Local Composition of Silicon Oxycarbides Obtained by Laser Spray Pyrolysis

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New nanosized Si/O/C composites have been synthesized by laser−aerosol interaction. The ^{29}Si spectra revealed a deep rearrangement of Si bonding in the samples with respect to the original aerosol. From the siloxane $(CH_3)_3SiOSi(CH_3)_3$ (MDSO) and the silane C_2H_5-$OSi(CH_3)_3$ (ETMS) aerosols with M environments, solids with a wide variety of SiO_xC_{4-x} environments were produced. These environments were shown to be randomly distributed. On the other hand, the same Q environment from the $Si(OC_2H_5)_4$ (TEOS) aerosol remained in the powders. This can be rationalized in terms of Si−O and Si−C bond exchanges. After pyrolysis and before crystallization, there was a clear deviation from the random model, indicating that the material started to organize. ^{13}C and ^{1}H NMR distinguished Si−C and aromatic free C. Both spectroscopies indicated that there was less C in the Si/O/C phase of the ex-MDSO powder than in the ex-ETMS one. The ex-MDSO Si/O/C was therefore less oxygenated, contained less carbon, and consequently the most condensed of the two. This study illustrates the great versatility of the method. The local environment of the Si in the precursor is modified through a limited bond redistribution and condensation during the synthesis and before pyrolysis. The choice of a Q organosilane, not allowing bond redistribution, leads to a highly porous, nanosized silica, because excess aromatic carbon is burned off by thermal oxidation. On the other hand, a choice of a precursor with a mixed SiO_xC_{4-x} environment leads after pyrolysis under an inert atmosphere to a mixture of Si/O/C and free aromatic carbon.

Introduction

The need of industry for new ceramics with ever improved thermomechanical properties has prompted numerous studies of silicon based nanosized composites in general[1,2] and of the silicon oxycarbide (Si/O/C) system in particular.[3] Indeed, incorporation of carbon in silica glasses is expected to reinforce its structural tetrahedral network via denser carbidic units.[4] Such black glasses are usually obtained with great versatility by pyrolysis of polysiloxane gels.[5−10] However, interesting new nanosized precursors to such composites have also been synthesized by laser−aerosol interaction. By taking advantage of the absorption of the laser IR light by Si−O−Si and Si−O−C bonds, this original method, which has also been successfully applied to the Si/C/N system,[11−13] results in a direct but incomplete pyrolysis of organometallics in a laser beam.[14] As the organometallic liquid is transported as an aerosol dispersed in a flowing inert gas, this pyrolysis is limited to a few milliseconds, namely, the residence time of the droplets in the section of the beam. Condensation reactions are thereby limited, and excessive loss to volatile silane is avoided. The resulting powders are ultrafine (20−30 nm), amorphous, and with high specific areas. They form a solid exorganometallic, whose mineralization is completed by further thermal treatment.

Compared to SiO_2, it is the substitution of divalent O by tetravalent C which provides for a greater degree of cross-linking and tightens the structure. Considering this, there is a direct relationship between the local environment at the molecular scale and the macroscopic

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(1) Komarneni, S. *J. Mater. Chem.* **1992**, *2*, 1219.

(2) Wakai, F.; Kodama, Y.; Sakaguchi, S.; Murayama, N.; Izaki, K.; Niihara, K. *Nature* **1990**, *344*, 421.

(3) Bowen, H. K. *Mater. Sci. Eng.* **1980**, *44*, 1.

(4) Homeny, J.; Nelson, G. G.; Paulik, S. W.; Risbud, S. H. *J. Am. Ceram. Soc.* **1987**, *70*, C114.

(5) Chi, F. K. *Ceram. Eng. Sci. Proc.* **1983**, *4*, 704.

(6) Babonneau, F.; Thorne, K.; Mackenzie, J. D. *Chem. Mater.* **1989**, *1*, 554.

(7) Bois, L.; Maquet, J.; Babonneau, F.; Mutin, H.; Bahloul, D. *Chem. Mater.* **1994**, *6*, 796.

(8) Babonneau, F. *Polyhedron* **1994**, *13*, 1123.

(9) Kamiyama, K.; Yoko, T.; Sano, T.; Tanaka, K. *J. Non-Cryst. Solids* **1992**, *119*, 14.

(10) Hatakeya, F.; Kanzaki, S. *J. Am. Ceram. Soc.* **1990**, *73*, 2107.

(11) Gonsalves, K. E.; Strutt, P. R.; Xiao, T. D.; Clemens, P. G. *J. Mater. Sci.* **1992**, *27*, 3231.

(12) Herlin, N.; Musset, E.; Luce, M.; Cauchetier, M. *J. Eur. Ceram. Soc.* **1994**, *13*, 285.

(13) Cauchetier, M.; Croix, O.; Herlin, N.; Luce M. *J. Am. Ceram. Soc.* **1994**, *77*, 993.

(14) Haggerty, J. S.; Cannon, R. W. In *Laser-Induced Chemical Processes*; Steinfeld, J. I., Ed.; Plenum Press: New York, 1981; pp 165−241.

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Table 1. Synthesis Parameters and Solid Production Yields

precursor	boiling point (°C)	liquid heating (°C)	wavelength (μm) and laser line	laser power (W)	liquid displaced (g/h)	powder production (g/h)	yield (w/w %)
$Si(OC_2H_5)_4$ or TEOS	165.8	120	9.293 (9R16)	340	55.1	10.3	19
$(CH_3)_3SiOC_2H_5$ or ETMS	75−76	65	9.293 (9R16)	345	92.3	22.3	24
$[(CH_3)_3Si]_2O$ or MDSO	99−101	80	9.488 (9P12)	335	157	73.5	47

mechanical properties of the solid. Such observations have prompted numerous solid-state nuclear magnetic resonance (NMR) studies of black glasses synthesized by different routes, clearly establishing the existence of the Si−C bond (mostly by ^{29}Si NMR) as well as the presence of a so-called free excess carbon phase by ^{13}C NMR.[15−21]

The aim of this work is to apply the same NMR methodology to characterize these new nanosized Si/O/C powders obtained by laser−aerosol interaction. More precisely, we tried to understand how the bonding in the aerosol affects the composition and the nature of the carbidic phase in the as-formed powder, as well as its mineralization under thermal treatment.

