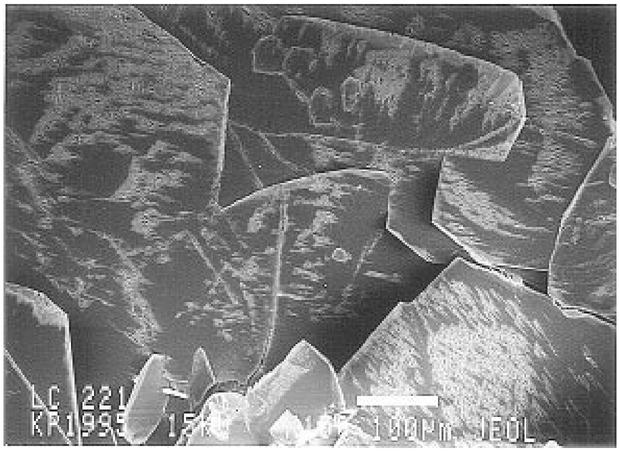

Figure 6. SEM of bulk material X1MNA (A/P = 0.2) showing plate-type fragmentation. Bar = 100 μm.

We were interested to see if similar behavior would result if dry monolithic additive-free glassy xerogels were exposed to solutions of types A and B organic additives. Thus a piece of monolithic xerogel X1, ~0.5 × 0.5 × 1.0 cm, was suspended in a saturated TCA solution in THF. The monolith fragmented into thin layers and granules within 12 h. A small piece of commercial cobalt(II)-doped silica gel (desiccant) behaved similarly when suspended in the TCA solution fragmenting into small granules within hours. Surface studies of the fragmented materials are underway.

These latter observations may be of interest in connection with use of additives as aids for the wet grinding of minerals where a variety of polymers and surfactants have been used as viscosity lowering agents for concentrated aqueous slurries.[19] In contrast with the effects of the TCA solution a piece of monolithic xerogel X1, ~0.5 × 0.5 × 1.0 cm, suspended in a concentrated THF solution of phenol remained intact during several weeks of observation. This is in keeping with the effects of phenol on monolith formation when used as an additive in sol–gel mixtures.

Porosity Measurements on Organic Additive-Treated Xerogel Materials following Soxhlet Extraction with THF. Continueous Soxhlet extraction (for several hours) of additive-treated materials with THF revealed that the incorporated TCA, ClBA, and PhOH is readily removed. The BET surface areas of these extracted materials are collated in Table 2.

Nitrogen sorption measurements on the residual silicate materials from X1TCA2, X1TCA3, and X1TCA4 and gave BET surface areas of 8.3, 72, and 8.67 $m^2\ g^{-1}$, respectively. The value for X1TCA3 is unexpectedly high compared to X1TCA2 and X1TCA4. These represent a considerable change compared to the additive-free material X1 which had a measured BET surface area of 460–600 $m^2\ g^{-1}$ and average micropore diameter of 20 Å. The extracted X1ClBA materials were essentially nonporous. The TEOS derived X3TCA2 material was also extracted with THF to remove TCA and the residual silicate had a measured BET surface area of 168 $m^2\ g^{-1}$, which is much lower than that reported for additive-free material produced in a similar fashion.

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Table 2. BET Surface Areas on Selected THF-Extracted Xerogels

xerogel[a]	bet surface area[b] (m^2 g^{-1})
X1[c]	460
X1TCA2	8.3
X1TCA3	72
X1TCA4	8.6
X1ClBA	<2
X1PhOH	357
X3TCA	168
X3PhOH	(323)[d] 790

[a] X1 derived from p-(Cl$_3$SiCH$_2$)$_2$C$_6$H$_4$; X3 derived from TEOS, TCA = *trans*-cinnamic acid; acid; ClBA = p-chlorobenzoic acid; PhOH = phenol. [b] Materials were extracted with THF. [c] Additive-free material (see ref 6). [d] Before extraction with THF.

In the case of the phenol-treated xerogel X1PhOH (A/P = 2), THF extraction removed ~50% of the encapsulated phenol from the monolithic xerogel (1.0 × 0.5 × 1.0 cm) without any visual cracking or fragmentation of the material, suggesting that in this case much of it is incorporated as an inert filler material. The measured BET surface area of the extracted phenol-treated material was 357 m^2 g^{-1} and average pore diameter (BJH adsorption) 32 Å which is close to that observed for the additive-free material. The phenol-treated xerogel X3PhOH (A/P = 0.46) had a BET surface area of 323 m^2 g^{-1}, but this increased to 790 m^2 g^{-1} following extraction of the phenol (100% recovered) into THF. These results on the extracted phenol-doped materials are particularly interesting and suggest that the phenol behaves as a template for the porous network since liberation of the phenol was not accompanied by collapse of the network.

