



NMR Studies on Hydrolysis and Condensation Reactions of Alkoxysilanes Containing Si–H Bonds

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Abstract. Hydrolysis and condensation reactions of four organically modified alkoxides, used for the preparation of silicon oxycarbide gel precursors, have been followed by ^{29}Si NMR. Triethoxysilane ($\text{HSi}(\text{OEt})_3$) and methyldiethoxysilane ($\text{MeHSi}(\text{OEt})_2$) react extremely fast compared to methyltriethoxysilane ($\text{MeSi}(\text{OEt})_3$) and tetraethoxysilane ($\text{Si}(\text{OEt})_4$). Co-hydrolysis reactions between different pairs of precursors— $\text{MeSi}(\text{OEt})_3/\text{Si}(\text{OEt})_4$; $\text{MeSi}(\text{OEt})_3/\text{HSi}(\text{OEt})_3$; $\text{MeHSi}(\text{OEt})_2/\text{Si}(\text{OEt})_4$; and $\text{MeHSi}(\text{OEt})_2/\text{HSi}(\text{OEt})_3$ —were investigated by solution state ^{29}Si and ^{17}O NMR. Despite significantly different reactivities between precursors, evidence for co-condensation reactions has been found for each system. Finally, two-dimensional ^{29}Si - ^1H heteronuclear correlation MAS-NMR spectroscopy was used to probe the local environments of the various Si sites in the product hybrid networks.

Keywords: precursor chemistry, hydrolysis, condensation, solution NMR, solid state NMR

1. Introduction

Hybrid silica xerogels containing Si–H and Si– CH_3 groups have been reported to be good precursors for silicon oxycarbide glasses [1]. Such glasses exhibit improved physical and mechanical properties compared to silica glasses and are excellent candidates for high-temperature materials [2]. Introduction of Si–H groups together with Si– CH_3 groups in a silica gel network can favor, after pyrolysis under argon, the formation of a carbon-rich silicon oxycarbide network, and strongly reduce the presence of free carbon [3].

The preparation of these gels usually involves the co-hydrolysis of two organically modified alkoxides, which serve as sources for Si–H and Si– CH_3 groups. The homogeneous distribution of Si–C bonds within the silica gel network, required to minimize phase separation in the final glass, may strongly depend on the reactivity towards hydrolysis of the different precursors.

In this work, four systems were investigated, which have already been reported as precursors for Si–C–O glasses [3]: $\text{MeSi}(\text{OEt})_3/\text{Si}(\text{OEt})_4$ (MTES/TEOS); $\text{MeSi}(\text{OEt})_3/\text{HSi}(\text{OEt})_3$ (MTES/TREOS); $\text{MeHSi}(\text{OEt})_2/\text{Si}(\text{OEt})_4$ (MDES/TEOS); and $\text{MeHSi}(\text{OEt})_2/\text{HSi}(\text{OEt})_3$ (MDES/TREOS), all with a 1/1 molar ratio between the two precursors, so that the number of Si–Me bonds per Si was constant (0.5), while the number of Si–H bonds per Si varied from 0 to 1. Hydrolysis and condensation reactions of the four individual alkoxysilanes were followed by ^{29}Si NMR to compare their reactivities. Then, co-hydrolysis reactions between the different pairs of precursors were investigated by solution state ^{29}Si and ^{17}O NMR to detect the formation of any co-condensed species. Finally, it was demonstrated that two-dimensional (2D) ^{29}Si - ^1H heteronuclear correlation MAS-NMR spectroscopy is a sensitive probe of the local environments of the various Si units in the product gel networks.

2. Experimental Section

All chemicals were used as received. Gels were prepared by co-hydrolyzing the corresponding two alkoxides in a 1/1 ratio under acidic conditions (EtOH/Si = 2; H₂O/OEt = 1; pH = 2(HCl)). The resulting solutions were aged in closed tubes at 60 °C for 24 h, for gelation to occur. Then, the gels were dried at 100 °C for several days.

