Pore topology control of three-dimensional large pore cubic silica mesophases†

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Facile synthetic modulation of the pore shape and pore entrance of large pore cubic silica mesophases with fcc and bcc three-dimensional structures was achieved by applying post-synthesis treatment with sulfuric acid.

Highly porous materials consisting of three-dimensionally (3-D) interconnected mesopores[1–4] are attracting wide current interest for applications as selective sorbents, catalyst supports, regulated flow and transport systems, matrices for biomolecule immobilization, or nanostructured host–guest systems. Mesoporous SBA-16[1,2] and related KIT-5[4] silicas, which consist of spherical cavities arranged in body-centered cubic (bcc $Im\bar{3}m$) and face-centered cubic (fcc $Fm\bar{3}m$) symmetries, respectively, are particularly interesting because of their highly interconnected 3-D structures with cage-like mesopores (>5 nm) bridged through smaller entrances. However, practical synthetic methods are still being intensively sought to tailor pore geometry, dimension and interconnectivity in an efficient and systematic manner. Besides, these structural and textural properties are affected by the process of removal of the block copolymer templates selected to open the pores[5–8] Calcination has been the most widely applied method[5] during which the template molecules are thermally decomposed and all pores are vacated in a single step. However, calcination is usually accompanied with extensive silanol condensation and marked shrinkage of the mesostructure.[5] Conversely, the novel method of sulfuric acid treatment recently reported for mesoporous SBA-15 silica having straight channel-type mesopores[9,10] enables consecutive generation of mesoporosity and microporosity. Moreover, this treatment facilitates further condensation of the silica framework to render the thus-treated material more stable against shrinkage at high temperature.[10] Therefore, we expect that acid treatment could be very suitable to tailor cage-like materials, with emphasis on the pore entrances regulating the access to the large cavities. In this communication, we report our preliminary findings concerning the sulfuric acid treatment of cage-like materials. While the highly ordered cubic structure is retained, remarkable differences in the size of the mesopores, the pore

entrance and pore volume are observed for the acid-treated materials compared to calcined materials.

The large pore 3-D cubic mesoporous silicas were prepared according to previously described procedures,[4,11] and subsequently treated with H_2SO_4.[9,10]‡ The surface properties are expected to be different for calcined and acid-treated materials, similarly to SBA-15 silica.[9,10] Argon was therefore chosen as the adsorbate to avoid specific interactions with different surfaces and to achieve higher accuracy for measurements in the micropore range. Fig. 1 shows the Ar sorption isotherms measured at 87 K for both series of template-free cubic bcc and fcc materials. The samples obtained after conventional calcination exhibit typical type IV isotherms with a capillary condensation step at high relative pressure and H2-type hysteresis loops. These characteristics are indicative of large mesopores with ink-bottle or cage-like shapes.[4,12] In contrast,
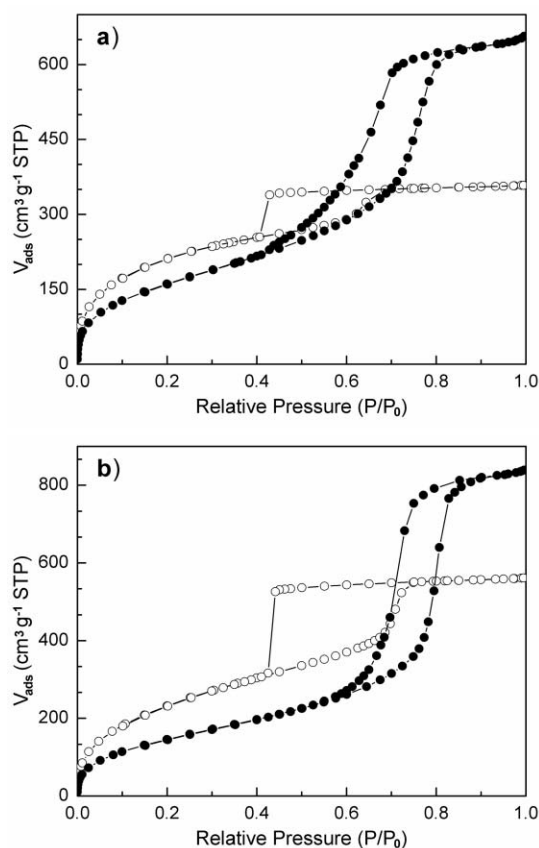

Fig. 1 Ar physisorption isotherms of cubic mesoporous silicas with fcc (a) or bcc (b) structures after conventional calcination at 550 °C (open circles) or H_2SO_4 treatment followed by calcination at 250 C (filled circles).

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the materials treated with H_2SO_4 show significantly higher adsorption capacity. Interestingly, the sorption isotherms for the acid-treated materials have H1-like hysteresis loops, which are remarkably different from those for the calcined samples. The H1-like hysteresis is usually attributed to uniform mesopores with cylindrical geometry.[13] Therefore, the difference in the features of the hysteresis loops seems to be correlated to different pore topology.

