



Porous silicon oxycarbide glasses from hybrid ambigels

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ABSTRACT

Highly porous ambigels (aerogel-like materials dried at ambient pressure) have been employed for the synthesis of porous siliconoxycarbide (SiOC) glass. Ambigels were synthesized from methyltriethoxysilane (MTES), (bistriethoxysilyl)methane (BTEM) and 1,2(bistriethoxysilyl)ethane (BTEE) as the starting precursors which were later pyrolysed yielding porous SiOC glass. The synthesized ambigels possess very high surface area and pore volumes and a maximum surface area of 1131 m²/g with a pore volume of 1.29 cm³/g could be achieved for the gels derived from BTEE. After pyrolysing the ambigels in inert atmosphere, the porosity has been retained and a surface area as high as 430 m²/g could be attained. Solid state NMR studies have been employed to verify the retention of Si–C bond in the pyrolysed glass.

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1. Introduction

Mesoporous materials have attracted a great deal of interest ever since they were reported less than two decade ago [1]. Research into mesostructured silica and other inorganic oxides has grown steadily in recent years and these materials have been synthesized as powders, monoliths and films [2]. These porous nanostructured systems find applications in diverse fields such as catalyst supports, molecular sieves, gas adsorbents and ceramics [3]. Unfortunately, many of these applications require very high thermal stability which these mesoporous materials lack.

Silicon oxycarbide (SiOC) glass is an amorphous solid where there is a partial replacement of Si–O bonds with Si–C bonds. They are stable at high temperature up to 1200 °C either in oxidizing and inert atmosphere [4,5]. Recently, [6] calorimetric measurements confirmed that SiOCs are thermodynamically stable compared to their crystalline constituents and this result has been associated with their very peculiar nanostructure [7].

SiOC glass can be prepared through pyrolysis under inert atmosphere of cross-linked polysiloxane networks (preceramic polymer) containing Si–R bonds. (R = H, CH₃, CH₂–CH₃, C₆H₅...) [8–10]. The preceramic polymer can be prepared from alkoxy silanes (by employing sol–gel chemistry) [8,9] or from polysiloxanes [10] or polycarbosilane [11].

Porous SiOC ceramics in bulk and cellular structures are reported via polymer pyrolysis from crosslinked polysiloxanes by Schmidt et al. [12]. The authors found that the pore characteristics

and specific surface areas of polymer-derived ceramics are strongly dependent on the composition of the preceramic material as well as on the maximum pyrolysis temperature. In addition to these, the heating rate also has an influence on the final pore characteristic of the ceramic.

Singh and Pantano synthesized high surface area hybrid gels and SiOC glasses from mixtures of methyltrimethoxysilane (MDMS) and tetraethoxysilane (TEOS) [13]. The gels were aged in ammonium hydroxide and the ²⁹Si MAS NMR spectra revealed that the Si–C bonds are unaffected by aging. On pyrolysis of the aged gels in non-oxidizing atmosphere, surface area could be retained (200 m²/g at 1200 °C).

Phenyltrimethoxysilane (PhTMS) and tetramethoxysilane (TMOS) derived hybrid aerogels and xerogels were used as precursors to produce porous SiC/SiOC glasses by Liu et al. [14]. By pyrolysing 25 mol% PhTMS and 75 mol% TMOS aerogel in argon, porous SiOC glass of high thermal stability and high surface area (581 m²/g at 1000 °C) was achieved.

Toury et al. synthesized periodic mesoporous silicas (PMOs) starting from two (bis-trialkoxysilyl)ethane [1,2(bistriethoxysilyl)ethane(BTEE) and 1,2(bis(trimethoxysilyl)ethane (BTME))] and ionic surfactant cetyltrimethylammoniumchloride (CTAC) [15]. The difference in alkyl groups causes a major change in the pore structure, with 2D-hexagonal symmetry for the material derived from BTEE and cubic Pm3n symmetry for that derived from BTME. The BTME derived sample retains the initial cubic structure even at 1000 °C and exhibits a large BET surface area of 735 m²/g. More over the ²⁹Si MAS NMR spectra confirms the retention of Si–C bonds.

PMO's from (bistriethoxysilyl)methane (BTEM) and cetyltrimethylammoniumchloride (CTAC) were also reported [16]. The

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synthetic conditions (pH, CTAC/BTEM ratio, post-treatments and concentrations) were used to study their effects on the structure of the as-prepared samples. The samples exhibited a 2D-hexagonal structure with a surface area of 950 m²/g. On pyrolysis at 800 °C, the samples exhibited a surface area of 800 m²/g with retention of Si–C bonds.

In a similar work by the same group, Pluronic F127 was used as the structure directing agent together with the bridged silane [1,2(bis(triethoxysilyl)ethane (BTEE)] [17]. The periodic mesoporous silicas were later pyrolysed in argon atmosphere to obtain porous SiOC glass which possessed a surface area of 260 m²/g. The ²⁹Si MAS NMR studies also revealed the retention of Si–C bonds.

