

Structural Characterization of Sol-Gel Derived Oxycarbide Glasses. 1. Study of the Pyrolysis Process

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A gel resulting from the cohydrolysis of dimethyldiethoxysilane, a siloxane precursor, and tetraethoxysilane, a silica precursor, has been pyrolyzed to a silicon oxycarbide network. This conversion has been carefully characterized using various structural techniques: thermogravimetric analysis coupled with mass spectrometry, multinuclear solid-state magic angle spinning nuclear magnetic resonance (^{29}Si , ^1H , and ^{13}C), infrared spectroscopy, and electronic spin resonance. The pyrolysis process can be divided in two main stages. In the 400–650 °C temperature range, redistribution reactions between Si–O and Si–C bonds occur with evolution of low molecular weight siloxanes. New Si sites are created, but the methyl groups remain intact. From 650 to 1000 °C, the conversion of the polymeric network into an inorganic material takes place. Cleavage of C–H, Si–C, but also Si–O bonds occurs with evolution of methane, hydrogen and water. Aromatic carbon units are formed. Heat treatment at 1000 °C in argon flow leads to the formation of an amorphous silicon oxycarbide phase, characterized by $\text{SiC}_x\text{O}_{4-x}$ units. The presence of a free carbon phase has also been shown.

Introduction

Mechanical properties of silica glass may be improved by cationic and also anionic substitution. Conventional melting processes were first used to substitute divalent oxygen atoms by tetravalent carbon atoms. Silicon carbide was used as carbon source. Its incorporation did not exceed 0.5 wt %, because the high temperatures required resulted in carbon oxidation. Nevertheless, mechanical properties were improved.^{1,2}

The sol-gel process is currently used to obtain oxide ceramics, allowing formation of monolithic pieces, fibers, and coatings. It appeared as a very attractive way to incorporate carbon in a silica network resulting in silicon oxycarbide glasses, also called "black glasses". Gels containing Si–C bonds can be easily obtained, using a hydrolysis reaction of modified silicon alkoxides $\text{R}_n\text{Si}(\text{OR}')_{4-n}$ where R is an alkyl or aryl group. Pyrolysis of such gels leads to an oxycarbide glass. During the firing process, Si–C bonds should be maintained and C–H bonds should be substituted by C–Si bonds. Several studies on the pyrolysis chemistry of siloxane materials containing Si–CH₃ or Si–C₆H₅ groups have already been reported in the literature.^{3–14} The formation of a silicon oxycarbide

phase was proven by ^{29}Si MAS NMR.⁷ However, in all cases, a free carbon phase was present in the glassy state. Successful attempts to minimize this carbon phase has been achieved, by introducing Si–Si¹⁵ or Si–H^{16,17} bonds in the gel precursor.

These polymeric-derived oxycarbides are of interest for their high-temperature strength and chemical stability. They also exhibit high resistance to crystallization and oxidation at temperatures above 1000 °C.¹¹ Potential applications have been considered in the field of glass fibers and composite matrices.^{18,19}

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The objective of the present work was not to prepare carbon free oxycarbide but to understand the chemistry involved in the firing process of siloxane gels containing Si-CH₃ groups. They have been prepared by cohydrolysis of tetraethoxysilane (TEOS) and dimethyldiethoxysilane (DEDMS) in a 1/1 ratio. They were pyrolyzed from 400 to 1000 °C under flowing argon and the samples have been carefully characterized by thermogravimetric analysis coupled with mass spectrometry (TG/MS), multinuclear solid-state magic angle spinning nuclear magnetic resonance (MAS NMR, ²⁹Si, ¹H, and ¹³C), electronic spin resonance (ESR), and infrared spectroscopy (IR).

Experimental Section

Sample Preparation. Gels were prepared by mixing TEOS (Fluka) and DEDMS (Fluka) in a 1/1 ratio. Acidic water (HCl, pH = 2) was then added (H₂O/TEOS = 6). No alcohol was used as solvent. Water was not miscible, but the solution became clear within a few minutes under magnetic stirring. The sol was then poured into plastic tubes and air dried at room temperature. The solution gelled within about 2 days. Samples were finely ground and pyrolyzed under flowing argon (10 °C/min) at various temperatures with a 10-min plateau at the maximum temperature.

