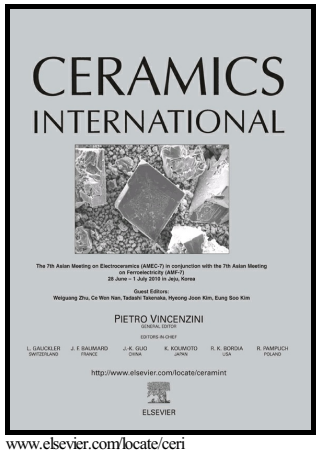

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Polymer-derived SiOC aerogel with hierarchical porosity through HF etching

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Abstract

Silicon oxycarbide (SiOC) aerogels have been synthesized from preceramic polymers via pyrolysis in inert atmosphere at 1200 and 1300°C. The as synthesized materials have a typical colloidal microstructure with mesoporosity in the range 10 – 50 nm and no microporosity. HF acid attack of the SiOC aerogels dissolves preferentially the SiO_2-rich phase and creates micro- and (small)mesopores (< 10 nm) in the aerogels microstructure finally leading to a materials with hierarchical porosity. The HF post-pyrolysis treatment is more efficient for the SiOC aerogels pyrolyzed at the maximum temperature, i.e. 1300°C, leading to a maximum value of specific surface area of 530 m^2/g and total porosity of 0.649 cc/g.

Keywords: Preceramic polymers, SiOC, high surface area, aerogels, HF etching.

1 Introduction

Materials having pores on two or more length scales are called hierarchically porous materials. Micropores are the ones below 2 nm, while mesopores are defined as the ones in between 2 nm to 50 nm and all pores bigger than 50 nm are called macropores according to IUPAC notation. Materials with hierarchical porosity potentially possesses several desirable characteristics, such as rapid transport with fast uptake and release, low pressure drop but great catalytic properties, efficient use of volume, high mechanical strength, etc.[1]

Preceramic polymers have been used for achieving ceramics with hierarchical porosity [1]. In our lab we have recently developed a new technique for the synthesis of aerogels from preceramic polymers [2]. Accordingly aerogels of the Si-C, Si-O-C and Si-C-N systems have been produced, characterized [3-5] and proposed as gas sensors [5] or anodes for Li-ion batteries [6]. These materials, with porosity up to 95 vol%, are formed mainly by large mesopores and macropore in the range size between 10 and 100 nm [2-4]. One possibility to introduce micro- and (small)meso-pores into a ceramic aerogel could be a post-pyrolysis etching treatment with either an HF solution or chlorine gas [7-9]. To the knowledge of the authors, only the selective Cl_2 etching has been used in combination with PDC aerogel formation while HF etching was never attempted before [10-11]. In the present work, the formation of polysiloxane aerogels is accomplished by using a commercial polysiloxane. The formed thermoset aerogels were pyrolyzed to form SiOC aerogels, which were then HF etched to obtain high surface area, hierarchically porous aerogels.

2. Experimental Procedure

2.1. Aerogel synthesis

A commercial polysiloxane, polyhydromethylsiloxane (PHMS) and tetramethyl-tetravinyl-cyclotetrasiloxane (TMTV) were purchased from Alfa Aesar (Alfa Aesar GmbH & Co., Ward Hill, MA, USA) and used as received without any further modification. Platinum-divinyl-tetramethyl-disiloxane complex solution in xylene, with Pt content of ~2% (Sigma-Aldrich, Saint Louis, MO, USA) was used for the preparation of the gel.

The PHMS was crosslinked via hydrosilylation reaction between the Si-H bonds of PHMS and the C=C groups of TMTV in the presence of diluted Pt catalyst and acetone as a solvent. The synthesis parameters were set-up in order to have 85% vol. of solvent, a 2:1 molar ratio between Si-H and C=C groups and a 10 ppm by weight of Pt relative to PHMS. The synthesis steps consists of charging 994 µl of PHMS, 660 µl of TMTV and 8797 µl of acetone into small glass vials, mixing for 15min to get homogenous solution with a magnetic stirrer and then adding 10 µl of diluted Pt solution. During loading of the reagents, Ar was gently fluxed to avoid excessive contamination of the reagents by oxygen and moisture. The glass container was sealed with the cap and introduced into a pre-heated oven and kept at a temperature of 60°C for 24 h, then allowed to cool slowly to room temperature. The wet gels were extracted from the glass vial and transferred to a 100 ml beaker, which was previously filled with 99.9% pure acetone and kept for 3 days. The acetone was renewed with a fresh one once per day in order to remove unreacted precursor and catalyst from the wet gel. Then the wet gel was loaded into a home built CO_2 supercritical dryer. The gels were washed with liquid CO_2 once a day for 8 days and then supercritically dried at 41 °C and 95 bar by slowly removing the supercritical fluid down to 1 bar at a rate lower than 1 bar/min.

