A silica cellular structure was synthesized as a novel means of enhancing the geometrical surface area of a silicon microchannel with cell diameter of ~10 \( \mu \text{m}\) and cell interconnectivity of ~0.4. Surface-selective infiltration, assembly, and partial sintering of polystyrene microspheres in the microchannel were used as mechanisms to create a sacrificial template. The polymer template was infiltrated with a silica precursor, and the infiltrated structure was dried and calcined at 500 \( ^\circ \text{C}\) to remove the polymer phase and subsequently sintered at 1100 \( ^\circ \text{C}\) to form dense silica skeleton. Volume shrinkage and crack formation during calcining and sintering of the infiltrated silica structure were strongly influenced by silica particle size in the precursor. In comparison with free-standing cellular specimens prepared by similar template methods, the shrinkage and cracking issues offered an interesting challenge for synthesizing the cellular structure which could be net-shaped into the spatial confinement of the microchannel geometry.

1. Introduction

Currently cellular ceramic and metallic materials are manufactured using polyurethane foams as sacrificial templates with typical cell sizes larger than 100 \( \mu \text{m}\). Recently, the use of polymer microsphere assembly as an inverted template has been explored as a versatile approach for synthesizing macroporous ceramic materials at laboratory scales.1–4 For example, Yang et al. demonstrated the synthesis of macroporous silicas with highly ordered pore sizes of 0.65 and 0.92 \( \mu \text{m}\) within a microchannel space. Sung et al. synthesized cellular SiC and SiCN structures in the cell diameter range of 1–5 \( \mu \text{m}\) for use as catalyst support structures in high-temperature fuel reforming reactions. The microsphere template-based synthesis approach offers two advantages: (1) desired cell size selection and control in the range of 100 \( \text{nm}\) to a few millimeters and (2) potential for near net-shape synthesis capability within the confined space of a microchannel, as a novel means of incorporating catalyst particles into microreactors for chemical process intensification and miniaturization applications.5–14

Despite significant advances in the fabrication techniques used for microreactor applications, catalyst integration into the confined space of microreactors remains an open issue. In the most straightforward approach, catalyst particles with size in the range of 10–100 \( \mu \text{m}\) can be directly packed into a microreactor to form a packed bed assembly of the particles. In this arrangement, filters are usually needed to hold the particles in place.11,15 The packed bed configuration can result in large pressure drop, and also increases risk of clogging caused by particle aggregation, breakage, and attrition during microreactor operation. Alternatively, catalyst particles can be deposited as a coating on the wall of a microreactor by washcoat or sol–gel methods.10,16,17 The catalyst coating approach results in lower pressure drop and improves mechanical stability in comparison with the packed bed approach, but at the expense of less catalyst loading per microreactor volume basis.

Our motivation behind this investigation was to use an interconnected open cellular structure which: (1) fills the fluidic path of a microreactor and (2) is infiltrated and coated with a layer of catalyst particles. For this application, a cellular structure can be basically viewed as an inverse packed bed structure with the same geometrical surface area. With a higher void fraction of the cellular structure, the pressure drop is greatly reduced.18 Furthermore, tortuous fluid pathways within the cellular structure enhance the degree of micromixing.18,19 As described elsewhere,20,21 we recently demonstrated that cellular structures can be readily and uniformly infiltrated and immobilized with a layer of ~1 \( \mu \text{m}\) catalyst particles by a layer-by-layer self-assembly method.

For an ideal cellular structure in which uniform spherical cells are arranged in a hexagonal close packed pattern, cell radius \((R_c)\), window radius \((R_w)\), and skeleton density \((\rho_s)\) are key structural parameters which define the structure’s pressure drop, micromixing, and mechanical properties. In considering the requirements anticipated for our microreactor applications,22 we initially selected the following synthesis targets: (1) a cell diameter on the order of 10 \( \mu \text{m}\) and (2) a cell interconnectivity \((R_w/R_c)\) of about 0.4. These structural parameters represented: (1) a geometrical surface area enhancement factor of 16 in reference to an unfilled 100 \( \mu \text{m}\times 500 \mu \text{m}\) microchannel22 and (2) a pressure drop of 340 Pa along the 6 cm length of the microchannel as estimated using the Ergun equation.15,23,24 The objective of this investigation was to develop a synthesis method with built-in mechanisms to tailor the cellular structure with particular focus on ascertaining: (1) the effects of particle size in the silica precursor sol on volume shrinkage and crack formation of the cellular structure during calcining and sintering steps and (2) the effects of the geometrical confinement of the cellular structure by the microchannel wall on the morphological evolution and stability of the cellular structure. Silica was selected as a model material for the scaffold phase synthesis via sol–gel.