In a recent work, 1,3,5-tris(dimethoxysilyl)cyclohexane was synthesized by adding chlorotrimethoxysilane to magnesium in tetrahydrofuran (THF) (Grignard reaction) at 50 °C [18]. There after 1,3,5-tris(dimethoxysilyl)cyclohexane was treated with ethylene glycol at 140 °C where transesterification takes place. The transesterified product was then sol–gel processed in HCl in presence of Pluronic P123 and KCl to obtain wet gels which were later supercritically dried to obtain aerogels. The monoliths were later pyrolysed in argon atmosphere at 1000 °C to yield silicon oxycarbide monoliths by maintaining the hierarchical porosity of the organo-silica gel.

Silica aerogel possess many unique physical and chemical properties and hence are widely used in fundamental and applied areas. They are by and large synthesized under supercritical conditions where the capillary stresses inside the wet alcogel can be nullified resulting in a highly porous network. However, the synthesis of the aerogels under ambient conditions (ambigels) is still under active investigation and has been widely reported in the literature [19–29]. In the present work, we studied the synthesis of highly porous SiOC glasses starting from hybrid ambigels obtained from two different arylene-bridged silicon alkoxides: 1,2(bis(triethoxysilyl)ethane (BTEE) and (bis(triethoxysilyl)methane (BTEM). Loy and Shea reported various arylene-bridged polysilsesquioxane xerogels and aerogels [30,31], but only recently these precursors have also been employed for the preparation of PMOs (periodically mesoporous silicas) which were later pyrolysed to produce ordered porous SiCO glass powders [15–18]. In this work, we will show that our synthetic approach can be adjusted for the synthesis of highly porous bulk SiOC glasses from hybrid ambigels, which can exploit to the utmost the potential applications of silicon oxycarbide glasses. Moreover, to investigate the role of the bridging organic group, porous SiOCs have also been synthesized from methyltriethoxysilane (MTES) which is a similar alkoxides bearing three ethoxy groups per silicon atom but with a terminal CH₃ group instead of a bridging arylene moiety (see Scheme 1).

The porosity features of the preceramic ambigels and also the pyrolysed glasses are presented in this study. The ²⁹Si magic angle spinning nuclear magnetic resonance (²⁹Si MAS NMR) studies were also employed to characterize the local environment around the

silicon atoms and to obtain information on the condensation degree of the gel network.

2. Experimental

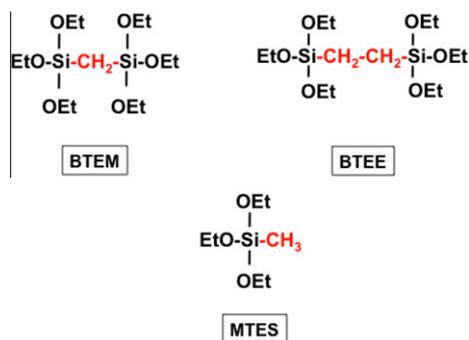
(Bis(triethoxysilyl)methane (BTEM), 1,2(bis(triethoxysilyl)ethane (BTEE), Aldrich Chemicals), methyltriethoxysilane (MTES) (ABCR, Germany), HCl (Aldrich Chemicals), ammonia (Aldrich Chemicals) and isopropanol (Aldrich Chemicals) were used as received. The molar ratio of alkoxide:isopropanol:acidic water:basic water was maintained at 1:5:4:4. The ambigels derived from MTES were labelled MTS and those derived from BTEE and BTEM were labelled as BTE and BTM, respectively. A higher water molar ratio was also used for the preparation of BTE gels and a ratio of alkoxide:isopropanol:acidic water:basic water, 1:5:8:0.5 was employed. The samples are labelled BTE8 where 8 stands for the molar ratio of water used (1:5:8:0.5). All the gels derived from BTEM were prepared only on the molar ratio of 1:5:8:0.5.

To prepare the silica sol, the following procedure has been used for all the investigated alkoxides. As an example, we describe the recipe in the case of the methyl-modified precursor. MTES in isopropanol was hydrolyzed with acidified water (3 M HCl) and was stirred for one hour. Then basic water (13.36 M NH₄OH) was added dropwise while stirring. In a typical experiment, silica sol was prepared by hydrolyzing 4.433 g MTES in 7.458 g isopropanol with 1.789 g water (acidified water). After stirring for 1 h, 3.480 g basic water was added dropwise. The sol was stirred for 5 min and was kept at 50 °C for gelation. The gelation time was noted and was found to be 120 min.

The alcogels were aged for one week at 50 °C in closed environment, and then were solvent exchanged with isopropanol (3× in 24 h) maintaining the gels at 50 °C. This was followed by aging the gels in 60 vol% of the starting MTES solution in isopropanol for 48 h at 50 °C. This sample was labelled MTS 60. A second aerogel sample was also prepared by aging the alcogels in 80 vol% silane solution and it was labelled MTS 80. The final solvent exchanged was done with isopropanol (3× in 24 h) to remove excess silane keeping the gels at 50 °C. The gels were finally dried slowly at 50 °C to preserve the porous network. Accordingly, the containers were sealed by covering them with aluminium foil and the foil was then sealed well with cellophane tape. This experimental set-up allows the slow drying of the gel. After 2 weeks, a pin hole is made on the cover to allow for the complete drying of the samples which normally takes 1 week.

