

Modification of SBA-15 pore connectivity by high-temperature calcination investigated by carbon inverse replication

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Two-dimensional hexagonally ordered CMK-3 carbons were synthesized using SBA-15 templates calcined at a temperature of 1153 K, whereas a disordered carbon was obtained using SBA-15 calcined at 1243 K, demonstrating that the pores connecting ordered mesopores in SBA-15 silica persist up to *ca.* 1153 K, but are eliminated at temperatures close to 1243 K.

During the last several years, SBA-15 silica¹ with a two-dimensional (2-D) hexagonal arrangement of uniform mesopores has attracted much attention and is being evaluated for numerous applications in the fields of catalysis, separations, water purification, and advanced optics devices (see for instance refs. 2 and 3 for references). This remarkable interest stems from the many desirable features of SBA-15, including tailored pore size, high degree of structural ordering, ease of synthesis, availability of economically facile synthesis pathways, high hydrothermal/thermal stability and so forth. Despite all this interest in the synthesis, modification and application of SBA-15, the very structural identification of this material was largely uncertain until recently. Initially,¹ SBA-15 was considered to be an extra-large-pore MCM-41⁴ analog with a honeycomb structure of disconnected channel-like pores. Later, much evidence for microporosity in numerous SBA-15 samples was reported,^{2,3,5–8} although some SBA-15 samples were claimed to be non-microporous in contrast to others,^{7,8} and the very evidence of microporosity was questioned⁹ by the authors who first suggested the presence of micropores in SBA-15.⁵ As we first pointed out,^{2,3} the development of microporosity in SBA-15 and its evolution during the synthesis are consequences of the fact that poly(ethylene oxide) blocks of the poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) template penetrate the silicate walls of as-synthesized SBA-15, which was convincingly shown by others.^{10,11} To end the controversy about the SBA-15 structure and to fully reveal its nature, we carried out an extensive study involving platinum³ and carbon¹² replication, as well as characterization *via* selective pore blocking *via* chemical modification.³ The latter method in addition to nitrogen and argon adsorption confirmed the presence of micropores and small mesopores (later referred to as complementary pores) of the size below 3.4 nm.³ In addition, the replication studies revealed for the first time the interconnected nature of SBA-15 porosity, since bundles of ordered platinum nanowires,³ and high-surface-area carbon (denoted as CMK-3) with uniform pores between 2-D hexagonal arrangement of uniform rods¹² were obtained through SBA-15 templating. It is otherwise known that similar structures cannot be obtained using MCM-41 as a template under analogous conditions.^{13–15} It is also noteworthy that replication is widely considered as a convincing and reliable tool of structure characterization,¹⁶ and carbon replication¹⁷ in particular has already been employed¹³ to confirm the worm-like interconnected nature of porosity in HMS silica.¹⁸ The SBA-15 samples studied by platinum and carbon replication were synthesized by employing aging at 373 K which is a standard procedure for SBA-15 synthesis¹ (referred to by some authors as hydro-

thermal treatment).⁸ Therefore, our findings about the interconnected nature of SBA-15 porosity are relevant to the overwhelming majority of SBA-15 preparations reported to date, including some of the materials, which were claimed non-microporous in contrast to other SBA-15 samples.^{7,8}

In the current study, we employed carbon replication to confirm that not only typical SBA-15 silica has interconnected porous structure, but also the connecting pores are exceptionally persistent and are not eliminated even after calcination at 1153 K, although there is evidence that they are largely eliminated at somewhat higher temperatures. The remarkably high thermal stability of connecting pores and the possibility of their elimination only at temperatures as high as *ca.* 1273 K were suggested in our earlier study based solely on nitrogen adsorption data.³

SBA-15 samples were prepared using the triblock copolymer, EO₂₀PO₇₀EO₂₀ (Pluronic P123, BASF) and tetraethoxysilane (TEOS, 98%, Acros). The details of the synthesis procedure are described elsewhere.¹² The synthesis procedure was similar to that originally developed by Stucky and coworkers,¹ except for the particle growth under static conditions and the starting composition of 10 g P123:0.10 mol TEOS:0.60 mol HCl:20 mol H₂O. The SBA-15 products were filtered off, dried without washing, and calcined in dry air flow at various temperatures. The carbon replication was performed with sucrose as described in detail elsewhere.¹² Briefly, the SBA-15 sample was infiltrated twice with sucrose in the presence of sulfuric acid and subsequently, the carbonization was completed by heating at 1173 K under vacuum. These calcined SBA-15 silicas are referred to as SBA-15-*x*, where *x* denotes the calcination temperature, whereas the SBA-15-*x* templated carbons are referred to as CMK-3-*x* or C-*x*, in the case of ordered and disordered carbons, respectively.

As can be seen in Fig. 1(a), SBA-15 retains a highly ordered hexagonal structure even after calcination at 1243 K, despite the large decrease (*ca.* 25%) in the unit-cell size. The structural shrinkage was accompanied by a major loss of the BET specific surface area and total pore volume (from 850 to 390 and 220 m² g⁻¹, and from 1.03 to 0.49 and 0.23 cm³ g⁻¹, after heating at 1153 and 1243 K, respectively) and significant pore size decrease, but the narrow pore size distribution persisted [Fig. 1(b)]. It should be noted that the specific surface areas, total pore volumes, and pore size distributions reported herein were evaluated as described in our previous work.^{2,3} When the resulting SBA-15 silica templates were employed in the carbon synthesis, only samples calcined at 823 and 1153 K afforded 2-D hexagonally ordered carbons, whereas SBA-15 template calcined at 1243 K rendered carbon with no long-range ordering [Fig. 1(a)]. All the carbon replicas exhibited high BET specific surface areas and total pore volumes (1160, 1160 and 750 m² g⁻¹, as well as 1.24, 1.08 and 0.53 cm³ g⁻¹, for CMK-3-823, -1153 and C-1243 samples, respectively). However, only CMK-3-823 and -1153 samples exhibited capillary condensation steps on nitrogen adsorption isotherms, and consequently, narrow mesopore size distributions [Fig. 1(c)], whereas C-1243 carbon was primarily microporous with a relatively small amount of