II. Experimental Procedure

The microreactor used in this study had a microchannel of 100 \( \mu \text{m}\) (width) \times 500 \( \mu \text{m}\) (depth) \times 10 cm (length). The microchannel was created by deep reactive ion etching (DRIE) on a 700 \( \mu \text{m}\) thick silicon wafer as shown in Fig. 1. Carboxyl modified polystyrene microspheres (Interfacial Dynamic Corporation, Portland, OR) with a mean diameter of 16 \( \mu \text{m}\) and with a coefficient of variation in the diameter of 10.8% were used to prepare a polymer microsphere template. The microspheres were suspended in water at a concentration of 0.039 g/mL. As illustrated in Fig. 1, polystyrene microspheres were infiltrated into the microchannel of the microreactor using a surface-selective infiltration method16 in which the top surface of the microreactor was made hydrophobic while the inner surface of the microchannel remained hydrophilic. Two small pieces of nylon filter paper with 0.2 \( \mu \text{m}\) pores were placed at the end sections of the
In order to study the effect of the silica precursor, four different colloidal precursor sols were prepared from (1) tetraethylorthosilicate (TEOS), (2) Ludox™ AS-30 silica colloid, (3) Aerosil™ OX 50 fused silica particles, and (4) 500 nm silica particles, respectively. Particle size distribution of these precursors was characterized by dynamic light scattering (DLS) using a Zetasizer Nano ZS system (Malvern Instruments, Malvern). The DLS results and other key characteristics of the silica precursors are summarized in Table I.

The TEOS precursor was a polymeric sol and the other three precursors were particulate sols. The TEOS precursor was prepared as follows: (1) 5 mL TEOS (Aldrich, Milwaukee, WI) was dissolved in 25 mL ethanol under stirring at room temperature; (2) 3 mL water and 0.85 mL HCl were added to catalyze the hydrolysis of TEOS; (3) the mixture was stirred for 30 min to 1 h before the use of the precursor for the infiltration experiments. The Ludox™ precursor was prepared from Ludox™ silica colloid AS-30 (Grace Davison, Columbia, MD), which was a 30 wt% dispersion of 1.9 nm dense silica particles in water with ammonium counter ions. The as-received colloid was diluted to 16 wt% to lower the viscosity from 0.014 to 0.002 Pa·s for the ease of infiltration into the polymer template. The Aerosil™ precursor was prepared by dispersing Aerosil™ OX 50 (Degussa, Parsippany, NJ) fused silica particles of 43 nm in de-ionized water and adjusted the pH value to about 9–10 with ammonia. The concentration of the Aerosil™ precursor was 16 wt%. Suspension of 500 nm silica particles in water at 2 wt% was purchased from Duke Scientific Corporation (Palo Alto, CA), and was used as received.

Calcination and sintering of the infiltrated structure were carried out in a Microtherm™ tube furnace (Mellen Company, Concord, NH), which was exposed to air. Typically, for calcination, temperature was increased to 500°C at a rate of 10°C/min. and was held for 6 h. For sintering, the temperature was further increased to 1100°C at a rate of 10°C/min. and was held for 10 h.

In order to evaluate the effects of geometrical confinement, two other synthesis procedures were developed as schematically illustrated in Fig. 2. In the first approach, a sacrificial polymer interlayer was deposited on the internal surface of the microchannel to weaken the bonding between the cellular structure and the microchannel wall. The interlayer was prepared by depositing a layer of 1 μm polystyrene microspheres followed by sintering to make the polystyrene layer continuous. The polystyrene-coated microchannel was then used as the substrate to detach the cellular structure during the follow-on calcination step. In the second approach, 16 μm microspheres were packed within a Gastight™ syringe (Hamilton Company, part # 7656-01, Reno, NV) with an internal diameter of 723 μm, and removed from the syringe as a free-standing polystyrene microsphere assembly. This microsphere assembly was sintered at 100°C and then infiltrated with a silica precursor, calcined, and sintered.

