Fabrication of high-surface area nanoporous SiOC ceramics using pre-ceramic polymer precursors and a sacrificial template: Precursor effects

Xiaojie Yan, Muhammad Sahimi, Theodore Tsotsis

*Mork Family Department of Chemical Engineering & Materials Science, University of Southern California,
Los Angeles, CA 90089-1211, USA*

Abstract: We report on the fabrication of silicon oxycarbide (SiOC) ceramics with high surface area, porosity and hierarchical pore structure, which are synthesized using pre-ceramic polymer precursors, such as hydridopolycarbosilane (HPCS), allyl-hydridopolycarbosilane (AHPCS) and their blends. Layered double hydroxides, modified by a common surfactant, namely, sodium dodecylbenzenesulfonate (SDBS), are used as the sacrificial templates, and a simple impregnation technique is employed, followed by pyrolysis and acid leaching. Characterization techniques, such as XRD, XPS, electron microscopy, elemental analysis, and nitrogen adsorption/desorption at its liquid temperature are used to verify that the SiOC materials have been successfully synthesized, and to study their chemical and structural characteristics. The emphasis is on the effects, which are shown to be significant, of the type of polymer precursor employed (AHPCS or HPCS), their weight ratio (in the case of blends), and the amount of polymer precursor used during the template impregnation. Depending on the polymer ratios and amounts utilized, SiOC particles with a variety of morphologies, ranging from plate-like to flower-like structures, have been prepared that have hierarchical structures and high surface areas, ranging from 531 m²/g to 1311 m²/g, and large pore volumes from 0.47 m³/g to 1.20 m³/g. The study provides guidance for the systematic design and fabrication of highly porous SiOC materials with potential for broad application in various fields, such as catalysis, sorption and membrane separations under harsh conditions, and biomedical device uses, among others.

Keywords: Silicon oxycarbide; Polymer precursor effect; Modified Layered double hydroxide template; Surface area; Pore structure

1. Introduction

Fabrication of inorganic nanoporous materials with high surface area and porosity that can withstand the harsh conditions that one encounters in the environments of practical applications has received considerable attention during the past decade or so. Among such inorganic nanoporous materials, silicon oxycarbide (SiOC) has garnered particular attention, due to its promising properties that include good chemical durability [1] and oxidation resistance [4], high-temperature stability [2], and thermal-mechanical durability [3]. SiOC materials exhibit good potential for broad applications in a number of fields, such as catalyst support and sorbents [5-6], lithium battery anodes [7-9], insulation materials and filters [10], gas sensors [11], light emitters [12], and drug delivery media [13], just to mention a few.

In recent years, the templating method has emerged as a simple but efficient technique to prepare SiOC materials with well-controlled pore structure characteristics. The technique involves selecting an appropriate pre-ceramic polymer precursor and porous template and infiltrating the precursor into the template's pore structure, followed by heat treatment to convert the polymer into the ceramic, and finally removing the template. For example, SiOC nanotubes with diameters between 250 and 350 nm were produced by pyrolyzing polycarbosilane (PCS) infiltrated into the cylindrical pores of an anodized aluminum oxide (AAO) template [14]. Three-dimensional (3D) diamond-like SiOC and silicon carbide high-temperature ceramic photonic crystals have been prepared by infiltrating allyl-hydridopolycarbosilane (AHPCS) into a patterned polyhedral oligomeric silsesquioxanes (POSS) template, followed by high-temperature ceramic conversion and hydrogen fluoride (HF) etching [15]. An ordered mesoporous SiOC monolith with a surface area of 616 m²/g has been synthesized by using liquid poly-(hydridomethylsiloxane) (PHMS) as the pre-ceramic polymer precursor, and mesoporous carbon CMK-3 as the template [16]. Porous SiOC ceramics with a surface area of up to 180.5 m²/g were obtained by using a polysiloxane preceramic polymer as a precursor and wood biomass as a template treated at a high temperature of 1400 °C [17].

