In-Situ X-ray Diffraction/Scattering Study of Mesoporous Silica Nanoparticles

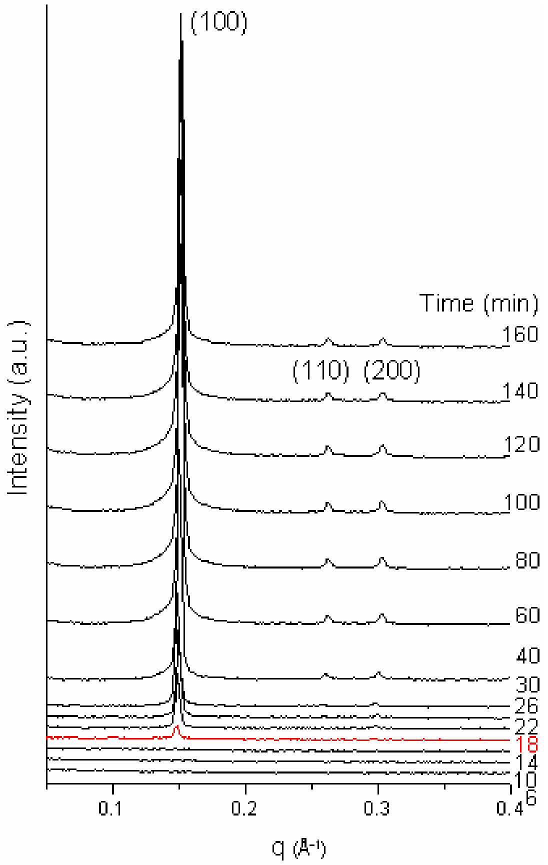
Ching-Yi Lin (林靜儀), Wei-Chia Huang (黃威嘉), and Chia-Min Yang (楊家銘)

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan

Ordered micro- and mesoporous materials are high-performance materials in their own right, but in addition they provide excellent opportunities for the creation of materials with additional functionality. Their regular pore system can be used to introduce molecules or particles that are stabilized by the solid framework and are spatially organized by the regular pore system. Mesoporous materials are generally synthesized via supramolecularly templating routes involving surfactants. In this field, one of the important topics is to control the ordered mesostructure and the morphology of the resulting materials [1]. Small mesoporous silica nanoparticles (MSNs) with dimensions of several hundreds of nanometers are of particular interests because they are potentially useful for biomedical applications. They have been engineered for gated drug delivery vehicles and for enhancing contrasts in the MRI imaging recently. For these applications, the size of the MSNs should be relatively small and uniform in size and shape. Various synthesis routes have been proposed for the control of morphology and size of MSNs and among them, controlled synthesis in the dilute solution of surfactants has been proven to be highly reproducible and controllable. In order to have even better control of the synthesis and to further modulate the mesoscopic structure, knowledge on the formation kinetics is crucial. In-situ X-ray diffraction/scattering is one of the best techniques for this type of kinetic studies, and we have recently established the experimental setup at Beamline 17B3 and have applied it to study the formation of trimodal micro/meso/macroporous SBA-15 silica materials [2].

The same setup has been applied in the past year to study the formation of mesoporous MCM-41 silica nanoparticles with p6mm symmetry. The synthesis started with the preparation of a dilute solution of a cationic surfactant cetyltrimethylammoniumbromide mixed with calculated amount of sodium hydroxide in the reactor. After slowly injecting tetraorthosilane into the reactor, the mixture was continuously pumped through a Kapton sealed thin container, through which the X-ray beam passed and then back to the reactor. Both the reactor and the container were thermostated to a desired temperature. The recorded X-ray intensity was converted and the resulting in-situ X-ray diffraction/scattering data were collected. Figure 1 shows the in-situ data of the synthesis of MCM-41 MSN. It can be clearly observed that one relatively sharp reflection appeared suddenly after a reaction time of 18 min, and two more reflections were observable 4 minutes later. These reflections can be indexed as the (100), (110) and (210) reflections of a 2-D hexagonal mesophase with ratios of the corresponding d-spacings of 1 : $1/\sqrt{3}$: 1/2. The calculated unit cell parameter (a_0) was 4.85 nm at 18 min. The intensity of (100) reflection continued to increase with time, which reflects an increase in the amount of ordered matter. On the other hand, the a_0 value remained the same during 18-30 min but started to decrease to 4.82 nm at 40 min and finally to 4.79 nm at 60 min. It suggests that for the MCM-41 MSNs the ordered structure forms at the very early stage of the synthesis, and the ordered domain continues to grow with certain degree of structural shrinkage. The same technique is applied to study the formation mechanism of other MSNs with different structures.

Figure 1. Time-resolved SAXS/XRD patterns of MCM-41 MSN materials.



Reference:
[1] Yang, C. M. and Chao, K. J.; J. Chin. Chem. Soc. **49**, 883 (2002).
[2] Hsu, Y. C.; Hsu, Y. T.; Hsu, H. Y.; and Yang, C. M.; Chem. Mater. **19**, 1120 (2007).