Experimental Section

Synthesis by Laser Spray Pyrolysis. The experimental device has been previously described.[13] To study the influence of the different O/Si atomic ratios on the final powder composition, the following liquid precursors were used: tetraethoxysilane, $Si(OC_2H_5)_4$ or TEOS; ethoxytrimethylsilane, $C_2H_5OSi(CH_3)_3$ or ETMS; and hexamethyldisiloxane, $(CH_3)_3SiOSi(CH_3)_3$ or MDSO. They were purchased from Fluka Chemie A.G. and used without further purification. They present strong absorption IR bands between 9 and 11 μm, which is the emission range of a high-power continuous-wave tunable CO_2 laser (fast axial flow PRC-Oerlikon 1500 W CO_2 laser modified to accept a grating).[22] The precursors were placed in a special glass jar which was heated between 60 and 120 °C depending on the boiling point of the liquid. They were introduced in the aerosol form with argon as carrier gas (2560 cm^3/min) through a glass tubing (diameter = 13 mm) orthogonally to the laser beam (expanded beam diameter = 25 mm). Characteristics of the aerosol (droplet size, density, etc.) produced by an ultrasonic spraying technique depend on the liquid precursor physical properties (viscosity, surface tension, volatility, etc.) and the frequency of the ultrasonic generator (Table 1).[23]

Thermal Mineralization. The heat treatments were carried out in a tubular furnace under air for oxidation or in a Pyrox GE80 graphite furnace for annealing under argon. The heating rate was 10 °C/min and the dwell time 1 h. Thermogravimetric analyses (TGA) at 10 °C/min were conducted under flowing argon.

Characterization. Methods used for the characterization of the powders have already been reported.[24] Chemical analysis for Si, O, C, H determination was performed by the Service Central d'Analyses of the CNRS. Specific surface area was determined by nitrogen absorption (BET method using a Micromeretics Flowsorb 2000). Samples were analyzed by infrared (IR) absorbance (Perkin-Elmer 580) in the 4000−400 cm^{-1} range using KBr pellets. X-ray diffraction patterns (XRD) were obtained on a Philips APD 1700 diffractometer at the Cu Kα radiation.

Magic-Angle Spinning Nuclear Magnetic Resonance (MAS NMR). The MAS NMR spectra of ^{1}H and ^{29}Si were recorded on a Bruker ASX 500 instrument at 500 and 99.3 MHz, respectively, while the $\{^1H-^{13}C\}$ cross-polarization CP/MAS NMR spectra were obtained on an ASX 100 at 25.1 MHz. The powdered samples were spun at 5 kHz in 7 mm zirconia rotors with polyimide endcaps.

One-pulse ^{29}Si spectra were recorded using a pulse width ($\pi/2$) of 4.7 μs. The recycle delay was 500 s, and around 200 transients were recorded for the as-formed powders. For pyrolyzed powders the recycle delay was cut to 20 s. Trials increasing by 1000-fold the recycle delay showed that those retained here were sufficient for quantitative analysis. This rapid relaxation behavior relative to usual carbides can be attributed to the highly disordered and default-rich character of the powders.[25]

$\{^1H-^{29}Si\}$ CP/MAS NMR spectra were obtained with $\pi/2$ proton pulses of 4 μs, contact times of 4 ms, and recycle delays of 5 s. Line broadening procedure (100 Hz) was applied before Fourier transform, and the chemical shifts were quoted relative to TMS with Q_8M_8 as a secondary reference.

One-pulse ^{1}H spectra were recorded using a pulse width ($\pi/2$) of 5 μs and recycle delays of 10 s. Moreover, testing on a 4 mm probe head showed that the spectra were not affected by the spinning speed in the range 5−16 kHz. For this reason, as mentioned above, a 7 mm probe head spinning at only 5 kHz, allowing for a larger amount of sample, was used. 160 transients were recorded with benzene as a secondary reference at 7.4 ppm from TMS.

The $\{^1H-^{13}C\}$ cross-polarization CP/MAS NMR spectra were obtained with $\pi/2$ proton pulses of 4 μs, contact times of 2 ms, recycle delays of 5 s, and about 50 000 transients. Continuous-wave decoupling was maintained during acquisition at the same power level as during Hartmann−Hahn contact. A line broadening of 50 Hz was applied. Spectra were referenced with glycine as a secondary reference at 176 ppm from TMS.

Results

As-Formed Powders. Table 1 summarizes the irradiation conditions and the results on powder production. The irradiation laser lines were chosen at the maximum of the IR absorption band between 9 and 11 μm for the three liquid precursors. The difference in powder production rate between TEOS and MDSO can be explained by the different number of Si−C bonds in the chemical formula of the liquid precursors, because the Si−C bond dissociation energy is lower than the Si−O bond dissociation energy (85 and 128 kcal/mol, respectively).

The powders were brown to black (presence of free carbon). Their composition (for the as-formed powders) and surface area are given in Table 2. They were amorphous through X-ray diffraction (Figure 1) and nanosized as shown previously by transmission electron

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(15) Kamiya, K.; Yoko, T.; Sano, T.; Tanaka, K. *J. Non-Cryst. Solids* **1990**, *119*, 14.

(16) Zhang, H.; Pantano, C. G. *J. Am. Ceram. Soc.* **1990**, *73*, 958.

(17) Hatfield, G. R.; Carduner, K. R. *J. Mater. Sci.* **1989**, *24*, 4209.

(18) Lipowitz, J.; Turner, G. L. In *Solid State NMR of Polymers*; Mathias, L., Ed.; Plenum Press: New York, 1991; p 305.

(19) Turner, G. L.; Kirkpatrick, R. J.; Risbud, S. H.; Oldfield, E. *Am. Ceram. Soc. Bull.* **1987**, *66*, 656.

(20) Tougne, P.; Hommel, H.; Legrand, A. P.; Cauchetier, M.; Luce, M. *Diamond Relat. Mater.* **1992**, *1*, 360.

(21) Sorarù, G. D.; D'Andrea, G.; Campostrini, R.; Babonneau, F.; Mariotto, G. *J. Am. Ceram. Soc.* **1995**, *78*, 379, and references therein.

(22) Luce, M.; Herlin, N.; Musset, E.; Cauchetier, M. *NanoStruct. Mater.* **1994**, *4*, 403.

(23) Langlet, M.; Joubert, J. C. In *Chemistry of Advanced Materials*; Rao, C. N. R., Ed.; IUPAC, Blackwell Scientific Publications: Oxford, 1992; pp 55-79.

(24) Herlin, N.; Armand, X.; Musset, E.; Martinengo, H.; Luce, M.; Cauchetier, M. *J. Eur. Ceram. Soc.*, in press.