Characterization. TGA experiments were run using a Netzsch STA409 thermobalance. About 20 mg of the sample was heated in an alumina crucible from room temperature to 1200 °C at 10 °C/min in an argon flow (50 mL/min). This analyser was interfaced to a Kenos KSM88 quadrupole mass spectrometer (MS). The volatiles evolved during the pyrolysis were collected by a stainless steel capillary heated to 150 °C. This capillary was placed in the furnace above the sample and was connected to the MS through a 32- μ m diaphragm. The ionization energy was 75 eV. During the pyrolysis, one scan from 2 to 150 amu was collected every 30 s and stored. It allows the different gases evolved during the pyrolysis to be identified. Loss of heavy condensable compounds such as oligomers may not be detected by MS although a weight loss will be apparent on the TGA curve. Evolution of water during the pyrolysis was detected in a continuous process using a quadrupole mass spectrometer (MS), Quadrex 200, 70 eV, electron impact) coupled to a TGA (B60 Setaram).

Elemental analyses were performed by the Service Central d'Analyse du CNRS, Vernaison, France.

Solid-state NMR spectra were recorded on a Bruker MSL 400 spectrometer. A pulse width of 2 μ s ($\theta \approx 30^\circ$) and recycle delays of 60 s were used for ²⁹Si spectra (79.5 MHz); 800–1000 transients were recorded for pyrolyzed samples. Short flip angles along with relatively long delays between pulses were chosen to overcome the problem of long relaxation times for ²⁹Si NMR. Cross polarization (CP) technique was also used to record ²⁹Si MAS-NMR spectra with contact times of 2 ms. Pulse widths of 2 μ s and delays of 2 s were used for ¹H (400 MHz) spectra. ¹³C CP MAS NMR spectra (100.6 MHz) were recorded with contact times of 1 ms and recycle delays of 6 s; 100 transients were accumulated for samples pyrolyzed to temperatures ≤ 600 °C. For pyrolysis temperatures greater than 600 °C, 1000–7000 transients were recorded. Spinning rates of 4 kHz were used for ²⁹Si and ¹³C NMR spectra, whereas a 15-kHz spinning rate was used for ¹H NMR spectra to get a better averaging of the dipolar interactions. Si sites will be labeled with the X, M_n, D_n, T_n, and Q_n notation, referring respectively to SiC_{4-x}O_x sites with x = 0, 1, 2, 3, or 4 and n the number of bridging O surrounding Si. The spectra were simulated with the program WINFIT.²⁰

Samples were analyzed by IR spectroscopy using KBr pellets between 200 and 4000 cm⁻¹ on a Perkin-Elmer 783 spectrometer.

ESR experiments were run at room temperature on a Varian E09 spectrometer with a microwave resonance frequency at about

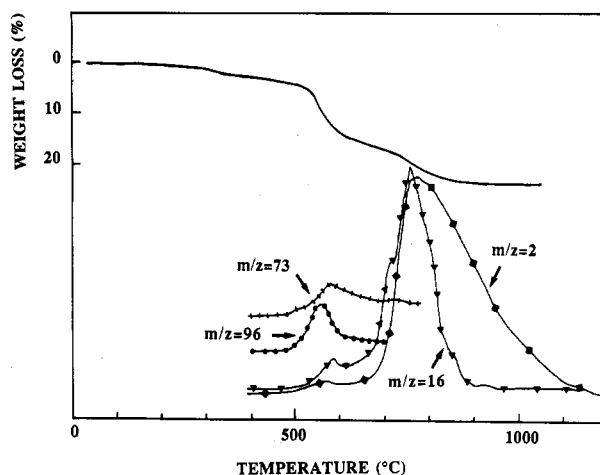


Figure 1. TG-MS analysis under argon (10 °C/min) of the dried gel.

Table 1. Pyrolysis Results: Ceramic Yields (Y) and Composition (wt %) of Residues

	%C	%H	%Si	%O ^a	Y	Δ Si	empirical formula
precursor	16.9	4.0	40.5	38.6			SiC _{0.97} H _{2.8} O _{1.67}
400 °C	16.7	4.2	41.2	37.9			SiC _{0.94} H _{2.8} O _{1.61}
600 °C	14.7	3.2	41.8	40.2	0.91	5	SiC _{0.82} H _{2.2} O _{1.68}
800 °C	11.5	1.4	45.8	41.3	0.80	8	SiC _{0.59} H _{0.8} O _{1.57}
1000 °C	11.2	1.0	46.5	41.2	0.78	14	SiC _{0.56} H _{0.6} O _{1.55}

^a %O has not been analyzed but was calculated assuming that %O = 100 - %C - %Si - %H.

9.1 GHz. Spin densities, in number of spins per gram of sample, were estimated by comparing integrated signal intensities of the sample with that of a reference sample containing a known number of Cu²⁺ ions.

Nitrogen specific surface area at 77 K was determined from BET analysis using a molecular cross-sectional area of 0.162 nm². Nitrogen adsorption isotherms were measured using Carlo Erba (Soptomatic 1800) equipment.