Local Chemical Structure of Additive-Treated Xerogel Materials Derived from 1,4-bis(Cl$_3$SiCH$_2$)$_2$C$_6$H$_4$. To gauge the possible relative influence of the additives TCA, ClBA, and PhOH on the condensation process, the entire product from each X1TCA, X1ClBA, and X1PhOH experiment was powdered and dried under vacuum at 80 °C. These powders were analyzed by solid-state ^{13}C and ^{29}Si NMR spectroscopy using cross-polarization (CP) and magic-angle spinning (MAS). The ^{13}C spectra all show strong peaks for the aromatic groups of the organosilicate matrix (133.7 and 129.6 ppm) and peaks assigned to the $-$CH$_2$$-$ groups of the matrix (22.0 and 1.2 ppm) with assignments confirmed by nonquaternary suppression experiments as discussed in our previous work.[6] The peak due to the carboxylic acid group of TCA is also clearly visible (167.5−173.0 ppm). Peaks assigned to T^n (n = 0−3)[2] environments were observed in the ^{29}Si NMR spectrum at −18.0, −53.5, −62.7, and −70.3 ppm, respectively. There is no direct evidence to suggest the presence of Si−O−C(O)CH=CHPh residues. The absence of any peaks associated with Q^4 environments suggests that there was no significant cleavage of the silicon−carbon bonds under these conditions. The relative peak areas were measured, enabling the percentage condensation to be calculated, and the results are reported in Table 3. [A key to T^n notation used in this work appears in an earlier paper.[6] The peak areas were measured as previously described. In this previous work we found that peak areas measured for 2 ms contact time were within 1% of those corrected for the cross polarization process. The peak areas in the present work are uncorrected for CP.]

Table 3. Areas of the T^n Environments and Percentage Condensation Measured from ^{29}Si CPMAS NMR Spectra

sample	T^0	T^1	T^2	T^3	% condensation
X1	5.2	5.3	51.3	38.2	74.2
X1TCA2	20.3	3.5	50.6	25.7	60.7
X1TCA3	5.2	6.6	54.5	33.7	72.4
X1TCA4	12.8	4.8	58.7	23.7	64.6
X1PhOH	10.6	3.8	35.6	49.9	75.0
X1ClBA	11.7	6.5	44.3	37.5	69.4
X1ClBA[a]	6.4	10.7	45.8	37.3	71.4
X1ClBA1	18.0	4.6	41.8	35.6	65.1
X1ClBA1[a]	14.7	9.8	34.3	41.2	67.43

[a] THF extracted material.

The results are reproducible and show no systematic relationship between TCA loading and changes in relative distributions of T^n environments or overall percentage condensation. The relative distribution of T^n environments in additive free X1 and X1TCA3 (A/P = 1) are very similar (see X1TCA2 and X1TCA4 for comparison) with higher percent condensation for X1TCA3, compared to X1TCA2 and X1TCA4; the BET surface area of X1TCA3, 72 m^2 g^{-1}, was also significantly higher than found for X1TCA2 and X1TCA4. Thus the differences in both percent condensation and surface area between X1TCA and the dopant-free X1, each show a nonsystematic TCA loading effect. The T^n distribution is different for the two X1ClBA samples studied. It is noteworthy that the THF-extracted materials exhibit increased condensation particularly with respect to T^0 levels. The T^n distribution in the phenol additive-treated material X1PhOH, which showed no fragmentation, was very different from that in additive-free X1 especially with respect to the higher levels of condensation (T^2 and T^3) although overall percentage condensation is similar in both cases.

Conclusions

The effects of some organic additives on monolith formation in organosilicate and silica xerogels have been examined and at high loading levels apparently differ for additives for which molecular stacking is a structural feature compared to those for which it is not. A considerable number of reports have been devoted to additive effects on sol−gel processed materials, but effects that may be specific to structural features of additives of the type described in this paper have not, to our knowledge, been reported. While much further work is required, it is certainly the case that properties of materials formed where the sol−gel mixtures contained high concentrations of additives are considerably modified compared to those that are additive-free. Additives such as TCA which form stacked structures promote densification of the xerogel networks, while additives such as phenol which do not stack may possibly act as templates during construction of the porous networks. A study of the phenol-treated material X1PhOH and X3PhOH before and after extraction of the phenol revealed this novel templating potential in the production of porous networks by sol−gel processing. Further studies are in hand. While TCA loading effects were noted, no systematic correlation could be found between TCA loading and the distribution of T^n environments in X1 doped materials (from ^{29}Si CPMAS NMR) or measured surface areas of X1TCA extracted materials. The induced fragmentation of monolithic samples suspended in solutions of TCA may be of interest in connection with use of additives as grinding or dispersing aids.[19] A detailed study of the products of this fragmentation process is underway. Work is also underway to further systemize and to extend this work to other systems.