The SiOC aerogels were obtained after high temperature pyrolysis of the PHMS/TMTV aerogels. The pyrolysis was performed in heavy duty tubular alumina furnace (Lindbergh Blue) up to 1200°C and 1300°C with the heating rate of 10°C/min and 5hr dwell time at the maximum temperature under Ar flow (100 ml/min). The furnace was purged for 25 hr with Ar before pyrolysis, to get rid of any trace of oxygen and moisture.

The etching process was performed on SiOC aerogel powder using hydrofluoric acid, HF, solution (40 wt.% in H_2O). 0.145 g of the powder aerogel sample was placed into a polyethylene container with ~80ml of the HF solution. Then the solution was gently stirred using a magnetic stirrer at room temperature for 22 hrs. Finally, the SiOC aerogel powders were filtered and rinsed off with deionized water to remove any residual HF and reaction products and kept in the oven at 100 °C for overnight to remove any residual water.

2.2. Aerogel characterization

The microstructure of the aerogels was studied using FE-SEM (Zeiss supra 60, Carl Zeiss NTS GmbH, Germany). Images were acquired in high-vacuum mode at 2.00kV. The pyrolytic transformation from the precursor aerogels to the ceramic ones was studied by thermal gravimetric analysis (TGA) using Netszch equipment (STA 409 model, Netzsch-Gerätebau GmbH, Selb, Germany) with a heating rate of 10°C/min up to 1300°C in Ar flow (the same condition as pyrolysis).

The crystallinity of ceramic aerogels before and after HF etching was analyzed by X-ray diffraction, XRD, using a custom made apparatus with CuKα monochromatic radiation in a Bragg-Brentano configuration with flat samples, fixed omega (fixed incident beam angle of 5

degrees), 10 minutes total acquisition time a with Curved Position Sensitive detector (INEL CPS 120).

FTIR spectra were collected on aerogels powders using Nicolet Avatar 330 Fourier transform infrared spectrometer (Thermo Electron Corporation, Waltham, MA, USA) in transmission mode using KBr. Spectra were recorded in the 4000 – 600 cm^{-1} range collecting an average of 64 scans with 4cm^{-1} resolution.

The pore structure of the SiOC powder (before and after HF acid etching) was analyzed by nitrogen sorption experiment at 77°K using Micrometrics ASAP 2020 instrument (Micrometrics, Norcross, GA, USA). The specific surface area (SSA) was calculated from the N_2 adsorption data at relative pressure (p/p_0) between 0.05-0.30, by applying the Brunauer-Emmett-Teller (BET) multi-point method. The pore size distribution (PSD) was evaluated by Barrett-Joyner-Halenda (BJH) method from desorption branch of the isotherm. The micropore volume was determined by the Harkins–Jura method.

3. Results and Discussion

3.1. Morphological Characterization

In **Fig. 1** a digital image showing both the cured thermoset aerogel and polymer derived SiOC ceramic sample pyrolyzed at 1300°C is reported. Characteristically, samples formed in the described procedure were 1-2 cm sized monolithic fragments, and upon pyrolysis white colored thermoset aerogels, see (Fig. 1(a), turns into black colored ceramic pieces, see Fig. 1(b). SEM images taken from those samples after curing at 60°C, pyrolysis at 1300°C, and HF etching are given, in **Fig. 1(c), (d),** and **(e)** respectively. As could be seen during pyrolysis the

microstructural features remained unchanged and the common colloidal aerogel microstructure is observed in all specimens. Apparently the pore shapes are irregular and randomly spread in the material as well the particle size does not change significantly during pyrolysis.