Normally two methods are reported in the literature for synthesising aerogels by ambient pressure drying. One is to cap organic groups so that there will be a spring back effect while drying [19,20] and the other is to strengthen the gel network by aging in silane solutions [21,25]. Hence the first solvent exchange step was followed by aging the gels with different silane concentration. The effect of concentration of the aging solution on subcritically dried silica aerogels (TEOS-derived) has been studied by Smitha et al. [25] and good quality aerogels were obtained for the 60% and 80% silane aged gels. Hence in our study we used 60% and 80% silane treatments. More over we use a low surface tension solvent 2-propanol (isopropanol) which will hence reduce the capillary pressure resulting in high surface area ambigels.

The BTE and BTM gels were prepared in the same way as described above with an exception that the results obtained on the silane treated samples are not presented here. We observe no effect at all of the silanisation step and we present only the results of the non-silanated gels which are labelled BTE 0 and BTM 0. As stated earlier a higher molar ratio of water was also used to prepare gels from the ethane-bridged siloxane and the corresponding gels were labelled BTE8 0.



Scheme 1. The structure of the three hybrid silicon alkoxides used in this study.

The bulk density of the dried gels was calculated from their mass and volume. The porosity was calculated following a method reported elsewhere [29]. The BET surface area of aerogels was determined by N₂ adsorption at 77 K (Micromeritics, Gemini Model 2010, USA). The specific surface area was determined using the BET equation with an accuracy of ±10 m²/g [32]. The total pore volume was calculated as,

$$\text{Pore volume, } V = V_a^* D$$

where V_a = volume adsorbed at P/P_0 0.99, D = density conversion factor (0.0015468 for nitrogen as adsorbate gas). The pore size distribution was obtained using the Barrett–Joyner–Halenda (BJH) method [33]. The micropore volume was determined by Harkins–Jura method. Assuming that the pores are cylindrical and open at both ends, the average pore size of a given sample is calculated using the equation,

$$\text{Average pore size} = 4V_{\text{total}}/\text{SBET}$$

The ²⁹Si MAS NMR spectra were collected with a MSL 300 Bruker spectrometer at 59.6 MHz. The powdered samples were put in 7 mm zirconia rotor and spun at 4 kHz. Spectra were referenced externally to tetramethylsilane (TMS) at 0 ppm.

The thermogravimetric analysis were performed in a DTA/TG thermoanalyser (Netzsch, STA 409), equipped with an alumina tubular furnace and alumina crucible. Analysis was performed by taking about 40–50 mg of gel sample under argon (100 ml/min) flow and a heating rate of 10 °C/min. A buoyancy correction was also applied to the TG data.

The pyrolysis of the gels were done in controlled atmosphere (flowing argon, 100 ml/min) at 1000 °C using a graphite furnace (Astro, Thermal Technology, USA). Monolithic pieces were pyrolysed at a heating rate of 5 °C/min and were soaked at the maximum temperature for 3 h.

Chemical analysis was performed on selected SiOC samples. O, C and H were measured and Si was estimated by difference to 100%. Elemental analysis was performed via hot gas extraction using an O-analyzer (TC-436, Leco Instrumente GmbH, Mönchengladbach, Germany) and via combustion analysis with a C-analyzer (C-200, Leco Instrumente GmbH, Mönchengladbach, Germany). H analysis has been performed by the “Mikroanalytisches Labor Pascher” Remagen–Bandorf, Germany.

3. Results and discussions

3.1. Ambigel characterization

We start presenting and discussing the data for the methyl-modified samples, MTS gels, and later we will compare the results with those obtained for the ethane- and methane-bridged alkoxides. The properties measured on the studied ambigels are reported in Table 1. Monolithic, white and opaque MTS ambigels have been obtained (see Fig. 1). The MTS 60 and MTS 80 have densities 0.33 and 0.12 g/cm³, respectively. The porosity calculated for MTS 60 and MTS 80 is found to be 84% and 95%, respectively. Den-

sity and porosity values of MTS 0 samples are also in the range typical of aerogels and suggest that the synthesis conditions, mainly the use of a low surface energy and high boiling point solvent coupled with a slow and controlled drying process, are very suitable for preserving the original pore structure. However, the post-synthesis silanization step is very effective for this system and can decrease down to ¼ the aerogel density (density of the MTS 80 is 0.12 g/cm³ compared to 0.4 g/cm³ of the MTS 0 sample) and up to 95% the porosity compared to the 80% of the non-silanated ambigels.

The adsorption–desorption isotherm (Fig. 2) of MTS 0 can be classified as Type IV according to the IUPAC nomenclature. At higher pressure, there is a hysteresis loop which is caused by the capillary condensation in the mesopores (2–50 nm). The hysteresis loop can further be classified as H3 with slit-shaped pores [34]. These isotherms are also characteristics of pores in the range of 2–200 nm. At lower pressures ($p/p_0 < 0.04$) the isotherms are not linear which indicates the presence of micropores in the material. We also noticed that the amount of nitrogen adsorbed by the MTS 80 aerogel is higher (~1000 cm³/g) at a relative pressure of 0.99 (not shown in Fig. 2) and this is due to the larger pore volume (1.47 cm³/g) compared to both the MTS 0 the MTS 60 samples.