Experimental Section

The organosilicate precursors 1,4-bis($Cl_3SiCH_2)_2C_6H_4$ and 1,4-bis{$(EtO)_3Si$}C_6H_4 were made as previously described.[5,4] The organic additives were commercially supplied. The gel-forming compositions are given in Table 1. Scanning electron micrographs were obtained using JEOL JSM-3S and JEOL Jem-1200 Ex II scanning transmision electron microscopes. Energy-dispersive X-ray analysis utilized a LINK QX 2000 system. Samples were attached to a carbon holder using colloidal silver solution, analyzed by EDAX and then gold sputtered for SEM analysis. Surface area measurements were obtained using a Micromeretics ASAP 2000 instrument. The ^{13}C and ^{29}Si NMR spectra were acquired using cross polarization (CP) magic angle spinning (MAS), and high-power proton decoupling on a Bruker MSL-300 spectrometer. Typical conditions were 2 ms contact time, 1 s recycle delay, a 90° pulse length of 4.07 μs and a spinning speed of 4.5 kHz. The ^{13}C and ^{29}Si frequencies were 75.5 and 59.6 MHz, respectively. All spectra were recorded at room temperature, and chemical shifts are quoted relative to TMS.

General Procedure for Additive-Treated Xerogel Materials. Additive-Treated Xerogel Materials from 1,4-bis($Cl_3SiCH_2)_2C_6H_4$ or 1,4-bis{$(EtO)_3Si$}C_6H_4. In general a clear solution of the organic additive and 1.0 g of 1,4-bis-{$(EtO)_3Si$}C_6H_4 or 1,4-bis($Cl_3SiCH_2)_2C_6H_4$ in 10 cm^3 of THF was prepared in an inert atmosphere in a Pyrex round-bottomed flask and subsequently treated with 0.11 cm^3 of water (see Table 1 for A/P ratios). This mixture was vigorously stirred to a clear sol, transferred to a polyethylene bottle and left to gel. No precipitation was observed, and clear transparent gels subsequently formed. In the absence of any added organic additive gelation occurs over a period of 8−24 h, and the resulting dried xerogel is a transparent glassy material. In the presence of organic additives gelation occurred within 24 h in every case and within minutes when pinacol was used as additive. The wet gels were left to age for a further 24 h, after which drying commenced through 2 small (diameter ~1 mm) pinholes in the polyethylene bottle for 5 days. The whole sample was subsequently exposed to air for further slow drying for 3 weeks.

Additive-Treated Xerogel Materials from TEOS. To a stirred warm solution of TCA (1.03 g, 6.95 mmol) in dry ethanol (7.8 cm^3) was added TEOS (4.7 cm^3, 24 mmol). Water (1.73 cm^3) was added in one go, and the whole solution vigorously stirred under a dynamic nitrogen flow for 1 h at room temperature, affording a pale green sol. After 48 h standing under static nitrogen a pale green transparent gel formed, which became colorless after a further 2 days. This gel was then dried through a pinhole for 3 days and then fully exposed to air. During the next 3 weeks the xerogel completely fragmented until the whole sample was converted into small granules. The experiment was repeated with TCA (2.01 g, 14 mmol) with identical results.

An identical procedure was followed using phenol as additive at two different loadings A/P = 0.24, 0.46. In these cases transparent monolithic xerogels were obtained and no fragmentation was observed.

Additive-Treated Xerogel Materials from 1,4-bis[(n-BuO)$_3SiCH_2]_2C_6H_4$ and *m*-Nitroaniline (m-$(O_2N)C_6H_4NH_2$). A solution of 1,4-bis[(n-BuO)$_3SiCH_2$)]$_2C_6H_4$ (2.35 g, 3.92 mmol) in *n*-butanol (10 cm^3) was added to *m*-nitroaniline (0.5 g, 3.62 mmol), and the mixture was stirred to a clear yellow solution. To this solution was added in one go HCl (1.00 cm^3 of 1 mol dm^{-3} solution in H_2O) followed by vigorous stirring for 0.5 h in a dynamic nitrogen atmosphere. The bright orange sol formed was left to stand for 19 days under static nitrogen, and the transparent gel was aged a further 2 days before drying through pinholes commenced and continued for 5 days. The hard monolithic gel formed at this point was fully exposed to air. Fragmentation to layers occurred spontaneously during the next 7 days.

Physical changes which occurred during the drying stages in each case are listed in Table 1. Sol−gel mixtures containing type B organic additives phenol, and pinacol behaved like the additive-free gels on drying, giving monolithic xerogels. Sol−gel mixtures containing type A organic additives *trans*-cinnamic acid, crotonic acid, benzoic acid, and *m*-nitroaniline underwent fragmentation to layers or granules during these stages. The rate of fragmentation was considerably faster (~minutes) when the whole surface of wet gel samples was exposed to air omitting an initial period of slow drying through pinholes.

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