The solution state NMR spectra were recorded on a MSL400 Bruker spectrometer. The samples were held in an 8 mm tube which was in turn placed in a 10 mm tube with C₆D₆ in the annulus as lock solvent. The references for chemical shift were tetramethylsilane for the ²⁹Si experiments and tap water for the ¹⁷O experiments. For the ¹⁷O NMR, 10 at.% enriched water (Isotec, Saint Quentin, France) was used as reactant. The notation X_{xy} will be used to describe the Si sites where X designates the type of Si sites, x the number of oxo bridges and y the number of silanol groups. X will be Q for SiO₄, T for MeSiO₃, T^H for HSiO₃ or D^H for HMeSiO₂ sites.

The 2D ²⁹Si-¹H heteronuclear correlation MAS-NMR experiments were performed on a Chemagnetics CMX-500 spectrometer. Experimental parameters used were as follows: 5 kHz spinning rate; 2.5 ms contact time, 3 s repetition time; 128 individual experiments with 8 scans each.

3. Results

3.1. Comparison of the Reactivities of the Various Precursors

The hydrolysis and condensation reactions of the four organically modified alkoxides, were followed by solution state ²⁹Si NMR (EtOH/Si = 2; H₂O/OEt = 1; pH = 2). The extent of condensation reaction was calculated for each precursor, according to the equation:

$$c = \sum_i \left(\frac{i \cdot x_i}{f} \right) \quad (1)$$

where x_i is the relative concentration of the X_{ij} silicon site, derived from NMR spectrum simulation, and f is the functionality of the monomer (2 for MDES, 3 for MTES and TREOS and 4 for TEOS).

The variation of c during the first two hours for the various precursors (Fig. 1) showed an extremely fast condensation rate for MDES and TREOS, compared

to MTES and TEOS. Within 10 min., condensation reactions were mostly completed for TREOS ($c > 80\%$) and MDES ($c > 90\%$), while they were in progress for MTES ($c \approx 15\%$) and just started for TEOS ($c \approx 5\%$). After 2 hours, c reached 40% for MTES and 20% for TEOS, and after 10 hours 55% for TEOS and 75% for MTES. These last results agree with previous report showing the higher reactivity of MTES, compared to TEOS, under acidic conditions [4]. Electronic inductive effects could be responsible for the high reactivity of the Si-H containing alkoxysilanes. However, the linear correlation existing between the paramagnetic screening factor and the net charge at the silicon atom in the [-40; -120 ppm] chemical shift range [5], indicates that the charge at the Si center in TREOS is intermediate between that of TEOS and MTES. Reactivity of TREOS would thus be expected to be intermediate between that of MTES and TEOS. Steric effects, with the presence of the very small H-substituent that will favor nucleophilic attack of the water molecule at the Si center, could therefore explain the differences in hydrolytic behavior. Similar observations have already been reported for alkoxysilanes with R groups of different sizes [6].

One point should be considered: due to the large difference in reactivities, co-hydrolysis of MDES and TEOS, or MTES and TREOS could lead to inhomogeneous distribution of the two types of Si units within the siloxane network, and thus of the Si-C bonds, that could promote the presence of C-rich regions in the final oxycarbide glass. Actually, Fig. 1 shows that addition of TREOS to MTES, or MDES to TEOS, leads to a marked increase in the extent of reaction of the less reactive units. Even if not a direct proof, this strongly suggests that co-condensation reactions between the two types of units occur.

3.2. Evidence for Co-Condensation Reactions

The four solutions (MTES/TEOS; MDES/TREOS; MDES/TEOS; MTES/TREOS) were hydrolyzed with a low amount of water ($h = 0.1$) and aged for 2 days. The resulting sols were characterized by ²⁹Si and ¹⁷O NMR to investigate the formation of co-condensed species. The presence of short oligomers (monomers, dimers and trimers) facilitated high resolution of the ²⁹Si NMR spectra. On the other hand, ¹⁷O NMR signals are always broad, and this is attributed to short relaxation times of the quadrupolar oxygen nuclei. Variable-temperature experiments were tried for increasing