(25) Carduner, K. R.; Carter III, R. O.; Milberg, M. I.; Grossbie, G. M. *Anal. Chem.* **1987**, *59*, 2794.

Table 2. Chemical Composition and Surface Area of the As-Formed Powders, Oxidized, and Pyrolyzed under Ar Samples

samples		weight change (%)	BET surface (m^2/g)	Si (mol/100 g)	C (mol/100 g)	O (mol/100 g)	H (mol/100 g)	chemical composition
TEOS	as-formed	0	172	1.35	0.78	3.13	1.62	$SiO_{2.32}C_{0.58}H_{1.20}$
	600 °C/air	−13.6	177					
	1200 °C/Ar	−18.3	47					
	1600 °C/Ar	−20.2	0					
ETMS	as-formed	0	239	1.52	2.41	1.67	1.76	$SiO_{1.09}C_{1.58}H_{1.16}$
	600 °C/air	−9	98					
	1200 °C/Ar	−15.9	41					
	1600 °C/Ar	−56.6	12					
MDSO	as-formed	0	161	1.82	2.51	1.12	0.98	$SiO_{0.61}C_{1.38}H_{0.54}$
	600 °C/air							
	1200 °C/Ar							
	1600 °C/Ar							

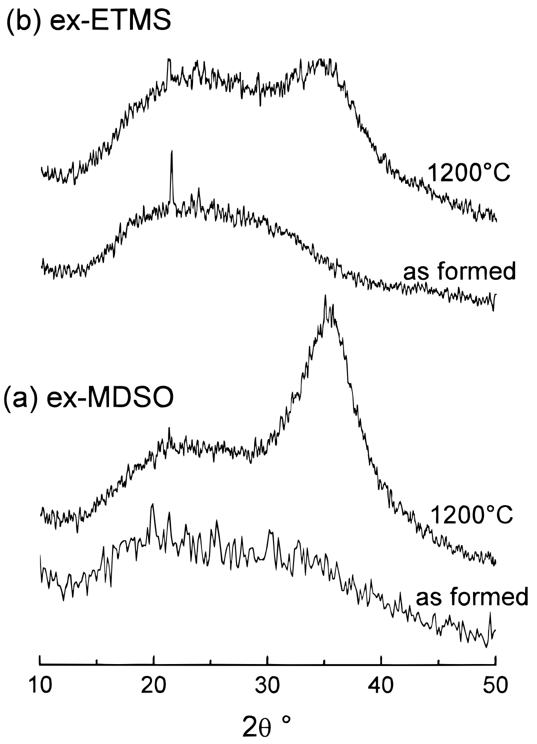

Figure 1. XRD spectra of the and as-formed and pyrolyzed (1 h under Ar) powders. (a) ex-MDSO, (b) ex-ETMS.

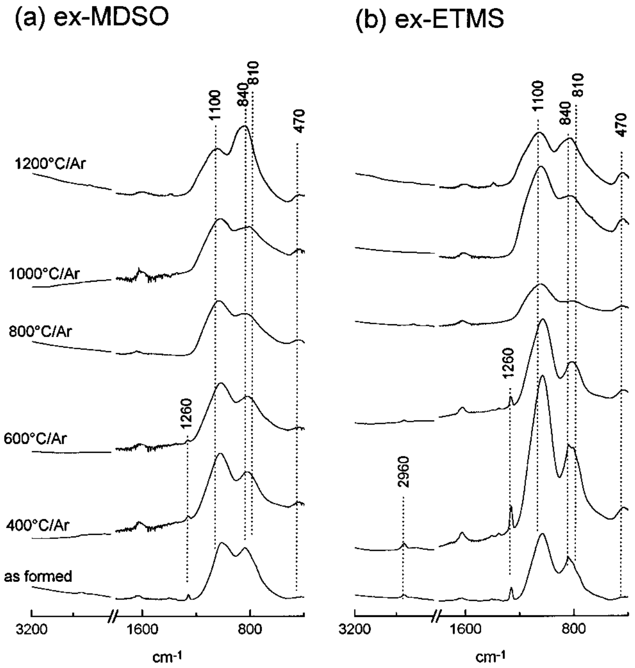

Figure 2. IR spectra of as-formed and pyrolyzed (1 h under Ar) powders: (a) ex-MDSO; (b) ex-ETMS.

microscopy.[24] The C/O atomic ratio increased from the ex-TEOS to the ex-MDSO sample following the atomic ratio in the liquid precursors.

IR spectra of ex-ETMS and ex-MDSO powders are shown in Figure 2. Contributions due to Si−O (ν_{as}[Si−O−Si] at 1100 and 810 cm^{-1}, δ[Si−O−Si] at 470 cm^{-1}) and Si−C (ν[Si−C] at 840 cm^{-1}) bonds were apparent. A well-resolved band at 1260 cm^{-1} (ρ_s[Si−CH$_3$]) indicated that methyl groups were retained during the synthesis,[24,26−28] as well as a minute amount of ethoxy groups (ν_{as}[SiOC$_2$H$_5$] at 2960 cm^{-1}).[29] It was also noted that the Si−H stretch band at 2080 cm^{-1} was not detected in those samples, confirming that no hydride groups formed.

The ^{29}Si spectra of the ex-MDSO and ex-ETMS as-formed powders exhibited two broad resonances around −65 ± 5 and −10 ± 20 ppm, while only one sharper, slightly asymmetrical line at −106 ppm was observed for the ex-TEOS as-formed powder (Figure 3−5). Chemical shifts have been established in silicon oxycarbides according to the first coordination sphere of Si:Q (SiO$_4$)

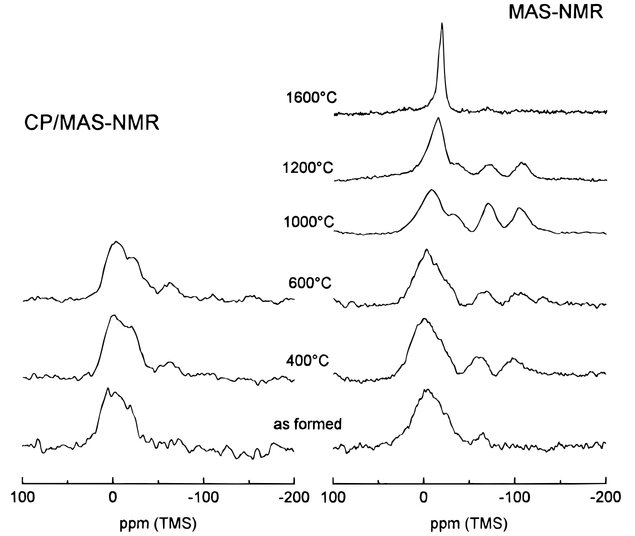

Figure 3. ^{29}Si one-pulse MAS and CP/MAS NMR spectra of as-formed and pyrolyzed (1 h under Ar) powders, ex-MDSO.

