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Polymer-Derived Ordered Mesoporous Silicon-Boron-Carbon-Nitrogen (Si/B/C/N) Ceramics

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Abstract

Ordered mesoporous silicon-based non-oxide ceramics are attracting increasing interest thanks to their outstanding high-temperature stability and their anticipated robustness. In this category of materials, periodic ordered silicon-boron-carbon-nitrogen (Si/B/C/N) frameworks represent an excellent opportunity for use in harsh environments in key fields like heterogeneous catalysis and/or hydrogen storage. In this review, the nanocasting approach to these materials is summarized on the basis of the synthesis of boron-modified polysilazanes, the solution infiltration of carbonaceous and silica templates, the pyrolysis of the composites followed by the template removal step. The as-obtained micron-sized powders are characterized and potential applications discussed.

Keywords: SiBCN, mesoporous powder, non-oxide ceramics, polymer-derived ceramics, nanostructured ceramics

I. Introduction

Polymer-Derived Ceramics (PDCs) are receiving increasing interest thanks to their particular suitability for high-impact applications such as in energy and environmental domains [1–12]. Associated mainly with non-oxide ceramics, this concept, known since the intensive work by Yajima on polymer-derived silicon carbide (SiC) fibers in the 1970s [1], allows the fabrication of simple borides, carbides, carbonitrides and nitrides of various main groups and transition elements with a number of favorable performance characteristics. By extending this concept to more complex compositions, it is possible to design homogeneous mixtures or solid solutions of two or more pure ceramic phases often displaying dramatically enhanced properties and even new properties in comparison to thermodynamically stable phases. In such "smart" and "adaptive" materials, the composition, shape, texture and morphology can be tuned on demand with the objective of achieving performances that go far beyond those of conventional ceramics. Combined with the ability to control the composition (and therefore the purity), shape and structure of the product and the possibility to mix two or more phases in the same material that is then homogeneous on nanoscale, PDCs appear to be strategic materials for modern science.

PDCs recently attracted interest for the preparation of periodic mesoporous frameworks inspired by the discovery of ordered mesoporous oxides in the early 1990s by Japanese and Mobil's scientists [13–15].

Mesoporous materials are materials with pores in the range of 2–50 nm according to the IUPAC classification [16]. The pores can have different shapes such as spherical or cylindrical and be arranged in varying structures. Mesoporous PDCs can be formed with a wide range of compositions expected to exhibit improved thermal and mechanical properties compared to their metal- and metalloid-oxide counterparts which represent one of the most important classes of catalytic supports of metallic (nano)particles in hydrogenation and oxidation reactions, as well as in environmental applications [17]. The introduction of porosity in PDCs could pave the way to use in key fields like catalysis support and also as scaffolds to confine chemical hydrogen storage materials. In particular, the use of PDC media should avoid the O-H---H-B interactions that exist in porous oxides used as host materials for boron hydrides and which are known to affect the nanoconfinement effect [18–19]. However, mesoporous PDCs have rarely been investigated in terms of synthesis and, as a consequence, in terms of applications. A major reason for this is that the synthesis of porous PDCs is quite challenging because their synthesis requires reaction conditions that exclude water and dioxygen.

Two methodologies for the synthesis of porous PDCs, hard and soft templating methods, are mainly reported in the literature [20–21]. This offers versatility with regard to pore morphology, pore size, pore arrangement and size distribution and potentially improved control over the nanostructure of supported catalysts. The so-called nanocasting, i.e. hard-template methodology, provides access to tunable pore morphologies by (*i*) replicating the nanostructure of a template material into a locally ordered pore system through the impregnation of the pore template with a preceramic polymer solution or melt, (*ii*) performing the subsequent pyrolysis then (*iii*) removing the template.

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Over the past decade, our group has focused on the preparation of ordered mesoporous boron- and silicon-containing non-oxide multiphasic ceramic systems [22–24]. In this category, PDCs containing Silicon, Boron, Carbon and Nitrogen (Si/B/C/N) elements which are derived from boron-modified polycarbosilazanes (BmPSs) of the type $[B(C_2H_4SiRNR')_3]_n$ ($R = H/CH_3/(NH)_{0.5}$ with $R' = H$ or $R = H/CH_3$ with $R' = CH_3$ or $R = H/CH_3/(N=C=N)_{0.5}$ with $R' = N=C=N$; $C_2H_4 = CHCH_3$, CH_2CH_2) have proven their outstanding thermo-structural properties in the 1990s [22–35]. Riedel *et al.* discovered their excellent stability at very high temperature (1800 °C) thanks to the existence of a solid solution in which the diffusion of silicon and boron yielding their respective nitrides and/or carbides is very slow [25]. Among non-oxide-type ceramics, they now represent the reference in terms of high-temperature stability, granting them potential applications in harsh environment as composites [27], ceramic fibers [28–34], and membranes [35].

In this article, we report the general procedure to prepare ordered mesoporous Si/B/C/N ceramics using silica and carbonaceous templates (Fig. 1) and BmPSs of the type $[B(C_2H_4SiCH_3NR)_3]_n$ ($R = H$, CH_3; $C_2H_4 = CHCH_3$, CH_2CH_2) as Si/B/C/N precursors.

The design, processing and properties of these micronsize mesoporous powders are described in detail. Morphological and (nano)structural characterizations by means of SEM, TEM, nitrogen physisorption (77 K), elemental analysis and X-ray diffraction are described. A major challenge in the preparation of ordered mesoporous PDCs is their applications. This will be discussed in the conclusion.