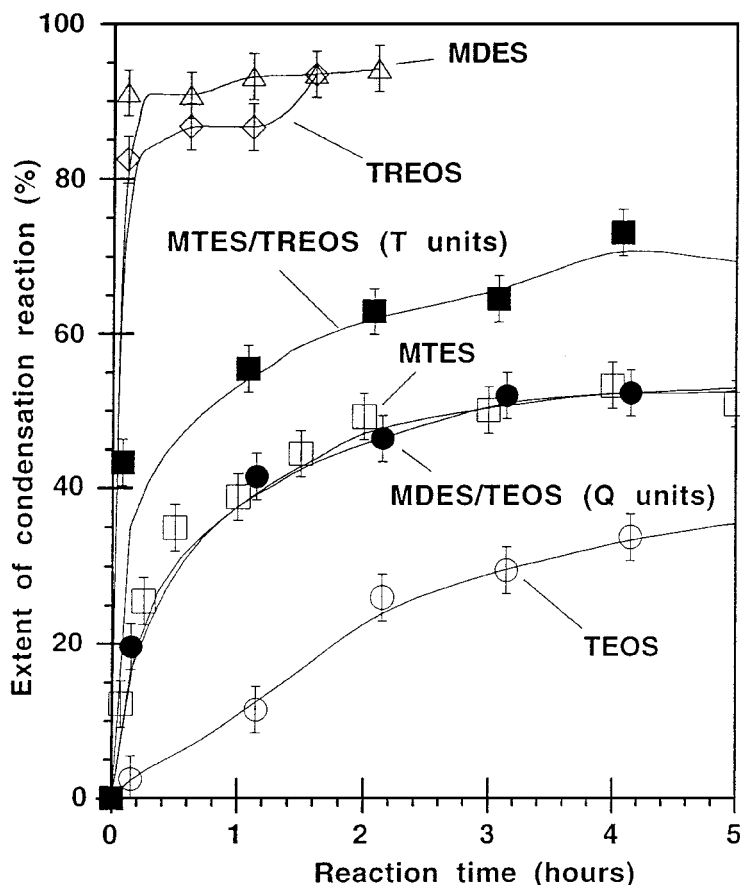
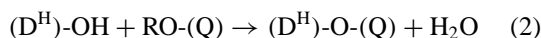


Figure 1. Evolution versus time of the extent of condensation reaction for MDES ($\text{MeHSi}(\text{OEt})_2$), MTES ($\text{MeSi}(\text{OEt})_3$), TREOS ($\text{HSi}(\text{OEt})_3$) and TEOS ($\text{Si}(\text{OEt})_4$), as well as MTES/TREOS (T units) and MDES/TEOS (Q units) mixtures. ($\text{EtOH}/\text{Si} = 2$; $\text{H}_2\text{O}/\text{OEt} = 1$; $\text{pH} = 2$).

resolution, but only a modest result was obtained on the MTES/TEOS system [7].

- **MTES/TEOS system:** evidence for co-condensation reactions between MTES and TEOS can be seen on the ^{29}Si and ^{17}O NMR spectra (Fig. 2(a)) as already reported in the literature [8–10].
- **MDES/TREOS system:** for the MDES/TREOS system, co-condensation could be clearly seen by the presence of new ^{29}Si resonance signals [11], but similar chemical shift values for $(\text{D}^{\text{H}})\text{-O}(\text{D}^{\text{H}})$, $(\text{T}^{\text{H}})\text{-O}(\text{T}^{\text{H}})$ and $(\text{D}^{\text{H}})\text{-O}(\text{T}^{\text{H}})$ sites prevented similar conclusions from the ^{17}O NMR experiments (Fig. 2(b)).
- **MDES/TEOS system:** formation of $(\text{D}^{\text{H}})\text{-O}(\text{Q})$ sites can be clearly seen on the ^{17}O NMR spectrum (Fig. 2(c)). The spectrum of the hydrolyzed solution of MDES presents mainly two peaks at 59.7 and 62.0 ppm assigned to $\text{D}_1^{\text{H}}\text{-D}_1^{\text{H}}$ and $\text{D}_1^{\text{H}}\text{-D}_2^{\text{H}}\text{-D}_1^{\text{H}}$ species. No clear evidence for $(\text{D}^{\text{H}})\text{-OH}$ groups was found. On