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(26) Bertoluzza, A.; Fagnano, C.; Morelli, M. A.; Gottardi, V.; Gugliemi, M. *J. Non-Cryst. Solids* **1982**, *48*, 117.

(27) Wu H.-J.; Interrante, L. V. *Chem. Mater.* **1989**, *1*, 564.

(28) Schmidt, W. R.; Interrante, L. V.; Doremus, R. H.; Trout, T. K.; Marchetti, P. S.; Maciel, G. E. *Chem. Mater.* **1991**, *3*, 257.

(29) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: New York, 1990; Chapter 5, pp 215−233.

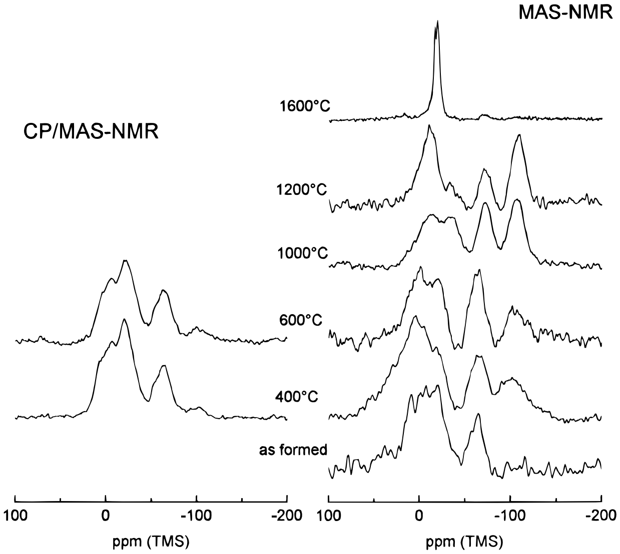

Figure 4. ^{29}Si one-pulse MAS and CP/MAS NMR spectra of as-formed and pyrolyzed (1 h under Ar) powders, ex-ETMS.

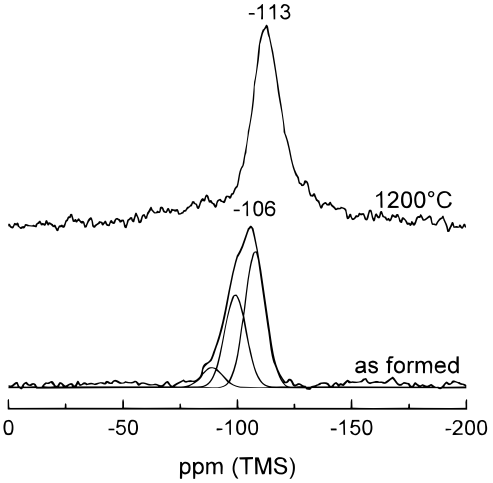

Figure 5. ^{29}Si one-pulse MAS NMR spectra of ex-TEOS as-formed and pyrolyzed (1 h under Ar) powders.

between −90 and −115 ppm, T ($SiCO_3$) between −55 and −75 ppm, D (SiC_2O_2) between −18 and −35 ppm, M (SiC_3O) between 8 and −2 ppm, and X (SiC_4) between 0 and −15 ppm.[30] The variability of the shifts is attributed to differences in the second coordination sphere, namely, the protonation of the C environment and the bridging character of the O.[31] Therefore, the ex-TEOS as-formed powder appeared as uniquely composed of Q units, while the ^{29}Si NMR of the ex-MDSO and ex-ETMS as-formed powders revealed mixed T, D, M, and X environment, with only the T environment being resolved.

The ex-TEOS as-formed powder did not give any CP/MAS ^{13}C signal. After a considerable amount of accumulation, signals were obtained for the ex-MDSO and ex-ETMS as-formed powders with two distinct resonances: a broad one at 130 ± 20 ppm and a sharper one at −2.5 ppm (Figure 6). The downfield resonance was characteristic of sp^2 aromatic C, while the upfield resonance was intermediate between resonances expected for Si−CH_3 sp^3 C in D (0 ppm) and T (−5 ppm) units. Extending downfield to 5 ppm, it was sufficiently broad to contain a contribution from bridging Si−CH_2−Si carbons (1.6−3 ppm).[28]

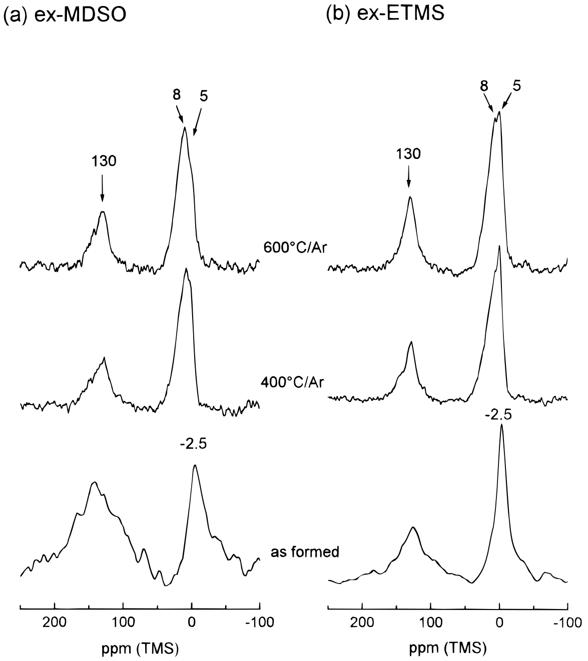

Figure 6. ^{13}C CP/MAS NMR spectra of the ex-MDSO and ex-ETMS powders: (a) ex-MDSO; (b) ex-ETMS.