Results

The general pathway in which a siloxane polymer is thermally decomposed into a silicon oxycarbide can be seen from TG/MS curves (Figure 1). An initial small weight loss (2.3%) can be detected from 200 to 400 °C with evolution of water ($m/z = 18$), which indicates a dehydration of the product, resulting from the condensation of the remaining hydroxyl groups. The second weight loss between 400 and 650 °C is more important (12.5%), involving a loss of volatiles with fragments $m/z = 96$, 133 and 73, 147. The first two fragments, due to [C₄H₁₂Si₃O₃²⁺] and [C₃H₉Si₂O₂⁺], are characteristic of cyclic siloxanes [(CH₃)₂SiO]₃.²¹ The fragment with $m/z = 73$ [C₃H₉Si⁺] is due to linear polysiloxane (CH₃)₃Si-O[(CH₃)₂SiO]_xSi-(CH₃)₃ ($x = 0$ or 1) and/or tetramethylsilane. The fragment with $m/z = 147$ [(CH₃)₅Si₂O⁺] is due to the fragmentation of polysiloxanes (CH₃)₃Si-O-Si(CH₃)₃ or (CH₃)₃Si-O[(CH₃)₂SiO]_xSi(CH₃)₃.²² The last weight loss (8%) occurred between 650 and 1000 °C with evolution of methane ($m/z = 16$) and hydrogen ($m/z = 2$).

Elemental analyses were performed on the fired samples (Table 1). Loss of silicon can be estimated using the formula introduced by Mutin et al.:¹⁵

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$$\Delta\text{Si} = 100[(\% \text{Si})_0 - Y(\% \text{Si})_T]/(\% \text{Si})_0 \quad (1)$$

where $(\% \text{Si})_0$ and $(\% \text{Si})_T$ are the Si mass percentages in the precursor and in the sample pyrolyzed at a temperature T , and Y is the mass yield. Loss of silicon occurs between 600 and 1000 °C. Evolution of the C/Si and H/C ratios were reported in Figure 2. From 400 to 1000 °C, both ratios decrease from 1 to 0.5 and from 3 to 1, respectively. These results can be correlated with evolution of gases, such as siloxanes, methane, and hydrogen.

Structural evolution of the pyrolyzed samples has been investigated using ^{29}Si , ^{13}C , and ^1H MAS NMR and infrared spectroscopy. The ^{29}Si MAS NMR spectra were recorded using single-pulse experiments (Figure 3a) as well as cross-polarization technique (Figure 3b). This technique is very efficient due to the large number of protons present in the samples pyrolyzed at $T \leq 800$ °C. The spectra of the gel consist of three resonances at -18, -100, and -110 ppm due to D_2 , Q_3 , and Q_4 sites respectively.²³ The spectra of the 400 °C sample does not show many changes, except a decrease in the Q_3 units due to condensation reactions which transforms the Q_3 into Q_4 units. It shows the good thermal stability of the samples. In the spectrum of the 600 °C sample, two additional resonances are observed at 7 and -67 ppm assigned to M (C_3SiO) and T (CSiO_3) units.²³ These units are formed by Si-O and Si-C bond redistribution as already mentioned in the literature.^{22,24} The following are possible redistribution reactions between the Si units:



NMR line widths remain constant up to 600 °C showing that the local order around silicon units is preserved during the redistribution reactions (Figure 4). But between 800 and 1000 °C, the widths of all the signals strongly increase from 500 to 1500 Hz, indicating a large disordering in the Si environments.

Evolution of the chemical shifts of D and T sites versus temperature (Figure 5), shows a pronounced upfield shift between 600 and 1000 °C. The values are characteristic of the presence of oxo bridges bonded to the Si sites. The observed shift in the peak positions can not be attributed to condensation of silanol groups. Similar observations were already reported in the study of the conversion of polycarbosilane into silicon carbide²⁵ and of polysilazane in silicon carbonitride.²⁶ They were assigned to changes in the environments of C atoms bonded to Si atoms, which become less protonated.

