Porous Ceramics

HIERARCHICAL POROSITY CERAMIC COMPONENTS FROM PRECERAMIC POLYMERS

P. Colombo[1*], L. Biasetto, E. Bernardo, S. Costacurta, C. Vakifahmetoglu
University of Padova, Dipartimento di Ingegneria Meccanica – Settore Materiali
via Marzolo, 9
35131 Padova, Italy
[1]Department of Materials Science and Engineering, The Pennsylvania State University
University Park
PA 16802, USA

R. Peña-Alonso, G.D. Soraru
University of Trento, Dipartimento di Ingegneria dei Materiali e Tecnologie Industriali
via Mesiano 77
38050 Trento, Italy

E. Pippel, J. Woltersdorf
Max Planck Institut für Mikrostrukturphysik
Weinberg 2
06120 Halle, Germany

ABSTRACT

Cellular SiOC ceramic components with a porosity > 70 vol% and cell size dimension ranging from 10 μm to a few mm approximately have been developed using a silicone resin. These cellular materials have been further functionalized by developing a high specific surface area (SSA), which is useful for applications such as absorbers or catalyst supports. Several approaches were followed to achieve this goal, including controlling the heating process to retain the transient porosity, depositing a SiO_2-based meso-structured coating on the surface of the SiOC cellular material, or etching the foams in HF. The samples were characterized using various techniques, including SEM, high resolution and analytical TEM methods and N_2 adsorption-desorption. The SSA value produced varied according to the processing strategy followed.

INTRODUCTION

Porous ceramic components, in particular cellular ceramics, find use in a very broad range of engineering applications, for instance as filters for molten metal or particulate in gas streams, as catalyst support, as load-bearing lightweight structures or as scaffolds for biomedical applications. Most of these applications have rather strict requirements in terms both of the amount of porosity and of its morphology (cell size, cell window size, interconnectivity between the cells) that can be met by choosing the appropriate fabrication method [1,2].

The development of components with hierarchical porosity (micro-, meso- and macro-porosity) is of particular interest because they possess at the same time high permeability and tortuosity of the flow paths (improving mixing and heat transfer), provided by the macro-pores (with a dimension d > 50 nm), and a high specific surface area (SSA), given by the micro- (d < 2 nm) and meso-pores (2 < d < 50 nm). Components with hierarchical porosity can thus be employed in separation, gas storage, removal of pollutants and catalysis applications.

---

* Member, The American Ceramic Society. Corresponding author: paolo.colombo@unipd.it

Preceramic polymers allow the fabrication of cellular ceramics (micro- and macro-cellular foams [1,2]) as well as of components with high SSA [3-6], taking advantage both of the shaping possibilities given by the use of a polymeric material and of the transient porosity that is generated upon pyrolysis. Moreover, functionalization of the porous components is possible, by simply adding suitable fillers to the preceramic polymers, in order to enhance/modify some physical properties (for instance electrical conductivity or magnetic properties) [7].

In this paper, we briefly discuss the use of several possible approaches for developing a high specific surface area in open-cell macro-porous ceramic components obtained from preceramic polymers.

EXPERIMENTAL

SiOC microcellular foams were prepared using a preceramic polymer (MK Wacker-Chemie GmbH, Germany) and poly-methylmetacrylate (PMMA) microbeads (Altuglas BS, Altuglas International, Arkema Group, Rho (MI), Italy) of nominal size ranging from 10 to 185 μm acting as sacrificial filler [4]. The powders were mixed at a constant weight ratio (20 wt% MK, 80 wt% PMMA) by ball milling for 1 hour and then warm pressed (130 to 180°C, 20 MPa). The warm pressing temperature was adjusted as a function of the PMMA microbeads size, in order to optimize the viscous flow of the molten polymer through the beads and the degree of crosslinking of the preceramic polymer. The green samples were then treated in air at 300°C for 2h (heating rate = 0.5 °C·min^{-1}) in order to burn out the PMMA microbeads and allow for the crosslinking of the preceramic polymer. Macro-cellular foams were produced by direct foaming according to the procedure reported in reference 3. All the foams, in their polymeric stage, were pyrolyzed under nitrogen flow at 1200°C for 2 hours (heating rate = 2 °C·min^{-1}). During pyrolysis, the preceramic polymer samples were subjected to a large volume shrinkage (~50%; about 23% linear shrinkage) due to the polymer-to-ceramic transformation, occurring with the elimination of organic moieties and leading to the formation of an amorphous Si-O-C ceramic.

