

Synthesis and characterization of polymer-derived SiCN aerogel

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Abstract

Synthesis and characterization of polymer-derived SiCN aerogels are reported. The wet pre-ceramic gels are synthesized via hydrosilylation reaction of a polysilazane with divinylbenzene as cross-linker in cyclohexane. Subsequently, the wet polymeric aerogels are dried using supercritical carbon dioxide for the removal of the solvent. The SiCN ceramic aerogels are obtained through pyrolysis in N₂ at 1000 and 1500 °C. The ceramic aerogels show a low density (< 0.1 g/cm³), high porosity (>90 %), high specific surface area (>150 m²/g) and display a hierarchical pores size distribution which ranges from micropore to mesopores to macropores.

Keywords: Polymer-derived ceramic, SiCN, Aerogel, Hydrosilylation

I. Introduction

Polymer-derived SiCN ceramic, a non-oxide material, has been shown to have high thermal stability [1], crystallization [2] and creep resistance[3]. Moreover, SiCN ceramic also exhibits many interesting physical properties such as ultrahigh-temperature semiconductivity [4], and intense photoluminescence which make them interesting materials for LED application [5]. Remarkably, the functional properties of SiCN ceramic can be tailored by controlling the chemistry of the preceramic polymers and the pyrolysis conditions. Accordingly, SiCN ceramics have gained a strong research interest and many applications for this kind of material have been proposed [6].

Although much work has been devoted to SiCN ceramics, few studies concerning porous SiCN bodies have been published. Different fabrication methods through the pre-ceramic polymer route have been reported in the literature: (i) direct foaming using a mixture of polysilazane precursor and polymethylmetacrylate (sacrificial fillers) or azodicarbonamide (a physical blowing agent) [7], (ii) sacrificial fillers using polysilazane precursors, which are infiltrated into colloidal silica or polystyrene [8-10] or nanocasted into mesoporous carbon template [11]. Porous SiCN ceramics have been found promising for some applications such as catalyst supports for fuel reforming [9], and anode material in lithium ion batteries [12].

Recently, Sorarù and his coworkers [13-14] have successfully prepared highly porous polysiloxanes and polycarbosilanes aerogels using supercritical drying technique and converted

them into SiOC and SiC/C ceramic aerogels. This new approach for producing porous ceramics derived from polymer precursors allows to easily change the composition of the ceramic aerogel and to reach porosity values over 90 % and specific surface area beyond 400 m²/g. It should be noticed here that obtaining highly porous ceramics via supercritical drying technique without the use of the fillers or sacrificial templates, is an advantage over the conventional methods previously reported.

The aim of this paper is to synthesize and characterize novel SiCN aerogels from a commercial polysilazane via hydrosilylation reaction using supercritical CO₂.

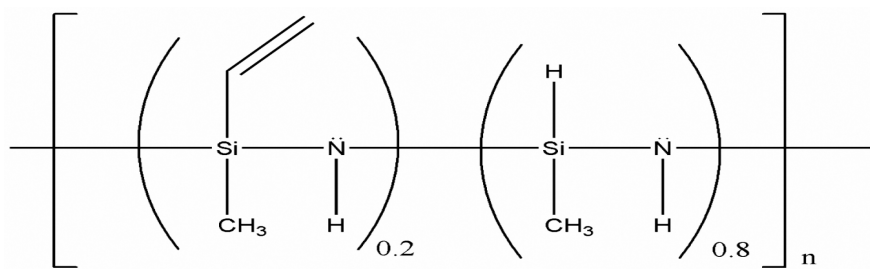
II. Experimental procedures

2.1 Aerogel synthesis

The procedure to synthesize the aerogels is similar to the one proposed in a previous article. [14]

A commercial polysilazane, Ceraset PSZ-20 (KiON Defense Technologies, Huntingdon Valley, USA) and divinylbenzene, DVB (Alfa Aesar, Ward Hill, MA, USA) were used as received. Platinum–divinyltetramethyldisiloxane complex in xylene, with Pt content of ~2% (Sigma-Aldrich, Saint Louis, MO, USA) was further diluted to obtain a solution containing 0.1 wt% of catalyst.

The polysilazane contains both Si-H and vinyl moieties, in a 4:1 ratio respectively, as summarized in **scheme 1**.



Chemical structure of PSZ-20 (do we need to refer to the catalog?)

