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Reaction pathways during the thermal conversion of polysiloxane precursors into oxycarbide ceramics

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Abstract

A detailed evaluation of the events that occur during the heating of organic–inorganic hybrid solids obtained by the sol–gel method has been established. The correlation of many characterization techniques, in particular TG/MS analysis associated with specific alkoxide structural units, has provided some explanations in terms of a set of mechanisms.

It will be shown that the residual Si–OH and Si–OEt, arising from incompletely hydrolyzed and condensed alkoxides, play an important part in the degradation of gel precursors. They undergo reactions with Si–H in the temperature range 200–700 $^{\circ}$ C and with Si–Me starting around 450 $^{\circ}$ C.

The thermal stability of Si–Me is strongly linked to the nature and distribution of the other functional substituents (Si–OH, Si–H) present in the gels. The cleavage of Si–Me may thus take place within a large temperature range varying from $450 \degree$ C to $1000 \degree$ C. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Precursors: organic; Pyrolysis; Glass; SiO_xC_y; Thermal conversion

1. Introduction

Silicon oxycarbide (SiO_xC_y) is an amorphous metastable phase in which the silicon atoms are bonded to oxygen and carbon simultaneously. Their synthesis is achieved through the pyrolysis of cross linked organically-modified alkoxy silane precursors, more commonly known as polysilsesquioxanes, of the general formula $[RSi-(O_{3/2})]_n$ (where R is hydrogen or a hydrocarbon group). These precursors are readily obtained by hydrolysis-condensation reactions of alkoxy silanes $[R_x Si - (OR')_{4-x}]$. During this step, Si-OR' bonds are converted into Si-O-Si via the hydrolysis of Si-OR' into Si-OH, followed by the condensation reaction of such hydrolyzed substituents leading to Si-O-Si networks. These organically modified alkoxy silanes provide a direct Si-C bond in the starting solution, which is preserved during hydrolysis, condensation and drying. The resulting oxycarbide gels, which have diverse applications,^{1,2} can be further processed to obtain dense glasses,³ porous glasses,⁴ powders⁵ or ceramic materials.⁶

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To synthesize silicon oxycarbide ceramics, pyrolysis at high temperatures is required. This is performed in order to dehydrogenate and crosslink the terminal organic groups; hence Si–O–Si bonds result from the hydrolysis–condensation reactions, whereas Si–C–Si bonds result mainly from the high temperature reactions occurring during the pyrolysis step.

The composition and the structure of glasses depend on the composition and the structure of the starting precursor units, and on the reactions that take place during pyrolysis.

Interesting studies have recently been published regarding the understanding of the pyrolytic process and many reactions have been proposed.^{2,7–10} There is, however, considerable disagreement over the reaction temperature range and types of reaction sequences taking place. These discrepancies in the published literature has led to the present work.

The objective of this study is, therefore, to investigate the influence of the structural changes of the precursors during thermal treatment, with a special emphasis on the temperature range of each reaction involved during the process.

This is achieved through the use of polymeric precursors of the formula $[R_xSi-(OEt)_{4-x}]$ where R is hydrogen and/or methyl.

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2. Experimental procedure

2.1. Synthesis

The present study covers predominantly the thermal conversion of D^HT^H gels having different ratios of D^H and T^H units. However, in order to attain a more pronounced insight into the evolution of these gel-structures, we have extended the study to other structures as well. Thus, various structures of silicon precursors have been used to make silicon oxycarbide glasses. Among them are (T^H) triethoxysilane HSi(-OEt)₃, (D^H) methyldiethoxysilane (CH₃)HSi-(OEt)₂, (O) tetraethoxysilane $Si(-OEt)_4$ and (T) methyltriethoxysilane CH₃Si(-OEt)₃. Samples were prepared by the hydrolysis and condensation of either a single alkoxide precursor (Gel T) or by the mixture of two alkoxide precursors (Gels D^HT^H, TT^H, D^HQ and TQ). To the stirred alkoxide precursor, ethanol was slowly added at room temperature (ratio EtOH/Si = 2). After 5 min of stirring, acidic H_2O (H_2O/Si = 2, pH 4.5 for $D^{H}T^{H}$ gels and pH 1 for T gel) was then slowly added drop by drop. For T gel, the mixture was slowly heated to reflux $(76 \,^{\circ}C)$ and maintained for 2 h. After slowly cooling to ambient temperature, the rate of stirring was increased and concentrated NH₄OH solution (0.5 ml per 10 ml of T precursor), was added drop by drop, to ensure optimal condensation. The resultant solutions were immediately poured into plastic test tubes and these tubes allowed to stand at ambient temperature for 7 days. All gels obtained were dried for 2 days at each temperature (40 $^{\circ}$ C, 60 $^{\circ}$ C, 80 $^{\circ}$ C, 100 $^{\circ}$ C and 120 $^{\circ}$ C). The gels are named as follows: T for the gel issued from CH₃Si(-OEt)₃, $D^{H}T^{H}$ (1/1, 1/2 and 1/9) for those issued from the different ratios of D^H (CH₃)HSi-(OEt)₂ and T^H triethoxysilane HSi(-OEt)₃, TT^H from CH₃Si(-OEt)₃ and HSi(-OEt)₃, TQ from CH₃Si(-OEt)₃ and Si(-OEt)₄, and D^HQ from (CH₃)HSi-(OEt)₂ and Si(-OEt)₄.