the contrary, the spectrum of a solution of TEOS hydrolyzed under the same conditions, showed a main peak at 14.6 ppm due to $(\text{Q})\text{-OH}$ groups and a peak at 29.7 ppm due to $(\text{Q})\text{-O}(\text{Q})$ sites, confirming the much lower extent of condensation reaction. The hydrolyzed solution of the mixture of MDES and TEOS is characterized by a main peak at 46 ppm which corresponds to $(\text{D}^{\text{H}})\text{-O}(\text{Q})$ sites, with two additional peaks due to $\text{D}_1^{\text{H}}\text{-D}_1^{\text{H}}$ and $\text{D}_1^{\text{H}}\text{-D}_2^{\text{H}}\text{-D}_1^{\text{H}}$ species. No evidence for $(\text{Q})\text{-OH}$ or $(\text{Q})\text{-O}(\text{Q})$ sites could be found, suggesting that either TEOS does not hydrolyze, due to its much lower reactivity, and thus $(\text{D}^{\text{H}})\text{-O}(\text{Q})$ sites are formed as follows:



or TEOS hydrolyzes, but then reacts preferentially with $(\text{D}^{\text{H}})\text{-OX}$ groups ($\text{X} = \text{H}$ or R).

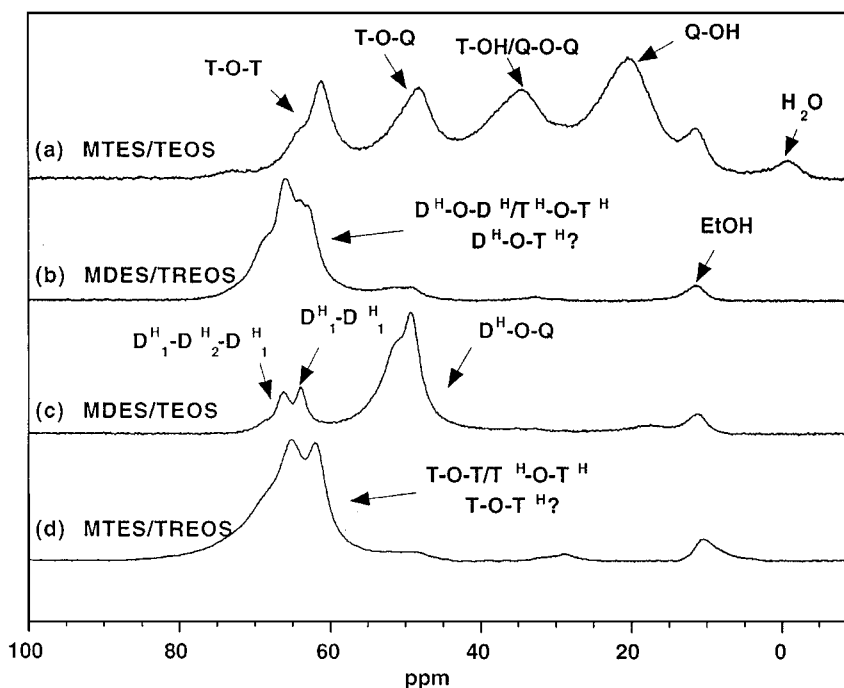


Figure 2. Solution state ^{17}O NMR spectra of hydrolyzed solutions of: (a) MTES/TEOS; (b) MDES/TREOS; (c) MDES/TEOS and (d) MTES/TREOS (EtOH/Si = 2; $\text{H}_2\text{O}/\text{OEt}$ = 0.1; pH = 2).

Co-condensation reactions were also confirmed by ^{29}Si NMR experiments, with peaks at -87.1 ppm ($\text{Q}_{10}^*-\text{D}^{\text{H}}$) and at -93.5 ppm ($\text{Q}_{20}^*-\text{D}^{\text{H}}$). Peaks due to Q_{10}^*-Q and Q_{20}^*-Q , expected at -88.1 and -95.4 ppm, were not present.