The ^{29}Si MAS NMR spectra were recorded with small pulse angles ($\approx 30^\circ$) and relatively long recycle delays (60 s), to allow quantitative analysis of the data. Due to the high number of scans necessary to get a reasonable signal-to-noise ratio (800–1000 for pyrolyzed samples), it was not possible to measure T_1 relaxation times. An attempt to use longer delays (300 s) showed no changes in the

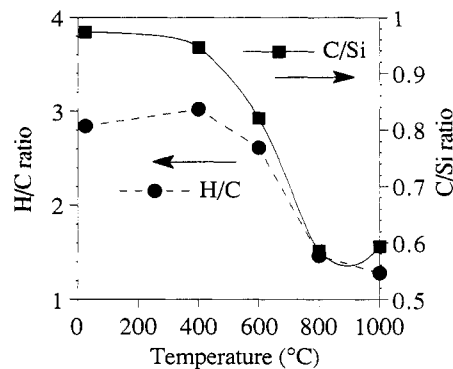


Figure 2. C/Si and H/C ratios from chemical analysis on pyrolyzed samples.

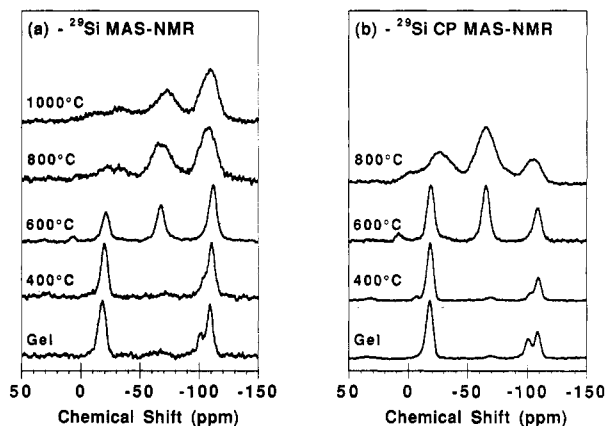


Figure 3. ^{29}Si MAS NMR spectra of pyrolyzed samples: (a) single-pulse experiments; (b) cross-polarized experiments.

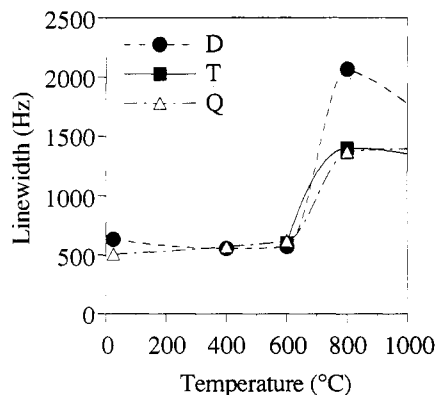


Figure 4. Variation of ^{29}Si NMR line widths versus pyrolysis temperature.

relative intensities of the various peaks. The set of chosen parameters was considered as a good compromise. The spectra were thus simulated and the percentages of various Si sites extracted. The number of Si-C bonds per Si sites was calculated by the following relation $n_{\text{Si-C}} = ([\% \text{T}] + 2[\% \text{D}] + 3[\% \text{M}] + 4[\% \text{X}])/100$ (Figure 6). The starting point is in agreement with the gel composition found from elemental analysis. Then the curve shows a decrease of the Si-C bonds above 400 °C which become more important between 600 and 800 °C.

However, the ^{29}Si NMR spectrum shows the presence of Si-C bonds even in the sample pyrolyzed at 1000 °C. The spectrum can be simulated with four components at -109 ppm (55%), -72 ppm (35%), -32 ppm (8%), and -8 ppm (2%). The first three resonances can be assigned respectively to Q, T, and D units. The last signal can be

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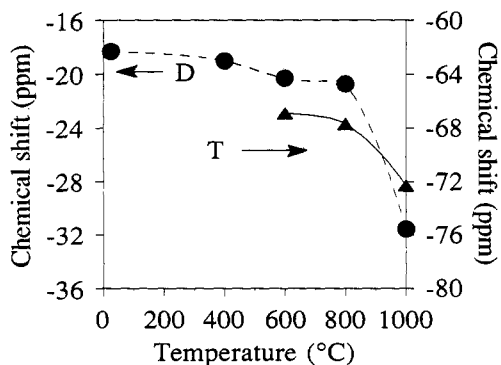


Figure 5. Variation of chemical shift values of the various $\text{SiC}_x\text{O}_{4-x}$ units in the pyrolyzed samples.

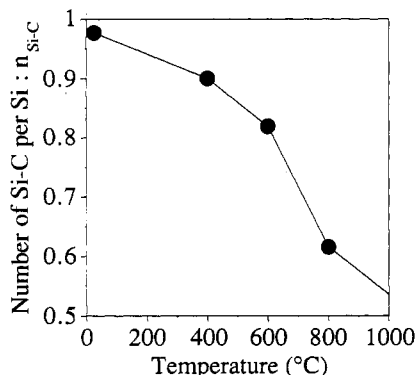


Figure 6. Evolution of the average number of Si-C bonds per Si site ($n_{\text{Si-C}}$) in the pyrolyzed samples.

due to M or X units. The number of Si-C bonds per Si can thus be estimated to 0.58 ± 0.01 . Assuming that each O is only bonded to Si,^{11,50} a O/Si ratio of 1.71 is found. Chemical analysis gave 1.57, so the O/Si ratio can thus be estimated using both analyses to 1.64 ± 0.07 .