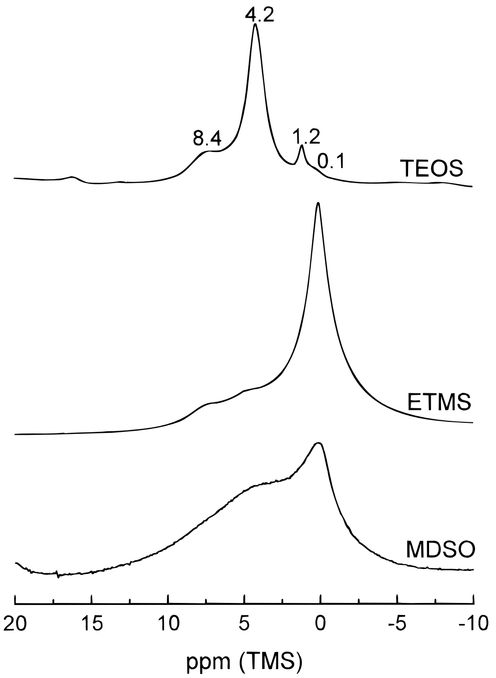

Figure 7. ^{1}H MAS NMR spectra of the as-formed powders.

All the ^{1}H spectra exhibited a broad component at 4.2 ppm (present only as a shoulder in the ex-ETMS as-formed powder) and a more or less resolved contribution around 8 ppm (Figure 7). A peak at 0.1 ppm was also present in all spectra except that of the ex-TEOS sample. In place a line at 1.2 ppm was observed in this sample. By comparison to the spectra of protons on silica surfaces, the resonance at 4.2 ppm can be attributed to physisorbed water or hydrogen-bonded Si−OH groups, while the peak at 1.2 ppm may correspond

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(30) Beshah, K.; Mark, J. E.; Ackerman, J. L. *J. Polym. Sci. B* **1986**, *24*, 1207. Marsmann, H.; In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1981; Vol. 17.

(31) Babonneau, F.; Bois, L.; Yang, C.-Y.; Interrante, L. V. *Chem. Mater.* **1994**, *6*, 51.

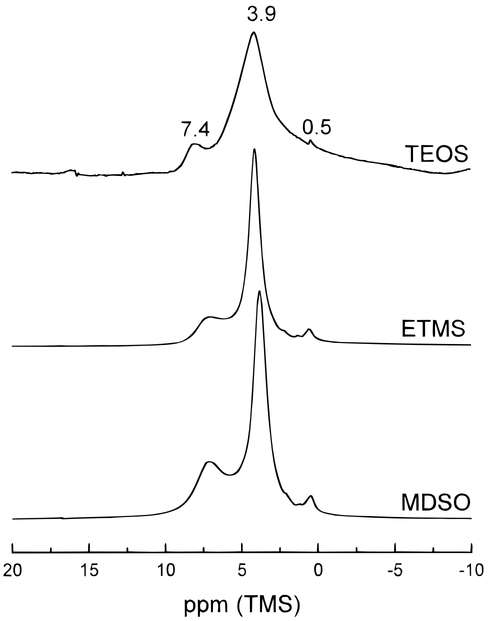

Figure 8. ^{1}H MAS NMR spectra of the samples oxidized 1 h in air at 600 °C.

to isolated, non-hydrogen bonded Si−OH or to residual ethoxy groups.[32,33] The resonance around 8 ppm can be attributed to protons on aromatic carbons. Strongly hydrogen-bound water can also resonate at such a frequency as is observed on zeolites and silica.[34,35] However this possibility was ruled out in these systems by checking that the 7−9 ppm line was unaffected by degassing under vacuum. For the one at 0.1 ppm, such a shielded shift certainly belongs to protons on Si-bonded carbon, but there is some ambiguity as to whether it reflects on a bridging Si−CH$_2$−Si or on a terminal Si−CH$_3$ environment.[36]

In conclusions, ^{13}C CP/MAS NMR allowed to distinguish aromatic and Si−C carbons establishing the presence of a free aromatic carbon phase. This phase was also detected by ^{1}H NMR which also allowed distinctions of resonances associated with silanol and methylsilane groups. Finally, ^{29}Si NMR probed the Si environment in the silicon oxycarbide phase.

Pyrolyzed Silicon Oxycarbides. Because of a loss of free carbon to CO$_2$ or CO, oxidation under air led to a whitening of the powders. The ^{29}Si spectra of all samples revealed a unique Q environment at −110 ppm (not shown). The ^{1}H resonance indicative of Si−C environments at 0.1 ppm decreased and shifted downfield to 0.5 ppm, leaving the proton spectra dominated by the 3.9 ppm resonance indicative of hydrogen bonded Si−OH protons and the 7−8 ppm resonance of the protons of the aromatic phase (Figure 8).

Ex-ETMS and ex-MDSO samples pyrolyzed under Ar at temperatures above 600 °C gave no CP/MAS ^{13}C spectra (nor CP/MAS ^{29}Si) due to the lack of protons. Indeed the IR ρ_s[Si−CH$_3$] and ν_{as}[SiOC$_2$H$_5$] bands, at 1260 and 2960 cm^{-1} respectively, disappeared at 800 °C. At inferior temperatures, little changes were observed except for a shift of the sp^3 resonance from −2.5 to 5−8 ppm (Figure 6). This shift reflected the increasing occurrence of bridging carbons.

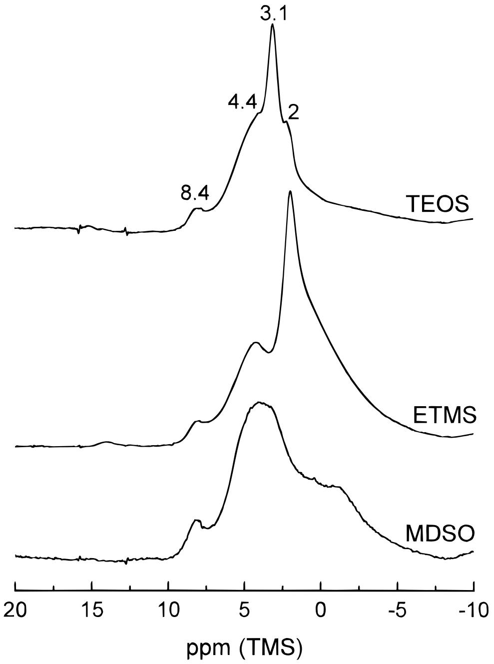

Figure 9. ^{1}H MAS NMR spectra of the samples pyrolyzed 1 h under Ar at 1200 °C.