A mesoporous silica precursor solution was prepared containing tetraethyl orthosilicate (TEOS) as the silica source, and the block copolymer Pluronic F127 (EO_{106}-PO_{70}-EO_{106}-EO=CH_2CH_2O, PO=$CH(CH_3)CH_2O$) as the structure-directing agent. A starting solution was prepared by mixing 4 g TEOS and 2.5 g EtOH, and successively adding 0.355 g of a 0.768 M HCl solution. The solution was then stirred for 45 minutes in order to pre-hydrolize the silane units, and added to a solution containing 12 g EtOH, 1.3 g Pluronic F127 and a 0.057 M HCl solution. This was stirred for further 15 minutes before impregnation into the SiOC foams. The SiOC foams were immersed into the silica solution and withdrawn after 1 minute; excess solution was then removed from the samples with absorbing paper. The impregnated samples were dried in air at ambient temperature for a few days. The impregnated samples were heat treated in order to remove the surfactant from the mesopores and promote further condensation of the silica framework. Calcination was carried out in air at 350°C for 1 hour (heating rate = 1°C·min^{-1}).

SiOC foams were etched using an HF solution (20 vol% in H_2O). Samples were placed in a polypropylene container with the hydrofluoric acid (HF) solution. The weight ratio between the SiOC samples and the HF solution was kept constant to 1:50. The solution was gently stirred at room temperature for 9h, and then the samples were extracted and rinsed with distilled water to remove any residual HF. They were then heated up to 110°C to eliminate the remaining water. Some samples were heat treated in air at 650°C for 2h after pyrolysis (before etching), to remove completely any traces of residual carbon possibly deriving from the incomplete burn out of the PMMA microbeads.

MK silicone resin was mixed (50 wt%) with a liquid poly-dimethyl-siloxane (Rhodorsil RTV 141, Rhodia, France), cast into a mold and, after crosslinking, the sample was pyrolyzed at 1200°C for 2 hours (heating rate = 2 °C·min^{-1}).

The samples were characterized using Scanning Electron Microscopy (SEM, JEOL JSM-6490, Japan), Transmission Electron Microscopy (Philips CM20 FEG microscope, operated at 200 keV), and nitrogen adsorption-desorption (ASAP 2020, Micromeritics; analysis performed at 77 K). Specific Surface Area (SSA) was determined from a BET (Brunauer, Emmet, and Teller) analysis [7]. Pore size distribution was calculated from the adsorption branch of the isotherm through the BJH analysis [8].

RESULTS AND DISCUSSION

Several approaches can be followed in order to produce porous components using preceramic polymers. Macro-porous cellular components with a large cell size (macro-cellular foams, average cell size from ~250 μm to ~3 mm) or a small cell size (micro-cellular foams, average cell size from ~1 μm to ~200 μm) can be fabricated using different procedures: macro-cellular foams can be obtained from direct foaming or by using polyurethane precursors as expanding agents [3,9], while micro-cellular foams are produced with the aid of sacrificial fillers [4,10]. Additionally, micro- and/or meso-porosity can be developed within cellular ceramics, thus obtaining ceramic components with hierarchical porosity.

Several routes that can be pursued to accomplish this goal are listed in Table I and are addressed in this paper.