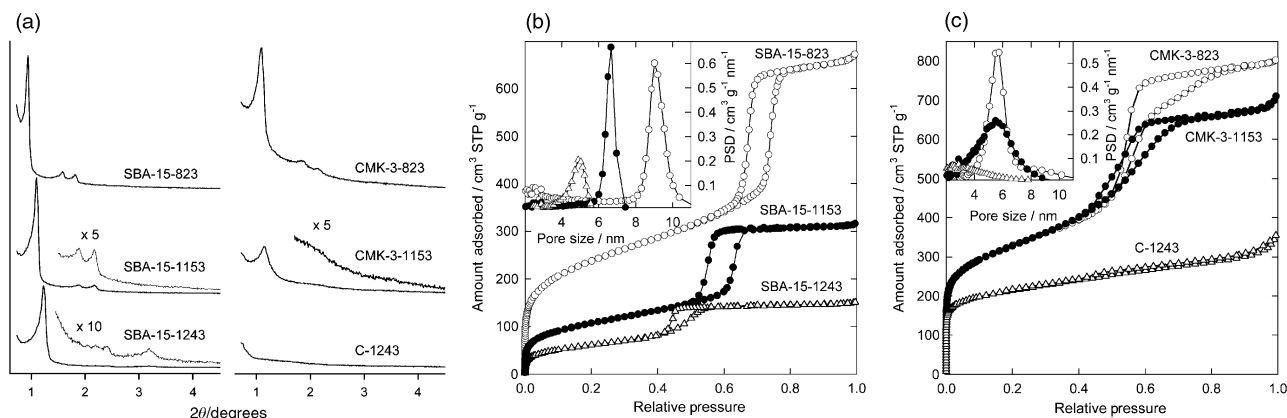


Fig. 1 (a) Powder X-ray diffraction spectra for the SBA-15 and carbon samples. (b) Nitrogen adsorption isotherms and pore size distributions for the SBA-15 silicas. (c) Nitrogen adsorption isotherms and pore size distributions for the carbons synthesized using the SBA-15 silica templates.

disordered mesopores, thus being similar to the high-surface-area carbon synthesized using MCM-41 as a template.¹⁴ It should be noted that the carbon framework of CMK-3 is microporous to some extent,¹² similarly to other ordered mesoporous carbons synthesized using the same carbon precursor.^{14,17} Therefore, the overall porosity of CMK-3 is a combination of uniform pores between ordered carbon rods, and micropores within these rods.

The successful synthesis of ordered mesoporous carbons using SBA-15 templates calcined at 823 and 1153 K showed that the structure of SBA-15 prepared under standard conditions is clearly interconnected, otherwise periodic carbon structures would not form. Indeed, as inferred from the structures of C-1243 carbon and carbons templated using MCM-41 silicas,^{13,14} disconnected uniform carbon rods do not exhibit a tendency to agglomerate in ordered structures. The carbon templated using SBA-15-1153 exhibited mesoporous structure similar to that of the material prepared from the SBA-15-823 template, thus suggesting that the large structural shrinkage during the high-temperature calcination did not result in the complete elimination of the complementary pores. However, it needs to be kept in mind that the complementary pores are likely to be largely depleted after such a treatment. One can infer this from the examination of the relation between the primary mesopore diameter (w), primary pore volume (V) and primary pore surface area (S) for the SBA-15 templates. Primary pores are defined here as primary (ordered) mesopores and complementary (connecting) pores. The factor wS/V is theoretically expected to be 4 for cylindrical and 4.2 for hexagonal pores. For highly ordered MCM-41 silicas, we found wS/V values of 4.5–5.0 and therefore we can consider this range of values as that characteristic of disconnected cylindrical (or hexagonal) mesopores of size of several nanometers. The difference between the theoretical and experimental values can be largely attributed to the overestimation of surface area using the BET method that was discussed elsewhere.¹⁹ For SBA-15 calcined at 823 K, the wS/V factor was equal to 7.6 (consistent with earlier studies),³ whereas for the samples calcined at 1153 and 1243 K, it was 5.3 and 4.9, respectively. So, on the basis of data for MCM-41, it is not unexpected that SBA-15 samples with $wS/V = 7.6$ and 5.3 were suitable as templates for ordered porous carbons, and SBA-15 with $wS/V = 4.9$ was not. However, it is surprising that as small a difference in wS/V factor as 0.4, and corresponding expected small difference in the pore structure may lead to completely different templating effects. This suggests that either even a small content of connecting pores in SBA-15 is capable of imparting stable CMK-3 frameworks, or connecting pores in SBA-15 are abundant and even their significant depletion leaves an appreciable population, or both of the above. Anyway, further studies of structures of SBA-15 and CMK-3 carbons are highly desirable. In addition, a search for

criteria useful for reliable prediction of pore connectivity of templates, and in particular, further work on refinement of the wS/V criterion, appear to be worthwhile. To this end, we should emphasize that w , S and V values need to be evaluated using reliable methodology, for instance the same as or equivalent to that employed herein.^{2,3} Where calculation procedures providing different results are used, the threshold value of the wS/V factor for connected pore structures would have to be re-evaluated. Moreover, the value of the wS/V factor should not be treated as fully conclusive as to pore connectivity. The final conclusions about the presence or absence of connecting pores should be based preferably on replication procedures, among which carbon replication appears to be the most convenient.

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