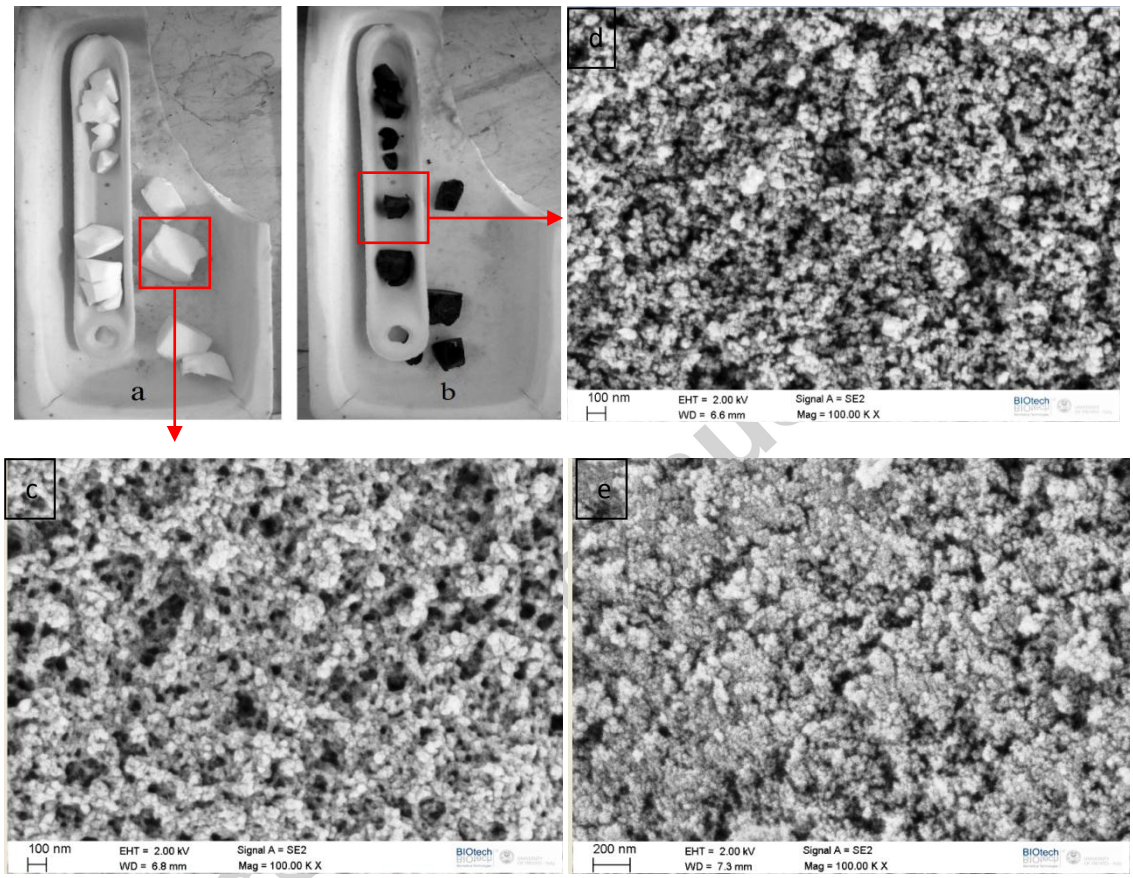

Figure 1. Digital photo images of sample (a) after curing, (b) after pyrolysis, and SEM images taken from the fracture surfaces of, (c) cured polymeric aerogel, (d) sample after1300^{o}C pyrolysis, and (e) pyrolyzed sample after HF etching.

3.2. Structural Characterization

Thermogravimetric analysis (weight change during heat-treatment) of thermoset aerogel sample obtained in Ar atmosphere is shown in **Fig. 2(a)**. The most observable weight loss occurred in the temperature range of 400-900°C. Prior to this temperature interval, the sample remains

thermally stable at its polymeric state nearly up to 400°C without any significant weight loss (note the initial weight increase in the curve is due to the buoyancy, i.e. an instrumental culprit). A weight loss ≤ 20% occurs up to 800°C. In the temperature range 400-800°C the loss is associated with the organic-to-inorganic transformations where low molecular weight hydrocarbons like methane and hydrogen evolves. Usually, free carbon is formed above 600°C and uniformly distributed in the SiOC phase. In addition to the organic-to-inorganic transformation, the material also undergoes a structural rearrangement through "redistribution reactions". These reactions, which are active in the 1100 – 1300 °C temperature range, involve the exchange between Si-O and Si-C bonds and lead to the formation of SiO_4 and SiC_4 units without any weight loss [12-13].