Table I. Possible strategies for producing hierarchical porosity ceramic components with high SSA from preceramic polymers, with typical SSA values obtained

Strategy	SSA (m^2/g)	Reference
Controlled thermal treatment of preceramic polymers	400-700*	[5,6]
Addition of high SSA fillers	400-650*	[5,6]
Deposition of zeolites	150-300	[11]
Deposition of meso-porous coatings	60	[12]
Infiltration of aerogels into foams	150-220	[13]
Etching	150-600	[14]
Mixing of preceramic polymers with different characteristics	20-30	[15]

* at 600°C

The first approach listed in Table I is the controlled thermal treatment of preceramic polymers. This approach takes advantage of the transient porosity generated upon heat treating a preceramic polymer in the temperature range at which the polymer-to-ceramic conversion occurs (generally 400-800°C) [16,17]. The build-up of internal pressure in the component, provoked mainly by the decomposition of the organic moieties in the preceramic polymer (with generation typically of CH_4 and H_2 gas) leads to porosity (with pore size typically below 50-100 nm). This (micro)porosity is transient, in that it is eliminated when the pyrolysis temperature leading to the completion of the ceramization process is increased. Figure 1a shows the gas evolution of MK polysiloxane, with its associated weight loss, which is maximum in the polymer-to-ceramic transformation temperature interval. Figure 1b reports the data for the pore volume present in a macro-cellular foam pyrolyzed at various temperatures. It can be seen that with increasing

pyrolysis temperature, the micro- and meso-pores are closed, with consequent drastic reduction of the Specific Surface Area values. A significant influence of the pyrolysis rate on the amount of the generated SSA at each temperature has also been reported (the slower the heating, the higher the SSA values) [5,6].

The amount of produced specific surface area is stable up to the pyrolysis temperature reached, even after prolonged heating at the same temperature. In one experiment, a macro-cellular foam was heated at 600°C for times ranging from 1 to 48h, and the SSA value decreased only of about 10% (to 380 m^2/g) after the longest heating time, confirming that the closure of the small pores is driven by a densification mechanism based on surface reaction/pyrolysis accommodated by viscous flow (and thus is temperature dependant) [17].

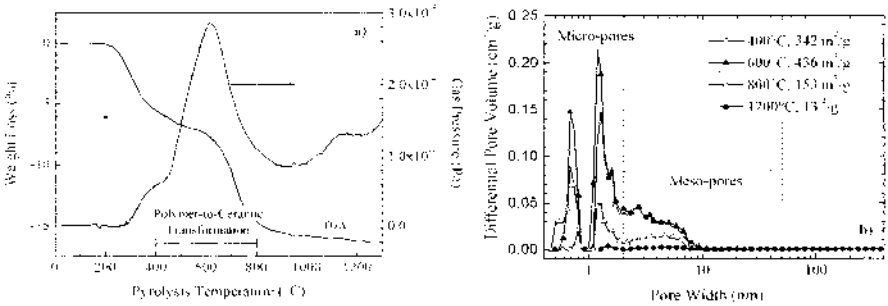

Fig. 1. a) Gas generation and weight loss upon pyrolysis; b) Evolution of micro- and meso-pore volume and of SSA with pyrolysis temperature (macro-cellular foam).

Despite the fact that high values of SSA can be achieved by controlling the heating schedule and limiting the pyrolysis temperature [5,6], it is very difficult to retain the micro- and meso-porosity when heating at temperatures above 600-800°C, which can be desirable for some applications. A possible solution is the second approach listed in Table 1: the mixing of micro-/meso-porous fillers with the preceramic polymer, followed by shaping into a cellular ceramic component. For instance, the addition of carbon black (activated carbon) powders to a polysiloxane, led to SSA values of about 100-130 m^2/g up to a pyrolysis temperature of 1200°C [5].

The third and fourth entries in Table 1 refer to the deposition of high SSA materials on the cell walls, namely zeolites and meso-porous coatings. Macro-porous ceramic foams, in fact, are an ideal candidate as substrates for the development of porous bodies with hierarchical (micro-, meso- and macro-) porosity. Their very large geometric surface area (for micro-cellular foams, in particular, of the order of a few $m \cdot cm^{-3}$) provides a wide region for the deposition of coatings of suitable materials possessing micro-/meso-porosity. Zeolites have been deposited both on macro-cellular foams [18] and on micro-cellular foams [19]. In the latter case, a high SSA value for the ceramic components with hierarchical porosity was achieved (221 m^2/g for ZSM-5 coatings, 293 m^2/g for silicalite-1 coatings, corresponding to a zeolite loading of about 80 wt%). We therefore decided to further develop this strategy by depositing a SiO_2 mesoporous layer obtained by block copolymer-templated self-assembly from a sol-gel solution [12].