The surface area of MTS 0, MTS 60 and MTS 80 gels are 471, 416 and 727 m²/g, respectively (Table 1). The reason for the highest value of surface area for MTS 80 aerogel is due to its higher total pore volume. The increase in total pore volume can be due to the fact that when more silane monomers are getting into the system, (pores surfaces and also in the gel network) the connectivity degree increases with a corresponding strengthening of the network resulting in lower density and higher porosity. The strengthened network of the MTS 80 sample is also able to preserve, during drying, a larger fraction of micropores compared to the MTS 60 aerogel, and this could be the reason for the slightly lower average pore size of the MTS 80 sample 80 vs. 94 Å, respectively (see Table 1). The pore size distribution of the aerogels are provided in Fig. 3a. The studied MTS ambigels have a broader pore size distribution from 20 to 800 Å.

The BTE 0 gel is cracked (see Fig. 1) and the corresponding properties are provided in (Table 1). Aerogels derived from supercritically dried bridged silsesquioxane gels with densities ranging from 0.1 to 0.7 g/cc were reported by Loy and Shea [30]. They also reported that after the hypercritical extraction of the wet polysilsesquioxane gels considerable shrinkage occurred. The gels however possess very high pore volume and very high surface areas. In our work a very high surface area of 1131 m²/g with a pore volume of 1.29 cm³/g was achieved. The shrinkage for BTE 0 and BTM 0 are 29% and 27%, respectively, while for MTS 0 the shrinkage was found to be only 14%. Nitrogen sorption measurements (Fig. 2) for the gels show Type IV isotherm with a H2 hysteresis loop. The desorption is greatly delayed indicating an open mesoporous system. The pore size distribution of the BTE gels obtained from the BJH analysis of the adsorption branch is provided in Fig. 3b. It can be inferred from the figure the presence of mesopores around 10 nm. Our synthetic procedure is so simple that by using a solvent (2-propanol) which has low surface tension coupled with slow drying, we are able to get high surface area materials with large pore volumes even without silane strengthening treatments.

By increasing the hydrolysis ratio (BTE8 series gels) we were successful in synthesising monolith transparent samples as shown in Fig. 1. For BTE8 0 sample the surface area was found to be 938 m²/g (Table 1). The nitrogen adsorption–desorption isotherm (Fig. 2) indicates that they are Type I isotherms, which can be further classified as Type Ib, where we have wider micropores. The pore size distribution of the BTE8 gels obtained from the BJH analysis of the adsorption branch (Fig. 3b) indicates the presence of pores around 2–4 nm. The acid catalyzed hydrolysis of silicon

Table 1
Properties of prepared ambigels.

Sample	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Pore diameter (Å)	Density (g/cm ³)
MTS 0	471	0.83	70	0.41
MTS 60	416	0.99	94	0.33
MTS 80	727	1.47	80	0.12
BTM 0	1085	0.80	30	0.87
BTE 0	1131	1.29	45	0.52
BTE8 0	938	0.61	26	0.86



Fig. 1. Photograph of MTEs derived ambigels.

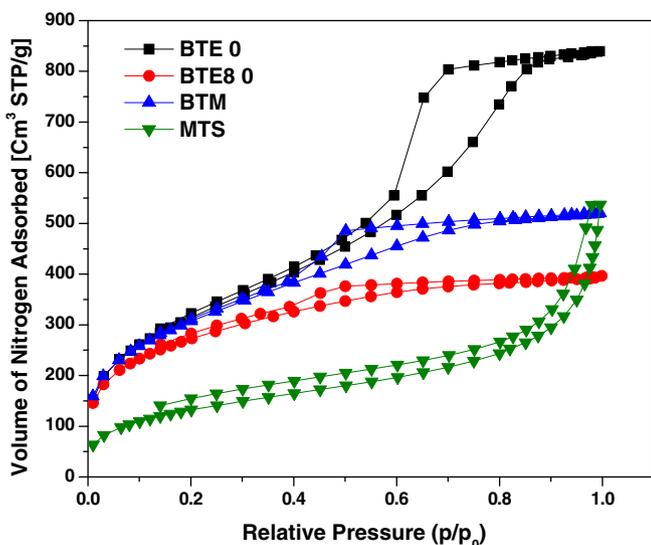


Fig. 2. Adsorption-desorption isotherm of ambigels.

alokoxide is first order with respect to the concentration of water [35]. Hence the rate of hydrolysis of the alkoxide precursors can be considered to increase with increasing water content. But an increase of water reduces the concentration of silicic acid per unit volume which also results in the lower oxide content in the final polymer material. Moreover, water separates the silanol molecules and hinders the crosslinking of the silane chain formation. The network formed under these circumstances will be fragile leading to

the formation of a lower total pore volume and hence a lower surface area after the final drying (see Table 1).

