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Recommended Citation

Leventis, Nicholas; Sotiriou-Leventis, Lia; Wang, Xiaojiang; and Mulik, Sudhir, "Conformal internal coating of macroporous co-continuous MCF-silicas with isocyanate derived polymers" (2006). Faculty Research & Creative Works. Paper 41.  
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CONFORMAL INTERNAL COATING OF MACROPOROUS CO-CONTINUOUS MCF-SILICAS WITH ISOCYANATE DERIVED POLYMERS

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Introduction
Since their discovery in 1992,1 templating sol-gel silica with structure-directing agents has resulted in new materials with ordered mesoporous (2-50 nm) structure that is investigated for application in areas as diverse as high surface area supports for catalysts or as nanostructured drug storage and release platforms.2 Structure-directing agents are typically surfactants ranging from cationic detergents such as alkyl-trimethylammonium salts with C8-C18 hydrocarbon chains to non-ionic tertiary amines, polyethylene oxide or amphiphilic triblock copolymers such as poly(ethyleneoxide)-block-poly(propyleneoxide)-block-poly(ethyleneoxide) (e.g., Pluronic P123). Depending on the surfactant and the conditions (e.g., kind and concentration of catalyst) the structure of the mesopores may vary (e.g., from cubic to hexagonal etc.). The surfactant forms templating micells, which can be enlarged by adding organic swelling agents as for example mesitylene to P123. The resulting materials are referred to as Mesoporous Cellular Foams (MCFs)3 and they contain a co-continuous three-dimensional macroporous (>50 nm) pore system consisting of interconnected spherical compartments with mesoporous walls.4 Owing to a combination of a low resistance to hydraulic flow with short diffusion path lengths within the mesoporous skeletal walls surrounding the macropores, such systems attract attention as chromatographic stationary phases,5 and in fact certain versions of this technology are already incorporated in monolithic separation columns marketed by Merck Co. under the trade name ChromolithTM.6

Typical preparation conditions for those materials involve phase separation induced by the templating agent, followed by gelation of an alkoxysilane. Ambient pressure drying removes the gelation solvent and a final high-temperature calcination removes the templating agent. These conditions induce shrinkage that not only makes reproducible in-place-of-use preparation of the monolith problematic but also causes chemical alteration of the silica surface, densification of the skeletal framework and partial collapse of the macropores.

Here we explore a different approach for minimizing shrinkage, reduce cracking, increase mechanical strength and reproducibility of templated silica type of materials. For this we employ a method we developed recently by which we use the native –OH group surface functionality of silica in order to direct the polymerization of a di-isocyanate.7 Bi-continuous macro/mesoporous monolithic silicas are prepared by Nakashishi’s modification of Stucky’s method,8 in which P123 (molecular weight~5,800) is used as templating agent while 1,3,5-trimethylbenzene (TMB) is employed as an expanding agent. The templating agent was washed off by Soxhlet extraction and the resulting wet gels were exposed to a solution of a di-isocyanate in acetone; unreacted di-isocyanate was washed off and the samples were dried with CO2 taken out supercritically. Comparative characterization was conducted for isocyanate-treated and non-treated samples. Isocyanate-treated monoliths undergo minimal shrinkage, they are much more robust than native samples while they maintain the surface area of the untreated monoliths.

Experimental
In a typical procedure, 4.0 g of P123 was dissolved in 12 g of a 1.0 M aqueous solution of nitric acid, and then a given amount of TMB was added under stirring. Following Nakashishi’s notation,7 for MP4 samples no TMB was used; for MP4-T045 samples we used 0.45 g TMB and, for MP4-T310 samples we used 3.10 g TMB. The same amount of TMOS (5.15 g) was then added to each sample at 0°C under vigorous stirring. After 10 min, the resultant homogeneous solution was poured into polypropylene molds (Wheaton polypropylene Omni-Vials, Part No. 225402, 1 cm in diameter). Molds were sealed with plastic cups and kept at 60 °C for gelation. The resulting wet gels were aged at 60 °C for about 5 times the gelation time and were removed from the molds. Such as-made wet gel monoliths were washed twice (~8 h each time) with ethanol and went to Soxhlet extraction using CHCl3 as solvent for 2 days to remove P123. Subsequently, wet gels were aged another four time with acetone (~8 h each time) and were either dried with supercritical CO2 to yield native dry silica monoliths, or were placed in a solution containing 11 g of Desmodur N3200 in 94 mL of acetone. After allowing a 24 h equilibration time, the samples were heated in the Desmodur solution at 55 °C for 3 days. After four more acetone washes (~8 h each time) such gels were dried with SCF CO2 to yield crosslinked monoliths. For comparison with the literature, native dry silica monoliths were also calcined at 650 °C for 6 h in air to yield calcined monoliths.