Figure 2a and 2b show some TEM micrographs of such coating deposited on the walls of a microcellular SiOC foam (average cell size 185 μm). TEM investigations revealed the mesoporous nature of the layer, with an average pore size of ~4 nm. The pores are assembled in an 3D ordered fashion, according to a BCC unit cell with a lattice parameter of about 13 nm. It can be observed that closer to the foam there was a lower degree of order in the pores, which became regularly arranged further away from the substrate. From SEM and TEM investigations, the coating thickness was assessed to be in the range 1 to 5 μm, depending on the region of the foam observed. In some areas the coating appeared to be partially detached form the substrate, either because of stress caused when sectioning the sample or because of uneven drying shrinkage. The issue will be further investigated in forthcoming experiments.

The nitrogen adsorption-desorption isotherms indicated that the coated microcellular SiOC foams followed the typical behavior of mesoporous materials, showing also the presence of micropores (deriving from the interconnection among the mesopores). The analysis of the data gave a SSA value of 60 m^2/g for the entire sample. Considering that the uncoated SiOC foam has a SSA value of only ~3 m^2/g, and taking into account the amount of meso-porous coating deposited on the foam (from weight change measurements before and after impregnation and calcination), this corresponds to a SSA for the meso-porous silica layer of about 560 m^2/g, which is typical for mesoporous materials. Thus, we can state that the nature and morphology of the foam substrate did not affect the self-assembling process of the molecular inorganic nano-building blocks, which is guided by the presence of supramolecular structure-directing agents formed by the self-assembly of amphiphilic species.

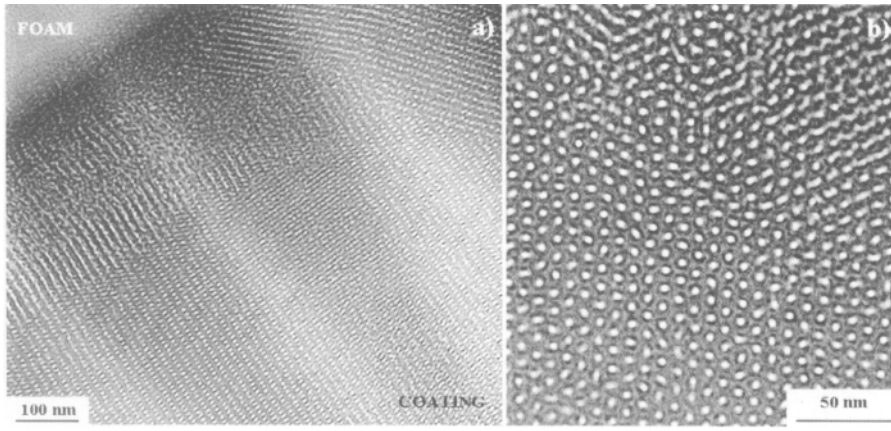

Fig. 2. a) Cross-sectional TEM of SiOC foam coated by a meso-porous SiO_2 layer; b) particular of the meso-porous coating, showing a 4-fould symmetry axes for the pores.

Besides meso-porous coatings, other infiltrants could be used for the generation of high SSA and hierarchical porosity in macro-porous ceramics: sol-gel derived aerogels, for instance, which have a SSA as high as 1000 m^2/g, can be infiltrated into open cell foams with or without the aid of vacuum [13]. If completely infiltrated, the resulting component has a reduced

permeability, but the ceramic foam structure provides strength and support to the otherwise mechanically weak aerogel material.