Table I. Characteristics of the Silica Precursors

| Precursor | Type of sol | \(D_{a v g}^{A}\) (nm) | CV%\(^A\) | Solid content (g·silica/mL) | Viscosity (Pa·s) |
|-----------|-------------|---------------------|------|---------------------------|----------------|---|
| TEOS      | Polymeric   | 2.6                 | 23   | 0.105                     | 0.002           |   |
| Ludox\(^h\) | Particulate | 1.9                 | 20   | 0.175                     | 0.002           |   |
| Aerosil\(^h\) | Particulate | 43                  | 66   | 0.175                     | 0.003           |   |
| 500 nm    | Particulate | 525                 | 28   | 0.020                     | N/A\(^A\)       |   |

\(^A\)Hydrodynamic diameter measured by dynamic light scattering. \(^h\)Coefficient of variation in diameter. \(^A\)Not measured, but expected to be the same as the viscosity of pure water. TEOS, tetraethylorthosilicate.

Fig. 2. (A) Synthesis procedure with the polystyrene sacrificial interlayer to prepare the cellular structure detached from the microchannel wall and (B) synthesis procedure used to prepare free-standing cellular samples. Note that the illustrations are not drawn to scale.
Cellular specimens were carefully prepared for characterization using a field emission scanning electron microscope (LEO Electron Microscopy Inc, Thornwood, NY). For the cellular structures synthesized within the microchannel, the silicon chip that contained the microchannel was directly attached to the scanning electron microscopy (SEM) specimen stage using a piece of carbon tape on the back. In this manner, any further cracking of the cellular structures during handling and characterization could be avoided. The free-standing cellular structures were carefully placed onto a piece of carbon tape which was already attached to the specimen stage, and a nitrogen jet was used to apply a gentle pressure to ensure good adhesion between the cellular sample and the tape surface. Cell size and window size were directly measured from SEM images. Specific surface area and micropore and mesopore measurements of the silica phase were carried out by nitrogen physisorption at 77 K using an Autosorb™ 1-C system (Quantachrome Instruments, Boynton Beach, FL). Samples used for the physisorption measurements were prepared by crushing the cellular structures to small particles and degassed at 300°C overnight.

Fig. 3. Calcined cellular silica specimens prepared from: (A) and (E) tetraethylorthosilicate, (B) and (F) Ludox™, (C) and (G) Aerosil™, and (D) and (H) 500 nm particle precursors after 6 hours at 500°C.
III. Results and Discussion

Cellular silica samples synthesized from the four silica precursors within the silicon microchannel after calcination at 500°C are compared in Fig. 3. Note that, for each precursor, at least three samples were prepared and we carefully selected the images shown in Fig. 3 as representative images of the samples. From the SEM images in Fig. 3, cell size was typically observed to be in the range of 12–14 μm. Cell interconnectivity was measured to be in the range of 0.3–0.4. Shrinkage of the cellular structure synthesized from the TEOS precursor, which will be referred to as the “TEOS sample,” was significant as evident from large cracks within the cellular structure and gaps appearing between the structure and the microchannel wall (Figs. 3(A) and (E)). In comparison, the “Ludox” sample” shrank less, but with the appearance of fine microcracks in the skeleton phase of the structure (Figs. 3(B) and (F)). The “Aerosil” sample” (Figs. 3(C) and (G)) and the “500 nm particle sample” (Figs. 3(D) and (H)) did not shrink noticeably in contrast to the TEOS and Ludox samples.

N$_2$ physisorption isotherms of the calcined silica phase of the TEOS and Ludox samples are shown in Fig. 4. The isotherm of the TEOS-derived silica phase was of Type-I, which is typically observed for microporous (i.e., pore diameter <2 nm) materials. On the other hand, the isotherm of the Ludox sample appeared to be a Type-II isotherm. Note that Type II is typically observed for mesoporous (i.e., pore diameter of 2-50 nm) materials. Micropores were present in both the samples, as evident from the V–t plot of these samples (Fig. 5). The average pore diameter in the silica phase gel from the TEOS precursor and the Ludox precursor was estimated to be ~1.1 and ~2.6 nm, respectively, based on calculations using a density function theory (DFT) method integrated with the Autosorb-1 software. Based on SEM observations, the average pore diameter in the calcined Aerosil precursor and the 500 nm particle samples was estimated to be on the order of 10 and 100 nm, respectively.