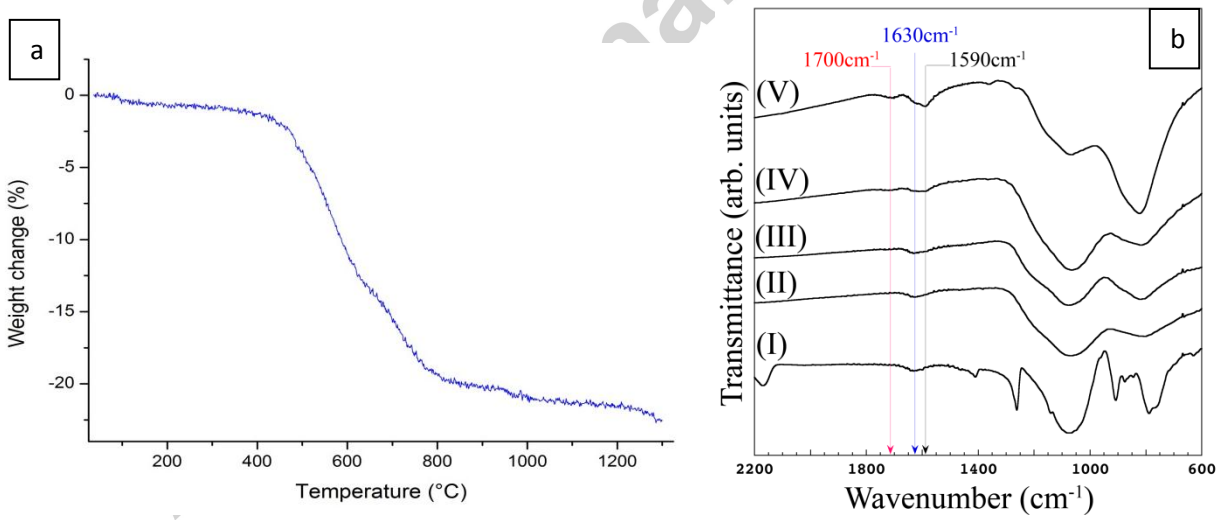

Figure 2. (a) TGA data of the cured sample derived from PHMS/TMTV (Ar, 10°C/min), (b) FTIR data including the thermoset aerogel (I), SiOC aerogel obtained at (II) 1200°C pyrolysis, (III) 1300°C pyrolysis, after HF etching of (IV) 1200°C pyrolyzed SiOC, and (V) 1300°C pyrolyzed SiOC.

FTIR spectra of the samples are shown in **Fig. 2(b)**. The peak at 2170 cm^{-1} (stretching) and 910 cm^{-1} (deformation) result from the presence of Si-H bonds and can only be seen in the starting thermoset aerogel. Additionally, sharp peak at 1265 cm^{-1} (stretching) and 785 cm^{-1} (rocking) are

due to Si-CH_3bond vibration: as expected these peaks disappear upon conversion of the polymeric aerogel into the SiOC ceramic aerogels.

Si-O bonds of the siloxane network give rise to broad and high-intensity peak at about 1070 cm^{-1}(stretching) which is visible in all samples. A strong Si-C bond vibration peak starts appearing at 810 cm^{-1}in the samples pyrolyzed at high temperature. The peak at ~1630 cm^{-1}comes from the presence of adsorbed water on surfaces of the samples.

Interestingly, the band related to the Si-O bonds at 1070 cm^{-1} strongly reduces in the HF treated samples confirming the selective dissolution of the SiO_2-based phase. In the FT-IR spectra of the HF etched samples (and particularly in the sample treated at 1300 °C) two new peaks appear. The small peak around 1700 cm^{-1} can be assigned to C=O bonds while the vibration at ~ 1590 $cm^{-1}$is due to C=C bonds of the free carbon phase. These vibration have been already reported in the literature for HF-etched SiOC glasses [14] however the formation mechanism of the C=O group is still not completely clear. In the literature has been proposed that C=O moieties are formed during the HF treatment through reaction with the free carbon phase [14].