II. Synthesis of Ordered Mesoporous Si/B/C/N Ceramics

Our group has been particularly active in the past decade in the design of precursors for boron nitride in form of nanoparticles [36] and derived nanopolyhedrons [37–38], fibers [39–41], nanofibers [42], nanotubes [43], coatings [44] and workpieces [45]. More recently, we focused on the synthesis of precursor-derived porous BN including ordered mesoporous [46] and micro-/mesoporous [47] BN microsized powders, as well as BN foams with hierarchically porosity [48].
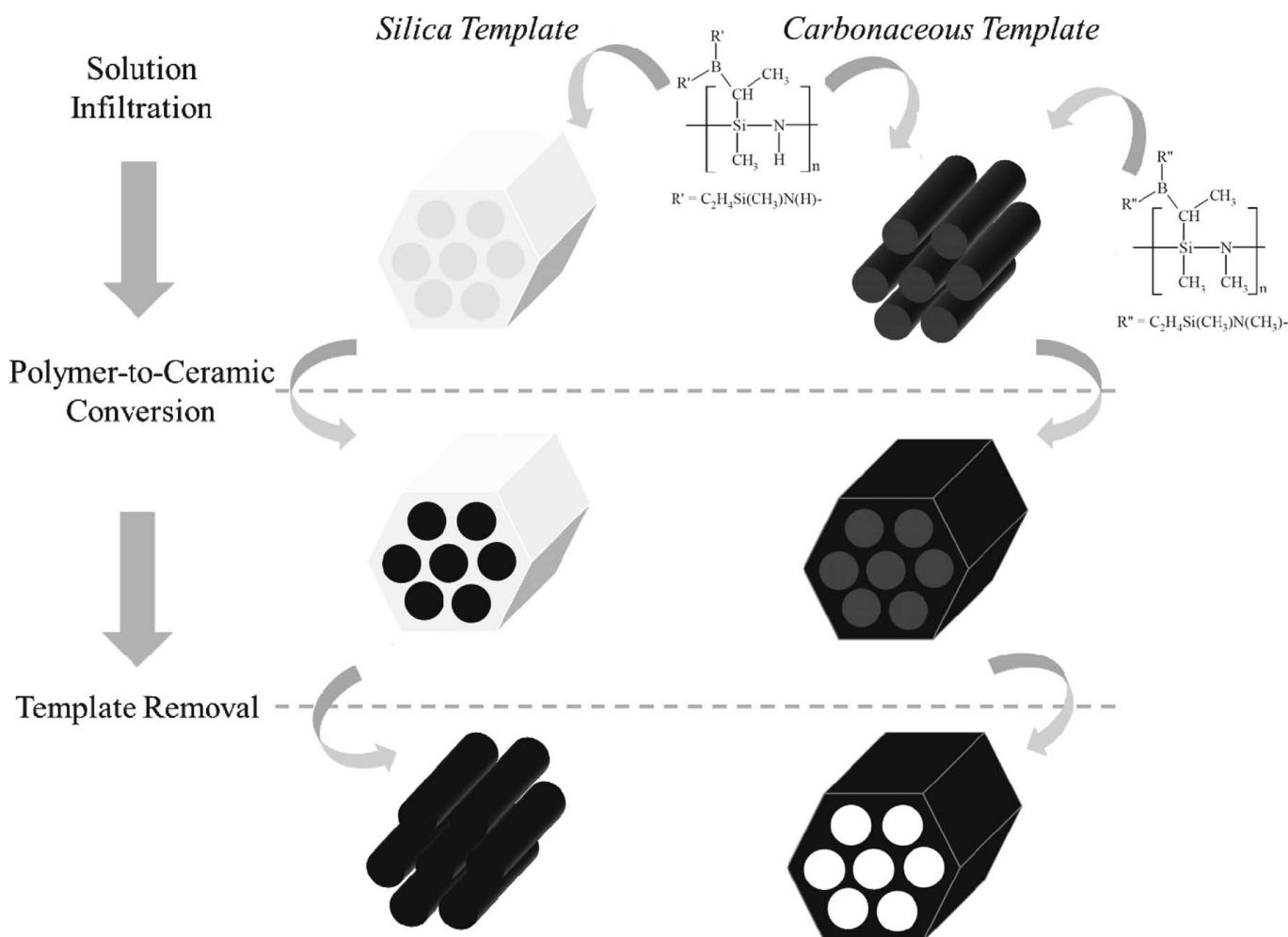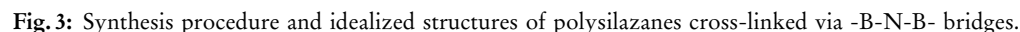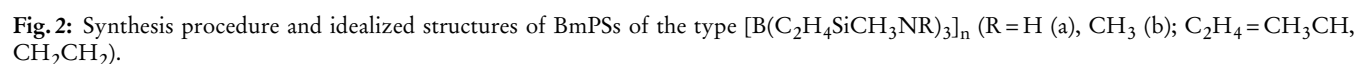

Fig. 1: Nanocasting procedure to prepare ordered mesoporous Si/B/C/N ceramics.

Fig. 2: Synthesis procedure and idealized structures of BmPSs of the type $[B(C_2H_4SiCH_3NR)_3]_n$ (R = H (a), CH$_3$ (b); C$_2$H$_4$ = CH$_3$CH, CH$_2$CH$_2$).