The conversion from a polymeric state to a glassy material was monitored by the changes in the IR transmission (Figure 7). The spectrum of the gel shows bands characteristic of D units at 1260 cm^{-1} [$\delta(\text{SiCH}_3)$], 865 cm^{-1} [$\rho_s(\text{SiCH}_3)$] and 800 cm^{-1} [$\nu_{\text{as}}(\text{Si-C})$; $\rho_{\text{as}}(\text{SiCH}_3)$] as well as bands due to the silica network, $\nu_{\text{as}}(\text{Si-O})$ at $1030\text{--}1080 \text{ cm}^{-1}$ and $\delta(\text{Si-O-Si})$ at 390 cm^{-1} .^{27,28} The bands due to O-H groups, $\nu(\text{O-H})$ around 3500 cm^{-1} or H_2O , $\delta(\text{H-O-H})$ at 1630 cm^{-1} are weak, revealing the hydrophobic character of these gels. The IR spectrum of the 600°C sample shows the same bands indicating that the methyl groups are retained in the network at this temperature. Great modifications occur from 600 to 800°C : the bands due to the CH_3 groups strongly decrease while new bands appear at 1360 cm^{-1} assigned to the stretching vibration of the SiCH_2Si groups,²⁹ and at 2100 and 880 cm^{-1} due to the formation of Si-H bonds.^{29,30} The absorption coefficient for the Si-H stretching vibration is high, and thus the weak band at 2100 cm^{-1} corresponds to a small amount of Si-H bonds present in the sample. Presence of OH groups and/or water is also clearly visible with a large band at 3400 and one at 1620 cm^{-1} . A shoulder is present around 3500 cm^{-1} which can be attributed to Si-OH groups. A broad band is also present at 1900 cm^{-1} and could be due to the presence of allene ($\text{C}=\text{C}=\text{C}$) sites in this sample.³¹

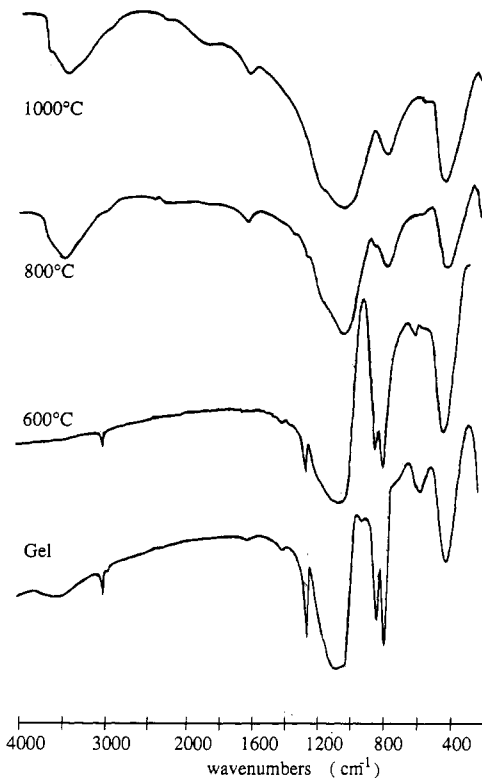


Figure 7. Infrared spectra of the pyrolyzed samples.

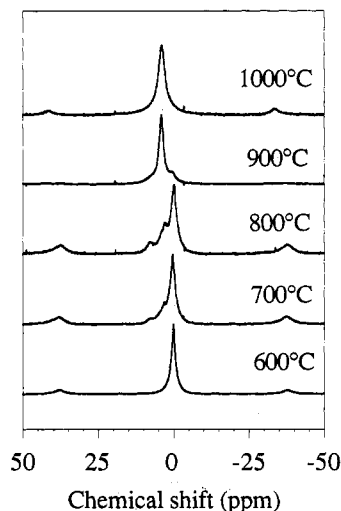


Figure 8. ^1H MAS NMR spectra of the pyrolyzed samples.