The PSZ-20 was crosslinked via the hydrosilylation reaction of the Si-H bonds (present only in the PSZ-20) with the vinyl groups (of both PSZ-20 and DVB) in presence of the Pt catalyst and using cyclohexane as solvent. The crosslinking was carried out in a closed pressure vessel with an internal Teflon liner at different temperature and time. The synthesis parameters were adjusted in order to have 90%vol of solvent, a molar ratio between Si-H and C=C groups equal to 1 and a 60 ppm of Pt with respect to PSZ-20 mass. In a typical synthesis 500 mg of PSZ-20, 300 mg of DVB and 5.77 g of cyclohexane were loaded into the Teflon container of the pressure vessel, mixed for five minutes with a magnetic stirrer and then 35 μ L of the 0.1% Pt solution were added. The manipulation of the reagents is performed under gentle Ar flow to prevent excessive contamination of the reagents by oxygen and moisture. The pressure vessel was introduced in a pre-heated oven and left at the preset temperature of 150 °C for 20 h. The wet gels were then removed from the pressure vessel and transferred in a beaker filled with cyclohexane. The wet gels were washed for 2 days in a 100 mL flask filled with fresh solvent, renewing the cyclohexane a total of 3 times, in order to remove the catalyst and eventually unreacted precursors. For the supercritical drying the cyclohexane was first gradually substituted with liquid CO₂ by replenishing the liquid inside the drier twice a day for 4 days. The final PSZ-

20/DVB aerogels are obtained after bringing the CO₂ in supercritical state (50°C - 100 bar) and then slowly removing the supercritical fluid down to 1 bar at a rate lower than 1 bar/min.

The PSZ-20/DVB aerogels were pyrolyzed in a tubular furnace (Lindbergh Blue) at 10 °C/min with 1 hour dwell time at the maximum temperature under nitrogen flow (100 mL/min). The furnace is purged for 60 min with flowing nitrogen before pyrolysis.

2.2 Aerogel characterization

FT-IR spectra were collected on a Nicolet Avatar 330 Fourier transform infrared spectrometer (Thermo Electron Corporation, Waltham, MA) using KBr technique in transmission mode. An average of 64 scans with 4 cm⁻¹ resolution was recorded for each specimen.

Solid state NMR analysis was carried out with an AVANCE 300 Bruker 7 mm probe-head (Bruker Instruments, Karlsruhe, Germany) operating at a proton frequency of 300.13 MHz. ¹³C MAS NMR spectrum of the synthesized polymer aerogel was acquired with CP pulse sequences under the following conditions: ¹³C frequency of 75.47 MHz, a $\pi/2$ pulse length of 3.0 μ s, a contact time of 2.5 ms, a proton decoupling length of 3.9 μ s, and a recycle delay of 5 s. The sample was packed in 4 mm zirconia rotors which were spun at a rate of 6 kHz under air flow. Adamantine was used as external secondary reference for the determination of the ¹³C chemical shifts.

The shrinkage progress of the aerogel samples during pyrolysis was detected by measuring the dimensions of the cylindrical aerogels with a digital caliper and the mass loss was evaluated

weighting the sample before and after the heat treatment. These measurements allowed also the calculation of the bulk density before and after pyrolysis.

The mass change during pyrolysis was also studied by thermal gravimetric analysis (TGA) using a Netzsch STA 409 instrument (Netzsch-Gerätebau GmbH, Selb, Germany) with a heating rate of 10°C/min up to 1500°C in Ar flow.

The porosity of the preceramic and ceramic aerogels was analyzed by nitrogen adsorption/desorption experiments at 77°K using a Micromeritics ASAP 2020 system (Micromeritics, Norcross, GA, USA). The specific surface area (SSA) was calculated from the N₂ adsorption data at relative pressures between 0.05 and 0.30, by employing the Brunauer-Emmett-Teller (BET) method.

The pore size distributions in the macro- and meso- range were calculated using the Barrett-Joyner-Halenda (BJH) method from the desorption branch of the isotherms while for the small meso- and microporosity range was used the Quenched Solid Density Functional Theory (QSDFT, nitrogen on carbon, assuming slit/cylindrical pores) from the adsorption branch of the isotherms.

The crystallinity of the ceramic aerogels was analyzed by X-Ray Diffraction (XRD) with a RigakuD/Max diffractometer (Rigaku, Tokyo, Japan) in the Bragg-Brentano configuration, using Cu K α radiation and a monochromator in the diffracted beam, in the range $2\theta = 20\text{--}80^\circ$ with a 0.05° step and 5 s acquisition time.