Fig. 3: Synthesis procedure and idealized structures of polysilazanes cross-linked via -B-N-B- bridges.

Whereas BN is a binary component that is produced on industrial scale, the synthesis of BN precursors is relatively complex, rendering this approach inappropriate in terms of cost for the production of less complex shapes like coatings and workpieces. The use of precursors becomes attractive for the production of complex ceramic shapes and textures as well as multiphasic non-oxide materials of covalently bonded ceramics. When both are targeted, the PDCs route is the exclusive approach for chemists. Indeed, it appeared obvious that improved control of compositional homogeneity and purity in multiphasic ceramic syntheses should be realized by use of single-source precursors as developed for high-quality metal oxide counterparts based on the coupling of metal alkoxide synthesis and sol-gel processing. A combination of the PDCs route and conventional shaping processes has been developed for Si/B/C/N ceramics.

(1)   Synthesis of boron-modified polysilazanes

There are two main single-source molecular systems that lead to Si/B/C/N ceramics. The first synthetic pathway pioneered by Riedel *et al.* focuses on the synthesis of boron-modified polysilazanes (BmPSs) of the type $[B(C_2H_4SiCH_3NH)_3]_n$ (C$_2$H$_4$ = CH$_3$CH, CH$_2$CH$_2$)[25]. They represent polysilazane rings that are cross-linked via -C-B-C- bridges (Fig. 2a).

The second approach proposed by Jansen *et al.* makes use of the synthesis of polyborosilazanes, i.e. polysilazanes cross-linked via -B-N-B- bridges (Fig. 3)[49].

Each of these approaches has its advantages and drawbacks in terms of polymer processing and ceramic properties. BmPSs probably offer better latitude in the tailoring of their processability to prepare shaped materials for the targeted applications. In our own group, we have explored additional examples of BmPSs synthesis, and some progress has been made in understanding some of the stepwise chemistry that takes place in the formation and decomposition of single-source precursor systems. For example, we have examined the synthesis of BmPSs of the type $[B(C_2H_4SiCH_3NCH_3)_3]_n$ (C$_2$H$_4$ = CH$_3$CH, CH$_2$CH$_2$) by the reaction of methylamine (MA) as a network building agent with tris(dichloromethylsilylethyl)borane (TDSB) as a molecular precursor (Fig. 2b)[24]. We found that a 9.0 : 1.0 reactant ratio produces a preceramic polymer of idealized composition ($[Si_{3.0}B_{1.1}C_{11.3}N_{3.3}H_{36.8}]_n$) with all the elements of the Si/B/C/N system. This polymer can be infiltrated in a carbon mesoporous template (CMK-3) to be further pyrolyzed at 1000 °C under nitrogen (ceramic conversion) then heat-treated at 1000 °C under ammonia (carbon template removal) to generate a periodic mesoporous Si/B/C/N framework[24]. Later, we re-investigated the synthesis of the BmPS of the type $[B(C_2H_4SiCH_3NH)_3]_n$ (C$_2$H$_4$ = CH$_3$CH, CH$_2$CH$_2$) which was pioneered by Riedel *et al.* using lithium amide (LiNH$_2$) instead of ammonia as a network building agent with TDSB (Fig. 4)[22].

Further unpublished extensions on this system revealed that LiNH$_2$ allowed us to precisely control the quantity of

—NH_2 groups introduced in the polymer building block of idealized composition ($[Si_3B_{1.1}C_{10.5}N_{3.0}H_{25.5}]_n$).
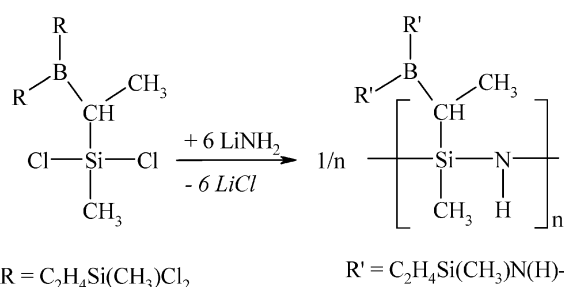

R = $C_2H_4Si(CH_3)Cl_2$ R' = $C_2H_4Si(CH_3)N(H)$-

Fig. 4: Reaction between TDSB and $LiNH_2$ leading to BmPSs of the type $[B(C_2H_4SiCH_3NH)_3]_n$ ($C_2H_4 = CH_3CH$, CH_2CH_2).

During the BmPS synthesis, a maximum degree of transformation of Si-Cl groups into $Si-NH_2$ and $SiN-HCH_3$ can be reached by reaction of TDSB with excess of NH_3 and MA, respectively. These groups polycondense at RT to build up the polymer network according to the ideal synthesis pathway depicted in Fig. 2. On the basis of former studies [25,32], the BmPSs considered here are expected to be composed of cyclic silazane units $[-Si-N-]_n$ bridged by BC_3 units. Formally, every chlorine atom present in TDSB (6 atoms) is substituted by a NH_2 or a $NHCH_3$ group depending on the linking agent. Subsequent condensation yields Si-N(H)-Si and $Si-N(CH_3)$-Si units. Ammonolysis with ammonia and aminolysis of TDSB therefore requires at least 9 *eq.* of linking agent referred to TDSB. With $LiNH_2$ (Fig. 4), 6 *eq.* referred to TDSB are required. All efforts to fully characterize these polymers have been successful, in particular by means of solid-state NMR and even molecular weight measurements, and proved that the real structure of BmPSs of the type $[B(C_2H_4SiCH_3NR)_3]_n$ (R = H, CH_3; $C_2H_4 = CHCH_3$, CH_2CH_2) differed from the ideal structure suggested in Figs. 2 and 4. For example, BmPSs of the type $[B(C_2H_4SiCH_3NCH_3)_3]_n$ ($C_2H_4 = CHCH_3$, CH_2CH_2) represent a complex polymeric network bridged via tri-coordinated $BC_{3-x}N_x$ units and tetra-coordinated BC_xN_{4-x} units connecting four- and/or six-membered -Si-N- rings. The latter are terminated by $-N(H)CH_3$ groups [32]. Therefore, the precise characterization of these precursors and more generally single-source precursors and preceramic polymers is a key step to further understand the chemistry involved during the polymer-to-ceramic conversion and finally generate materials with the desired nano- or microstructure and as a consequence tailor-made material properties.