2.2. Pyrolysis

Different analytical techniques were used to investigate the thermal stability of the gels. Thermogravimetry analysis (TGA) (Netzsch STA 409 apparatus) coupled with a quadrupole mass spectrometry (MS) (Quadrex 200, Leybold Heraeus, 70 eV, electron impact) was applied to simulate the behavior of powders during the annealing process and to determine the evolved gaseous species.

The experiments were carried out under a dynamic inert gas atmosphere (helium: 99.999 purity) at a flow rate of $25 \text{ cm}^3/\text{min}$. The samples (400 mg, particle size between $100 \,\mu\text{m} < d < 350 \,\mu\text{m}$.) were heated in Al₂O₃ crucibles up to $1000 \,^\circ\text{C}$, with a heating rate of $10 \,^\circ\text{C/min}$. The structures of the samples were identified before and after heating by X-ray diffraction (PW 1130 Philips diffractometer with monochromatic Cu K α radiation).

The quantitative chemical analysis of the precursor gels and their pyrolysis products were carried out by CNRS, Service Central d'Analyse, France. The silicon content was determined by ICP (inductive coupled plasma) from an aqueous solution of sodium and/or potassium silicate resulting from chemical attack of the sample. The carbon and hydrogen content was established by high-temperature combustion and IR spectroscopy. The oxygen content is obtained by difference. The stoichiometry of the oxycarbide phase residue (1000 °C) is derived from elemental analysis, assuming that the SiO_xC_y network is built of Si–O and Si–C bonds only (no Si–Si or C–O bonds), and that all oxygen atoms are bonded to silicon while neglecting, as a first approximation the presence of residual C–H.

This study was performed within a European community research program (Oxycarbide glasses FMRX-CT9801621), where other groups have analyzed the same samples by other characterization methods such as 29 Si, 13 C, MAS-NMR and TEM. $^{11-15}$

3. Results

3.1. Thermogravimetric analysis and ceramic yield

TG studies under flowing helium of the three cross-linked gels $D^{H}T^{H}$, shown in Fig. 1, reveal that each gel has a different thermal behavior. It can be seen that the mass loss is influenced by the ratio of D^{H}/T^{H} units. The smaller the D^{H}/T^{H} ratio, the larger is the ceramic yield. The values, which vary from 87% to 91% to 94% belong, respectively, to $D^{H}T^{H}$ 1/1, 1/2 and 1/9.

The weight loss proceeds in several steps, which are more or less significant depending on the structure of gels. These decomposition steps that indicate the presence of different chemical processes, were further characterized by the mass spectrometry experiments detailed below.

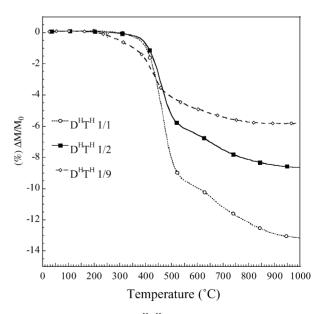


Fig. 1. TGA profiles of DHTH gels pyrolyzed under helium.

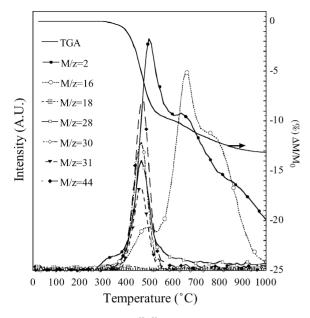


Fig. 2. TG/MS analysis of DHT^H 1/1 gel pyrolyzed under helium.

