

Thermally induced structural changes in SBA-15 and MSU-H silicas and their implications for synthesis of ordered mesoporous carbons

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SBA-15 and MSU-H silicas were synthesized and subjected to calcination at temperatures in the range from 823 to 1273 K. The porous structures of the resulting samples were studied using X-ray diffraction and nitrogen adsorption. The pore connectivity was elucidated using the inverse carbon replication procedure. The structures of carbon inverse replicas were studied using XRD and nitrogen adsorption.

1. INTRODUCTION

The recent development of ordered mesoporous carbons using ordered mesoporous silicas as templates [1,2] opened remarkable new opportunities in the synthesis of ordered mesoporous materials suitable for numerous advanced applications [1-5]. The necessary condition for the formation of ordered mesoporous carbon replica is a three-dimensional (3-D) connectivity of pores in the structure of the template [3]. The first reported ordered mesoporous carbon, CMK-1, was synthesized using MCM-48 silica template [1,2] that exhibits two interwoven, but disconnected 3-D porous systems. Consequently, CMK-1 exhibited an ordered structure, but the latter was different from that of the template because of the mutual displacement of the two interwoven carbon frameworks after the silica template dissolution [1]. The first ordered mesoporous carbon that faithfully replicated the structure of the silica template was synthesized using SBA-15 silica as a template [4]. SBA-15 exhibits a two-dimensional (2-D) hexagonally ordered structure with large mesoporous channels that are connected through complementary pores (micropores and mesopores) in the pore walls, as was demonstrated earlier using platinum inverse replication [6]. Consequently, SBA-15-templated carbon, referred to as CMK-3, is a 2-D hexagonal array of carbon rods. The formation of connecting pores in the SBA-15 structure was explained as an effect of occlusion of poly(ethylene oxide) chains of the triblock copolymer structure-directing agent in the silica framework [6]. It was further hypothesized that this behavior is common for silicas templated by polymers and oligomers with poly(ethylene) oxide blocks [6]. This contention was confirmed by a successful synthesis of CMK-3 carbons not only using SBA-15 templates assembled from TEOS as a silica source under acidic conditions in the presence of triblock copolymer structure-directing agent, but also using silica templates prepared in the presence of triblock copolymers or oligomers under different conditions. These templates include MSU-H silica synthesized from sodium silicate under nearly neutral conditions in the presence of triblock copolymer [7,8] and SBA-15 silica synthesized from sodium silicate

rather than from TEOS [8]. Moreover, CMK-3 carbons were successfully synthesized using 2-D hexagonal silica templates synthesized in the presence of oligomers [9].

Despite the fact that CMK-3 carbons can be formed using silica templates synthesized under various conditions in the presence of polymeric or oligomeric structure-directing agents, some differences in the structure of these templates are expected that may influence the structure of the resulting carbon replicas. In particular, it was reported that SBA-15 silica synthesized at 403 K exhibits relatively large tunnels or holes in the pore walls, which provide connectivity between the ordered, large mesopores [10]. These connecting pores are observable by transmission electron microscopy (TEM) as ruptures in the pore walls, whereas connecting pores present in SBA-15 synthesized at 373 K are not readily observable by TEM. It was also suggested on the basis of nitrogen adsorption data that the heat treatment of SBA-15 synthesized at 373 K leads to depletion and perhaps even to closure of the connecting pores [6].

These findings highlighted the need for a systematic study of pore connectivity in 2-D hexagonally ordered mesoporous silicas synthesized under various conditions in the presence of polymeric and oligomeric structure-directing agents. In particular, an effect of calcination temperature on the pore connectivity in these silicas deserves much attention, as the successful elimination of connecting pores without the destruction of the periodic structure of the material would lead to extra-large-pore MCM-41 analogues [11] that are desirable as templates for nanowires and as model adsorbents. It is also interesting to investigate the effect of the calcination of the silica template on the structure of its carbon inverse replica. This contribution reflects our ongoing research effort in these important directions.

2. EXPERIMENTAL

SBA-15 and MSU-H silicas were synthesized as described elsewhere using Pluronic P123 poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer as a structure-directing agent [8,12,13]. After the removal of the copolymer via calcination, inverse carbon replicas were synthesized as reported earlier [4].

3. RESULTS AND DISCUSSION

It is convenient to elucidate the pore connectivity in ordered silicas on the basis of the structural properties of their carbon inverse replicas [3,8,11,14]. We have already employed this methodology in studies of structural changes in SBA-15 brought about by calcination at temperatures above 823 K [11] (823 K is a standard calcination temperature for silicas synthesized using surfactant, oligomeric and polymeric structure-directing agents). SBA-15 silica selected for this study was synthesized initially at 308 K and later aged at 373 K, which are typical conditions for the SBA-15 synthesis [12]. It was found that thus synthesized SBA-15 sample retained its ordered structure after calcination at 1153 and 1243 K, although its unit-cell size and pore diameter were reduced and its adsorption capacity was diminished to a half and to one fourth, respectively, when compared to the sample calcined at 823 K. The SBA-15 samples calcined at 823 and 1153 K were successfully used as templates for the synthesis of ordered CMK-3 carbons, whereas the inverse replication of the SBA-15 silica calcined at 1243 K afforded a disordered high-surface-area carbon with a broad distribution of pores in the micropore and mesopore ranges. We interpreted this result as evidence that connecting pores in pore walls of large mesoporous channels of SBA-15 synthesized at 373 K are

eliminated at 1243 K, thus leading to the formation of large-pore MCM-41 analogue. Unfortunately, this MCM-41 analogue exhibited a low adsorption capacity and relatively small pore diameter (about 5 nm).