We recently reported synthesizing high surface area silicon oxycarbide materials with a large pore volume and a hierarchical pore structure, using polymer blends of AHPCS and hydridopolycarbosilane (HPCS) [18]. We did this by simply infiltrating the polymer precursors into the interlayer space of a low-cost layered double hydroxide (LDH) template, followed by

pyrolysis to generate the ceramic and subsequent acid (HCl) leaching to remove the LDH template. To make the LDH interlayer space accessible to the pre-ceramic polymer precursor, it was modified prior to impregnation using a common surfactant, namely, sodium dodecylbenzenesulfonate (SDBS). The resulting SiOC materials had a high surface area of 812 m²/g and a pore volume of 0.8 cm³/g.

In this paper, we report the results of our continued investigations of the preparation of nanoporous SiOC materials via pre-ceramic polymer infiltration in the LDH templates, with emphasis on the impact of the preparation conditions that determine the structural characteristics of the final materials. In particular, our focus is on the effects of the type of polymer precursor employed (AHPCS or HPCS), their weight ratio (in the case of their blends), and the amount of polymer precursor per unit mass of template used during the impregnation step. The type and amount of the polymer precursor utilized is shown to critically determine the morphology of the SiOC particles produced. By choosing the appropriate precursor and the amount infiltrated into the LDH template, SiOC materials with high surface areas, larger than 1300 m²/g, and large pore volume of ~1.20 cm³/g have been prepared. Moreover, the fundamental insight generated by the study provides guidance for the systematic design and fabrication of highly porous SiOC materials with potential for broad applications in various fields.

2. Experimental

2.1 Materials fabrication

The AHPCS and HPCS (purchased from Starfire Systems, Inc.), SDBS (from Sigma-Aldrich Co.), tetrahydrofuran (from VWR International), and hydrochloric acid (37 wt.%, from VWR International) were all used without further purification. The MgAl-LDH powder was provided by the Sasol Corporation (Sasol Mg-70, with a Mg/Al ratio of 3.0). The fraction of the LDH powder with particles sizes smaller than 25 μm (prepared by separating from the original powder using a 500-mesh sieve) was modified by the SDBS according to the calcination/regeneration method that was described in our previous paper [18], the surfactant-modified LDH hereafter referred to as the SDBS-LDH.

To study the effect of the pre-ceramic precursor (type and amount) on the properties of the resulting ceramics, the SDBS-LDH material was impregnated with various AHPCS/HPCS/THF

solutions with differing concentrations. For that, 1 gr of the SDBS-LDH material was mixed (impregnated) with an AHPCS/HPCS/THF solution. Specifically, for the impregnation step the solution is added to the LDH template powder drop-wise with continuous stirring, until an initial wet appearance is observed. We define the amount of the solution added up to that point as the *incipient wetness volume* (IWV) corresponding to that mass of template. For volumes larger than the IWV, the impregnating solution occupies not only the interlayer LDH space, but also coats the particle surface and occupies the space in between the particles, as manifested by the fact that the impregnated powder acquires a progressively wetter appearance. This, of course, has implications for the final structure of the resulting ceramics, as will be discussed further below. For example, the pre-ceramic polymer solution in the intraparticle region may act as a “glue” holding the LDH particles together during the subsequent pyrolysis and template removal steps, which in the present work were identical to those described previously [18].

The resulting composite material was heated in a tubular furnace with a rate of 1 °C/min according to the following procedure: first, the material’s temperature was raised to 200 °C in an argon atmosphere, where it was held for 1 h. Then, the temperature was increased to 400 °C and was kept there for one more hour, and finally to 750 °C where it was held constant for two additional hours. The material was then cooled down to room temperature with a rate of 5 °C/min. To remove the LDH sacrificial template from the resulting composite, acid leaching was used by immersing the material into a HCl solution (18.5 wt.%) for two days. The resulting black powder was washed several times with de-ionized water, and then dried in air for two days.