3.2. Thermogravimetry coupled with mass spectrometry

The TG/MS analyses of the three gels are given in Figs. 2–4. Due to the presence of numerous different fragments, to provide a clear presentation of the MS profile curves, only those ions of most importance to our discussion have been selected and displayed.

On heating from room temperature to 400 °C the gels with ratio 1/1 and 1/2 exhibit a mass loss of ~0.7%, while the gel with ratio 1/9 shows a loss of 1.6%. The gases detected correspond to water (m/z = 18, 17, 16) and ethanol (m/z = 31, 45, 27), with trace amounts of hydrogen (m/z = 2) and, particularly for the D^HT^H 1/9, ethane (m/z = 28, 30, 26).

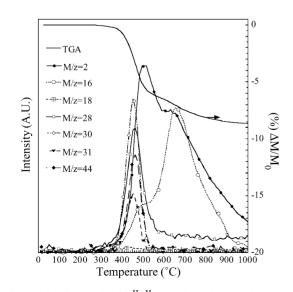


Fig. 3. TG/MS analysis of DHTH 1/2 gel pyrolyzed under helium.

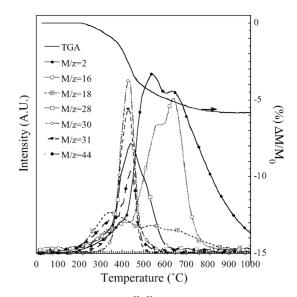


Fig. 4. TG/MS analysis of DHT^H 1/9 gel pyrolyzed under helium.

Between 400 °C and 600 °C the mass loss observed for each gel is different. For D^HT^H gels 1/1, 1/2 and 1/9 the mass loss observed is 9.3%, 5.8% and 3.3%, respectively. Detected in this region is a range of volatile silicon-containing species whose compositions depend on the ratio D^H/T^H: for D^H/T^H 1/1 all silanes of formula $(CH_3)_xSiH_{4-x}$, with 0 < *x* < 4 are detected; for D^H/T^H 1/2, species of 0 < *x* < 2; for D^H/T^H 1/9, only CH₃SiH₃ and SiH₄. Whatever the ratio of D^H/T^H, SiH₄ (*m*/*z* = 30, 31) and CH₃SiH₃ (*m*/*z* = 44, 45) are detected by MS.

In the range 600–1000 °C, the escape of hydrogen (m/z = 2) and methane (m/z = 16, 15, 14) are predominantly detected by MS. It is interesting to note that the MS profiles for methane and hydrogen from the gels are quite different; this will be described in more detail hereafter.

4. Discussion

Below 400 °C, the low weight loss observed by TGA and the nature of species (H₂O, C₂H₅OH, H₂ and C₂H₆) detected by MS, suggests the presence of unreacted residual Si–OH and Si–OEt moieties, which when heated undergo hydrolysis/condensation. The degree of condensation of the gels have been quantified by ²⁹Si NMR experiments and have been reported in the literature.^{11,14–16} These data are summarized in Table 1. Additional evidence comes from the C/Si ratios determined by chemical analysis (Table 2).

Actually, if $D^{H}T^{H}$ 1/1 and 1/2 are assumed to be fully condensed, then their C/Si empirical ratios are found to be equivalent to their theoretical ones. For $D^{H}T^{H}$ 1/9, the content of carbon present in the gel is greater than if it was theoretically fully hydrolyzed/condensed. Considering the possible origins of extra carbon in $D^{H}T^{H}$ 1/9, the most plausible answer for this is due to the presence of unreacted ethoxy groups.

Table 1 Degree of condensation of gels D^HT^H 1/1, 1/2, 1/9, T, TQ, TT^H and D^HQ quantified by $^{29}Si~NMR^{11,14-16}$

| Gels | Degree of condensation (²⁹ Si NMR) (%) |
|-----------------------------------|--|
| D ^H T ^H 1/1 | 100 |
| $D^{H}T^{H} 1/2$ | 100 |
| D ^H T ^H 1/9 | 93 |
| Т | 97 |
| TQ | 90 |
| TT ^H | 97 |
| D ^H Q | 93 |

These data suggest that condensation reactions that involve hydroxy and ethoxy groups may be occurring, following Eqs. (1) and (2).

$$\equiv Si-OH + HO-Si \equiv \rightarrow Si-O-Si \equiv + H_2O \tag{1}$$

$$\equiv Si - OC_2H_5 + HO - Si \equiv \rightarrow \equiv Si - O - Si \equiv + C_2H_5OH$$
(2)