It is interesting to note that in the case of the SBA-15 sample synthesized under conditions discussed above, the increase in the calcination temperature did not lead to any appreciable change in the pore diameter of the inverse carbon replica. This is rather unexpected because the higher calcination temperature results in structural shrinkage, which is expected to increase the pore wall thickness and thus to lead to larger pore diameter of the inverse carbon replica. However, it needs to be kept in mind that the pore wall of SBA-15 synthesized under conditions considered is highly porous and that the increase in the calcination temperature appears to lead to its consolidation. Therefore, the effect of structural shrinkage, which is expected to increase the pore wall thickness, is likely to be counterbalanced by the wall consolidation with reduction of the volume of the complementary pores in the walls. These two opposite effects may lead to a relatively constant pore wall thickness for SBA-15 samples synthesized at 373 K and calcined at different temperatures.

In addition to SBA-15 silicas synthesized at 373 K, MSU-H silicas synthesized at the same temperature were studied. As reported elsewhere [7,8], MSU-H synthesized at 333 K as well as at 373 K is suitable as a template for the synthesis of CMK-3 carbons. The resultant inverse carbon replica exhibits properties similar to those for CMK-3 carbon prepared using SBA-15 template [7,8]. MSU-H silica calcined at 973 and 1073 K was also suitable for the synthesis of CMK-3 carbons, whose properties were similar to those of typical CMK-3 carbons (see Figure 1). This indicates that the connectivity of pores in MSU-H silica synthesized at 373 K was retained at 973 and 1073 K. In contrast to the results of calcination at temperatures up to 1073 K, higher calcination temperatures for the MSU-H sample considered allowed us to obtain ordered mesoporous carbons with very interesting, novel properties. These properties can be explained as results of structural changes of the MSU-H template upon heating. We intend to continue this research to gain a better understanding of these fascinating phenomena and their implications in the synthesis of ordered mesoporous carbons, and we plan to report these results later.

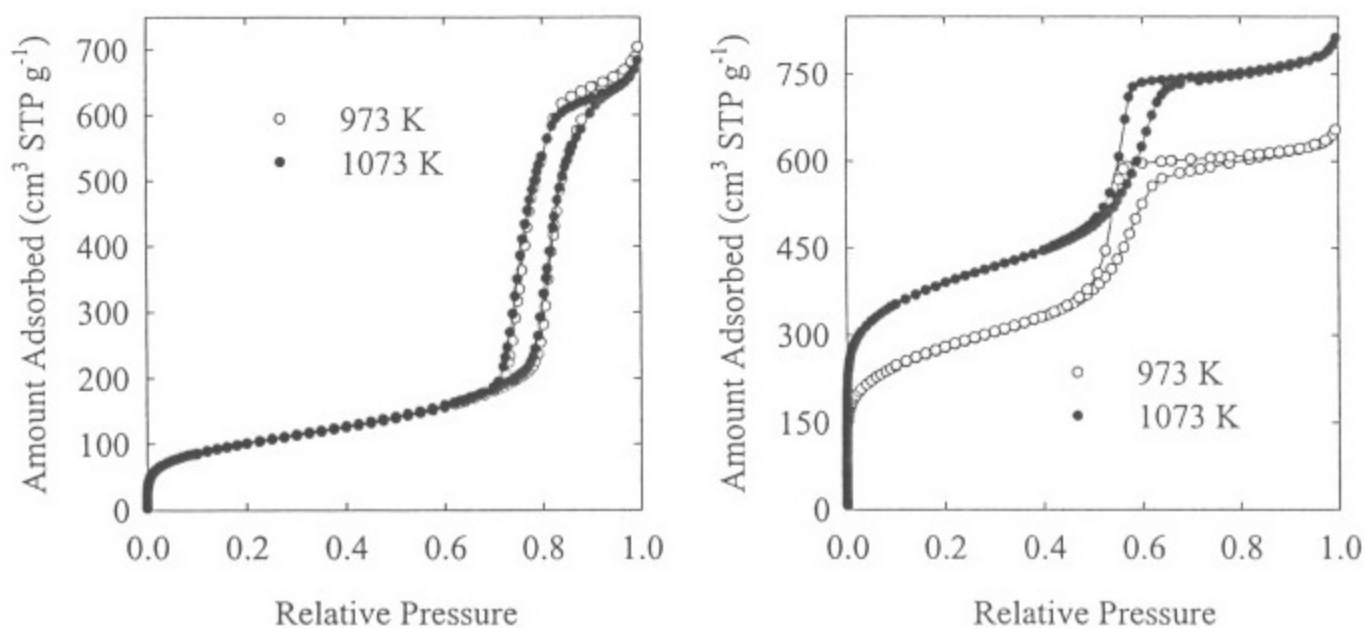


Fig. 1. Nitrogen adsorption isotherms for MSU-H silicas calcined at 973 and 1073 K (left graph) and for their inverse carbon replicas of CMK-3 type (right graph).