Finally, the properties of the BTM gels are provided in Table 1. The ambigel has a surface area of 1085 m²/g, the isotherm (Fig. 2) are of Type Ib and the pore size distribution (Fig. 3b) indicate the presence of pores which is also around 2–4 nm.

Fig. 4 shows the ²⁹Si MAS NMR spectra of three studied ambigels obtained without silane treatment. For the MTS 0 sample two peaks are observed: a major one at –65 ppm and a less intense one at –56.6 ppm. These two peaks correspond to *T*₂ and *T*₃ Si units, respectively [36]. Accordingly, *T*₃ refers to a CSiO₃ silicon site in which all three oxygens form oxo-bridges while *T*₂ indicates the same Si site in which only two oxygens are oxo-bridges and one oxygen is terminal. The terminal group can be either an OH or a residual organic group. The ²⁹Si MAS NMR spectrum of the BTE 0 gel shows a broader peak centered at –56 ppm (*T*₂ sites) with two shoulders at –64 (*T*₃ sites) and at –46 ppm (*T*₁ sites, i.e. CSiO₃ sites with two terminal oxygen and one oxo-bridge) [15]. The ²⁹Si MAS spectrum of the BTM gel is similar to the one of BTE and shows a main *T*₂ peak at –56 ppm with the two shoulders at –46 ppm (*T*₁) and at –65 ppm (*T*₃). The peak at around 60 ppm is characteristic of *T*₂ units with one terminal Si–OX (X = H and R) group [16]. The experimental ²⁹Si MAS NMR spectra have been deconvoluted and the amount of the individual components has been evaluated (Table 2).

The average number of oxo-bridges per Si atom can be evaluated from the quantitative MAS NMR analysis (Table 2). Accordingly, each Si atoms in MTS display 2.82 oxo-bridges while for the BTE and BTM gels, the number of oxo-bridges is lower (2.19 and 2.25, respectively). However, taking into account that for the methane and ethane-bridged siloxanes each Si atom also bears a

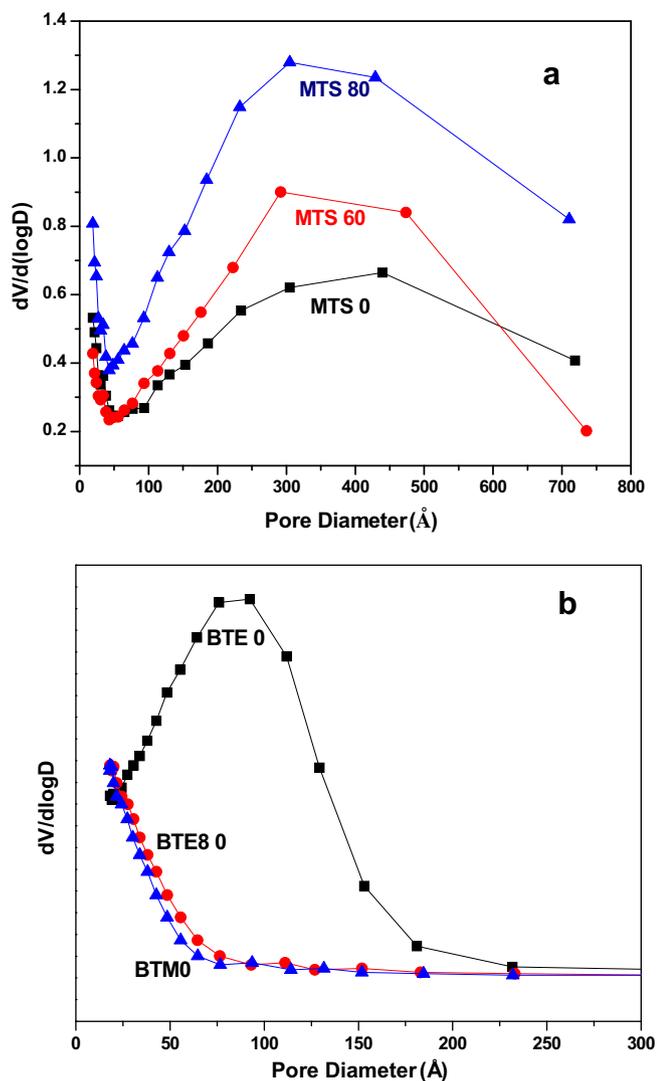


Fig. 3. (a) Pore size distribution of the MTS derived ambigels and (b) pore size distribution of BTE 0 BTE 8 and BTM 0 ambigels.

Si–R–Si bridge (R = CH₂ and C₂H₄) then the total connectivity (total number of bridges, –O– and –R–, per Si atom) is higher for the BTM (3.25) and BTE (3.19) compared to the MTS gel (2.82). This result indicates that the gel networks originated from the bridged siloxanes is more interconnected compared to the one bearing a –CH₃ terminal group and also explains the broader ²⁹Si MAS NMR peaks for the BTE and BTM gels compared to the one for the MTS gel. Moreover, the higher average connectivity of the BTM and BTE gels can also explain why the bridges siloxane can form more easily (without the use of the silanization treatment) a highly porous aerogel compared to MTS. The higher connectivity developed in the BTM and BTE gels leads to a stronger silica-based network which can withstand more easily the drying stresses without collapsing and preserving the porosity of the network.