(2) Infiltration-pyrolysis-template removal cycle

We firstly described the mesoporous templates, i.e. silica and carbonaceous templates, we have used for infiltration by the polymers we detailed previously.

(a) Carbonaceous templates

Carbonaceous templates were selected to be infiltrated first. At the beginning of our study, we anticipated that the use of the carbonaceous templates would prevent the possible interfacial contamination of PDCs which exist in silica templates as a result of diffused oxygen. Later,

we discovered that carbonaceous templates also contained oxygen at their surface.

The CMK-3 carbonaceous template has three main advantages: (1) chemical inertness towards the material confined in the nanochannels of the template at high temperature; (2) thermal stability without marked structural shrinkage; (3) hydrophobic nature which facilitates the filling of the guest polymer into the mesoporous space. It was prepared using mesoporous SBA-15 silica as a template and sucrose as a carbon source 50.

SBA-15 is a mesoporous silica (SiO_2) that has cylindrical pores arranged in a hexagonal order synthesized by hydrothermal synthesis according to established procedures. For this material, the pore size refers to the width of the cylindrical pores which can be tuned between 4 – 26 nm [51–52] even though pore sizes above 12 nm are rare. The length of the pores varies from ~ 200 nm [53] to several microns. Around each mesopore is a microporous network called the corona [54]. This network interconnects the mesopores with each other and is responsible for the high surface area of SBA-15. Typical textural parameters of the SBA-15 we prepared are reported in Table 1.

Table 1: Textural properties of SBA-15 and CMK-3 templates.

	d_{100} spacing (nm)	Cell parameter a (nm)	BET surface area ($m^2 \cdot g^{-1}$)	Pore diameter (nm)	Wall thickness (nm)	Pore volume ($cm^3 \cdot g^{-1}$)
SBA-15	9.41	10.86	745	6.8	4.06	1.03
CMK-3	8.44	9.74	1052	3.5	-	0.97

SBA-15 was added to a sucrose solution in a double infiltration procedure before carbonization under vacuum at 900 °C (1 K min^{-1}) and kept 3 h at this temperature (Fig. 5).

The SBA-15@Carbon composite was immersed in hydrofluoric acid at RT to be washed thoroughly with deionized water, methanol and acetone. After this procedure, the CMK-3 template exhibited a highly ordered 2D hexagonal mesostructure with a specific surface area of 1052 $m^2 \cdot g^{-1}$ and pore diameters of 3.5 nm (Table 1).

(b) Silica templates

Despite the possible interfacial contamination of PDCs with the oxygen present in mesoporous silica, in a second strategy we investigated the solution infiltration of silica templates. A *P6m* ordered mesoporous silica was prepared based on a procedure described by Martens *et al.* [55]. In our process, we modified some parameters like the synthesis temperature (70 °C instead of 20 °C and 90 °C) and the calcination procedure to evacuate the pore, which was performed at 500 °C with a dwelling time of 6 h instead of a two-step process (300 °C (8 h) + 550 °C (8 h)). Textural characteristics of the silica template we prepared (labeled **MartSiO$_2$**) are reported in Table 2.
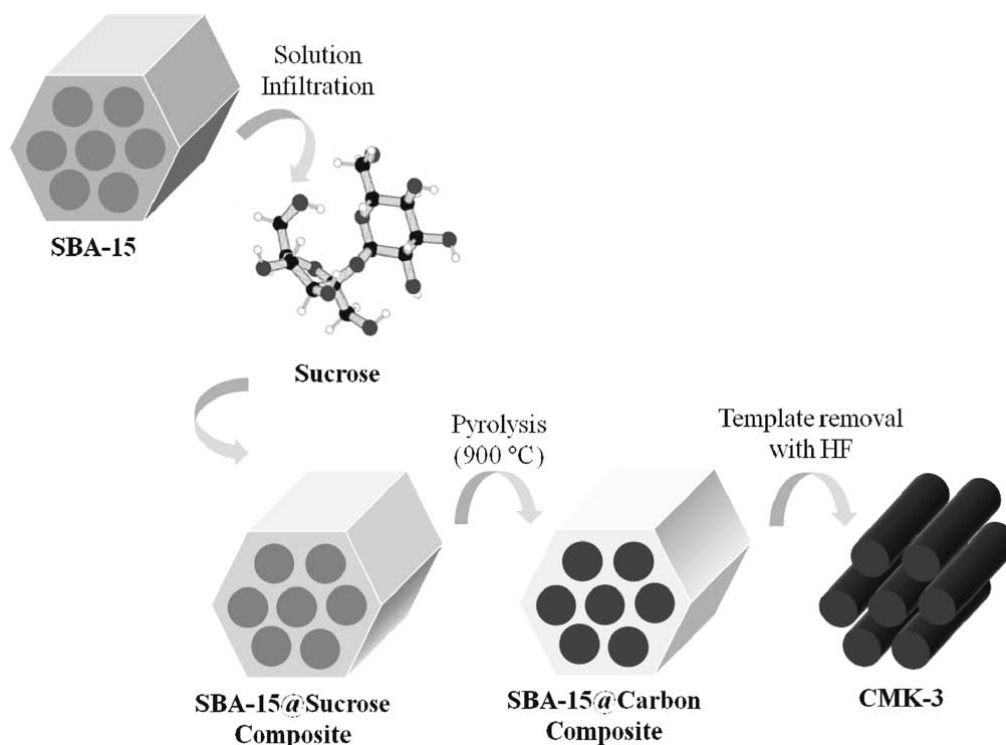
Fig. 5: The structure of the mesoporous silica SBA-15 and its carbonaceous CMK-3 replica.