Four of the samples were prepared with the AHPCS/HPCS/THF pre-ceramic solutions with weight ratio compositions of 1:2:2, 2:1:2, 3:0:2 (pure AHPCS in the THF solvent) or 0:3:2 (pure HPCS in the THF) by employing the IWV of the impregnating solution of ~ 0.2 ml solution/g of the template. In order to investigate the impact of using “excess” solution during impregnation, two additional SiOC materials were prepared with the AHPCS/HPCS/THF solutions with weight ratios of 1:2:2 or 2:1:2, employing 0.35 ml solution/g of template, for which the properties of the materials were discussed before [18].

2.2 Characterization

When studying the impact of the choice of pre-ceramic precursor on the properties of the resulting ceramics, one key consideration is the ease by which the polymer accesses the internal

pore structure of the template. A potential indicator of that is the radius of gyration of the polymer precursors, which in this study was measured by the dynamic light scattering (DLS) technique, utilizing a DynaPro Titan instrument (U.S.A). The resulting ceramics were characterized by X-ray diffraction (XRD) analysis using a Rigaku X-ray diffractometer (Japan), with the CuK α line as the X-ray source and a monochromator positioned in front of the detector. Scanning was performed over a 2θ angle ranging from 10° to 90° with a scanning rate of $4^\circ/\text{min}$ and step rise of 0.05. X-ray photoelectron spectroscopy (XPS) measurements were also carried out with the samples, performed using a Thermo ESCALAB 250 spectrometer (U.S.A). A monochromatic AlK α radiation source ($h\nu = 1486.6 \text{ eV}$) was used with a spot size of $400 \mu\text{m}$. Pass energies of 100 eV for the survey scan and 20 eV for the high-resolution scan were used with the analyzer. Low-resolution survey scans were also acquired at binding energies between 1 eV and 1400 eV with a resolution of 1 eV. The high-resolution scans of the C-1s and Si-2p regions were acquired with a resolution of 0.05 eV. The data analysis was carried out using the XPSPEAK software, version 4.1. For calibration purposes, the binding energy (B.E.) of carbon in the C 1s spectra was taken as 284.6 eV to compensate for charging effects. The resulting SiOC ceramic samples were also examined by scanning electron microscopy (SEM) employing a JEOL JSM 7001 instrument (U.S.A) at room temperature, and a 15 kV acceleration voltage. Nitrogen adsorption-desorption isotherms of the porous ceramic samples were also measured with a Micromeritics ASAP 2010 adsorption analyzer (U.S.A) at -196°C (77 K). Prior to the measurement, the porous SiOC material was degassed overnight at 110°C . (We have found that the degassing of these materials overnight at 110°C is an effective technique for generating reproducible adsorption/desorption data without risking substantial impact on the structure of the materials themselves). The Brunauer–Emmett–Teller (BET) [19] method was utilized to calculate the surface area. The mesopore evaluations were based on the desorption branch of the isotherms using the traditional Barrett-Joyner-Halenda (BJH) method [20], while the original Horvath-Kawazoe (HK) [21] method for slit-like pores is used in the determination of micropore region.

3. Results and discussion

The original LDH template has a confined interlayer space with lamellar distance of < 0.8 nm [18]. Modifying its structure with the SDBS, employing the aforementioned calcination/regeneration method, significantly expands its interlayer distance to ~ 3 nm, as determined by XRD analysis [18]. Such an expanded interlayer region may, potentially, still not be sufficiently large (absent further restructuring during the preparation procedure), however, to readily accommodate some of the pre-ceramic precursor molecules used in our studies. We, therefore, evaluated the radius of gyration of the various polymer solutions utilized via the DLS technique as a potential indicator of the ability of the pre-ceramic precursor molecules to access the internal interlayer space. For that, we measured the radius of gyration of pure HPCS (in THF), pure AHPCS (in THF), and one of their mixtures. Table 1 shows the measured radius of gyration values, which for the pure AHPCS/THF=1:1 solution, for example, is 6.4 nm, which is more than twice as large as the interlayer distance of the SDBS-LDH. Thus, at least in theory, most of the AHPCS precursor molecules in the solution should remain outside the template's layered structure, likely attaching themselves to the external surface of the microcrystallites comprising the particles of the SDBS-LDH template (It should be noted, however, that the radius of gyration of a polymer in solution, as measured by the DLS technique, offers only a very "rough" indicator of the size of the polymer, particularly as it relates to its ability to enter a pore space. Polymers are known, for example, to "align" differently within a constricted pore space than they do in solution).