3.2. Oxycarbide characterization

The chemical analysis of the pyrolysed glass gave the following results: O 46.2 wt%, C 8.18 wt%, H 0.44 wt% for BTM–SiCO and O 39.3 wt%, C 14.8 wt%, H 0.93 wt% for BTE–SiCO. The percentage of silicon was estimated by difference to 100. Accordingly, the chemical formula of the two glasses is: SiC_{0.42}O_{1.79} and SiC_{0.77}O_{1.52} for BTM–SiCO and BTE–SiCO, respectively (see Table 3).

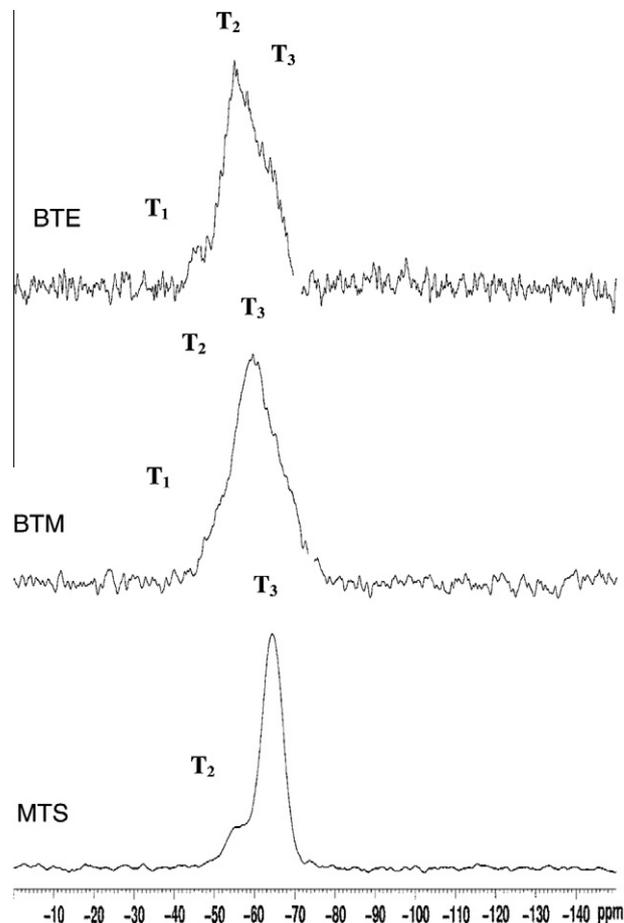


Fig. 4. ²⁹Si NMR of ambigels.

Table 2

Analysis of the ²⁹Si MAS NMR determined for pyrolysed ambigels.

Sample	T ₁ (%)	T ₂ (%)	T ₃ (%)	No. of oxo-bridges/Si	Total No. of bridges (oxo + Si–C)/Si
MTS 0	–	16.74	83.26	2.82	2.82
BTM 0	7.6	59.3	33.1	2.19	3.25
BTE 0	3.9	73.1	23.0	2.25	3.19

Table 3

Analysis of the ²⁹Si MAS NMR determined for ambigels.

Sample	Q (%)	T (%)	D (%)	Composition from ²⁹ Si NMR	From chemical analysis	C _{free} [*] /Si
BTM 0–SiCO	61.3	28.6	10.1	SiC _{0.12} O _{1.76}	SiC _{0.42} O _{1.79}	0.3
BTE 0–SiCO	62.6	32.7	4.7	SiC _{0.11} O _{1.78}	SiC _{0.77} O _{1.52}	0.66

* The amount of C_{free}/Si has been estimated by comparing the C obtained from the ²⁹Si NMR and the total from chemical analysis.

The thermogravimetric analysis was performed under argon atmosphere up to 1300 °C (Fig. 5). BTM and BTE ambigels show a high ceramic yield, around 75 wt%, while for the MTS system the ceramic yield is only around 40 wt%, quite below the value usually reported in the literature for methyl-containing precursor (80 wt%) [37]. The low ceramic yield of the MTS gel, associated with a main decomposition step between 500 and 800 °C, could be attributed to its high porosity combined with a high pore size that facilitate the decomposition process by favoring the escape of the gaseous

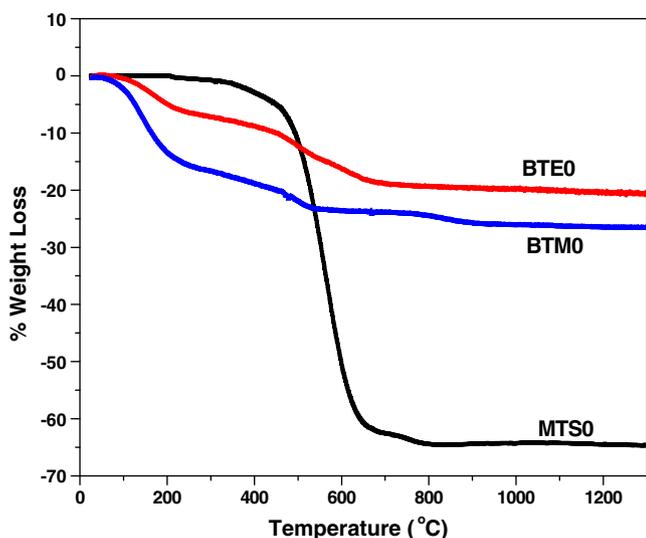


Fig. 5. TGA analysis performed under argon flow on SiCO precursor.