Other reactions that appear to be present due to these non-condensed units and which may also increase the cross linking in the gel network, are shown by Eqs. (3) and (4):

$$\equiv Si - OH + H - Si \equiv \rightarrow \equiv Si - O - Si \equiv + H_2 \tag{3}$$

$$\equiv Si - OEt + H - Si \equiv \rightarrow \equiv Si - O - Si \equiv + C_2 H_6 \tag{4}$$

It seems that the cleavage of Si–H bonds by Si–OH takes place above 200 °C, lower than the temperature mentioned in the literature.¹⁷ These observations are supported by the study of the non-fully-condensed gels D^HQ and D^HT^H 1/9, where MS analysis reveals that H₂, the resulting product of reaction (3), starts above 200 °C with a maximum temperature around 300 °C (first peak of H₂ in D^HQ gel) as is portrayed in Fig. 6.

For the second observed mass loss, in the region 400–600 °C, which is the largest and most important, the value obtained appears to be dependent on the ratio of D^{H}/T^{H} . Generally, the larger the quantity of the T^{H} unit in the gel the smaller the observed mass loss. The mass loss mainly corresponds to the formation of various volatile silicon species. These species, detected by MS, are attributed to redistribution reactions (also called exchange reactions) whereby the exchange of Si–O bonds with Si–H bonds and/or Si–C bonds occurs. These redistribution reactions (very common in organosilicon chemistry), have been well documented in the literature. It thus seems unnecessary to detail these reactions here.^{14–20}

Table 2 Theoretically determined C/Si ratios

| Gels | Empirical formula | Theoretical C/Si ratio |
|--|---|------------------------|
| $\begin{array}{cccc} D^{H}T^{H} & 1/1 \\ D^{H}T^{H} & 1/2 \\ D^{H}T^{H} & 1/9 \end{array}$ | $\begin{array}{c} SiC_{0.53}O_{1.29}H_{2.48}\\ SiC_{0.35}O_{1.28}H_{1.93}\\ SiC_{0.24}O_{1.48}H_{1.40} \end{array}$ | 0.5 0.33 0.09 |

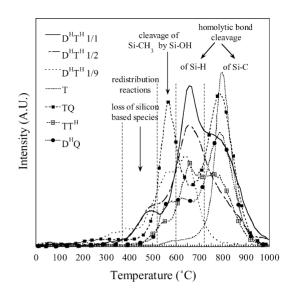


Fig. 5. Evolution of CH₄ evolved during the heating of gels D^HT^H 1/1, 1/2, 1/9, T, TQ, TT^H and D^HQ .

Also detected by MS in this range of temperature is the evolution of hydrogen, methane and ethylene (m/z = 28, 27, 26). These species can be explained by mechanisms of fragmentation of volatile silicon compounds. The energy required for these transformations is believed to be gained from the electron beam of the MS and/or the thermal heat of the furnace. Another possibility for the presence of hydrogen is from the decomposition of SiH₄. This reaction is known to occur at $450 \,^{\circ}C.^{15,17}$

In order to reinforce the proposed reactions which will be discussed in detail later, it seemed useful to use other structures of copolymers such as TQ, D^HQ and TT^H.

For a comparative analysis, we have reported in Figs. 5 and 6, the evolution of methane and hydrogen issued

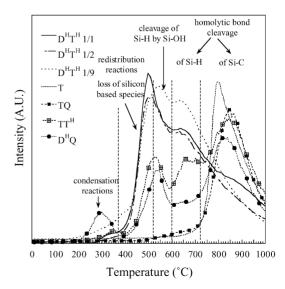


Fig. 6. Evolution of H_2 evolved during the heating of gels $D^H T^H$ 1/1, 1/2, 1/9, T, TQ, TT^H and $D^H Q$.

during the heating of various structural units of gels. In Fig. 5, the MS profile of TQ gel, lacking in Si–H bonds, is particularly interesting as the release of methane shows two distinct peaks with near equal intensities. The results of ²⁹Si solid MAS-NMR revealed that the TQ gel is not fully condensed and ethoxy (OEt) and hydroxyl (OH) residual groups are still present in the gel. This information is also supported by MS analysis where water and ethanol species resulting from condensation reactions of OEt and OH residual groups have been detected around T = 300 °C. Some of the remaining OH bonds will react with CH₃–Si by condensation reaction leading to Si–O–Si bridges and release methane according to Eq. (5).

$$\equiv Si-CH_3 + \equiv Si-OH \rightarrow \equiv Si-O-Si \equiv + CH_4$$
(5)

This reaction which takes place precisely between 450 °C and 650 °C corresponds to the first peak of methane in TQ gel. This reaction occurs in all of the partially condensed gels which contain Si–CH₃ bonds: TT^H , D^HQ and D^HT^H 1/9 (the less condensed gel in the series of D^HT^H). Indeed, the evolution of CH₄ with a maximum of intensity around 550 °C is more pronounced for D^HT^H 1/9 compared to D^HT^H 1/2 and D^HT^H 1/1.