The radius of gyration of the pure HPCS/THF=1:1 solution is 1.5 nm, which is half the size of the interlayer distance of the SDBS-LDH, hence indicating that the polymer in this solution will likely penetrate readily into the template's pore space. The HPCS is a small molecular weight (MW) polymer (with a MW in the range 132 – 352 Da [18]) and is fairly volatile. For example, when we subjected the HPCS/THF solution to the same heating protocol as that applied in this paper to produce the SiOC ceramics, the solution completely volatilized and the HPCS completely disappeared. When the same heating protocol was applied to the HPCS-impregnated SDBS-LDH template, however, a SiOC material was obtained, as further detailed below, indicative of the fact that the HPCS is held quite tightly inside the LDH pore structure, and that

pyrolysis and the onset of the “polymer-to-ceramic” transition processes begin prior to (and likely hinder) volatilization.

As one may have expected, the radius of gyration for the AHPCS/HPCS blends in THF falls somewhere in between those for the pure HPCS and AHPCS solutions. For example, the radius of gyration for an AHPCS/HPCS/THF=1:2:2 solution, also listed in Table 1, is 2.3 nm. Thus, it should be clear why the type of the precursor used and its volume to the template mass ratio should have such an impact on the properties and structural characteristics of the resulting ceramics: they are both important in determining the positioning of the precursor molecules relative to the pore structure of the template, which in turn determines the type (and number) of pores that are formed during pyrolysis and the subsequent acid-leaching step.

Figure 1 shows the XRD patterns of the six different silicon oxycarbide materials that we prepared. The materials fabricated using pre-ceramic precursor solutions with different compositions (and/or solution amounts per mass of template) are all fairly amorphous, characterized by relatively broad peaks. The peak in the range (21° - 24°) has been previously reported to be due to the silica glassy network present in the SiOC materials [16], while the weak peak between (40° - 50°) is most likely due to free, graphitic-like carbon being present in the SiOC materials [16], an observation which is also consistent with the elemental analysis of these materials, see discussion below.

The results of the XPS-elemental analysis of the various ceramic samples are shown in Table 2. Combined with the XRD data, they indicate that all samples contain Si, O, and C, as one would expect from the analysis of a silicon oxycarbide material. Their relative abundance, however, is not completely in line with the typical fractional composition $[\text{SiO}_{4-x}\text{C}_x]$ of silicon oxycarbide, indicating a “surplus” of C (It should be noted, however, that XPS probes mostly the materials’ near surface region, and the presence of irreversibly adsorbed CO_2 cannot be completely excluded. Thus, this may lead to the overestimation of the carbon amount on the surface).

High-resolution C 1s and Si 2p XPS analysis results for all the six samples further confirm the successful fabrication of SiOC materials. High-resolution C 1s XPS results of samples prepared employing the IWV of the impregnating solution (~ 0.2 ml solution/g of template) are presented in Figures 2(a) (b) (c) and (d), while the corresponding Si 2p XPS results of the same samples are shown in Figures 3(a) (b) (c) and (d). Results of the two remaining samples prepared using an