Another strategy that has been used to increase the specific surface area in cordierite honeycombs is etching [20], which has also been applied with success to SiOC materials in powder form [14,21]. Because of the nano-structured microstructure that SiOC ceramics possess, which is comprised of nano-domains (typical size 1-5 nm) based on clusters of silica tetrahedra encased within an interdomain wall constituted from mixed bonds of SiOC and from a network of sp^2 carbon [22]. HF attack provokes the preferential removal of silica from the material. This leads to the development of micro- and meso-porous structures with a high SSA [14]. The etching experiments performed on an as-pyrolyzed foam gave only a limited increase in the specific surface area (30 m^2/g). The reasons for this discrepancy with the results published by other authors concerning SiOC glass powders could be several. We can exclude a non complete infiltration of the foam by the HF solution, because we performed etching tests on crushed foams as well, but we did not observe a significant difference in the SSA data. Therefore, a possibility could be the presence of some residual carbon at the surface of the cells (deriving from an incomplete burn-out of the PMMA microbeads), which could act as a barrier towards chemical attack [23]. We therefore proceeded to heat treat a SiOC foam in air at 650°C, in order to remove any residual C present. After etching of the oxidized foam, an increase of SSA (46 m^2/g) was indeed observed, but not as significant as one could have supposed. Therefore, the reason for the limited development of specific surface area with etching in our present experiments must lie elsewhere. At this stage of the investigation, we believe that a possible motivation could be related to the size of the silica nano-domains in our SiOC ceramic; if they are too small, this would hinder the access of the etchant to the silica tetrahedra [14]. Small Angle X-ray Scattering experiment will have to be performed to clarify this issue. In Figure 3a and 3b are shown the absorption-desorption isotherms, which indicate the presence of both micro-pores and meso-pores, as well as the pore size distribution for both the as-pyrolyzed and oxidized SiOC etched foams. We can observe that most of the pores have a dimension below 10 nm, but the distribution is very broad (slightly more so for the oxidized SiOC foam).

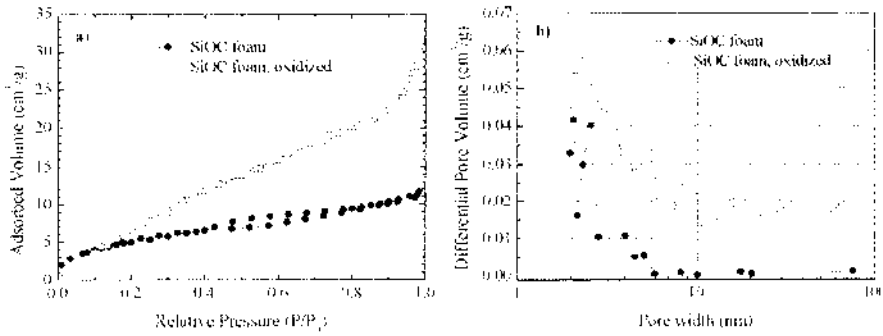

Fig. 3. a) Absorption-desorption isotherms for etched SiOC foam (as received and after oxidation at 650°C); b) Pore size distribution.

The last strategy listed in Table I is the mixing of precursors with different architecture (poly-silsesquioxanes typically possessing a cage-like structure or linear poly-siloxanes). This is another promising strategy for the generation of (macro-)porous ceramics from preceramic polymers [15]. Some preliminary work conducted in our laboratory has shown that porous structures of various morphology can be produced depending on the composition of the starting mixture. As a typical example, in Figure 4a and 4b are shown SEM micrographs of a porous ceramic obtained by mixing a silsesquioxane (MK resin) with a linear silicone (RTV 141). The generation of porosity is due to the different behavior that the two polymers have upon pyrolysis, in terms of weight loss, shrinkage and amount of gas generated (all much higher for the siloxane with a linear structure than for the silicone resin, with a more complex structure). It can be seen that a large amount of open porosity was generated in the sample, and that the specimen had quite a complex morphology. Besides large pores of a few hundred microns in size, a large amount of smaller, micron-sized pores and cavities is present. At this stage of the investigation we do not have any information relative to the amount of specific surface area produced by this processing method, but literature data indicate that relatively high SSA values could be achieved [15].