The microstructure of the aerogels was studied using a Supra 40 Zeiss FE-SEM (Carl Zeiss NTS GmbH, Oberkochen, Germany).

III. Results and discussion

3.1 Synthesis of pre-ceramic aerogel

3.1.1 FT-IR and ^{13}C MAS NMR

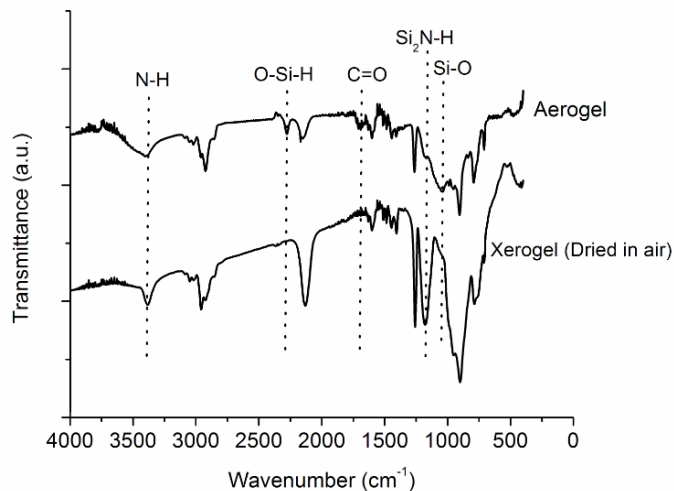


Figure 1. FT-IR spectra of the synthesized aerogel and xerogel.

FT-IR spectrum of the studied aerogel is shown in **Figure 1** and the main absorption bands of the spectrum are listed in **Table 1**. The FT-IR spectrum of the xerogel dried at ambient conditions was also recorded to compare with the synthesized aerogel and to investigate any possible reactions of the supercritical CO_2 with the polymer backbone. The FT-IR spectrum of the synthesized aerogel shows all the functional groups due to starting materials, for example N-H stretching (3383 cm^{-1}), Si- CH_3 deformation (1254 cm^{-1}) and C=C stretching (1591 cm^{-1}). In spite of the use of the stoichiometric ratio between the Si-H and C=C bonds, the FT-IR results indicate an incomplete hydrosilylation reaction between PSZ and DVB, evidenced by the presence of residual Si-H units of the starting PSZ at 2127 cm^{-1} (Si-H stretching). A possible reason for the incomplete consumption of the Si-H bonds could be due to steric crosslinked with, as found also in the case of polysiloxane/DVB system [Influence of the Polymer Architecture on the High Temperature Behaviour of SiCO glasses: a Comparison between Linear- and Cyclic-

derived Precursors, P. Dibandjo, S. Diré, F. Babonneau, G.D. Soraru, *J. Non-Cryst. Solids*, **356** 132–140 (2010).]. The FT-IR analysis shows the presence of O atoms in the aerogel which is verified by a new absorption at 1700 cm^{-1} assigned to C=O bonds (stretching) and by the Si-O absorption at 1080 cm^{-1} . Interestingly in the frequency region typical of Si-H bonds a new peak is also present in the aerogel spectrum at 2275 cm^{-1} which could be due to Si-H bonds present in silicon atoms sharing also bonds with oxygen atoms. [16]

These peaks are not observed in the FT-IR spectrum recorded for the xerogel. In addition, the peak at 3383 cm^{-1} assigned to N-H bonds is broader in the aerogel compared to the xerogel and the absorption assigned to the $\text{Si}_2\text{N-H}$ groups is present as a shoulder in the FT-IR spectrum of the aerogel while is a well defined peak in the spectrum of the xerogel.

The ^{13}C MAS NMR spectrum of the studied aerogel (**Figure 2**) shows main peaks at ~ 0 ppm, due to the CH_3 groups in the starting polysilazane, at $\sim 45 - 41$ ppm, at ~ 30 ppm at ~ 15 ppm due to aliphatic $-\text{CH}-$, $-\text{CH}_2-$ and $-\text{CH}_3$ groups respectively. Carbon atoms of the aromatic rings give rise to the peaks at 145 and 128 ppm while residual vinyl groups leads to resonances at 138 and 113 ppm. Interestingly, the resonance at ~ 157 ppm proofs the presence of C=O groups in the aerogel structure. The quantitative analysis reveals that the amount of carbonyl moieties is roughly 2.7 % compared to the CH_3 groups of the starting polysilazane.