“excess volume” of pre-ceramic polymer solution (~ 0.35 ml solution/g of template) have been previously presented in our recent paper [18] (see Figures 5(a) (b) and 6(a) (b) in that paper). High resolution C1s spectra all reveal typical peaks of carbide carbon ($\text{Si}_x\text{C}_y\text{O}_z$ or SiC) centered at 283.4 eV [22], elemental carbon (C) centered at 284.6 eV, and adsorbed carbon (CO_2) centered at around 286.9 eV [16, 23]. The dominance of the $\text{Si}_x\text{C}_y\text{O}_z$ species is further revealed from the high-resolution Si 2p XPS spectra – see further discussion below. The sample fabricated from pure HPCS exhibits, in addition, a peak at ~ 281.0 eV, which can be clearly attributed to carbide carbon from pure silicon carbide [24], due to an environment of pure Si-C without much O existence. The high resolution Si 2p spectrums for all the samples indicate the presence of silicon oxycarbide materials. Peaks between 100.3 eV and 102.5 eV are attributed to the existence of $[\text{SiOC}_3]$, $[\text{SiO}_2\text{C}_2]$ and $[\text{SiO}_3\text{C}]$ species. The presence of $[\text{SiO}_4]$ is revealed from the peaks centered between 102.5 eV to 103.5 eV [23, 25]. This could possibly be due to the existence of excess O within the template interspace structure. Moreover, the Si 2p spectra of the sample prepared from pure HPCS contains a strong peak centered at 99.5 eV, which is due to $[\text{SiC}_4]$ [25]. The HPCS is a SiC precursor that requires a relatively low temperature (600°C) for transformation into the ceramic, compared to the AHPCS that typically requires temperatures $\sim 850^\circ\text{C}$ to convert into SiC. It comes as no surprise, therefore, that a good fraction of the HPCS converts into SiC during heating at 750°C .

The morphology of the ceramic materials was investigated by the SEM, with images at various magnifications shown in Figures S1 – S3 of the Supplementary Section. All the samples are comprised of particles with particle sizes between 5 to $30\ \mu\text{m}$, other than the sample prepared from the AHPCS/HPCS/THF=2:1:2 solution, employing the IWV of the impregnating solution, for which (for reasons that are still not entirely clear) the particles are substantially larger. The particle sizes of the resulting SiOC ceramics are pretty much in line (with the notable exception of the aforementioned 2:1;2, 0.2 ml/g sample) with the particle sizes of the original LDH particles, indicating that the pre-ceramic polymer precursor acts potentially as the “glue” that holds together the microcrystals comprising the original LDH particles, with the resulting SiOC particles retaining the size of the original LDH particles, and in the case of the 2:1:2, 0.2 ml/g sample even resulting in particle aggregation and enlargement. Despite the fact that at low resolution the SiOC particles retain the size/shape of the original LDH template particles, at higher resolution one observes substantial macroporosity or even larger pores, particularly for

the materials prepared via the use of excess impregnating solution for which a substantial fraction of the pre-ceramic polymer precursor ends-up in the intracrystallite space.

N₂ sorption measurements were also conducted on the “pristine” (i.e., without having undergone pyrolysis first) SDBS-LDH template, samples resulting from the pre-ceramic polymer precursor solutions themselves after pyrolysis (i.e., without any template being present), and samples prepared from the polymer precursors utilizing the SDBS-LDH template after pyrolysis and acid leaching, in order to elucidate the effect of the polymer precursor (i.e., its composition and volume relevant to the mass of template) on the surface area, pore volume, and pore structure of the resulting materials, and the results are shown in Table 3.

The SDBS-LDH template, itself, has a very low surface area, less than 1 m²/g. (It should be noted here that conditioning the template sample for the BET analysis by vacuuming it overnight at 110 °C may have impacted its structure [26]; however, any changes that may have taken place are unlikely to account for the substantial differences between the template surface areas and those of the pyrolyzed samples). However, its presence is key to preparing SiOC materials with high surface areas and pore volumes. The template plays a number of important roles: For example, by acting as a host to the pre-ceramic polymer precursor, constraining its motion during heating-up and pyrolysis and, thus, preventing its volatilization. It was noted previously, for example, that without the template being present, the HPCS alone completely volatilizes and does not produce any ceramic material. On the other hand, after being impregnated inside the SDBS-LDH template, it produces a SiOC ceramic with a surface area of 1087 m²/g and a pore volume of 0.94 cm³/g. Further, the template appears to prevent the microporosity/mesoporosity that is generated during polymer precursor pyrolysis from being removed as the temperature of pyrolysis is increased. As Table 3 indicates, for example, pyrolysis of AHPCS/HPCS pre-ceramic precursor mixtures without the template being present produces only “dense” materials (though from BET analysis alone one cannot completely preclude the existence of dead-end pores in such materials). By confining the pre-ceramic polymer precursor in its interlayer region, on the other hand, the LDH template contributes to the formation of significant microporosity (as manifested by the large portion of micropore volume present in all samples) from the evolving gases from the processes that take place during the polymer-to-ceramic transition.