The ^{29}Si spectra became more distinctive for the ex-ETMS and ex-MDSO samples upon treatment under inert atmosphere due to a progressive decrease of the line widths (Figure 3). At 1200 °C, the Q (−113 ppm), T (−70 ppm), D (−35 ppm), and X (−15 ppm) resonances were resolved. The latter contained a downfield shoulder that could be indicative of an M (ca. 10 ppm) resonance. The ^{29}Si CP/MAS spectra (obtained below 600 °C) privileged the resonances of the most carbidic environments. The Q resonance was almost suppressed, while the X resonance was the most favored. This proved that the main proton-bearing species were the Si−C carbons instead of silanols. Concerning the ex-TEOS sample, its one-pulse ^{29}Si spectrum showed again only one line at −113 ppm after pyrolysis (Figure 5). The main difference from the spectrum of the as-formed powder was that the line was symmetrical. For all samples, after 1600 °C treatment only the X resonances of a crystalline mixture of β- and α-SiC polytypes at −16 and −19 ppm was present (Figure 3).[37,38] The proton spectra presented the same type of resonances as for the samples pyrolyzed under air: 7−9 ppm for protons on aromatic carbons, 3.1 and 2 ppm resonances for hydrogen-bonded and isolated OH, respectively, and a broad resonance around 0 ppm for protons on silicon-bonded carbons (Figure 9). This assignment is in line with what has been observed on pyrolyzed sol−gel precursors.[39,40]

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(32) Bronnimann, C. E.; Zeigler, R. C.; Maciel, G. E. *J. Am. Chem. Soc.* **1988**, *110*, 2023.

(33) Maciel, G. E.; Ellis, P. D. In *NMR Techniques in Catalysis*; Bell, A. T., Pines, A., Eds.; Marcel Dekker: New York, 1994; p 231 and references therein.

(34) Hunger, M.; Freude, D.; Pfeifer, H.; Bremer, H.; Jank, M.; Wendlandt, K. P. *Chem. Phys. Lett.* **1983**, *100*, 29.

(35) Dorémieux-Morin, C.; Heeribout, L.; Dumousseaux, C.; Fraissard, J.; Hommel, H.; Legrand, A. P. *J. Am. Chem. Soc.* **1996**, *118*, 13040.

(36) Engelhardt, G.; Jancke, H.; Mägi, M.; Pehk, T.; Lippmaa, E. *J. Organomet. Chem.* **1971**, *28*, 293.

(37) Apperley, D. C.; Harris, R. K.; Marshall, G. L.; Thompson, D. P. *J. Am. Ceram. Soc.* **1991**, *74*, 777.

(38) Carduner, K. R.; Shinozaki, S. S.; Rokosz, M. J.; Peters, C. R.; Whalen, T. J. *J. Am. Ceram. Soc.* **1990**, *8*, 2281.

(39) Babonneau, F.; Bois, L.; Livage, J. *J. Non-Cryst. Solids* **1992**, *147*, 280.

Discussion

Characterization of the Powders at the Atomic Scale. The structure and chemistry of Si/O/C glasses prepared by conventional pyrolysis have been extensively investigated.[5−10, 15−21,41,42] First a gel is obtained by polymerization of an organometallic precursor via the formation of siloxane bonds. Then the tetrahedral network is densified by thermal mineralization of the organic carbons into bridging carbidic carbons on one hand, and a free aromatic carbon phase on the other hand. Furthermore it was demonstrated by ^{29}Si MAS NMR that the first coordination shell of the silicon is also affected during mineralization through a Si−O and Si−C bond exchange mechanism.[43]

For laser-obtained Si/O/C, the situation is slightly more complex. During the synthesis, because of the thermal redistribution of the photon energy, a partial mineralization is simultaneous with the photon-induced siloxane polymerization. To progress in the laser synthesis of Si/O/C nanopowders, it is necessary to assess the extent of the network density and its evolution during pyrolysis.

A further difficulty is that polymerization results not from a hydrolysis but from the recombination of photon-induced radicals. A significant amount of dangling bonds are therefore present in the as-formed powders. Moreover a wide dispersion of chemical shifts is expected due to the brutal quenching experienced by the powder at the exit of the laser beam. These two facts led to broad ^{29}Si NMR spectra (Figure 3). In gel precursors it is often possible to calculate the connectivity of the structure through the small ^{29}Si NMR chemical shifts due to changes in the second coordination sphere.[44] Obviously, the ^{29}Si spectra in our material were too broad for such an analysis, but we will show that we were still able to qualitatively estimate the condensation of our powders through indirect evidence.

Pyrogenic Silica from TEOS. The case of the ex-TEOS powders involving only Q environments was relatively straightforward and is exposed here as reference for the analysis of the more complex ex-MDSO and ex-ETMS powders. The original Q environment from the TEOS liquid precursor remained in the as-formed powder. All the ex-TEOS powders exhibited only a Q resonance by ^{29}Si NMR. However, this resonance was shifted upfield from −106 to −113 ppm upon thermal treatment. Moreover, the peak became more symmetrical. In fact, the Q line before thermal treatment was the summed contribution of three environments (Figure 5) according to the degree of condensation of the tetrahedra, as is classically the case in silica:[45] Q^4(4Si), Q^3(3Si, OH), Q^2(2Si, 2OH) resonating respectively at −107, −99, and −88 ppm. Neglecting the unreacted ethoxy groups, the intensities of these contributions allowed us to derive the composition of the silicate phase in the ex-TEOS as-formed powders (Table 3): $SiO_{1.7}(OH)_{0.6}$. The validity of this treatment was confirmed by comparison to the chemical analysis (Table 2) leading to $SiO_{1.7}(OH)_{0.6} + 0.6CH$. Clearly the excess of oxygen in the as-formed powders was thus due to the incomplete condensation of the tetrahedral network. After dehydration during thermal treatment, all tetrahedra were fully condensed and only the Q^4 environment contributed. Proton NMR confirmed that Q coordination was conserved in the ex-TEOS powders. Indeed, the spectra corresponded exactly to what would be expected from a mixture of pyrogenic silica (adsorbed water and hydrogen-bonded Si−OH between 3 and 4 ppm, and isolated Si−OH between 1 and 2 ppm) and a free aromatic carbon phase (protons around 8 ppm).[46,47] Consequently, no Si−C resonance was obtained for the ex-TEOS powders by CP/MAS ^{13}C NMR (in those materials, the aromatic C resonance is too broad to be distinguished alone from the baseline).