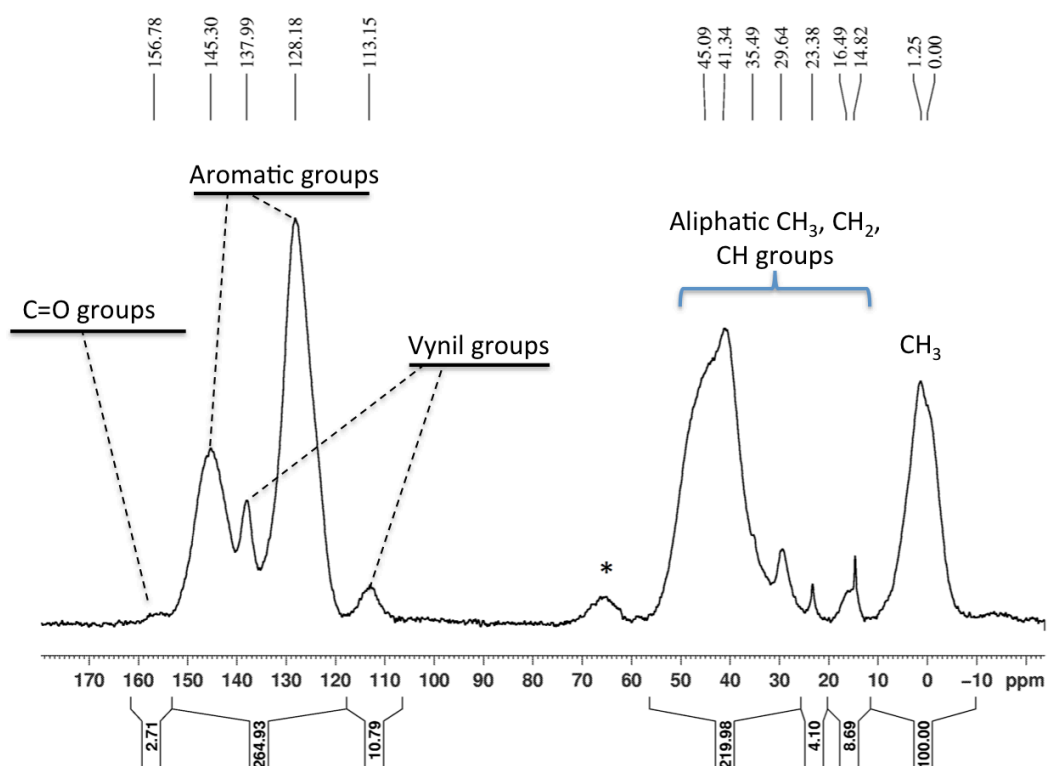
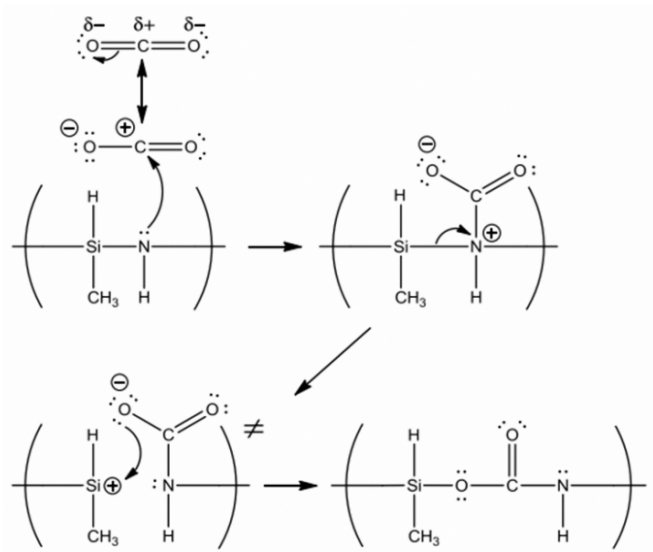


Figure 2. ^{13}C MAS NMR spectrum recorded on the studied pre-ceramic PSZ-20/DVB aerogel. *Spinning side bands. Sharp peaks at ~ 23 and ~ 15 ppm are due to pentane contamination used in the preparation of the samples for the NMR analysis.

According to the literature (put here the two papers suggested by the reviewers), the proposed insertion mechanism of the CO_2 into the polysilazane chain is illustrated in Scheme 2.