It is clear from Table 3 that pyrolysis in the presence of the template results in materials, after acid leaching, that have very high surface areas ranging from 531 m²/g to 1311 m²/g. The SDBS-

LDH template contributes in various ways, as noted above, in creating the hierarchical pore structure of the resulting materials. For example, via the removal of the individual sheets of its interlayer structure during the acid-leaching step, when the precursor is confined in that region, or via the removal of whole (or parts thereof) LDH micro-crystallites when the precursor is unable to completely penetrate into their pore structure. XRD and EDX analysis, presented in [18,23], for example, find no evidence that any template is left behind (within the precision, of course, of such measurements), which is not that surprising given the harsh conditions for leaching these materials (a 2-day immersion in 18.5 wt.% HCl solution). High-resolution SEM analysis presented in [18] and companion high-resolution TEM analysis presented in [23] clearly indicate the mesopore space where the template was located prior to its dissolution by HCl.

Though the role the template plays during the formation of the SiOC materials is understood in broad terms, the phenomena that take place, however, during the preparation of such materials are, in fact, significantly more complex, as evidenced by the differences in the surface area and pore volume among the various materials prepared under different conditions. For example, the material prepared from the AHPCS/HPCS/THF=1:2:2 solution when using the IWV of the impregnating solution has a surface area of 1230 m²/g and a total pore volume of 1.08 cm³/g. On the other hand, the material prepared using an excess amount of the same impregnating solution (0.35 ml/g) has a surface area of 531 m²/g and total pore volume of 0.47 cm³/g, which are less than half of that of the material prepared with the lesser amount of precursor. As discussed earlier, when using the IWV of the impregnation solution, a large fraction of the precursor finds its way inside the template's interlayer region. In contrast, when utilizing an excess amount of the impregnating solution, a significant fraction of the polymer precursor ends-up coating the outside surface of the microparticles or fills the intraparticle region. It appears that a “free-standing” polymer precursor blend with such composition contributes little to the microporosity of the final ceramic (in line with the observation that only dense ceramics are produced from these pre-ceramic polymers in the absence of a template). And, apparently, its presence makes it more difficult for the ceramic resulting from the polymer precursor to be confined within the LDH template and to preserve its own microporosity (e.g., by providing a continuous pathway for the polymer to transport from the interlayer region to the outside).

The material prepared from using the same excess amount (0.35 ml of solution/g of template) of the AHPCS/HPCS/THF = 2:1:2 impregnating solution has a higher surface area, 812 m²/g and

pore volume, $0.80 \text{ cm}^3/\text{g}$, than the ceramic prepared by the AHPCS/HPCS/THF = 1:2:2 impregnating solution. This means that the polymer residing outside the LDH interlayer region, has less of a negative impact on the final microporosity of the resulting ceramic in the case of the more viscous, higher MW 2:1:2 blend than in the case of its less viscous, lower MW counterpart. In fact, the material prepared with this polymer blend using the excess amount has only slightly less surface area ($812 \text{ m}^2/\text{g}$ vs. $876.3 \text{ m}^2/\text{g}$) and pore volume of ($0.80 \text{ cm}^3/\text{g}$ vs. $0.82 \text{ cm}^3/\text{g}$) than the material prepared using the IWV of the same polymer precursor blend.