Table 2: Textural properties of the silica template (labeled **MartSiO$_2$**).

	d$_{100}$ spacing (nm)	Cell parameter a (nm)	BET surface area (m$^2 \cdot$g^{-1})	Pore diameter (nm)	Wall thickness (nm)	Pore volume (cm$^3 \cdot$g^{-1})
MartSiO$_2$	10.1	11.6	877	6.5	5.1	1.02

In particular the specific surface area (SSA) was measured to be 877 m^2 g^{-1} with a pore volume of 1.02 cm^3 g^{-1}, both being superior to the values reported by Martens *et al.* [56].

(c)   *Infiltration-pyrolysis-template removal cycle*

Here, we used BmPSs of the type [B(C$_2$H$_4$SiCH$_3$NR)$_3$]$_n$ (R = H, CH$_3$; C$_2$H$_4$ = CHCH$_3$, CH$_2$CH$_2$). The BmPS of the type [B(C$_2$H$_4$SiCH$_3$NH)$_3$]$_n$ was used to infiltrate both silica and carbonaceous templates while the BmPS of the type [B(C$_2$H$_4$SiCH$_3$NCH$_3$)$_3$]$_n$ was only investigated for the infiltration of CMK-3.

The direct solution infiltration of the previously described templates with BmPSs in THF at room temperature for 48 h under static vacuum proved to be an effective method to fully infiltrate the pores of the template. The weight ratio of polymer: template has to be optimized for the preparation of high-quality periodic mesoporous Si/B/C/N ceramics. It is fixed based on the solubility and ceramic yield of polymers. We found that a polymer: template ratio of 1.2 was required for complete absorption of the polymer into the channels of the template. An important step for the successful synthesis is the subsequent filtration step to selectively remove the precursor molecules deposited outside while the capillary forces keep the precursor molecules effectively inside the pores. A further crucial part is the post-treatment of the infiltrated template

at low pressure (5.10^{-2} mbar at 30 °C) in order to slowly remove the solvent while generating a black powder. Lastly, the subsequent heat-treatments also proved to be challenging. The ceramic yield has to be the highest possible to limit the volume shrinkage occurring during the ceramic transformation. This is particularly true for porous PDCs. However, combining solubility and high ceramic yield in the same polymer is challenging and most of the time, these two properties are incompatible. As an illustration, the BmPS of the type [B(C$_2$H$_4$SiCH$_3$NCH$_3$)$_3$]$_n$ is easily soluble in THF or toluene and even meltable, but exhibits an extremely low ceramic yield which is predominantly affected by the volatilization of low-molecular-weight species during the BmPS-to-Si/B/C/N conversion [33]. Thermal degradation under nitrogen occurs in a continuous single-step weight loss from 80 °C up to 550 °C associated with a weight loss of approx. 90 % after thermolysis at 1000 °C. Therefore, the BmPS-to-Si/B/C/N conversion is expected to be associated with the collapsing of the porous structure. The first solution focuses on the application of a curing process under ammonia at 200 °C (dwelling time of 2 h) prior to decomposition under nitrogen at 1000 °C. This strategy allowed a decrease in the weight loss by 28 %. The second solution is to design the polymer chemistry with the objective to maintain good solubility while decreasing the weight loss associated with the polymer-to-ceramic conversion. The strategy is to incorporate at molecular scale units that do not modify the solubility of the polymer while reacting during the polymer decomposition to increase the ceramic yield. We used the BmPS of the type [B(C$_2$H$_4$SiCH$_3$NH)$_3$]$_n$ which exhibits NH units that are more thermally reactive than NCH$_3$ sites present in the BmPS of the type [B(C$_2$H$_4$SiCH$_3$NCH$_3$)$_3$]$_n$. It enables a higher ceramic yield (54 % measured at 1000 °C after

TGA under nitrogen) which does not require a particular cross-linking step prior to the pyrolysis under nitrogen at 1000 °C. The number of impregnation-pyrolysis cycles has to be optimized in order to completely wet the template. We applied a double impregnation-cross-linking cycle before the pyrolysis to 1000 °C under nitrogen to generate Template@Si/B/C/N composites. After the polymer-to-ceramic conversion, our standard protocol to remove carbonaceous template uses ammonia atmosphere [22–24] with heat treatment to 1000 °C while keeping the sample at this temperature for 5 h. We obtained periodic mesoporous Si/BC/N frameworks labeled *omp-Si/B/C/N-C1* and *omp-Si/B/C/N-C2* which are obtained from BmPS of the type $[B(C_2H_4SiCH_3NCH_3)_3]_n$ and $[B(C_2H_4SiCH_3NH)_3]_n$, respectively. In the case of the use of silica as template, the Silica@Si/B/C/N composite was immersed in a solution of hydrofluoric acid, and washed thoroughly with deionized water, methanol, and acetone while forming the expected ordered mesoporous Si/B/C/N materials labeled *omp-Si/B/C/N-S*.