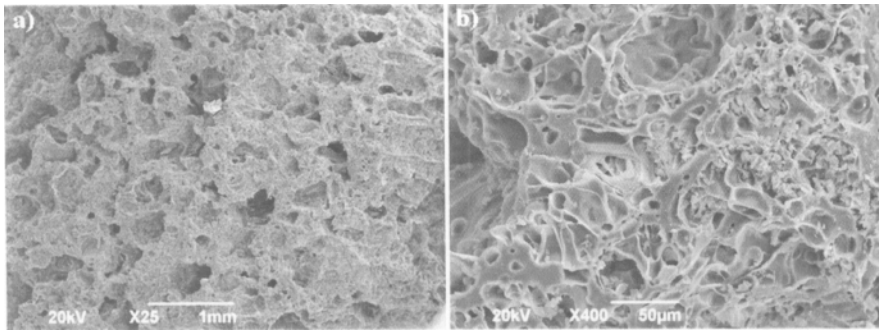

Fig. 4. SEM micrograph of the fracture surface of a macro-porous ceramic obtained by mixing preceramic polymers with different characteristics. a) general view; b) higher magnification detail.

Finally, it is worth noting that in some current applications (e.g. Diesel particulate filters with a wash-coat [21]), the amount of SSA present in the component is typically well below 100 m^2/g, so the required target value for high SSA in hierarchical porosity ceramics should be assessed depending on the application considered.

CONCLUSIONS

Using preceramic polymers, in particular polysiloxanes, it is possible to fabricate macro-porous (micro- and macro-cellular) ceramics. Several strategies are available for adding to these structures a high specific surface area (SSA), thus creating ceramic components with hierarchical porosity. Interrupting the pyrolysis process in the polymer-to-ceramic temperature range allows to retain the transient porosity in the material, but increasing pyrolysis temperature leads to a drastic reduction of the SSA. The addition of (micro- and meso-)porous fillers seems a good way of retaining high SSA values at high pyrolysis temperature. The deposition of coatings possessing

(micro- and meso-)pores is also a viable route to produce ceramic components with hierarchical porosity. Infiltration of the macro-porous ceramic components with aerogels is another possibility worth further exploring. Etching can also be used, but in the present experiments only a limited increase in SSA was observed, possibly due to the intrinsic nature of the SiOC ceramic tested. The mixing of preceramic polymers with different characteristics upon pyrolysis allows to fabricate (macro-)porous ceramics with a varied pore morphology.

ACKNOWLEDGMENTS

The authors wish to thank Dr. S. Carturan of Laboratori Nazionali di Legnaro (LNL) Padova, Italy, for BET measurements and the helpful discussions. P. C., G.D. S. and C. V. acknowledge the support of the European Community's Sixth Framework Programme through a Marie-Curie Research Training Network (PolyCerNet MRTN-CT-019601). R. P.-A. gratefully acknowledges the Spanish Ministerio de Educación y Ciencia for the financial support for a post-doctoral fellowship.

REFERENCES

[1]M. Scheffler and P. Colombo, Eds. *Cellular Ceramics: Structure, Manufacturing, Properties and Applications*. Wiley-VCH Verlag GmbH, Weinheim, Germany, 2005.

[2]P. Colombo, "Conventional and novel processing methods for cellular ceramics." *Phil. Trans. R. Soc. A*, **364[1838]**, 109-124 (2006).

[3]P. Colombo and J. R. Hellmann, "Ceramic foams from preceramic polymers," *Mat. Res. Innovat.*, **6** . 260-272 (2002).

[4]P. Colombo, E. Bernardo and L. Biasetto, "Novel Microcellular Ceramics from a Silicone Resin," *J. Am. Ceram. Soc.*, **87 [1]**, 152–154 (2004).

[5]H. Schmidt, D. Koch , G. Grathwohl and P. Colombo, "Micro-Macro Porous Ceramics From Preceramic Precursors", *J. Amer. Ceram. Soc.*, **84[10]**, 2252-2255 (2001).

[6]M. Wilhelm, C. Soltmann, D. Koch and G. Grathwohl, "Ceramers – functional materials for adsorption techniques," *J. Europ. Ceram. Soc.*, **25**, 271-276 (2005).

[7]P. Colombo, T. Gambaryan-Roisman, M. Scheffler, P. Buhler, P. Greil, "Conductive Ceramic Foams From Preceramic Polymers", *J. Amer. Ceram. Soc.*, **84[10]**, 2265-2268 (2001).