What complicates the interpretation of the various experimental observations is the fact that the LDH template, itself, is known to undergo substantial structural transformations during the heating protocol that leads to the formation of the ceramics [26]. For example, absent such transformations, and based on its measured radius of gyration alone, the pure AHPCS should not be accessing the interlayer region. However, the ceramics produced using the AHPCS/HPCS/THF=3:0:2 impregnating solution have ultra-high surface area of $1311 \text{ m}^2/\text{g}$ and total pore volume of $1.20 \text{ m}^3/\text{g}$ with a substantial fraction of mesoporosity. It is likely that the transformations that occur during the heating step act synergistically with the pre-ceramic polymer to generate a ceramic with substantially superior properties. Additional evidence for the important (and complex) role that the template plays in the preparation of these ceramics is provided by the material that is prepared using the pure HPCS/THF solution, which also has a very high surface area of $1087 \text{ m}^2/\text{g}$ and a total pore volume of $0.94 \text{ m}^3/\text{g}$. As noted previously, in the absence of the template, the HPCS precursor would completely volatilize during the heating step, generating no ceramic. In fact, the HPCS is a well-known precursor of SiC, but only via a chemical vapor deposition route. This, then, showcases the importance of the LDH template that helps to confine the HPCS in its interlayer region, preventing its volatilization, and making it possible to produce a ceramic via the significantly simpler pre-ceramic polymer pyrolysis route.

Figure 4 reports the sorption isotherms for all the 6 samples prepared with the use of the SDBS-LDH template. A steep increase between relative pressures of 0.0 to 0.4 indicates the existence of micropores. The pore size distribution (PSD) in the micropore region as calculated using the conventional (slit-pore) HK method is shown in Figure 5, indicating pores in the range 0.5-0.6 nm. Hysteresis loops in the adsorption isotherms between relative pressures of 0.4 to 0.8 are indicative of the presence of mesoporous structures [27], with PSD calculated by the BJH

method shown again in Figure 5. The significant fraction of mesoporosity, see also Table 3, is mainly due to the contributions of the LDH template after it has been removed via acid leaching, while microporosity is due to pre-ceramic polymer pyrolysis and its transformation into a SiOC ceramic while it is being confined within the template structure.

4. Conclusions

Silicon oxycarbide materials with ultra-high surface area have been fabricated using a convenient route by impregnating pre-ceramic polymer precursors into the interlayer space of a surfactant-modified LDH template, followed by pyrolysis and subsequent template removal via acid leaching. The key emphasis in this study was on investigating the effect on the structural properties of the resulting ceramics of the polymer precursor type (AHPCS or HPCS, or their blends), and the amount of precursor utilized.

The results of elemental analysis combined with XRD and XPS characterizations indicate that all the materials produced are silicon oxycarbide with potentially silica and free carbon co-existing, except for the ceramic prepared from the pure HPCS precursor, which contains a significant amount of silicon carbide as well, which is attributed to the relatively low ceramic forming temperature for this particular precursor. The amount of the precursor utilized has a substantial impact on the properties of the resulting materials. Using only the so-called “incipient wetness volume”, which in this research is determined to be ~0.20 ml/g template, means that, for the most part, the precursor is confined within the interlayer region of the template. Using additional amounts of precursor, beyond the IWV, then implies that increased amounts of precursor will likely end-up outside the interlayer region, for example, located in the intracrystalline space of the LDH particles, or even on the external surface of the particles themselves. What this implies for the properties of the resulting ceramics depends on the type of pre-ceramic precursor solution used, as the influence of the template, which is strong when the precursor is located entirely in its interlayer region - witness the ability to produce ceramics from the pure HPCS - “waned”. A key finding of this study is that, by the appropriate choice of the template, precursor type, and preparation conditions (e.g., the ratio of precursor volume to template mass), one can prepare materials with super-high surface areas ranging from 531 m²/g

to 1311 m²/g, and large pore volumes from 0.47 m³/g to 1.20 m³/g. Ceramic materials' fabrication aiming at materials with different surface area, pore porosities and structures can then be tuned by applying this route.

Acknowledgements

The National Science Foundation is gratefully acknowledged for financial support. We thank Dr. Patrick Haller of for the DLS analysis and Dr. Howard Shen from Starfire Systems for helpful discussions concerning the pre-ceramic polymer precursors. We are also grateful to Professor Xinhai Yu of the East China University of Science and Technology for his help in the characterization of the materials, as well as many useful discussions.