It is well known that negative capillary pressure develops and causes volume shrinkage as a gel is being dried during the initial stage of calcination. According to the Laplace equation,25 the capillary pressure is inversely proportional to pore size. Obviously, pores in gels consisting of larger silica particles are larger, and consequently the capillary pressure is lower. Therefore, the volume shrinkage of the Aerosil and 500 nm samples observed after the calcination step was relatively smaller in comparison with that observed for the TEOS and Ludox samples.

The capillary pressure can also lead to cracking if a gel cannot shrink freely and uniformly during drying as evident from the calcined samples. As expected from the particle size effect,26 the Aerosil and 500 nm particle samples did not crack significantly (Figs. 3(C) and (D)) as these precursors contained larger silica particles than the TEOS and Ludox precursors. However, from a practical processing perspective, there were several limitations on controlling crack formation by simply increasing silica particle size. First, silica particles were needed to be small enough to enter and completely infiltrate the interstitial space of the polystyrene microsphere template. Second, the strength of the gel decreases with increasing particle size,27 which could result in collapse of the gel structure during handling.

Different cracking patterns observed for the TEOS and Ludox samples could be explained by their gel structures. The gel structure derived from the TEOS precursor was a cross-linked network with polymeric clusters interpenetrated with each other and linked by multiple siloxane bonds. When the drying stress became high enough to break the gel, relatively large cracks originated from a few defective regions within the gel structure and propagated. In contrast, the dense spherical particles from the Ludox precursor had most likely small contact area between the particles. The particles were held together mainly by van der Waals forces, possibly along with a limited number of siloxane bonds. Under drying stress, numerous microcracks originated at many locations in the gel derived from the Ludox precursor due to the weaker bonding between the particles.

The cellular samples after 1100°C sintering are shown and compared as a function of the silica precursor in Fig. 6. The sintered specimens exhibited further volume shrinkage in comparison with that observed from the calcined samples previously shown in Fig. 3. The degree of shrinkage observed from the sintered specimens was the highest for the TEOS sample (Fig. 6(A)) and the lowest for the 500 nm particle sample (Fig. 6(D)). It appeared that the Ludox and Aerosil samples (Figs. 6(B) and (C) respectively) shrank by similar amounts.

At higher magnifications, quite different types of morphology were observed in the skeleton phase of the sintered samples. In the TEOS sample, pores smaller than 100 nm were observed most likely due to “bloating.” The bloating phenomenon is
known to occur as a result of water and/or ethanol vapor production during continued condensation of TEOS-derived gels.\textsuperscript{28} In comparison with Figs. 3(F) and 6(F), it appeared that fine microcracks observed from the calcined Ludox\textsuperscript{s} sample were somewhat healed after sintering. On the other hand, the larger cracks observed in this sample (Figs. 3(B) and 6(B)) basically remained in the structure after sintering with larger crack width. The Aerosil\textsuperscript{s} sample exhibited an interesting morphology (Fig. 6(C)) with the appearance of large \( \sim 50 \) \( \mu \)m holes that were resulted from the coalescence of individual cells of the structure. The 500 nm sample was only partially sintered, as evident from the presence of inter-particulate pores on the order

Fig. 6. Sintered cellular silica specimens prepared with: (A) and (E) tetraethylorthosilicate, (B) and (F) Ludox\textsuperscript{s}, (C) and (G) Aerosil\textsuperscript{s}, and (D) and (H) 500 nm particle precursors after calcining at 500 °C for 6 h followed by sintering at 1100 °C for 10 h.
of ~100 nm in the SEM images in Fig. 6(H). In contrast, the silica skeleton phase of the TEOS, Ludox®, and Aerosil® samples which contained smaller silica particles appeared to be fully sintered at least within the SEM resolution. Our observations on this silica particle size dependence were consistent with the well-known effects of small pore size and larger number of pores in the promotion of viscous flow sintering.28,29

Fig. 7. Cellular silica specimens synthesized within the polystyrene-coated microchannel with: (A) and (C) tetraethylorthosilicate precursor after the 500°C calcination step and (B) and (D) Ludox® precursor after the 1100°C sintering step.