Furthermore, for the higher temperature (1300°C) pyrolyzed and HF etched samples the peak intensity of Si-C bond increase much more, due to the formation of nanocrystalline SiC at higher temperature (see **Fig. 2**(**b, V**)). Generally, increasing the pyrolysis temperature triggers the phase separation of the SiOC amorphous network into carbide and oxide (silica) rich domains [12], with the formation of nanocrystalline SiC. This makes the HF etching of SiOC much easier compared to lower temperature pyrolyzed ones [15].

XRD patterns for the un-etched samples are similar to those already reported in the literature for SiOC glasses pyrolyzed in the same temperature range [15-16]. They show a broad halo at 2θ ~22° similar to the peak observed in amorphous silica and attributed to a short-range order in the

packing of silica tetrahedra. The XRD patterns recorded on the samples pyrolyzed at 1200 and 1300°C after the HF etching are reported in **Fig. 3**. The pattern of the aerogel pyrolyzed at 1200°C and then HF etched does not show any clear difference compared the same sample before etching. On the other hand, the spectrum of the 1300°C sample clearly reveals: (i) a strong reduction (but not its complete disappearance) of the silica halo and (ii) the diffraction peaks due to nanocrystalline SiC at 2θ ~ 35°, 60° and 71°.These results suggest that the HF etching dissolves preferentially the silica phase -leaving behind a Si-C rich ceramic aerogel- and this effect is more pronounced for the sample pyrolyzed at the higher temperature. However, the removal of the silica phase is never complete and residual silica is still present in both HF treated aerogels, in agreement with the FT-IR data. Finally, for both samples the XRD patterns show a new, quite sharp peak at 2Θ ≈ 18°; a similar peak has been already reported in the literature for HF-etched SiOC glasses and has been assigned to the formation of F-intercalated graphite [17-18].