The ^1H NMR spectra of the pyrolyzed samples are shown in Figure 8. The gel is characterized by two signals due to Si- CH_3 groups^{32,33} (0 ppm) and Si-OH groups (3 ppm).³⁴ The spectrum of the 600°C sample exhibits only the resonance at 0 ppm. The disappearance of the peak due to Si-OH groups confirms that condensation reactions occurred between silanol groups. New peaks appear in the samples pyrolyzed at 700 and 800°C at 3 ppm, 4.2 ppm, and 8 ppm. The two first peaks can be assigned respectively to terminal species SiH or SiOH groups and H_2O and this suggests the cleavage of Si-O bonds.^{34,35} The other peak at 8 ppm corresponds to another transformation

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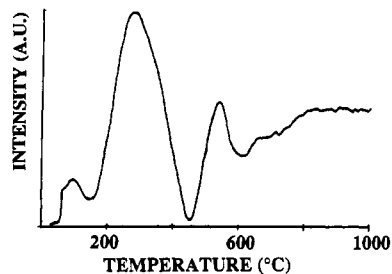


Figure 9. Detection of water via TG/SM experiment.

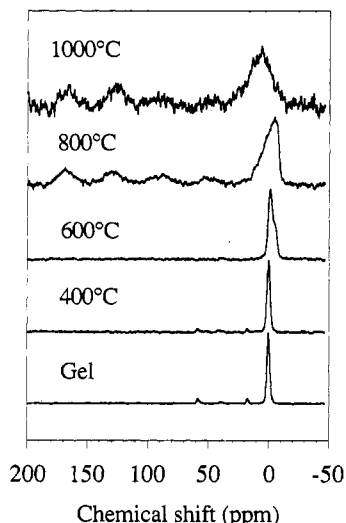


Figure 10. ^{13}C CP MAS NMR spectra of the pyrolyzed samples.

of the system: the formation of aromatic carbon.³⁶ This will be confirmed by ^{13}C NMR results. At 900 °C, the spectrum is strongly modified with a dominant resonance at 4 ppm, which reveals the presence of water.³⁴

Water was also detected by IR in the samples pyrolyzed above 900 °C. It could be due to the in situ generation of water during the pyrolysis process and/or adsorption of water from the atmosphere. The point has been investigated using TGA/MS analysis (Figure 9). Between 200 and 400 °C, water evolution is due to the condensation of silanol groups present in the starting gel. Above 600 °C and up to 1000 °C, a weak signal is detected showing the in situ formation of water during the polymer to glass conversion, but it is a minor reaction.

The ^{13}C CP MAS NMR spectra are shown in Figure 10. The spectrum of the starting gel is dominated by a peak at 0 ppm due to CH_3 groups in D units.³⁷ The minor components at 17.5 and 58.4 ppm are due to residual ethoxy groups.³⁸ The spectrum of the 400 °C samples does not change. At 600 °C, the peaks due to ethoxy groups have disappeared, while the peak due to CH_3 groups now exhibits a shoulder at ≈ -5 ppm. This new component is certainly due to methyl groups in T units, in agreement with the ^{29}Si NMR data.^{39,40} The spectrum of the 800 °C sample is totally different. The low signal-to-noise ratio,

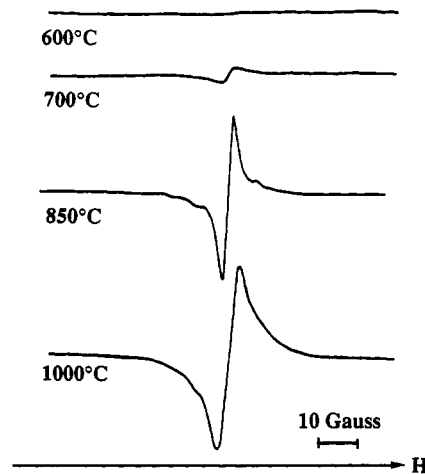


Figure 11. ESR spectra of the pyrolyzed samples.

despite a greater number of scans, indicates a poor efficiency of cross-polarization technique due to a loss of protons in the sample indicated by elemental analysis. The peak due to aliphatic C atoms is very broad with new components between 0 and 20 ppm. It shows a distribution of C environments, which are less and less protonated.^{41,42} A new peak is now present due to C sp^2 atoms.⁴³ Such signals have already been observed in the pyrolysis of preceramics polymers and assigned to the formation of a free carbon phase.^{44,45} The signals at 90 and 170 ppm are spinning sidebands.