Fig. 8. Free-standing cellular silica samples synthesized from: (A) and (C) tetraethylorthosilicate precursor after the 500°C calcination step and (B) and (D) Ludox® precursor after the 1100°C sintering step.
Calcined TEOS and sintered Ludox samples synthesized with the polystyrene sacrificial interlayer deposited on the Si microchannel wall are shown in Figs. 7A and (B), respectively. The gap between the cellular structure and the microchannel wall was clearly observed for the samples due to: (1) volume shrinkage of the cellular structure and (2) removal of the sacrificial polystyrene interlayer during calcination. Fine microcracks were observed for the TEOS and Ludox samples as shown in Figs. 7(C) and (D), respectively. Each sample showed a similar cracking behavior to that of the sample prepared without the polystyrene interlayer (Figs. 7(C) and (E) for the TEOS samples and Figs. 7(D) and 6F for the Ludox samples). The results show that the polystyrene sacrificial layer was useful in detaching the cellular structure from the microchannel wall, but did not prevent crack formation.

A free-standing cellular silica sample synthesized from the TEOS precursor using the mold approach after 500°C calcination is shown in Figs. 8(A) and (C). Also, a free-standing specimen synthesized from the Ludox precursor after 1100°C sintering is shown in Figs. 8(B) and (D). Cracking was not observed in these samples, as evident from the SEM images. However, due to compression of polystyrene microspheres and free shrinkage of the structure, cells in the free-standing samples appeared to be more deformed and smaller in comparison with the samples prepared under the microchannel confinement. The final diameter of the sintered Ludox sample was measured to be ~450 μm which corresponded to a ~40% linear shrinkage from the internal diameter of 725 μm of the syringe mold used to prepare the free-standing polystyrene microsphere template. The experimental results indicated that cracking in the TEOS and Ludox samples can be reduced by removing the geometrical confinement imposed by the microchannel.

Although it was relatively easy to set initial cell size and cell interconnectivity using the microsphere template approach, our results revealed that synthesizing a silica skeleton that exactly duplicated the inverse structure of the template presented an interesting challenge. This difficulty was largely due to the volume shrinkage and cracking of the silica gel infiltrated into the interstitial space of the polymer template during calcining and sintering. The sacrificial layer approach posed a dilemma in that it may prevent crack formation, but at the expense of creating a gap between the cellular structure and the microchannel wall. If the gap is continuous along the length of the microchannel, a fluid stream will preferentially flow along the gap instead of the tortuous fluidic pathway within the cellular structure. In this situation, the benefits of high geometrical surface area and mixing enhancement provided by the cellular structure would not be utilized.

Ideally, for uniform flow distribution, it is desirable to have a cellular structure that completely fills up the microchannel volume, although the structure may contain mesopores and non-propagating microcracks (e.g., calcined Ludox, and Aerosil samples shown in Fig. 3). While such a structure may not be strong for use as a free-standing material, the microchannel confinement can be viewed as beneficial in terms of protecting the weak, brittle structure during handling and use for various microfluidic-based reaction applications.

IV. Conclusions

The polystyrene microsphere template method was developed to produce the silica cellular structure within the microchannel of the silicon microreactor. In this method, polystyrene microspheres were infiltrated into the microchannel space of the Si-based microreactor, and were assembled to create an inverse template of the final cellular structure. The polymer template was subsequently infiltrated with a silica precursor sol containing silica particles. Four different precursor sols were used mainly to ascertain the effects of silica particle size in the range of 2–500 nm on the shrinkage, cracking, and sintering behaviors of the silica skeleton phase. With these precursors, the cell size of 12–14 μm was typically obtained from the 16 μm polystyrene microspheres used for the template preparation. The cell interconnectivity of ~0.4 was achieved by partially sintering the polystyrene microsphere assembly at 100°C for 180 s.

Although it was relatively easy to set initial cell size and cell interconnectivity using the microsphere template approach, the results revealed that synthesizing a silica skeleton that exactly duplicated the inverse structure of the template was difficult due to the volume shrinkage and cracking of the silica gel infiltrated into the interstitial space of the polymer template during calcining and sintering. Volume shrinkage and cracking of the cellular structure under the microchannel confinement were largely dictated by particle size in the silica precursor sol. The silica precursor sol with large and dense particles (i.e., ~40 nm in the Aerosil precursor) effectively reduced the degree of shrinkage and cracking during calcining. From the microreactor application perspective, the geometrical confinement imposed by the microchannel can be beneficial in terms of projecting the weak, brittle cellular structure during handling and use.

References