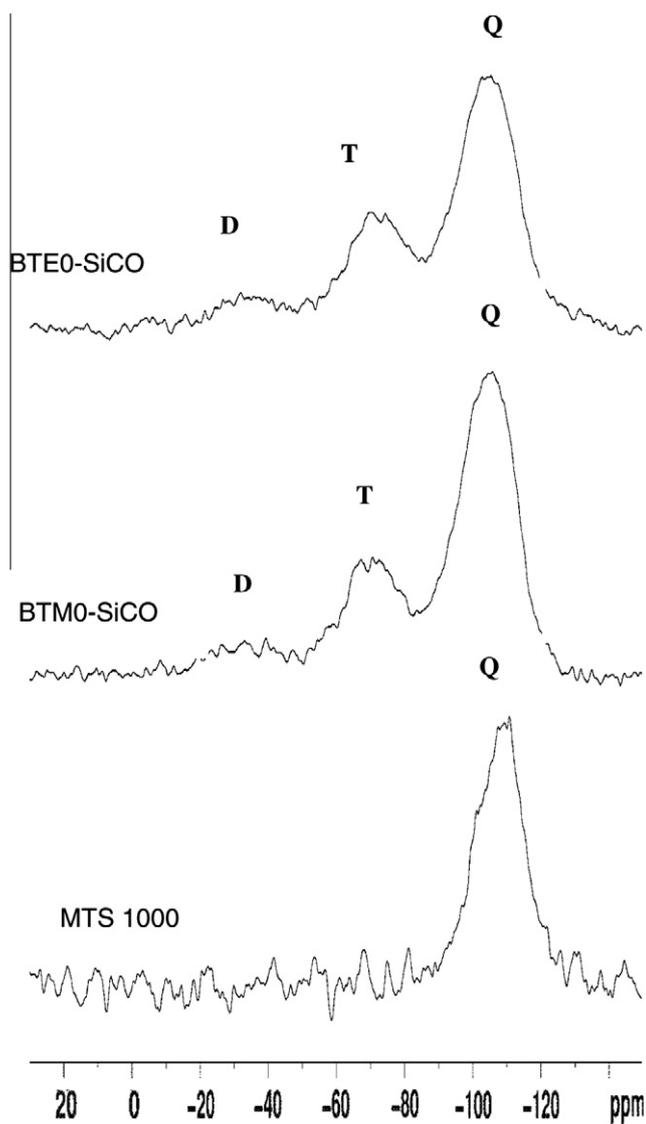


Fig. 6. ^{29}Si NMR of pyrolysed gels.

species produced during the organic-to-inorganic transformation. The TG curves of the BTM and BTE samples shows: (i) a weight loss step below 150 °C due to the evolution of adsorbed water and alcohol; (ii) from ca 200 °C up to 450 °C a steady weight loss most likely associated with the evolution of water and ethanol produced by the condensation reactions of the residual Si-OH and Si-OEt of T_2 and T_1 Si units as revealed by the NMR study (Fig. 8); (iii) from 500 to 900 °C, in the temperature range where the ceramization reactions take place, the weight loss is around 10 wt% in line with the results reported in the literature for similar bridged precursors [15].

The ^{29}Si MAS spectrum (Fig. 6) of the pyrolysed BTE and BTM gels are both characteristic of silicon oxycarbide network with a distribution of mixed $\text{SiC}_x\text{O}_{4-x}$, $x = 0, 1$ and 2 units. For the BTE-SiCO glass the three signals at -105, -72 and -35 ppm can be identified as Q units ($x = 0$, 62.6%), T units ($x = 1$, 32.7%) and D units ($x = 2$, 4.7%), respectively. The stoichiometry of the SiOC phase obtained from the quantitative analysis is provided in Table 3 and is calculated assuming that carbon is bonded to four silicon atoms. By comparing the composition estimated by NMR with the results of chemical analysis, the following composition of the glass can be obtained as $\text{SiC}_{0.12}\text{O}_{1.78} + 0.66 \text{C}_{\text{free}}$. A similar quantitative analysis performed on the ^{29}Si MAS spectrum of the pyrolysed BTM gel leads to the following composition $\text{SiC}_{0.12}\text{O}_{1.76} + 0.3 \text{C}_{\text{free}}$. The