[8](a) S. J. Gregg and K.S.W. Sing, *Adsorption, surface area and porosity*, Academic Press, London, 1982, pp. 285-286. (b) E. P. Barret, L. G. Joyner, and P. H. Halenda, "The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms," *J. Am. Chem. Soc.*, **53**, 373-380 (1951).

[9]P. Colombo and M. Modesti, "Silicon oxycarbide ceramic foams from a preceramic polymer", *J. Am. Ceram. Soc.*, **82** [3], 573-578 (1999).

[10]P. Colombo, E. Bernardo, "Macro- and Micro-cellular Porous Ceramics from Preceramic Polymers", *Comp. Sci. Tech.*, **63**, 2353 2359 (2003).

[11]A. Zampieri, P. Colombo, G.T.P. Mabande, T. Selvam, W. Schwieger and F. Scheffler, "Zeolite coatings on microcellular ceramic foams: a novel route to microreactor and microseparator devices," *Adv. Mater.*, **16 [9-10]**, 819-823 (2004).

[12]S. Costacurta, L. Biasetto, P. Colombo, E. Pippel and J. Woltersdorf, "Hierarchical Porosity Components via Infiltration of a Ceramic Foam." submitted to *J. Am. Ceram. Soc.*

[13]L. Biasetto, P. Colombo, L. VanGinneken, J. Luyten, unpublished results.

[14]R. Peña-Alonso, G.D. Soraru, R. Raj, "Preparation of Ultrathin-Walled Carbon-Based Nanoporous Structures by Etching Pseudo-Amorphous Silicon Oxycarbide Ceramics," *J. Am. Ceram. Soc.*, **89[8]**, 2473-2480 (2006).

[15]F. Berndt, P. Jahn, A. Rendtel, G. Motz and G. Ziegler, "Monolithic SiCO Ceramics with tailored Porosity," *Key Eng. Mater.*, **206-213**, 1927-1930 (2002).

[16]E. Kroke, Y-L. Li, C. Konetschny, E. Lecomte, C. Fasel and R. Riedel, "Silazane derived ceramics and related materials," *Mater. Sci. Eng. R*, **26**, 97-199 (2000).

[17]J. Wan, M.J. Gasch and A.K. Mukherjee, "In Situ Densification Behavior in the Pyrolysis Consolidation of Amorphous Si-N-C Bulk Ceramics from Polymer Precursors," *J. Am. Ceram. Soc.*, **84[10]**, 2165 69(2001).

[18]F.C. Patcas, "The methanol-to-olefins conversion over zeolite-coated ceramic foams", *J. Catal.*, **231[1]**, 194-200, (2006).

[19]A. Zampieri, P. Colombo, G.T.P. Mabande, T. Selvam, W. Schwieger and F. Scheffler, "Zeolite coatings on microcellular ceramic foams: a novel route to microreactor and microseparator devices," *Adv. Mater.*, **16 [9-10]**, 819-823, (2004).

[20]Q. Liu, Z. Liu, and Z. Huang, "CuO Supported on Al_2O_3-coated cordierite-honeycomb for SO_2 and NO removal from flue gas: Effect of acid treatment of the cordierite", *Ind. Eng. Chem. Res.*, **44**, 3497-3502 (2005).

[21]A.M. Wilson, G. Zank, K. Eguchi, W. Xing, B. Yates, and J.R. Dahn, "Pore Creation in Silicon Oxycarbides by Rinsing in Dilute Hydrofluoric Acid," *Chem. Mater.*, **9[10]**, 2139-2144 (1997).

[22]A. Saha, R. Raj and D.L. Williamson, "A Model for the Nanodomains in Polymer Derived SiCO," *J. Am. Ceram. Soc.*, **89[7]**, 2188-2195 (2006).

[23]G. D. Soraru, S. Modena, E. Guadagnino, P. Colombo, J. Egan and C. Pantano, "Chemical Durability of Silicon Oxycarbide Glasses," *J. Am. Ceram. Soc.*, **85[6]**, 1529-1536, (2002).

[24]C. Agrafiotis and A. Tsetsekou, "The effect of powder characteristics on washcoat quality. Part I: Alumina washcoats", *J. Euro. Ceram. Soc.*, **20**, 815-824 (2000).