- **MTES/TREOS system:** as for the MDES/TREOS system, ^{17}O NMR (Fig. 2(d)) is not a good technique to characterize the formation of (T)-O-(T^{H}) sites, because of the similarity between the chemical shift values of (T)-O-(T) sites ($\delta = 57$ ppm) [9] and (T^{H})-O-(T^{H}) sites ($\delta = 58\text{--}60$ ppm) [11]. Evidence for the formation of co-condensed species was obtained from the ^{29}Si NMR spectrum with peaks at -49.7 ppm ($\text{T}_{10}^*-\text{T}^{\text{H}}$) and -57.3 ppm ($\text{T}_{20}^*-\text{T}^{\text{H}}$), instead of -50.2 ppm and -58.3 ppm for T_{10}^*-T and T_{20}^*-T , respectively. Similarly, to the MDES/TEOS system, the less reactive units (i.e., T units) seemed to condense preferentially with the most reactive ones (i.e., T^{H} units). No signal due to T^*-T species was seen.

At low hydrolysis ratio ($h = 0.1$), evidence for the formation of co-condensed species was found in all the four systems, even when a large difference in reactivity exists between the precursors, such as in the

MDES/TEOS and MTES/TREOS systems. This suggests that the condensation mechanism, as described in Eq. (2), should occur to a large extent.

For a higher h value ($h = 1$), extensive condensation leads to a broadening of the ^{29}Si resonance signals, preventing any definitive conclusions on the formation of co-condensed species, and their stability versus time. For the MTES/TEOS system with $h = 0.5$, the condensation reactions were followed by ^{17}O NMR [10]: a peak due to (T)-O-(Q) sites was clearly identified around 45 ppm, whose intensity increased versus time. For the other three systems, a loss of ^{17}O NMR signal was observed for $h = 1$, preventing any site identification. This suggests that in the presence of a highly reactive precursor (MDES and/or TREOS), high molecular weight polymers are rapidly formed, incorporating through co-condensation reactions, the less reactive units, which cannot be detected.

3.3. $2\text{D } ^{29}\text{Si}-^1\text{H}$ Heteronuclear Correlation MAS-NMR Spectroscopy on Gel Networks

Product gel networks can be investigated by $2\text{D } ^{29}\text{Si}-^1\text{H}$ heteronuclear correlation MAS-NMR spectroscopy.

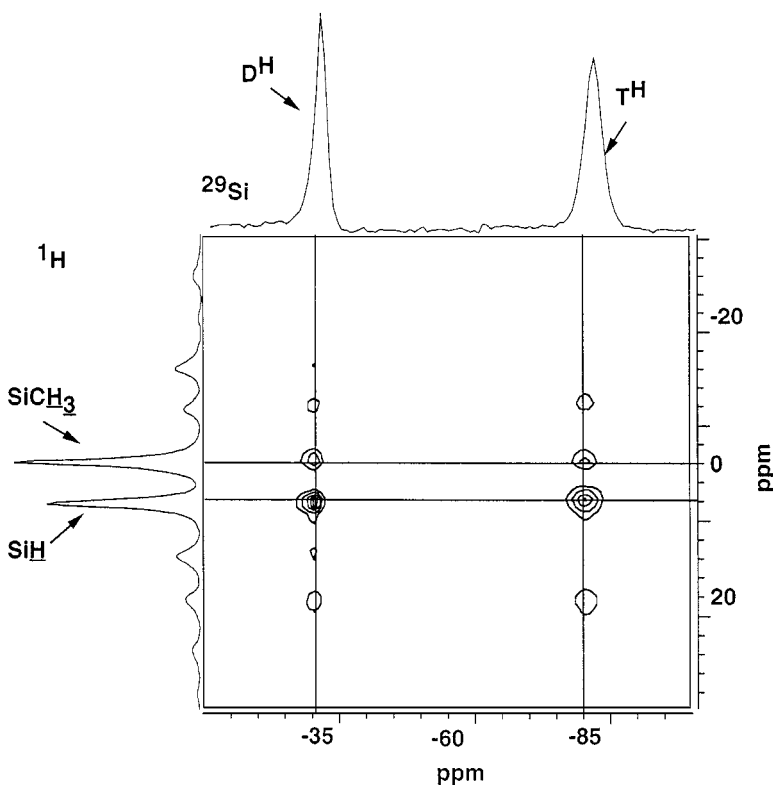


Figure 3. A 2D ^1H - ^{29}Si heteronuclear correlation NMR spectrum (contour plot) obtained for a gel prepared from co-hydrolysis of MDES and TREOS in a 1/1 ratio ($\text{EtOH}/\text{Si} = 2$; $\text{H}_2\text{O}/\text{OEt} = 1$; $\text{pH} = 2$).