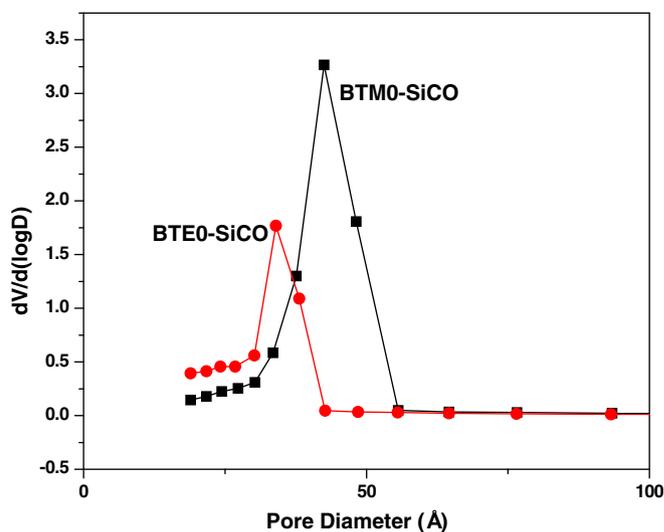


Fig. 7. Pore size distribution of BTM0-SiCO and BTE0-SiCO.

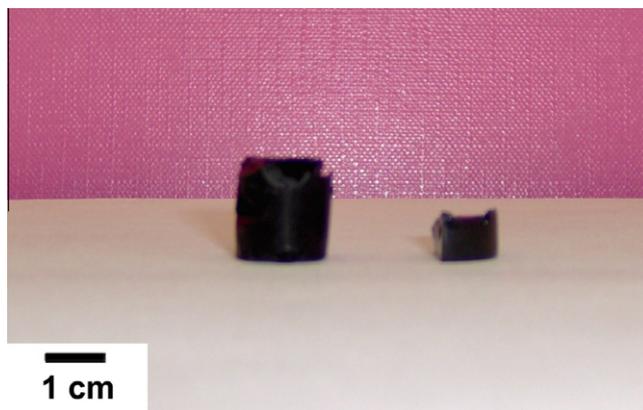


Fig. 8. Photograph of pyrolysed glass.

Table 4
Properties of pyrolysed ambigels.

Sample	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (Å)
BTE 0	1131	1.29	45
BTE-SiCO	430	0.46	42
BTM 0	1085	0.80	30
BTM-SiCO	452	0.33	29
MTS 0	471	0.83	70
MTS 0-SiCO	143	0.89	237
MTS 60	416	0.99	94
MTS 60-SiCO	132	0.67	201
MTS 80	727	1.47	80
MTS 80-SiCO	168	0.80	185

amount of carbon bonded to silicon is similar in the two SiOC glasses derived from the bridged alkoxides while the amount of free carbon is lower (almost half) for the BTM sample reflecting the lower C content of the starting gel.

Surprisingly, the pyrolysed spectra of the MTS gels (Fig. 6) do not show any peaks corresponding to the retainment of Si–C bonds. During pyrolysis of the gels we have unusual large weight loss which is probably due to a large loss of silanes preventing the retention of Si–C bonds. It is well known that gaseous silane species such as (CH₃)₄Si or (CH₃)₃Si–O–Si(CH₃)₃ can form during pyrolysis of methyl-modified silica gels by redistribution reactions of Si–O and Si–C bonds [38]. The evolution of these bulky species is certainly favored by the high porosity and the large pore size of the MTS sample. Accordingly, the retention of the Si–C bonds for the two bridged siloxanes could be due two factors: (i) the organic C atoms are already part of a network forming Si–R–Si bridges while for the MTS they form a terminal CH₃ moiety and (ii) the small size of the pores (for both samples below 10 nm) hinder the outward diffusion of the larger silane molecules while do not hinder the escape of the smaller H₂ and CH₄ species.

Highly porous oxycarbide glasses could be produced, as can be seen from the surface areas and porosity values of the pyrolysed gels provided in Table 4 (we are not giving the data for the MTS sample since, as showed by NMR study they do not form an oxycarbide material). The samples obtained from the bridged precursors show the highest values of surface area, in the range 430–450 m²/g coupled with very low and narrow pore size distribution in the range 30–50 nm (Fig. 7).

Finally, the photograph of the pyrolysed glass is provided in Fig. 8 and shows that monolithic crack-free SiCO samples are obtained after pyrolysis at 1000 °C.

4. Conclusion

Highly porous ambigels were successfully employed as precursors for obtaining porous siliconoxycarbide glass. Our synthetic procedure is so simple that by using a solvent (2-propanol) which has low surface tension coupled with slow drying we are able to get high surface area materials with large pore volumes even without silane strengthening treatments. The ambigels possessed very high surface areas and pore volumes and a maximum surface area of 1131 m²/g with a pore volume of 1.29 cm³/g was obtained for

BTE 0 gels. On pyrolysis, the ambigels retained very high surface areas and a maximum surface area of 452 m²/g with a pore volume of 0.33 cm³/g was obtained for BTM gels. During the polymer to ceramic conversion, the ceramic yield was found to be very high for the bridged precursors. The ²⁹Si MAS spectrum confirmed the retention of Si–C bonds in the pyrolysed glass.

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