It is worth noticing that the final structure reported in Scheme 2 contains all the chemical bonds shown by the FT-IR and NMR analysis, in particular: the $\text{C}=\text{O}$ bonds observed in the ^{13}C NMR spectrum at 158 ppm and in the FT-IR spectrum at 1700 cm^{-1} ; the Si-O bonds responsible for the FT-IR absorption at 1008 cm^{-1} and the Si-H bonds of the O-Si-H units at 2275 cm^{-1} .



3.2 TGA analysis

The TGA recorded for the synthesized preceramic aerogel is shown in **Figure 3**.

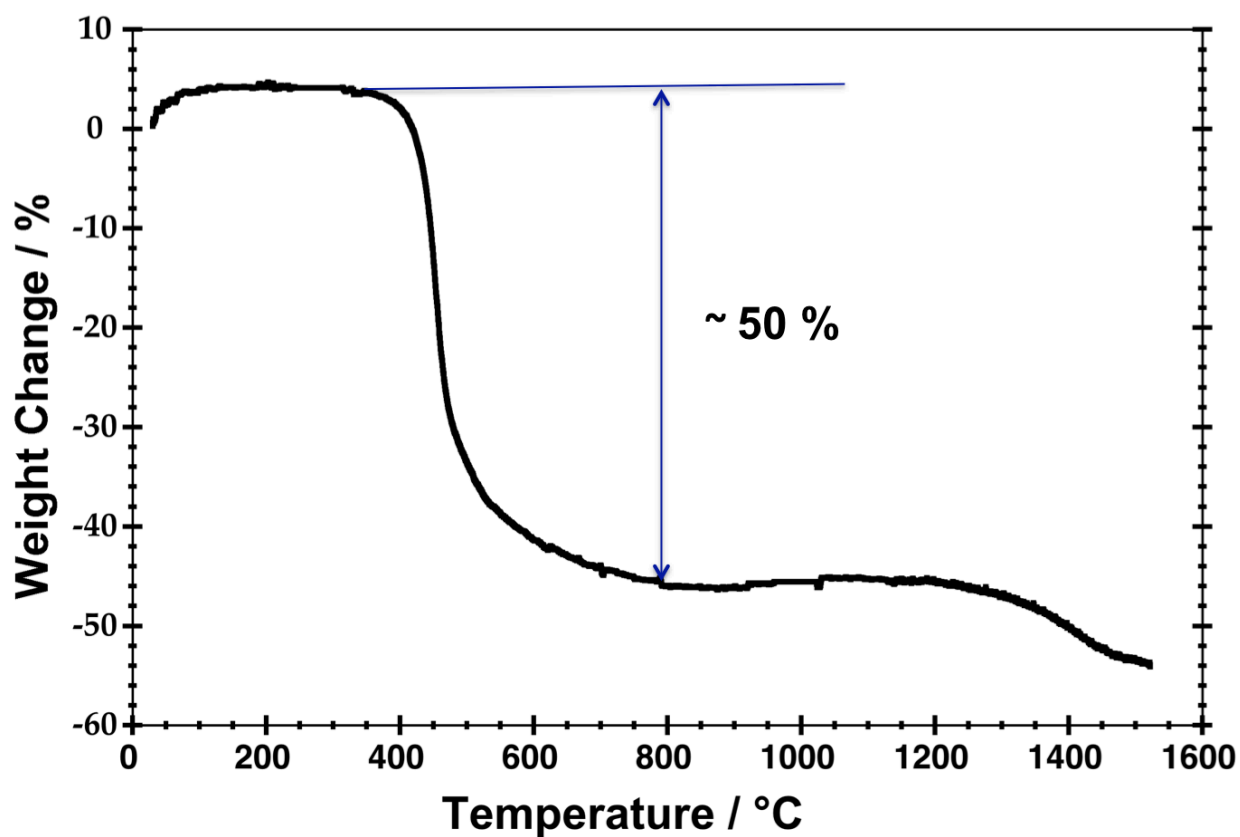
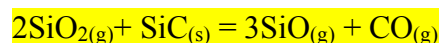
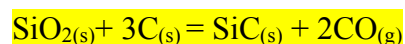


Figure 3. TGA of the studied PSZ-20/DVB aerogel in N₂ flow up to 1500 °C

The slight weight increase observed below 100°C is due to the buoyance effect of our instrument. The studied aerogel is stable up to 400 °C. Kraushaar et al. [11] studying the decomposition of similar compounds obtained by inserting CO₂ into Si-N bonds of diaminosilanes, observed a high weight loss below 200°C. The higher thermal stability that we detected in the present case is most probably related to the polymeric nature of our materials in contrast to the low molecular weight of the samples studied in [11].