The elongation (tailing) of the desorption curve for the acid-treated fcc material is indicative of small fractions of pores with distributions of pore entrance sizes. The lower limit of the closure of the hysteresis loop occurs at a relative pressure slightly higher than that corresponding to the lower limit of the condensed fluid stability, which may exclude cavitation.[12] On the other hand, the isotherm of the acid-treated bcc material exhibits a distinctive hysteresis shape: The loop is narrower than that of the fcc phase and the closure of the desorption branch takes place well above the limit of stability of the fluid. This suggests the presence of pores with wide entrances of more uniform size. Analysis methods based on non-local density functional theory (NLDFT) were chosen to characterize the textural properties of the samples, and the results are shown in Table 1. Significantly larger pore volumes were measured for acid-treated materials compared to calcined samples. However, the highest surface areas are observed for calcined samples, a fact which might originate from a substantial contribution of intrawall microporosity usually present in the silica materials templated by polyalkylene oxide-based block copolymers.[13,14]

Both calcined samples show a bimodal pore size distribution (PSD), with a broad distribution of small pores centered at 1.9 nm accompanying the main mesopore cages of 5.7 nm for the fcc sample and 6.8 nm for the bcc material (see ESI† Fig. S1). On the other hand, the samples with H_2SO_4 treatment exhibit larger pores with one main maximum in PSD centered at 7.9 nm for fcc and 8.8 nm for bcc samples, respectively. Moreover, these acid-treated samples seem to exhibit very low microporosity in the pore walls, as also concluded from analyses of comparative plots (Table 1). This is in contrast with the observations made for hexagonal mesoporous SBA-15 silica made with a different triblock copolymer with shorter hydrophilic ethylene oxide (EO) chains (Pluronic P123, $EO_{20}PO_{70}EO_{20}$). This reduced microporosity in the acid-treated materials might be related to pronounced segregation of silica and large EO domains in the mesophase,

caused by extensive silica condensation triggered in wet acidic conditions. Further investigation is in progress to clarify this particular aspect. Compared to strategies based on blends of the copolymers or extensive thermal treatments,[15,16] the method based on H_2SO_4 treatment emerges as a potential alternative to achieve uniform expansion of the pore size and pore entrances.

The powder X-ray diffraction (PXRD) patterns of the acid-treated mesophases, depicted in Fig. 2, are shifted to the lower two-theta region as compared to the calcined samples but still can be clearly indexed to the same fcc and bcc phases. This suggests that no collapse of the mesostructure or major structural transformation in terms of symmetry occurs during the treatment with H_2SO_4. The unit cell parameters (Table 1) are, however, noticeably larger for the acid-treated materials. Thus, the larger mesopore size and pore volume observed for acid-treated materials might result from reduced shrinkage of the mesostructure. TEM investigations further confirm highly ordered cubic structures after the harsh acid treatment, as exemplified in Fig. 3 for the case of the bcc mesophase (see also ESI† Fig. S2). Direct visualization of the pore geometry and connectivity of the acid-treated silica is made possible by imaging these materials with the pores infiltrated with platinum.[10,17] This method is used here in combination with gas physisorption in an attempt to obtain more detailed information. Fig. 3b shows an example of the TEM image of such a composite of acid-treated bcc mesophase with infiltrated Pt. The metal nanostructures reflect a highly interconnected 3-D cubic network of large mesopores. Furthermore, the shape of the infiltrated Pt seems to be necklace-like along the pore axis, which may suggest a pseudo-cylindrical pore geometry consisting of arrays of regularly undulating channels rather than discrete spherical cavities. Such a pore system may originate from structural rearrangement induced during silica condensation in the acid treatment, generating wide pore entrances and, most likely, pronounced modulation of pore surface curvature. Comprehensive high-resolution transmission electron microscopy investigations will be useful to clarify all these structural aspects.

To check whether the open pore system is indeed created upon H_2SO_4 treatment but not as a consequence of suppressed

Table 1 Structural properties of the fcc and bcc samples after calcination at 550 °C or H_2SO_4 treatment followed by calcination at 250 °C[a]

Symmetry	Method[b]	a/nm	S^c/ m^2 g^{-1}	V_t/cm^3 g^{-1}	V_m^e/ cm^3 g^{-1}	D^c/ nm
fcc	A	20.9	833	0.45 (0.45)[d]	0.13 (0.16)	5.7
	B	21.8	662	0.82 (0.83)	0.04 (0.00)	7.9
bcc	A	16.2	786	0.70 (0.71)	0.08 (0.06)	6.8
	B	18.4	581	1.05 (1.07)	0.02 (0.00)	8.8