The simultaneous presence of Si–OH and CH₃–Si bonds gives rise to the CH₄ in the temperature range 450-650 °C.

Moreover, in this same temperature range, the release of hydrogen was also observed, specifically for the less condensed compounds containing Si–H bonds ($D^{H}T^{H}$ 1/9, $D^{H}Q$ and TT^{H}). It seems that the condensation reaction of Si–OH bonds is not limited only to CH₃–Si bonds. Si–OH bonds also react with Si–H, in that temperature range, according to the Eq. (6).

$$\equiv Si-H + \equiv Si-OH \rightarrow \equiv Si-O-Si \equiv +H_2 \tag{6}$$

This is conveyed in the example of TT^H and D^HQ where a distinct peak of H_2 is observed, whereas in TQ, lacking in Si–H bonds, no trace of H_2 release is visible.

It is worth noting that the hydrogen as well as the methane issued from the thermal decomposition of silane, mentioned previously, is found at a slightly lower temperature (around 500 °C) than that compared to the hydrogen and methane produced by Eqs. (5) and (6). This can be easily seen by comparing the H₂ profiles of the more condensed gels $D^{H}T^{H}$ 1/1 and 1/2 with that of $D^{H}T^{H}$ 1/9 where the reaction (Eq. (6)) is more significant.

Around 660 °C, a further release of CH₄ and H₂ occurred for all gels containing both Si–H and CH₃–Si bonds (D^HT^H series, TT^H and D^HQ).

Some^{2,3,10,16,17} have believed that the losses of CH₄ and H₂ are assigned to the following reactions:

$$\equiv Si-CH_3 + \equiv Si-CH_3 \rightarrow \equiv Si-CH_2 - Si \equiv + CH_4$$
(7)

 $\equiv Si-CH_3 + \equiv Si-H \rightarrow \equiv Si-CH_2 - Si \equiv +H_2$ (8)

$$\equiv Si-CH_3 + \equiv Si-CH_3 \rightarrow \equiv Si-CH_2-CH_2-Si \equiv +H_2 \quad (9)$$

Based only on these reactions, one would expect more methane from T gel which contains enough CH_3 –Si groups. However, this did not happen. The cleavage of CH_3 –Si in T gel does not occur in the temperature range 600–700 °C but at higher temperature around 800 °C.

This indicates that other reactions different from those given in Eqs. (7)–(9) must be involved in the process.

Following the comparative study of the various structures used in this work, we suggest in fact, that the Si–H bonds take part in the reaction process and set off the cleavage of Si–CH₃.

The Si–H is considered as a radical initiator for the breaking of CH_3 –Si according to Eqs. (10)–(14).

• Initiation:

$$\equiv \mathrm{Si-H} \stackrel{\Delta}{\to} \equiv \mathrm{Si}^{\bullet} + \mathrm{H}^{\bullet} \tag{10}$$

• Propagation:

$$\equiv \text{Si-CH}_3 + \text{H}^{\bullet} \rightarrow \equiv \text{Si-CH}_2^{\bullet} + \text{H}_2$$
(11)

$$\equiv Si - CH_2^{\bullet} + CH_3 - Si \equiv \rightarrow \equiv Si - CH_2 - Si \equiv + {}^{\bullet}CH_3$$
(12)

$$\equiv Si-CH_2-Si \equiv + {}^{\bullet}CH_3 \rightarrow \equiv Si-{}^{\bullet}CH-Si \equiv + CH_4 \quad (13)$$

• Termination:

$$\equiv \mathrm{Si}^{\bullet} + \equiv \mathrm{Si}^{\bullet}\mathrm{CH}_{-}\mathrm{Si}^{\equiv} \to \mathrm{HC}(\mathrm{Si}^{\equiv})_{3} \tag{14}$$

In the absence of Si–H in the structure of the precursor, it follows that the homolytic cleavage of Si–CH₃ occurs at higher temperatures, above 750 °C. This, explains the delayed release of CH₄ and H₂ from TQ and T gels compared with the ones containing Si–H groups such as in the D^HT^H, D^HQ and TT^H series. From these results, the reactivity of substituents as a function of temperature may be drawn up in order as illustrated in Fig. 7.