The TGA analysis shows a mass loss (≈ 50 %) between 400 and 800 °C with a major effect (≈ 40%) between 400 and 500°C. It is reported in the literature that the grafted divinylbenzene groups, which have vinyl units bonded to one Si atom in the polymer are partially eliminated in this temperature range (400/500 °C). [19-20] Moreover, high porosity of the studied aerogel is supposed to be responsible for a large weight loss because of an easy escape of the gaseous species during the heat treatment.

Above 800°C the TGA curve shows a weight stability up to ~ 1200°C. Above 1250°C and up to 1500°C a weight loss of ~ 10% is observed with the highest rate of weight change around 1400°C. This effect is related to the removal of the oxygen – either incorporated during the supercritical synthesis as O-C=O moieties or picked-up during the early stages of pyrolysis from oxygen impurities present in the gas and/or in the furnace chamber - via carbothermal reduction with formation of gaseous CO and SiO, as shown in the following reactions:



3.3 High temperature structural evolution: XRD and FT-IR

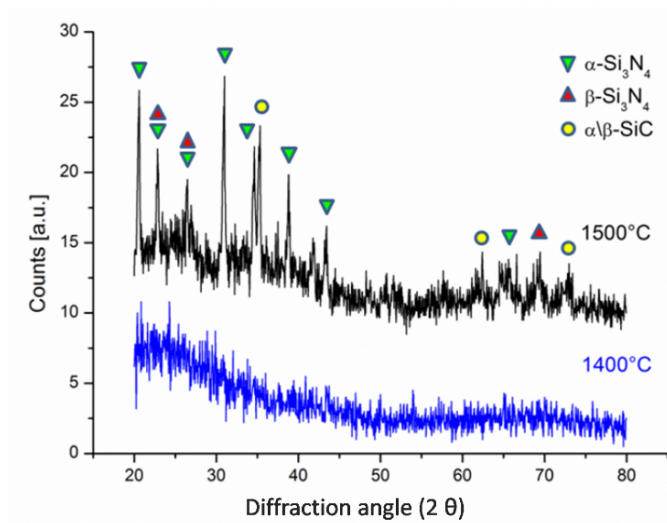


Figure 4. XRD patterns of the aerogel pyrolyzed at 1400 and 1500 °C

The XRD patterns of the ceramic aerogels pyrolyzed at 1400 and 1500 °C were recorded and shown in **Figure 4**. The studied aerogel remains X-ray amorphous up to 1400 °C. At 1500°C XRD result shows the formation of crystalline Si₃N₄ and SiC. This observation indicates a major structural modification occurring between 1400 and 1500 °C.

The FT-IR spectra (**Figure 5**) recorded for these ceramic aerogels treated at 1400 and 1500°C show a clear disappearance of Si-O peaks at 1500 °C in agreement with the TGA result which shows a mass loss above 1400 °C assigned to the evolution of SiO/CO gases.

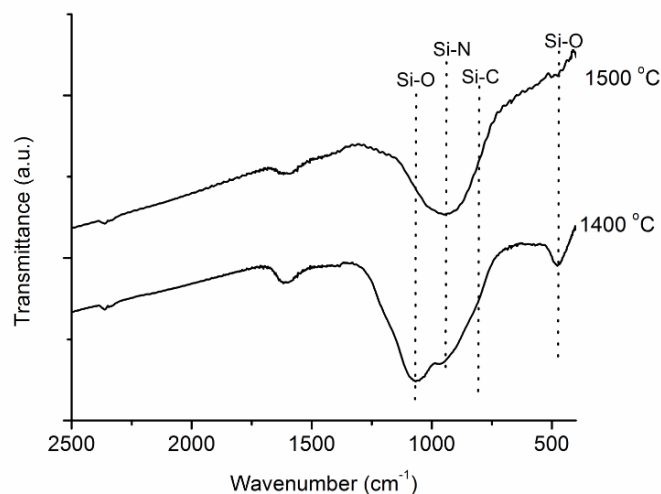


Figure 5. FT-IR spectra of the aerogel pyrolyzed at 1400 and 1500 °C for 1 h.

3.4 Physical properties and microstructure of SiCN aerogels

The properties of the aerogels are reported in **Table 2**.