(3) Characteristics of ordered mesoporous SiBCN

Using the two BmPS systems, Low-Angle XRD (LA-XRD) and HRTEM analyses (Fig. 6) revealed that, as a negative replica of the CMK-3 template, the obtained amorphous *omp-Si/B/C/N-C1* and *omp-Si/B/C/N-C2* micro-sized powders exhibited open, continuous, and ordered 2-D hexagonal frameworks, while elemental analy-

ses indicated the formation of Si/B/C/N materials without any clear contamination with oxygen ($Si_{3.0}B_{1.0}C_{4.2}N_{3.5}$ for *omp-Si/B/C/N-C1* and $Si_{3.0}B_{1.0}C_{4.2}N_{2.4}$ for *omp-Si/B/C/N-C2*).

The cross-section HRTEM image (Fig. 6) clearly displays a hexagonal (honeycomb-like) arrangement of the mesopores with diameters around 5 nm.

The nitrogen-adsorption isotherms of the *omp-Si/B/C/N-C1* and *omp-Si/B/C/N-C2* samples are shown in Figs. 7 (a) and (b).

Table 3 reports the corresponding BET results. Based on the IUPAC classification of the sorption isotherms [16], the *omp-Si/B/C/N-C1* and *omp-Si/B/C/N-C2* samples exhibit isotherms of type IV featuring a pronounced step owing to capillary condensation of N_2 in the primary mesopores. A steep increase and a H1-type hysteresis loop occur in the isotherms owing to the capillary condensation at a relative pressure (P/P_o) from 0.40 to 0.80 typical for ordered mesoporous materials with cylindrical pores and a narrow pore size distribution. The samples exhibited high surface area (600–636 m^2 g^{-1}), high pore volume (0.61–0.93 cm^3 g^{-1}), and narrow pore size distribution (3.6–4.6 nm).