[a] a: unit cell parameter; S: surface area; V_t: total pore volume; V_m: micropore volume; D: mesopore diameter. [b] Method A: conventional calcination at 550 °C; method B: H_2SO_4 treatment followed by 250 °C calcination. [c] Calculated by the NLDFT method using the adsorption branch. [d] Pore volume at $P/P_0 = 0.99$. [e] Evaluated from the cumulative pore volume obtained by the NLDFT method for all porosity below 2 nm. In parentheses are the values obtained from α_s plot using Ar on nonporous silica as reference isotherm.
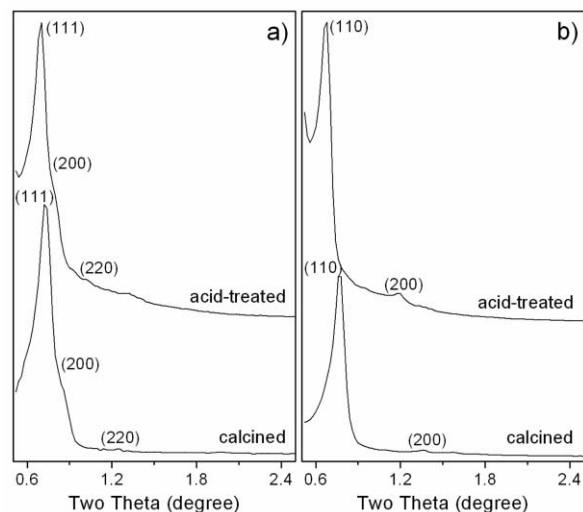

Fig. 2 PXRD patterns of calcined and acid-treated samples with fcc (a) or bcc (b) structures.
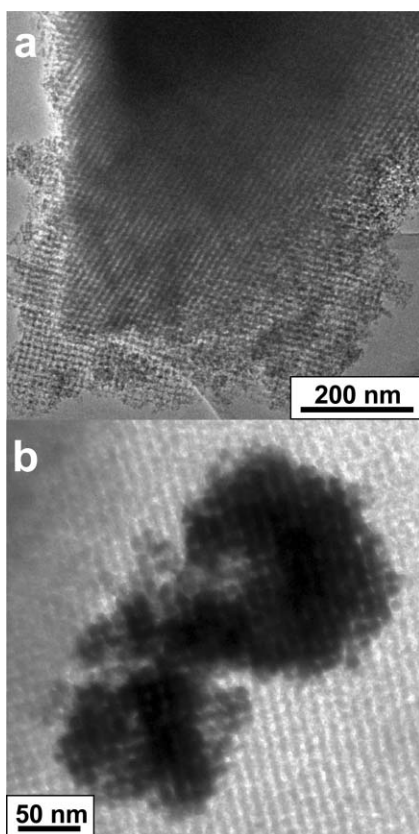
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Fig. 3 (a) TEM image of the cubic bcc silica obtained after H$_2$SO$_4$ treatment and subsequent calcination at 250 °C viewed along the [100] axis. (b) TEM image of the composite of the same silica with infiltrated Pt.

framework shrinkage, we performed Soxhlet extraction of the copolymer with pure ethanol. This soft treatment enabled the removal of large amounts of copolymer without initiating silica condensation.[18] Nitrogen physisorption (see ESI† Fig. S3) measurement of these extracted materials resulted in type IV isotherms with H2 type hysteresis identical to those of the calcined counterparts. This hence provides clear evidence that the mesophase topology is initially cage-like prior to template removal. We can speculate that during the H$_2$SO$_4$ treatment, the extensive silica densification facilitated by the highly acidic environment, combined with oxidative cleavage of the copolymer,[19] provoke profound restructuring of the framework.

In conclusion, a new method to control the pore topology of large pore cubic silica mesophases through post-synthesis treatment with sulfuric acid has been demonstrated. The thus-treated materials exhibit larger unit cell parameters, larger pore volumes and larger mesopore diameters than those for the materials prepared *via* conventional calcination. In addition, the treatment results in materials with pseudo-cylindrical mesopores while maintaining the overall cubic symmetry.

Acknowledgements

Notes and references

‡ Both SBA-16 and KIT-5 silicas were synthesized with Pluronic F127 (EO$_{106}$PO$_{70}$EO$_{106}$) as the structure directing agent and TEOS as the silica source. The reactions were performed at low HCl concentration (0.4 M) at 45 °C for 24 hours, followed by subsequent hydrothermal aging at 100 °C for another 24 hours. The details of the synthesis are reported elsewhere.[4,11] For the template removal, the as-synthesized silica–Pluronic mesophases were either extracted in a HCl–ethanol mixture and then calcined at 550 °C,[11] or subjected to H$_2$SO$_4$ treatment.[9,10] Briefly on the treatment, 2 g of the as-synthesized mesophase was stirred in 250 mL 48 wt% H$_2$SO$_4$ solution at 95 °C for 24 hours. After cooling, the solid was recovered by decantation and filtration, and then washed with distilled water and acetone successively, yielding a white powder. To achieve complete removal of residual organic species, the powder was further heated at 250 °C in air for 3 hours.[10] Pt/silica composites were prepared and visualized following methods described previously.[10,17] Ar physisorption isotherms were measured at 87 K using a Micromeritics ASAP 2010 sorption unit. The kernel of NLDFT equilibrium capillary condensation isotherms of Ar at 87 K on silica assuming cylindrical pores was selected for the model isotherm. Small deviation may occur in the case of cage-like materials since the pore geometry is closer to spherical, which could lead to possible underestimation of pore sizes. PXRD patterns were obtained on a Mac Science 18MPX diffractometer in the reflection mode using Cu Kα radiation. The TEM images were obtained with a JEOL JEM-2010 electron microscope.

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