Based on the X-ray diffraction and elemental analyses of specimens pyrolyzed at 1000 $^{\circ}$ C, all the D^HT^H systems

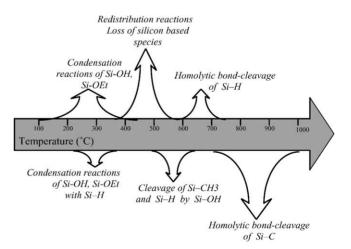


Fig. 7. Reactivity of functional groups during the conversion of polymeric-gel into oxycarbide ceramic.

Table 3 Elemental analysis of all systems D^HT^H from RT to $1000\,^\circ C$

| $\mathrm{D}^{\mathrm{H}}/\mathrm{T}^{\mathrm{H}}$ | SiCO composition | Stoichioemetric formula: SiC _x O _{2(1-x)} + (a C or b Si) |
|--|--|---|
| 1/1 (gel) 400 °C 600 °C 800 °C 1000 °C | $\begin{array}{c} SiC_{0.53}O_{1.29}H_{2.48}\\ SiC_{0.40}O_{159}H_{1.48}\\ SiC_{0.43}O_{1.48}H_{1.36}\\ SiC_{0.40}O_{1.57}H_{1.05}\\ SiC_{0.39}O_{1.38}H_{0.54} \end{array}$ | $SiC_{0.31}O_{1.38}H_{0.54} + 0.07C$ |
| 1/2 (gel) 400 °C 600 °C 800 °C 1000 °C | $\begin{array}{c} SiC_{0.35}O_{1.28}H_{1.93}\\ SiC_{0.32}O_{1.42}H_{1.38}\\ SiC_{0.30}O_{1.47}H_{0.72}\\ SiC_{0.28}O_{1.44}H_{0.59}\\ SiC_{0.30}O_{1.49} \end{array}$ | $SiC_{0.25}O_{1.49} + 0.05C$ |
| 1/9 (gel) 400 °C 600 °C 800 °C 1000 °C | $\begin{array}{l} SiC_{0.24}O_{1.48}H_{1.40}\\ SiC_{0.12}O_{1.60}H_{0.84}\\ SiC_{0.12}O_{1.63}H_{0.38}\\ SiC_{0.13}O_{1.70}H_{0.26}\\ SiC_{0.14}O_{1.61} \end{array}$ | $SiC_{0.15}O_{1.70} + 0.06Si$ |

studied are essentially amorphous and can be described as a mixture of oxycarbide phases with the presence of either excess carbon for $D^H T^H$ 1/1 and 1/2 or excess silicon for $D^H T^H$ 1/9 (Table 3).

5. Conclusion

Due to the diversity of structural units of the precursors used and their latent functional groups involved in the heating processes, it seems that the SiC_xO_y ceramic residues are the result of a complex cascade of reactions. Si–H, Si–OH and Si–CH₃ follow a variety of decomposition pathways that result in materials with a wide range of phase compositions. However, based on the results, we can suggest that the major reaction pathways by which organosilicon polymers evolve into ceramics, are sequenced as follows:

Condensation reactions of Si–OH, Si–OEt > condensation reactions of Si–OH, Si–OEt with Si–H > redistribution reactions (i.e. exchange reactions) > nucleophilic attack of Si–OH with Si–CH₃ and Si–H > homolytic bond-cleavage of Si–H > homolytic bond-cleavage of Si–C.

The loss of $-CH_3$ groups could be caused early in the pyrolysis process by nucleophilic attack of uncondensed Si–O–H groups (450 °C < T < 650 °C), or by homolytic cleavage initiated by the radical issued from the homolytic cleavage of Si–H bonds (600 °C < T < 750 °C). In the absence of Si–H in the structure of the precursor, it follows that the homolytic cleavage of Si–CH₃ occurs at higher temperatures, above 750 °C.

The detailed studies of these specific gel structures not only have provided a better understanding of the structural evolution during the polymer-to-ceramic conversion but also provide an insight on the thermal reactivity of each latent functional group in relation with its environment. This information should be useful to design the preceramic polymer and the thermal treatment protocol used in pyrolysis to achieve a ceramic residue with desired properties for a particular application.

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