Table 3. ^{29}Si NMR Peak Positions and Integrated Intensities for the As-Formed and Pyrolyzed 1 h under Ar up to 1000 °C Powders

samples			Q		T		Σ(D,M,X)	
			δ (ppm)	%	δ (ppm)	%	δ (ppm)	%
ETMS	as-formed		∼−110	0	−65	20	−10 ± 20	80
	400 °C/Ar			15		25		60
	600 °C/Ar			15		25		60
	1000 °C/Ar			25		25		50
random	prediction			9		29		62
MDSO	as-formed		∼−106	0	−65	15	−10 ± 20	85
	400 °C/Ar			10		10		80
	600 °C/Ar			10		10		80
	1000 °C/Ar			20		20		60
random	prediction			1		9		90
TEOS	as-formed	Q^4	−107	55				
		Q^3	−99	37				
		Q^2	−88	8				

Relationship between Si Bonding in the Aerosol and Tetrahedral Condensation in the Powders. For the M precursors, the breadth of the lines and the multiplicity of silicon environments in the formed powders precluded a direct analysis of the connectivity of the siloxane network. However, it could be estimated that nonbridging oxygens were a minor occurrence, even in the as-formed powders. Compared to the ex-TEOS sample, the silanol proton NMR resonances were negligible and the Si−C protons dominated the spectra at 0.1 ppm (Figure 7). Even more convincingly the ^{29}Si Q resonances were not enhanced by cross-polarization (Figures 3 and 4).

Having established that siloxane condensation was nearly complete in the as-formed powders, it was interesting to examine the extend of carbidic bridges. The ^{1}H NMR resonance of the Si−C protons at 0.1 ppm was more intense in the spectrum of the ex-ETMS as-formed powder than in the spectrum of the ex-MDSO powder (Figure 7). It was also directly possible by CP/MAS ^{13}C NMR to follow the aromatic and Si−C groups, and the same trend was confirmed: the Si−C resonance at −2.5 ppm was stronger for the ex-ETMS as-formed powder. Thereby both ^{1}H and ^{13}C NMR indicated that there was less C in the silicon oxycarbide phase of the ex-MDSO as-formed powder than in the ex-ETMS one. This was also reflected in a lower C content and C/Si

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(40) Babonneau, F.; Bois, L.; Yang, C.-Y.; Interrante, L. V. *Chem. Mater.* **1994**, *6*, 51.

(41) Renlund, G. M.; Prochazka, S.; Doremus, R. H. *J. Mater. Res.* **1991**, *6*, 2716, 2723.

(42) Zhang, H.; Pantano, C. G. *J. Am. Ceram. Soc.* **1990**, *73*, 958.

(43) Belot, V.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *J. Polym. Sci., Part A*: *Polym. Chem.* **1992**, *30*, 613.

(44) Sorarù, G. D.; D'Andrea, G.; Campostrini, R.; Babonneau, F. *J. Mater. Chem.* **1995**, *5*, 1363.

(45) Léonardelli, S.; Facchini, C.; Fretigny, C.; Tougne, P.; Legrand, A. P. *J. Am. Chem. Soc.* **1992**, *114*, 6412.

(46) Liu, C. C.; Maciel, G. E. *J. Am. Chem. Soc.* **1996**, *118*, 5103.

(47) Espinose de la Caillerie, J.-B. d'; Aimeur, M. R.; El Kortobi, Y.; Legrand, A.-P. *J. Am. Chem. Soc.*, submitted.

Table 4. ^{29}Si NMR Peak Positions and Integrated Intensities, with Derived Compositions, for the Powders Pyrolyzed 1 h under Ar at 1200 °C

pyrolyzed samples	SiO_4		$SiCO_3$		SiC_2O_2		SiC_3O		SiC_4		stoichiometry from NMR analysis
	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	δ (ppm)	%	
ETMS	−107	33	−70	11	−35	10	6	10	−11	35	$SiC_{0.50}O_{0.99}$
MDSO	−107	15	−71	14	−38	16	5	16	−13	40	$SiC_{0.63}O_{0.75}$
TEOS	−113	100		0		0		0		0	$SiO_{2.00}$

ratio from chemical analysis. The ex-MDSO as-formed powder was therefore not only less oxygenated, as predicted from the lower O content of the aerosol and indicated from the lower O/Si chemical analysis ratio (Table 2), but also contained less carbon. This argued for a higher degree of carbidic condensation. IR and CP/MAS ^{29}Si NMR also supported the conclusion that there were less nonbridging terminal Si−CH_3 groups in the ex-MDSO sample. The IR bands of the residual methyl groups at 1260 cm^{-1} was comparatively less intense than on the ex-ETMS sample. In addition, CP enhancement of the ^{29}Si NMR signals of the carbidic environments through protons of the terminal methyl groups was less effective.

In conclusion, the ex-MDSO as-formed powder must be the most condensed of the two. Indeed, according to chemical analysis, its composition is closer to the fully condensed stoichiometry (although chemical analysis does not account for the free carbon content which can be different in both samples). This can be rationalized by the higher initial condensation of the siloxane precursor MDSO and might explain the lower surface area of the ex-MDSO products.

Structural Homogeneity. The ^{29}Si spectra (Figures 3 and 4) revealed a deep rearrangement of Si bonding in the as-formed powder samples with respect to the original aerosol. From the MDSO and ETMS aerosols with M environments, powders were formed with a wide variety of SiO_xC_{4-x} environments. As previously stated, such exchange mechanisms have already been evidenced during the synthesis of sol−gel derived oxycarbide glass by pyrolysis. This further supported the idea that, although the reaction mechanisms in the laser beam are still obscure at the moment, modeling of the reaction as an instant and partial pyrolysis followed by rapid and immediate quenching is valid.