Results and Discussion
Following Nakashishi’s procedure we prepared silica wet gel monoliths templated with P123,7 in the presence and in the absence of TMB as expanding agent. However, instead of air-drying followed by calcination, our monoliths were subjected first to a Soxhlet extraction that removes the templating agent and subsequently were either dried with liquid CO2 that was eventually taken out supercritically, or were further subjected to a crosslinking process that involves treatment with a di-isocyanate according to procedures described recently in conjunction with mechanical reinforcement of silica aerogels. Scheme 1 summarizes the preparation procedures.

![Scheme 1. Preparation of MCF silica and crosslinking with a di-isocyanate.](Image)

Based on our prior work with isocyanate crosslinking of silica aerogels,7 the di-isocyanate is expected to attach itself on the silica backbone through carbamate (–Si-O-CO-NH) groups. Meanwhile, Thermogravimetric Analysis (TGA) data of native MCF samples show a first gradual mass loss below 100 °C (Figure 1) showing that native MCF samples retain up to 12-13% w/w water (coming from the gelation step), even after all processing and SCF CO2 drying. During treatment with Desmodur N3200 (an oligomeric di-isocyanate derived from hexamethylene di-isocyanate supplied by Bayer), adsorbed water is expected to hydrolyze dangling isocyanate groups of Desmodur N3200 already attached to the silica backbone, yielding dangling –NH2 groups, which in turn react with more di-isocyanate in the mesopores leading to bridging by polyurea. The IR spectra of isocyanate versus native samples (Figure 2) confirm massive uptake of polymer showing the characteristic C-H stretches just below 3000 cm−1 as well as the characteristic diazetidinedione carbonyl stretch at ~1767 cm−1 of the hexamethylene disiocyanate backbone.

![Figure 1. TGA data for a native MCF monolith (MP4-T310, density= 0.19 g cm−3) and its crosslinked counterpart (X-MP4-T310, density = 0.58 g cm−3).](Image)

Sample notation according to ref. 3.
Owing to polymer uptake, the density of isocyanate treated samples has more than doubled relative to the density of the native MCF silicas (Table 1), but by the same token the same samples have also undergone less shrinkage during processing (Figure 3). The percent weight of polymer in the isocyanate-treated samples is calculated from the density increase and diameter difference data, and is cited in Table 1. The agreement with the TGA data of Figure 1 is good.

Table 1. Pertinent Data For Templated And Crosslinked Silicas. (“X” Denotes Crosslinked MCF Samples With An Isocyanate-Derived Polymer.)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>diameter (cm)</th>
<th>density (g cm⁻³)</th>
<th>% polymer (w/w)</th>
<th>BET surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP4</td>
<td>0.80</td>
<td>0.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-MP4</td>
<td>0.91</td>
<td>0.76</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>MP4-T045</td>
<td>0.74</td>
<td>0.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-MP4-T045</td>
<td>0.91</td>
<td>0.66</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>MP4-T310</td>
<td>0.85</td>
<td>0.19</td>
<td></td>
<td>528</td>
</tr>
<tr>
<td>X-MP4-T310</td>
<td>0.91</td>
<td>0.58</td>
<td>73</td>
<td>487</td>
</tr>
<tr>
<td>Cal-MP4-T310</td>
<td>0.71</td>
<td>0.23</td>
<td></td>
<td>410</td>
</tr>
</tbody>
</table>

In analogy to silica aerogels, isocyanate-treated MCFs are mechanically very strong materials (formal mechanical characterization in progress), but from a practical point of view the question is whether isocyanate treatment compromises their microscopic structure. In that regard, SEM (Figure 4) shows that polymer loading has not visually affected the structure or size of the macropores. That is, morphological features of similar sizes are visible in the native as well as the isocyanate-treated samples. The next question is whether the polymer clogs the mesopores, or it has been conformally coated their surfaces. This is an important issue for separation applications where macropores facilitate hydraulic flow, while thin mesoporous walls with large surface area facilitate diffusion and provide lots of active sites that increase the theoretical plates. As shown in Table 1, the BET surface area of isocyanate treated samples remains extremely high, indicating that the polymer is coated conformally around the mesoporous walls as well.

Conclusions

The mesoporous surfaces of silica-derived co-continuous mesoporous cellular foams (MCFs) have been conformally coated with isocyanate derived polymers, in analogy to polymer crosslinked silica aerogels. The resulting materials undergo minimal shrinkage upon drying with SCF-CO₂, they require no calcination, they are extremely robust, and although their density has increased 3-fold by the polymer uptake, nevertheless, they retain all the macroporosity and 92% of the mesoporous surface area of their native counterparts. Based on those properties, we expect that such polymer-modified mesoporous cellular foams will find applications as platforms for separations.

References