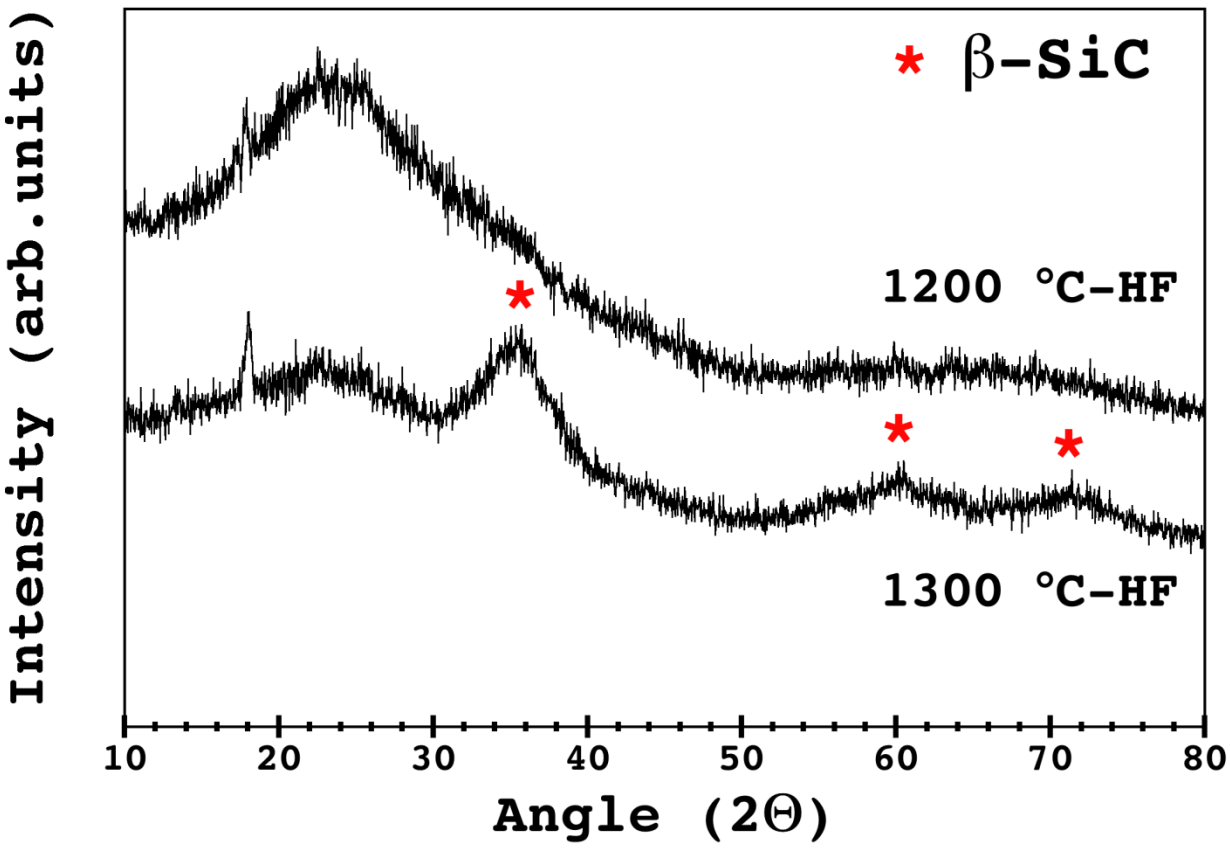

Figure 3.XRD patterns of the SiOC aerogels pyrolyzed at 1200°C and 1300°Cafter HF acid attack

3.3. Porosity Characterization

The N_2 adsorption-desorption isotherms were collected on SiOC aerogel powders before and after HF etching(**Fig. 4(a)** and **4(c)**). According to IUPAC, the shape of isotherms can be classified as type IV. In fact a hysteresis loop, which is caused by the capillary condensation of gas in the mesopores, is present in the adsorption/desorption isotherms. The hysteresis loop is located in the P/P_0 range 0.8-0.9, suggesting the presence of large mesopores. The measured SSA values and corresponding pore volumes are given in **Table 1**.