Since the synthesized aerogels were obtained in a well defined cylindrical shape, the bulk density and the linear shrinkage of the samples can be easily measured. An extremely low density value (59 kg/m^3) is measured for the starting pre-ceramic aerogel. The density increases up to 92 and 96 kg/m^3 for the ceramic aerogels pyrolyzed at 1000 and 1500 °C, respectively. However, these values are still 30-40 times lower than those reported for the SiCN bulk ceramics obtained from Ceraset, $\sim 2000 \text{ kg/m}^3$. [21-22]

From the measured bulk and skeletal density the vol% of porosity can be estimated. Accordingly, all the studied aerogels exhibit very high porosity, estimated to be around 95 %.

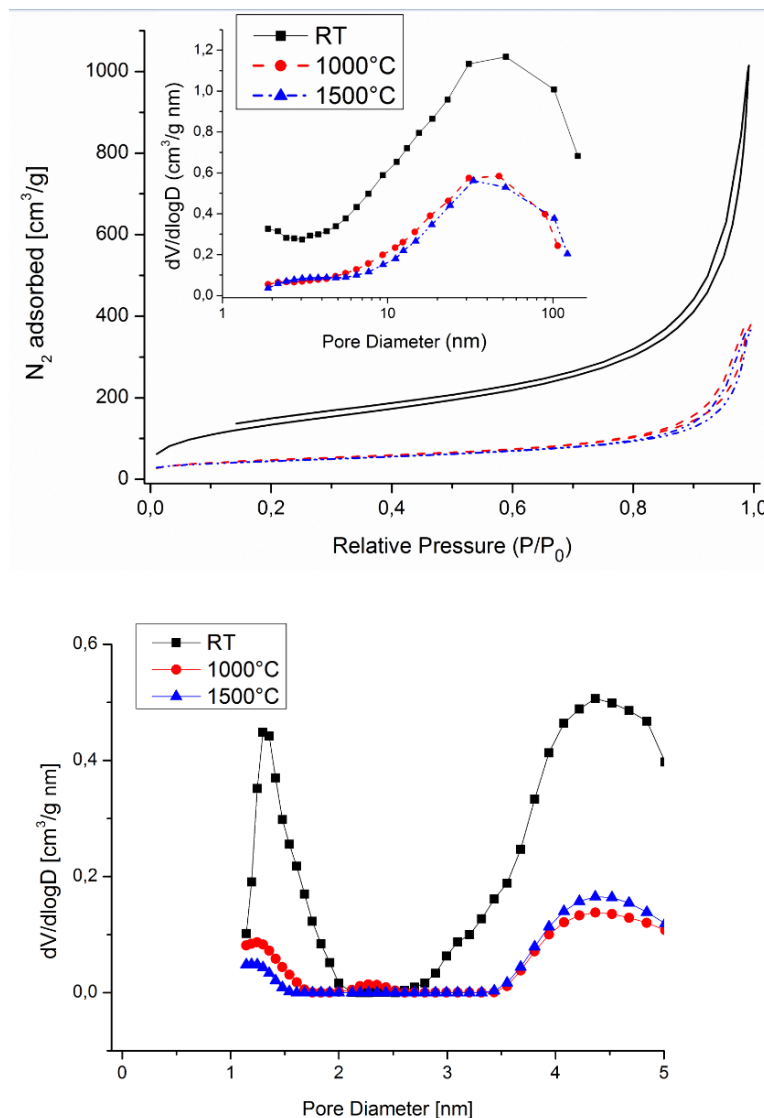
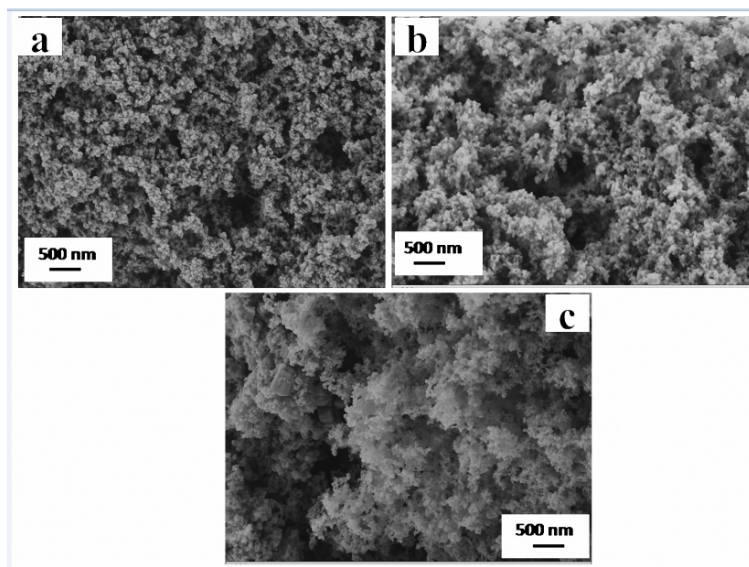


Figure 6. (a) N_2 adsorption/desorption isotherm and pore size distribution of preceramic aerogel and ceramic aerogel obtained at 1000 and 1500 °C; (b) QSDFT pore size distributions for the small meso- and microporosity.

