Time-resolved SAXS Study of a New Mesoporous Silica MMT-1 Materials

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Most of the surfactant-templated mesoporous materials [1] display pore topologies closely related to those for the liquid-crystal-like phases typical of surfactant-water systems [2]. Among them, the materials (for example SBA-8) [3] with 2D centered-rectangular (plane group *c2mm*) lattice, correlated to the ribbon-intermediate phases, may be regarded as deformed structures of the hexagonal mesophase in which the cylindrical micelles are flattened [4]. The elliptical channels resulted from the structural deformation are of special interest because of the additional anisotropy of the channels, but it remains a challenge to discover new synthetic strategies to control and extend the degree of the structural deformation.

Here we report the synthesis of *c2mm* mesoporous silica materials with tunable lattice dimensions and tunable elliptical channel section [5]. The synthesis was performed in a dilute solution of cationic cetyltrimethylammonium bromide and nonionic tetraethylene glycol dodecyl ether using tetraethoxysilane as a silica source and sodium hydroxide as a base catalyst. By increasing the molar ratio of the nonionic surfactant in the surfactant mixture, the structure of the resulting materials evolved from *p6mm* to *c2mm* symmetry suggested by the powder X-ray diffraction patterns of the materials. As indexed with a rectangular lattice, the ratio of the unit cell parameter *a* and *b* increased from $\sqrt{3}$ (~1.73) to 2.73. The results clearly show that the hexagonal structure is transformed to *c2mm* mesophases which can be modulated by simply adjusting the molar fraction of nonionic surfactant.

The formation of the MMT-1 material was studied by time-resolved small-angle X-ray scattering (SAXS), and the results are shown in Fig. 1. A mesostructured phase was formed at about 19 min after adding tetraethoxysilane, suggested by the appearance of a Bragg reflection (q=0.134 $Å^{-1}$) corresponding to a d-spacing of 4.7 nm. The reflection evolved and split immediately after its appearance, and the two reflections continued to sharpen, increase in intensity and move away from each other. Additional high-ordered reflections appeared at a reaction time of 30 min and remained in position after then. The patterns could be indexed assuming a 2D-rectangular lattice. The fact that the calculated *a*/*b* ratio increased from 1.73 to 2.57 within ~10 minutes clearly shows a rather rapid structural deformation within that period.

Based on the data, we speculate that the condensation of the silicate species adsorbed preferentially onto the cetyltrimethylammonium cations might induce a segregation of the two surfactants, similar to that observed in a ribbon-like liquid crystal formed by mixed amphiphiles with different nature of the polar heads [4]. The segregated nonionic surfactant might form the flattened parts of the deformed rod-like micelles in the surfactant-silica mesophase with more silicate species around the highly curved parts of the elliptical micellar rods where the cetyltrimethylammonium cations are concentrated.

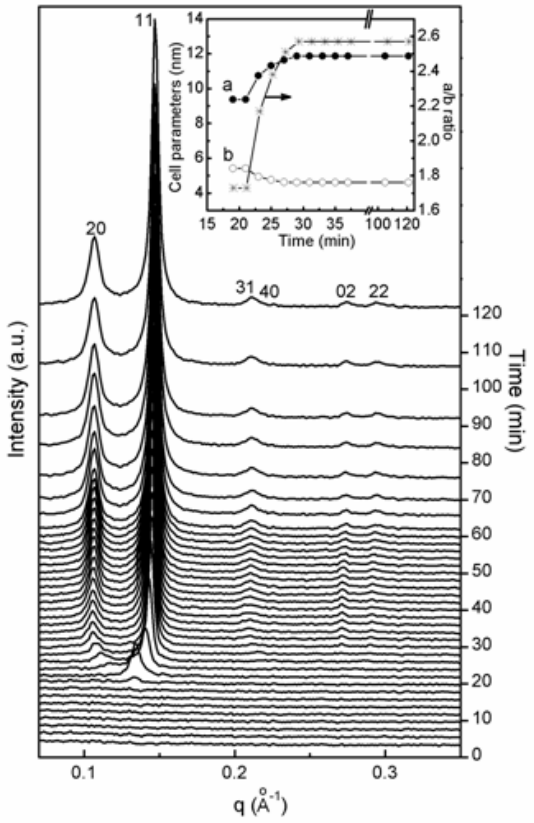

Fig. 1: Time-resolved SAXS patterns of MMT-1 materials.

References

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