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Table Captions:

Table 1: Radius of gyration of the pre-ceramic polymer precursors, obtained by the DLS analysis.

Table 2: The XPS elemental composition of the $\text{Si}_x\text{C}_y\text{O}_z$ samples, prepared by impregnation. Also shown is the excess carbon.

Table 3: The pore structure characteristics of the resulting ceramics. The doublet (x, y) indicates the weight ratio between AHPCS and HPCS, and the amount of polymer solution used in ml/g is also indicated. The first sample is pristine, un-pyrolyzed SDBS-LDH with no polymer precursor infiltrated. The second, third and fourth samples were prepared from various polymer blends, as indicated, after pyrolysis without using the SDBS-LDH template. All other samples were fabricated using polymer precursors and SDBS-LDH as the template, with BET analysis performed after template removal via acid leaching.

Table 1:

Polymer solution (weight ratio)	Radius of gyration
AHPCS/THF=1:1	6.4 nm
HPCS/THF=1:1	1.5 nm
AHPCS/HPCS/THF=1:2:2	2.3 nm

Table 2:

Samples	Atomic ratio			Composition
	Si	O	C	
(1:2:2, 0.35 ml/g)	1	2.2	2.8	$\text{SiO}_{2.2}\text{C}_{1.8}+\text{C}_{1.0}$
(1:2:2, 0.20 ml/g)	1	1.7	2.4	$\text{SiO}_{1.7}\text{C}_{2.3}+\text{C}_{0.1}$
(2:1:2, 0.35 ml/g)	1	1.8	3.1	$\text{SiO}_{1.8}\text{C}_{2.2}+\text{C}_{0.9}$
(2:1:2, 0.20 ml/g)	1	1.7	2.9	$\text{SiO}_{1.7}\text{C}_{2.3}+\text{C}_{0.6}$
(3:0:2, 0.20 ml/g)	1	1.7	2.3	$\text{SiO}_{1.7}\text{C}_{2.3}$
(0:3:2, 0.20 ml/g)	1	2.1	2.3	$\text{SiO}_{2.1}\text{C}_{1.9}+\text{C}_{0.4}$

Table 3:

Sample	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{meso} (cm^3/g)
SDBS-LDH	<1	<0.01	<0.01
(1:2:2, N/A)	0	0	0
(2:1:2, N/A)	<1	0	0
(3:0:2, N/A)	0	0	0
(1:2:2, 0.35 ml/g)	531	0.47	0.25
(1:2:2, 0.20 ml/g)	1230	1.08	0.57
(2:1:2, 0.35 ml/g)	812	0.80	0.46
(2:1:2, 0.20 ml/g)	876	0.82	0.46
(3:0:2, 0.20 ml/g)	1311	1.20	0.65
(0:3:2, 0.20 ml/g)	1087	0.94	0.54

Figure Captions:

Figure 1: The XRD patterns of the samples prepared under various conditions.

Figure 2: The XPS high resolution C 1s spectra of the samples: (a) is for the (1:2:2, 0.20 ml/g) sample, (b) is for the (2:1:2, 0.20 ml/g) sample, (c) is for the (3:0:2, 0.20 ml/g) sample, while (d) is for the (0:3:2, 0.20 ml/g) sample, respectively.

Figure 3: The XPS high resolution Si 2p spectra of the samples: (a) is for the (1:2:2, 0.20 ml/g) sample, (b) is for the (2:1:2, 0.20 ml/g) sample, (c) is for the (3:0:2, 0.20 ml/g) sample, while (d) is for the (0:3:2, 0.20 ml/g) sample, respectively.

Figure 4: Nitrogen sorption isotherms of the ceramic samples.

Figure 5: The HK pore size distributions and BJH pore size distributions of the ceramic samples.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

AHPCS:HPCS:THF + Modified LDH

Pyrolysis
+
Acid leaching