Short chemical etching with dilute HF eliminates the silica template, resulting in the formation of *omp-Si/B/C/N-S* as an open, continuous and highly ordered 2D hexagonal Si/B/C/N framework as demonstrated by means of LA-XRD and HRTEM analyses (Fig. 8).
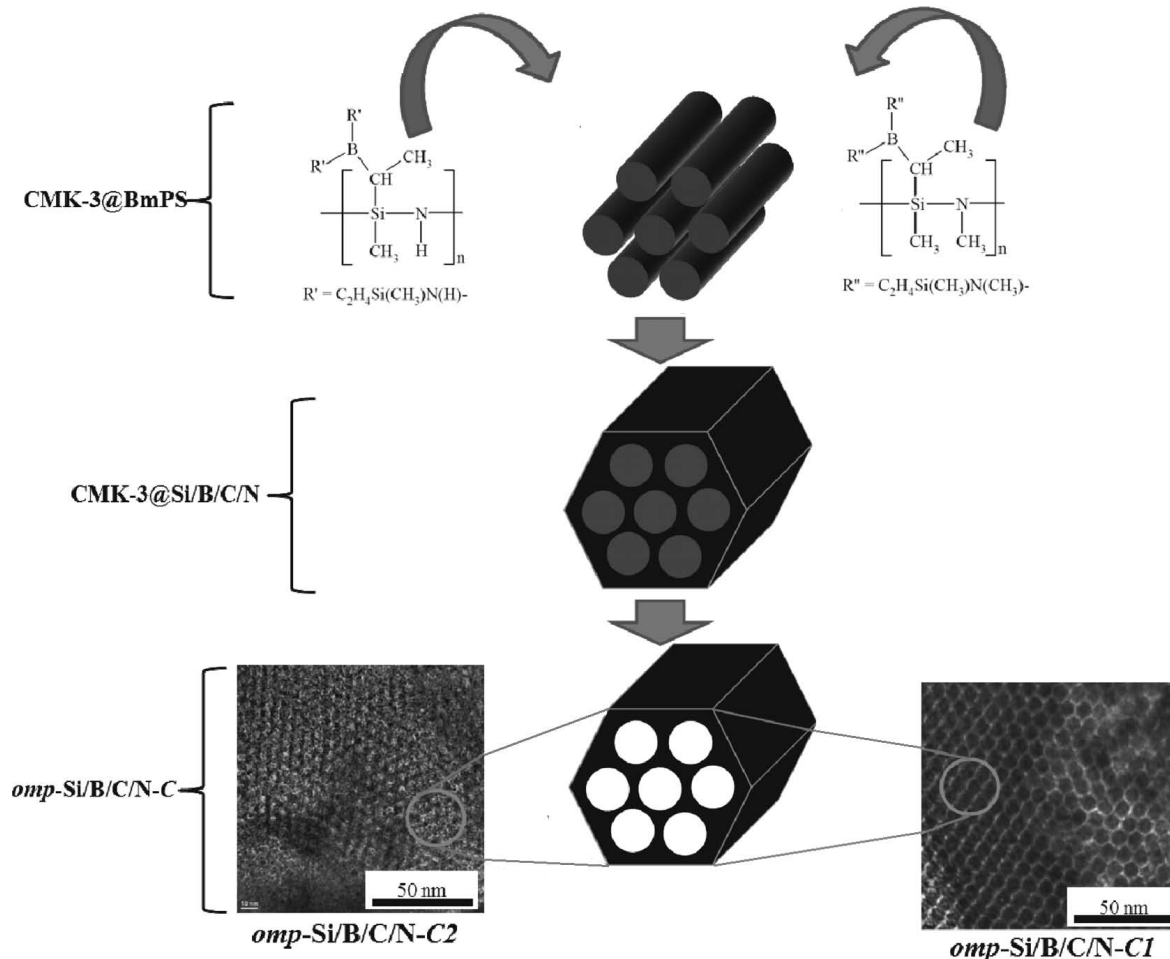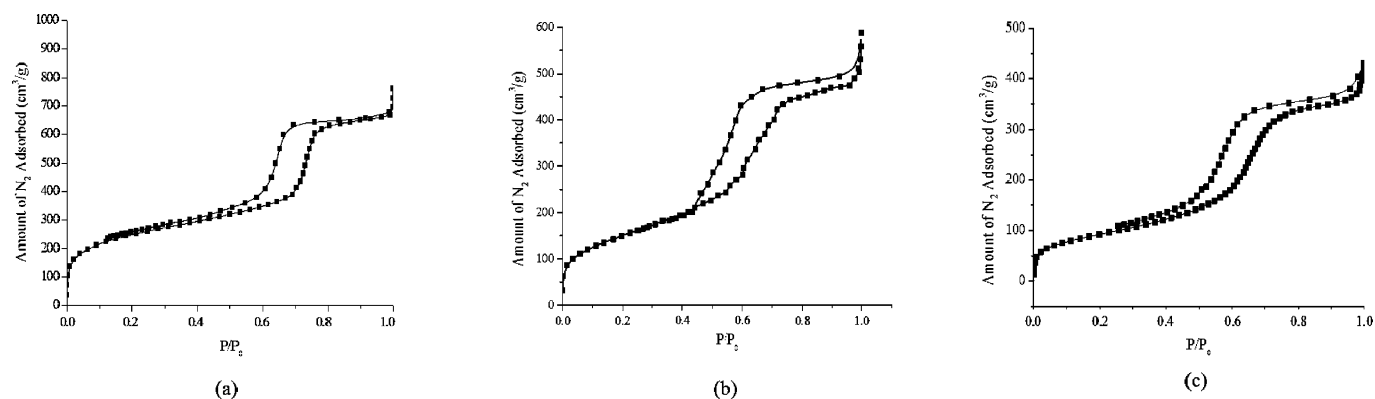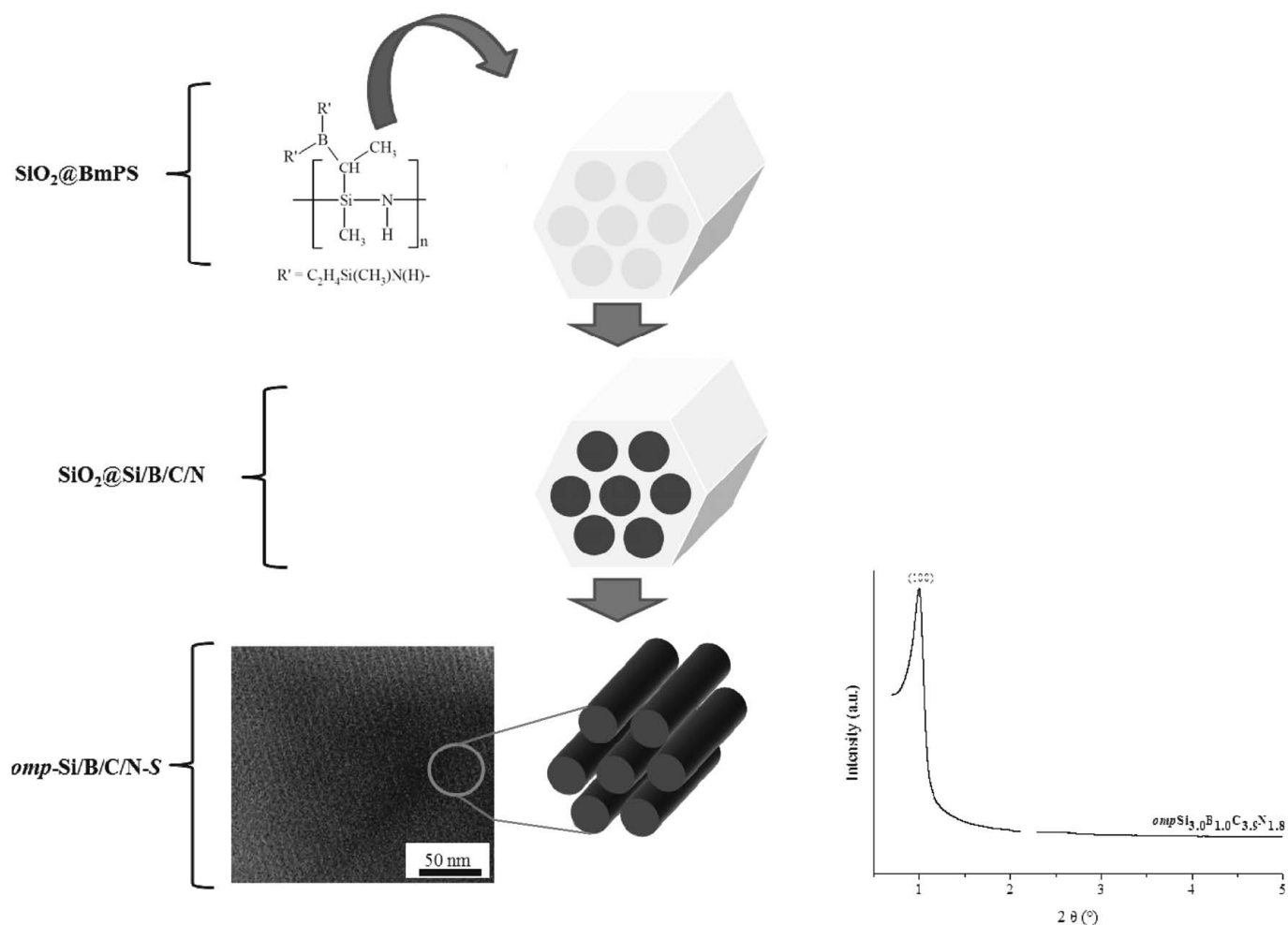