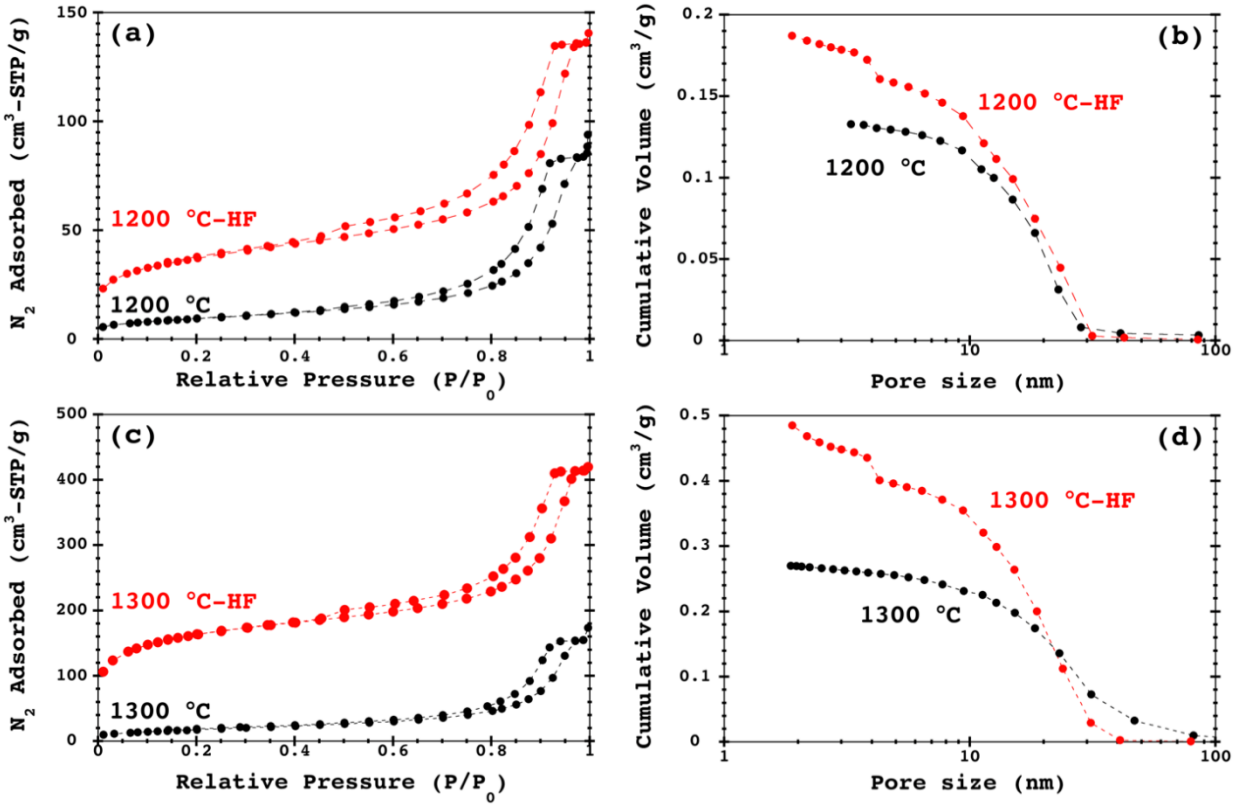

Figure 4. (a) and (c): N_2 adsorption/desorption isotherms of the samples pyrolyzed at 1200 °C and 1300 °C before and after HF etching; (b) and (d): cumulative pore volume as a function of the pore size for the samples pyrolyzed at 1200 °C and 1300 °C before and after HF etching.

The cumulative pore volume as a function of the pore size for the produced samples is given in **Fig. 4(b)** and **4(d)**. As can be clearly seen, while the non-etched samples had pores, roughly speaking, in the range 10 – 50 nm, for the HF etched samples new porosity appears below 10 nm. Indeed, for the samples pyrolyzed at 1200 °C the volume of mesopores (after HF) in the range 2-10 nm is ca 0.05 cm^3/g while in the same pore size range (2-10 nm) the sample pyrolyzed at 1300 °C shows a pore volume of ca 0.15 cm^3/g. Moreover, also the micropore volume reported in **Table 1,** show a similar trend: before etching the micropore volume is zero

for both samples while after etching the micropore volume is still very low for the sample pyrolized at 1200 °C (0.03 cm^3/g) but it reaches 0.19 cm^3/g for the aerogel treated at 1300°C. Taken all together this information truly demonstrate the presence of hierarchical porosity and also suggest that, by increasing the pyrolysis temperature, the phase separation of the SiOC glass is promoted at the micro/small-meso scale and results into a more efficient etching process. Accordingly, a remarkable increase of the SSA up to 530 m^2/g and TPV 0.65 cc/g has been observed for the aerogel pyrolyzed at 1300°C. Finally for both samples the curve of the cumulative volume shows a step between 3 and 4 nm implying a higher frequency of formation of pores close to that size. The reason for this experimenatl evidence is not yet clear even if the presence of silica clusters in the nanometer size (2-4) has been reported in the literature based on small angle x-ray scattering studies [19].

Table 1: Nitrogen sorption results.

Sample	SSA (m^2/g)	Micropore volume (cm^3/g)	Total Pore Volume (cm^3/g)
Pre-ceramic aerogel	78	0	0.42
1200°C (5h)	33	0	0.14
1300°C (5h)	64	0	0.27
1200°C (5h) + HF	125	0.03	0.22
1300 (5h) °C + HF	530	0.19	0.65

4. Conclusions

A silicon oxycarbide aerogels have been synthesized from a thermoset PHMS/TMTVS aerogel through pyrolysis in Ar flow at 1200 and 1300°C. The SiOC aerogels have SSA in the range 30 -60 m^2/g and are constituted by large mesopores in the range 10 - 40 nm. We have shown that it is possible to introduce micro and (small)meso-pores in the ceramic aerogel through a HF etching process. The hydrofluoric acid selectively removes the silica clusters present in the structure of the silicon oxycarbide glass thereby creating a high surface area and high porosity materials. Indeed, this treatment significantly enhanced the SSA value and pore structure of powdered aerogels. SSA values reaching ~530 m^2/g and total pore volume of 0.65 cc/g including a micropore volume of 0.19 cc/g were obtained. Finally we have shown that the acid treatment is more efficient if the SiOC glasses are well phase separated which implies the use of a high pyrolysis temperature (1300 °C better than 1200 °C).

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