The N_2 adsorption-desorption isotherms recorded for the studied aerogels are shown in **Figure 6a**. The results indicate that all the aerogels are mesoporous materials according to IUPAC classification.[23] All three isotherms do not show a well defined saturation plateau indicating a considerable fraction of macropores or large mesopores. The high SSA value of the

preceramic aerogels ($489 \text{ m}^2/\text{g}$) is related to the presence of micropores ($\leq 2 \text{ nm}$) as can be seen from the relevant QSDFT pore size distribution reported in **Figure 6b**. The organic-to-inorganic transformation leads to the closure of the micropores and a corresponding decrease of the SSA down to $165 \text{ m}^2/\text{g}$ at 1000°C . Increasing the pyrolysis temperature up to 1500°C does not substantially change the SSA. The large mesopores shown by the PSD curves with a maximum around 30–40 nm are stable through the pyrolysis process and do not sinter.

As seen in the SEM micrographs (**Figure 7**), all the SiCN aerogels have a colloidal microstructure with particles smaller than 100 nm and high porosity which remains up to the pyrolysis temperature of 1500°C . The SEM analysis shows a broad pore sizes range and the presence of macropores in the ceramic samples.



IV. Conclusions

Novel SiCN aerogels were successfully prepared via Pt-catalyzed hydrosilylation reaction between polysilazane and divinylbenzene in highly diluted conditions. As a consequence of using supercritical CO₂ drying, O atoms are incorporated in small amount into the synthesized aerogel as O-C=O moieties. We present for the first time the reaction between PSZ-20 and CO₂ and we also propose a reaction mechanism.

Polymeric aerogel shows a high SSA value of 490 m²/g and a low density value of 60 kg/m³. Monolithic highly porous SiCN ceramic aerogels have been produced, with densities of 90-100 kg/m³, SSA of above 150 m²/g, and amorphous structure until 1400°C.

Acknowledgements

The present work was financially supported by European Community ITN7 through MC-ITN FUNEA-Project 26487. The authors would like to thank Prof. Alberto Quaranta of the University of Trento, Italy for designing the experimental setup for the gas sensing measurements. The authors also would like to thank Dr. Emanuela Callone from the University of Trento, Italy for kind assistance in NMR measurement.

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Table 1. Main FI-IR absorptions of the synthesized preceramic SiCN aerogel

Wavenumber (cm ⁻¹)	Assignments [17-18]
3383	ν N–H (stretching)
3048	ν Csp ² –H (stretching)
2957, 2898	ν Csp ³ –H (stretching)
2275	ν Si–H (O–Si–H stretching)
2127	ν Si–H (N–Si–H stretching)
1700	ν C=O (stretching)
1440 - 1591	ν C=C (stretching)
1401	δ C–H (CH ₃ deformation)
1254	δ C–H (Si–CH ₃ deformation)
1173	ρ (Si ₂ N–H) (rocking)
1080	ν Si–O–Si (stretching)
902	ν Si–N–Si (stretching)
784	δ Si–C (deformation)
708	ρ C–H (Si–CH ₂ rocking)

Table 2: Properties of the studied preceramic and ceramic aerogels

Sample	Density (kg/m ³)	Linear shrinkage (%)	SSA (m ² /g)	TPV* (cm ³ /g)	Skeletal density (g/cm ³)	Porosity (Vol%)
Preceramic	59 ± 2	-	489 ± 10	1.57	-	94
Ceramic _1000	92 ± 1	38.1 ± 0.6	165 ± 10	0.58	1.80 ± 0.05	95
Ceramic _1500	96 ± 4	41.6 ± 0.1	153 ± 10	0.56	2.24 ± 0.09	96

Uncertainties of density and linear shrinkage are the standard deviation of 5 caliper measurements

Error bars for SSA values are given based on BET multiple linear regression

Uncertainties of skeletal density values are the standard deviation of 5 measurements using helium pycnometer

The porosity values are calculated based on the measured skeletal density

* Measured from the N₂ adsorption experiments.