Fig. 6: Synthesis of *omp-Si/B/C/N-C1* and *omp-Si/B/C/N-C2* by negative replica of CMK-3.

Table 3: Textural properties of ordered mesoporous Si/B/C/N samples.

	d_{100} spacing (nm)	Cell parameter a (nm)	BET surface area ($m^2 \cdot g^{-1}$)	Pore diameter (nm)	Wall thickness (nm)	Pore volume ($cm^3 \cdot g^{-1}$)
omp-Si/B/C/N-*C1*	7.13	8.23	600	3.6	-	0.61
omp-Si/B/C/N-*C2*	6.9	7.94	636	4.6	3.34	0.93
omp-Si/B/C/N-*S*	8.8	10.2	337	4.6	5.6	0.55

Fig. 7: Nitrogen-adsorption isotherms of the **omp-Si/B/C/N-C1** (a) **omp-Si/B/C/N-C2** (b) and **omp-Si/B/C/N-S** (c) samples.

Fig. 8: Synthesis of **omp-Si/B/C/N-S** by negative replica of silica template.

When viewed down the [100] direction of the sample (Fig. 8), the HRTEM image shows one-dimensional channels that represent hexagonally ordered pores arranged in a linear array. The distance between the centers of the adjacent channels is approximately 5.6 nm.

The *omp-Si/B/C/N-S* sample exhibits a specific surface area of 337 m^2 g^{-1}, high pore volume (0.55 cm^3 g^{-1}) and a narrow pore size distribution centered on 4.6 nm by N$_2$ sorption with an amorphous network remaining stable during continuous heat treatment to 1480 °C in a nitrogen atmosphere.

IV. Conclusions and Outlook

In this review, first examples of ordered mesoporous silicon-boron-carbon-nitrogen (Si/B/C/N) frameworks prepared based on a nanocasting approach are reported. Samples displaying *p6mm* hexagonal symmetry were synthesized according to a solvent nanocasting route using mesoporous carbonaceous (CMK-3) and silica as hard templates and boron-modified polycarbosilazanes (BmPSs) of the type [B(C$_2$H$_4$SiCH$_3$NR)$_3$]$_n$ (R = H/CH$_3$; C$_2$H$_4$ = CHCH$_3$, CH$_2$CH$_2$) as preceramic polymers (=Si/B/C/N precursors).

The solution infiltration-ceramic conversion-template removal cycle performed under nitrogen at 1000 °C (2 h, ceramic conversion) then in an ammonia atmosphere at 1000 °C (5 h, carbonaceous template removal) or in diluted HF (silica template removal) resulted in the formation of periodic mesoporous Si/B/C/N frameworks with surface areas of 337 to 636 m^2·g^{-1}, a narrow pore size (3.6 – 4.6 nm) and pore volumes varying from 0.55 to 0.93 cm^3·g^{-1}. In this complex process, the principal issues include the selection of the polymers in terms of solubility and ceramic yield, the infiltration process and the template removal step. By means of characterization with electron microscopy, X-ray diffraction, and N$_2$ sorption, it was demonstrated that the amorphous micron-size powders exhibit excellent mesopore uniformity and periodicity. Our objective in this context is for scientists to obtain more information about the synthesis, properties and potential applications of this particular composition of ceramics. Indeed, such micron-sized ordered mesoporous Si/B/C/N powders with short, unhindered mesochannels and therefore favorable mass transfer should be beneficial for catalysis. Furthermore, as we already mentioned in our introduction, the presence of porosity in Si/B/C/N systems is expected to pave the way to use in hydrogen storage as porous media or even as a separation barrier for fluid separation in harsh environments.

However, structured micrometer-sized powders are associated with some difficulties in practical use. For practical applications, shaping of porous solids is an essential processing step and elaborating porous monoliths that are capable of bearing hierarchical porosity are the materials of choice to be used as catalyst supports. For instance, SPS of ordered mesoporous ceramic powders leading to hierarchically porous monoliths [57] or mixing preceramic polymers with sacrificial fillers or foaming agents then pressing the solid mixture into pellets to be pyrolyzed and transformed directly into components possessing also macroporosity [58] are key strategies to extend the range of appli-

cations for these materials. These opportunities are now being addressed. It is anticipated that this will lead to host of structural and functional applications for a new generation of materials.

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