ESR experiments (Figure 11) show the appearance of a signal at $g = 2.0024$ when the samples are heated above 600 °C. Its intensity increases with temperature until 1000 °C where a concentration of 2×10^{19} spin/g was estimated. The signal presents no hyperfine structure except in the 850 °C sample. Such a g value, typical of organic free radicals, was already reported for dangling bonds on C atoms.⁴⁶ This confirms that during the decomposition of the organic groups, radicals, such as C^{\bullet} are created. Similar ESR results have already been reported in the study of the conversion of polycarbosilane in SiC ,⁴⁴ vinylic polysilane to silicon nitride,⁴² and polysilazanes in silicon carbonitride.⁵⁰ In this last paper, the authors assigned the observed signals to pyrolytic carbons containing highly delocalized electrons.⁵⁰

The evolution of density and specific surface area versus temperature is illustrated in Figure 12. The density increases with temperature from 1.1 to 1.8 g/cm^3 as the polymeric network converts to a glass. There is a significant change above 700 °C. In contrast, the surface area initially increases and then decreases above this temperature. This suggests that pores develop in the powders during the early stages of pyrolysis, when volatile species are evolving from the polymer. The surface area reaches values as high as 590 m^2/g at 700 °C. The subsequent decrease at higher temperatures indicates that pores are eliminated via shrinkage and densification.

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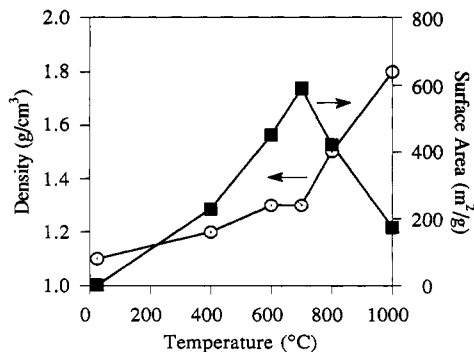


Figure 12. Variation of density and specific area versus pyrolysis temperature.

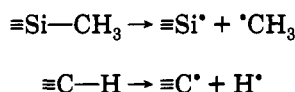
Discussion

The use of various techniques, mainly spectroscopic, to characterize the pyrolysis products allows a detailed description of the conversion of the gel into a silicon oxycarbide network. It can be divided in two main overlapping stages: redistribution reactions ($450\text{ }^\circ\text{C} < T < 800\text{ }^\circ\text{C}$) and polymer-to-glass transition ($650\text{ }^\circ\text{C} < T < 1100\text{ }^\circ\text{C}$).

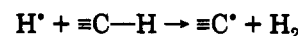
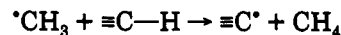
The gel is thermally stable up to $400\text{ }^\circ\text{C}$ as shown by NMR and IR. The only volatile detected in this temperature range is water, formed by condensation of residual silanol groups.

Between 400 and $650\text{ }^\circ\text{C}$, the main phenomenon is a redistribution of the Si-O and Si-C bonds. It was clearly demonstrated by ^{29}Si NMR and to a less extent by ^{13}C NMR. Such reactions are very common in solution chemistry of organosilicon compounds⁴⁷ and have recently been observed also in solid state.^{22,24} They are associated with a loss of siloxanes as evidenced by TG/MS in the present study. Fragments coming from linear siloxanes containing M units have been detected. But no M units were present in the starting gel. So the formation of M units from the starting D units according to reactions 3 and 4 has to be considered. It has to be pointed out that during this stage, the methyl groups are not decomposed as shown by ^{29}Si , ^{13}C , and ^1H NMR and TG/MS showing the high thermal stability of the Si-CH₃ groups.

Between 650 and $1000\text{ }^\circ\text{C}$, the transformation of the polymeric network into an inorganic material occurs, characterized by a loss of methane and hydrogen detected by TG/MS. The ESR results as well as the high temperatures involved suggest that this transformation occurs via a radical mechanism. The thermal stability of the various bonds present in the gel primarily depends on their dissociation energy. The weakest bonds in the silsesquioxane gels are the Si-C and the C-H bonds, which have dissociation energies around $90\text{--}100\text{ kcal mol}^{-1}$. The formation of methane and hydrogen is well accounted for by the following reactions: The first step is the homolytic cleavage of Si-C and C-H bonds:

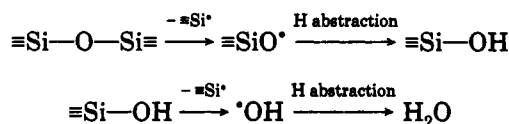


The second step is the abstraction of hydrogen by the radicals from the C-H bonds:



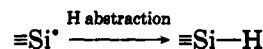
The fact that very little ethane is formed shows that combination reactions are negligible in the gas phase. On the other hand, the formation of the Si-C-Si bridges and of the free carbon in the solid probably results from the combination of the various $\equiv\text{Si}^\bullet$ and $\equiv\text{C}^\bullet$ radicals.