This sequence was first introduced to characterize surface species on silica and zeolite [12] and has already been applied to different siloxane-silica systems prepared from MTES and TEOS [13], or PhTES and TEOS [14].

Figure 3 shows the results of the ^{29}Si - ^1H connectivity experiment carried out on a gel prepared by co-hydrolyzing MDES and TREOS. One should first note that MAS at 5 kHz gave good resolution on the one-dimensional (1D) ^1H NMR spectrum. This is related to the presence of motions that could partially average the strong ^1H - ^1H dipolar couplings. In this particular system, the average functionality of the Si units was rather low ($f = 2.5$) and a glass transition temperature at -43°C has been reported [11]. It was possible to distinguish clearly the $\text{Si}-\text{CH}_3$ ($\delta = 0$ ppm) and $\text{Si}-\text{H}$ ($\delta = 4.5$ ppm) signals, and thus to identify the sources of polarization transfer. This is why this 2D sequence is so powerful compared to the equivalent 1D sequence: protons responsible for the polarization transfer to a given Si site can be identified, and thus spatial prox-

imity established. In this example, there is, as expected, a connectivity between the D^{H} units and the protons of the methyl groups, but more interestingly, there is also a connectivity between these protons and the T^{H} units which indicates the proximity between the D^{H} units (bearing CH_3 groups) and the T^{H} units, and the absence of clearly separated domain structures.

4. Conclusions

The objective of this paper was to characterize with NMR techniques four different alkoxy silane systems, which have been reported as precursors for silicon oxycarbide glasses, $\text{MeSi}(\text{OEt})_3/\text{Si}(\text{OEt})_4$ (MTES/TEOS); $\text{MeSi}(\text{OEt})_3/\text{HSi}(\text{OEt})_3$ (MTES/TREOS); $\text{MeHSi}(\text{OEt})_2/\text{Si}(\text{OEt})_4$ (MDES/TEOS); and $\text{MeHSi}(\text{OEt})_2/\text{HSi}(\text{OEt})_3$ (MDES/TREOS). It is important to know whether the $\text{Si}-\text{C}$ bonds are uniformly distributed within the product siloxane network, which could help the formation of a compositionally homogeneous oxycarbide network, after pyrolysis.

Hydrolysis and condensation reactions of the four organically modified alkoxides involved in the preparation of the starting gels, have been followed by solution state ^{29}Si NMR. Under acidic conditions ($\text{pH} = 2$) and with a hydrolysis ratio of 1 ($h = \text{H}_2\text{O}/\text{OEt}$), the alkoxysilanes with Si—H bonds (TREOS and MDES) reacted extremely fast compared to MTES and TEOS: this was attributed to steric, rather than electronic effects. The small H-group facilitated the nucleophilic attack of the water molecule at the Si center. However, despite large differences in reactivities that exist between several precursors, evidence for co-condensation reactions was found in all four systems hydrolyzed with a low amount of water ($h = 0.1$), using solution state ^{29}Si and ^{17}O NMR techniques. For a higher hydrolysis ratio ($h = 1$), the fast condensation reactions in MDES/TREOS, MDES/TEOS and MTES/TREOS lead to a broadening of the ^{29}Si resonance signals as well as a loss of the ^{17}O signal intensity, preventing any precise information concerning the formation and stability of co-condensed species in those systems.

Finally, two-dimensional ^{29}Si - ^1H heteronuclear correlation MAS-NMR spectroscopy was found to be a sensitive probe of the local environments of the various Si sites in hybrid networks. It has been demonstrated that the two types of Si units in a gel prepared from MDES and TREOS were mixed in the product network. However, the details concerning the degree of mixing have not been established in a quantitative

manner by the present results. Further investigations are in progress on the other systems.

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