Within the assumption that all the oxygen atoms belong to Si−O−Si bridges and that silicon atoms are bonded to carbon and oxygen atoms only, Mutin and coworkers derived a simple formula for the ^{29}Si NMR relative intensity I_x of a SiO_xC_{4-x} resonance in a random glass[48] (the same type of calculation has also been performed for the Si/C/N system):[49]

$$I_x = \frac{4!}{x!(4-x)!}[r/2]^x[1 - r/2]^{4-x}$$

where r is the O/Si ratio. Fortunately, in our powders which were, as demonstrated above, only partially mineralized, no assumption on the bridging character of the C need be made. One drawback is that in ignoring the stoichiometry of the Si/O/C phase we were prevented from calculating the free carbon content. The intensities were obtained by integration of the NMR spectra (Tables 3 and 4). For the samples pyrolyzed at 1200 °C where mineralization and thus condensation reached total completion (no methyl or ethoxy IR bands and no CP signals above 600 °C), r is approximated from the NMR spectrum itself according to:

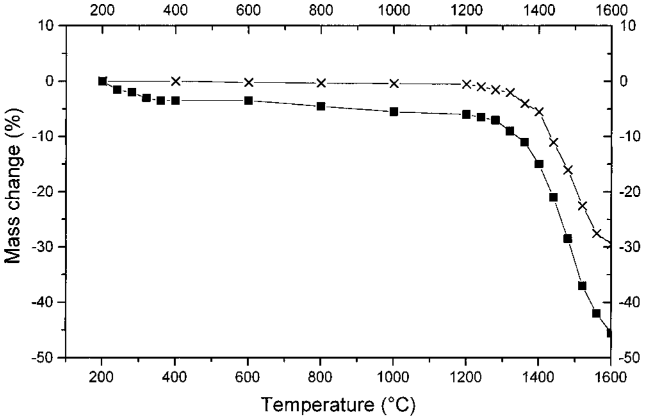

Figure 10. TGA curves of treatment under Ar: (×) ex-MDSO; (■) ex-ETMS.

$$r = \sum_{i=0}^{4} I_i i/2$$

For the as-formed powders, despite the fact that the NMR lines were not resolved, r could be obtained from the chemical analysis. Indeed, both elements O and Si belonged to the Si/O/C phase exclusively, as the ^{13}C NMR revealed no resonance indicative of an alkoxy ligand around 50−60 ppm[50] and as the IR band of the unreacted ethoxy groups was exceedingly weak. For the Si/O/C phases, it was therefore possible from the ^{29}Si NMR spectra to test if O and C were randomly distributed around Si, or if a particular, even if unknown, arrangement of tetrahedral types were privileged. For the ex-ETMS and ex-MDSO as-formed and pyrolyzed up to 1000 °C powders, only the T and Q resonances were resolved, but it was possible to test if the summed intensities were nevertheless compatible with a random model of Si−O and Si−C distribution within the solid (Table 3). The agreement was acceptable (within ±10% which is the accuracy of the NMR decomposition) with the exception of the ex-ETMS as-formed powder. Interestingly, this sample was not compositionally stable below 400 °C as evidenced by TGA (Figure 10). This suggested that mineralization was less advanced on the ex-ETMS powder. After pyrolysis at 1200 °C there was a clear deviation from the random model (Figure 11). This tended to indicate that although the material was still X-ray amorphous (Figure 1) and compositionally stable (Figure 10), it already started to organize. More precisely, the intensities corresponding to the pure SiO_2 and SiC environment grew relative to the random

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(48) Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *J. Mater. Sci.* **1995**, *30*, 2313.

(49) Suzuki, M.; Hasegawa, Y.; Aisawa, M.; Nakata, Y.; Okutani, T. *J. Am. Ceram. Soc.* **1995**, *78*, 83.

(50) Rakita, P. E.; Worsham, L. S.; Srebo, J. P. *Org. Magn. Reson.* **1976**, *8*, 310.

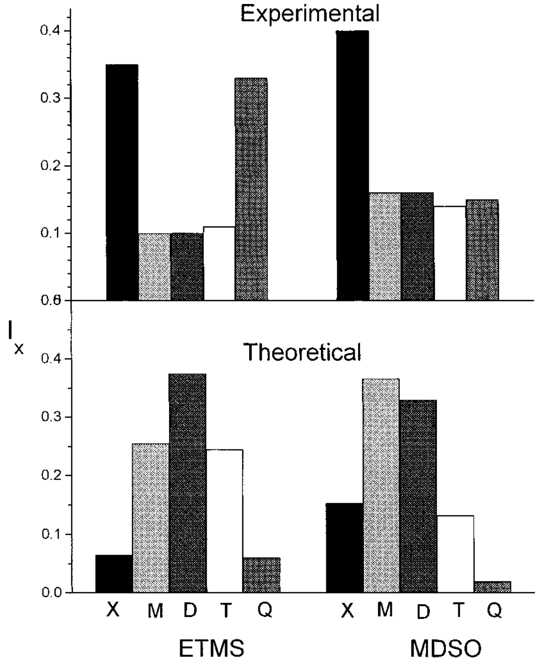

Figure 11. ^{29}Si MAS NMR relative intensities for the ex-MDSO and ex-ETMS samples pyrolyzed 1 h under Ar at 1200 °C (see Figure 3 and Table 4), and the predicted values assuming a random model taking *r* values derived from the ^{29}Si NMR data (0.99 and 0.75 for ex-ETMS and ex-MDSO, respectively).

model, possibly because of phase demixing as suggested by the growth of the broad XRD reflection between 35 and 40° 2θ.

Conclusion

This study illustrates the great versatility of the synthesis method. The local environment of the Si in the precursor was modified through a limited bond redistribution and condensation during the earlier stage of the synthesis, leading to a total randomization of the Si environment. Condensation, on the other hand, depended on the precursors choice and reaction conditions. The choice of a Q precursor, not allowing bond redistribution, led to the synthesis of a nanosized silica, and excess aromatic carbon was burned off by thermal oxidation. Alternatively, a choice of a precursor with a mixed SiO_xC_{4-x} environment led to a mixture of mineralized SiOC and free aromatic carbon after pyrolysis under inert atmosphere. The local structure (*i.e.*, degree of tetrahedral condensation and homogeneity of composition) and the surface area of the mineralized phase, depending on thermal bond redistribution and carboreduction can be tailored by the choice of the precursor, noticeably through the O content, and the thermal treatment. Regarding this last point, ^{29}Si NMR was sensible to heterogeneity in the local composition at temperatures below the onset of crystallization. Assuming that the energy absorbed from the laser is thermally redistributed to all the bonds, the original chemical structure of the organometallic should be indifferent, while the determining parameter should be simply its Si/O/C atomic composition. Remarkably, we have shown here that this is actually not the case as the choice of a siloxane precursor rather than a silane led to significantly more condensed powders.

This multinuclear NMR study of silicon oxycarbide powders synthesized by laser–aerosol interaction revealed three possible levels of understanding relative to the influence of the composition of the aerosol: it was possible to relate the O and C content of the powders to the original composition of the organometallic liquid; to relate the Si environment in the powders to the original one in the liquid; and finally to determine at what scale the composition is homogeneous, that is, if C and O were randomly distributed in the tetrahedral network.

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