The Si-O bonds, with a dissociation energy of ca. 110 kcal mol^{-1} , are the more stable bonds in the gels, and their homolytic cleavage is expected to occur at a higher temperature than the cleavage of Si-C and C-H bonds. The suspected formation of water above $800\text{ }^\circ\text{C}$ could indicate the occurrence of such cleavages, leading intermediately to the formation of silanol groups



However, the O/Si ratio of the sample does not significantly decrease between 800 and $1000\text{ }^\circ\text{C}$ (actually ^{29}Si NMR shows an increase of O/Si), which suggests that the water elimination is a side reaction.

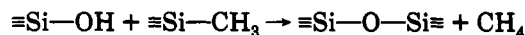
The $\equiv\text{Si}^\bullet$ radicals, arising from the cleavage of Si-O or Si-C bonds, may either combine with other radicals or abstract hydrogen (from H₂ for example) thus explaining the intermediate formation of Si-H groups detected in small amount by IR spectroscopy:



The ^{29}Si CP MAS NMR spectrum of the $800\text{ }^\circ\text{C}$ sample is in agreement with a low amount of Si-H bonds. Presence of H-SiO_{1.5} or H-Si(CH₃)O sites should give resonance peaks around 85 and 35 ppm , which cannot be clearly detected in the CP NMR spectrum.

The evolution of methane and hydrogen is concurrent with the formation of aromatic carbon which was directly observed from the ^1H and ^{13}C NMR results. This result suggests the formation of a free-carbon phase during the pyrolysis. Formation of graphitic carbons units occurs during the pyrolysis of organic compounds⁴⁸ or organosilicon polymers.⁴⁹

The ^{29}Si NMR spectra showed a decrease of the number of Si-C bonds between 400 and $800\text{ }^\circ\text{C}$. This decrease may have two origins: (1) the elimination of volatile cyclic and linear siloxanes, D_x and MD_xM, arising from the redistribution of Si-O and Si-C bonds, which lead to a loss of D and M units; (2) the substitution of the Si-C bonds by silanols, according to



The decrease of the number of C-H bonds was directly observed by the decrease of the H-C_{sp³} resonance intensity in the ^1H NMR spectra, the decrease of the IR band due to $\nu(\text{C}-\text{H})$ and the lowfield shield of the H-C_{sp³} resonance in the ^{13}C NMR spectra. Such reactions also affect the

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^{29}Si NMR chemical shift values, which present a continuous high-field shift versus pyrolysis temperature.

The surface area of the pyrolyzed samples greatly increases during the polymer-to-glass transition, due to the cleavage of numerous bonds and evolution of volatile species. Water from the air can thus be largely absorbed at the surface of the sample, and this can account for the strong IR band due to OH groups.

At 1000 °C, the chemical shifts observed for the D, T, and Q units are very close to that reported for silicon oxycarbide fibers containing less than 0.1 wt % hydrogen.⁵⁰ This suggests that in the sample pyrolyzed at 1000 °C the hydrogen content in the silicon oxycarbide phase is low, and that most of the hydrogen atoms detected by elemental analysis come from adsorbed water (the specific surface area is still high, close to 200 m²/g) and from the free carbon phase. The bonding of the C atoms in the oxycarbide phase is still open to question. In the glass obtained at 1000 °C, ^1H and ^{13}C NMR spectra are consistent with a predominantly CSi_4 environment, as in silicon carbide; however, the presence of residual C-H or C-C bonds cannot be rejected.

An estimation of the maximal amount of free carbon in the glass obtained at 1000 °C may be derived from the empirical formula, assuming that all the oxycarbide C

atoms are bonded to four Si in CSi_4 units. For a mean formula $\text{SiO}_{1.65}\text{C}_{0.56}$, one finds that ca. 70% of the C atoms are in the free carbon phase, which corresponds to ca. 8 wt % of free carbon in the glass. The glass obtained at 1000 °C can be described as an amorphous silicon oxycarbide phase with a residual aromatic carbon phase.

Conclusion

A gel prepared by cohydrolysis of dimethyldiethoxysilane and tetraethoxysilane has been converted with high ceramic yield into a silicon oxycarbide network by pyrolysis. ^{29}Si , ^{13}C , ^1H MAS NMR, TG/MS, ESR, and IR have been used with success to monitor the various structural changes that occur during the pyrolysis of the polysiloxane precursor. These changes include condensation reactions via hydroxyl groups, redistribution reactions involving the exchange of Si-C and Si-O bonds and finally extensive C-H, Si-C, and Si-O cleavage. At 1000 °C, the amorphous glass obtained from the gel consists in an amorphous silicon oxycarbide phase and with a residual free carbon phase.

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