FORMATION MECHANISM OF MCM41 IN LAURYLAMINE/TETRAETHOXYSILANE SYSTEM USING SAXS BY SYNCHROTRON RADIATION

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We succeeded in the formation of silica nanotubes at pH 4.5 in laurylamine hydrochloride (LAHC)/ tetraethoxysilane (TEOS) system and elucidated the formation processes. [1,2] We also found that the integrated ordered microstructure such as hexagonal array was successfully formed in the same system only in the narrow pH region from 10 to 11.5 and that the liquid-liquid interface between the organic and the aqueous phases played an important role for the formation of the integrated ordered microstructure. [3] However, the formation processes of the integrated ordered microstructure have not yet been elucidated. In this paper, we elucidate the formation processes, which are very rapid and complete within 3 min, by small angle X-ray scattering (SAXS) measurements using synchrotron radiation.

We used a laurylamine (LA)/ TEOS system. The mixture of TEOS and LA was contacted with water. Synchrotron radiation at SPring 8 was used to measure the shape and size of the products of very rapid reactions by SAXS using strong X-ray (10^{13} photons/sec). First, the half volume of a cell for SAXS measurement was filled with water. The pass-length of the cell was 3 mm. The height of a X-ray was adjusted to the interface. The diameter of the X-ray was 200 μm. Then, a mixed solution of LA and TEOS was poured into the cell, and the reactions started. The intensity of the scattering X-ray was detected using CCD camera with image intensifier.

The formation processes of the integrated ordered microstructure of silica on the liquid-liquid interface were measured at the interval ranged from 1 sec to 6 sec for 10 min by SAXS method. Figure 1 shows an example of the results obtained at various time. The SAXS pattern obtained at 3 sec has no peak in the range of meso-size region, indicating that no integrated ordered structure formed. On the other hand, the SAXS patterns obtained in the range from 51 sec to 591 sec have clear peaks at the scattering vector s=0.27 1/nm, indicating formation of integrated ordered structure. The obtained s-value corresponds to the periodical distance 3.7 nm.

The obtained result at 3sec was plotted in Guinier plot for sphere. We got straight line, indicating particle formation of 0.35 nm. The intensity due to particles was subtracted from the observed intensity, and the difference intensity I-diff was obtained. The I-diff was plotted in Guinier type plot for cylinder formation as shown in Figure 2. Straight line showed clearly formation of cylinder. Thus, we assume formation of a co-axial cylinder comprised of the hydrophobic core surrounded by the hydrophilic shell composed of silica and hydrophilic head of surfactants. Putting electron density for each phase, we calculated the scattering intensity of the co-axial cylinder. Figure 3 shows the result with the parameters assumed. The experimental intensity agreed quite well with the calculated one, indicating that cylinders were formed first at random configuration. Then these cylinders were oriented on the 2-dimensional interface, followed by the formation of 3-dimensional integrated ordered microstructure.

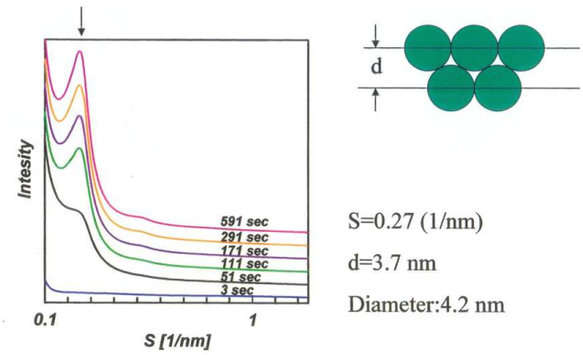

Figure 1. SAXS results obtained in the range from 3 sec to 591 sec. The mol ratio of TEOS to LA, [TEOS]/[LA]=0.5. The SAXS pattern obtained at 3 sec has no peak in the meso-size region. The SAXS patterns obtained in the range from 51 sec to 591 sec have clear peaks at about S=0.27 1/nm, corresponding to the periodical distance 3.7 nm.

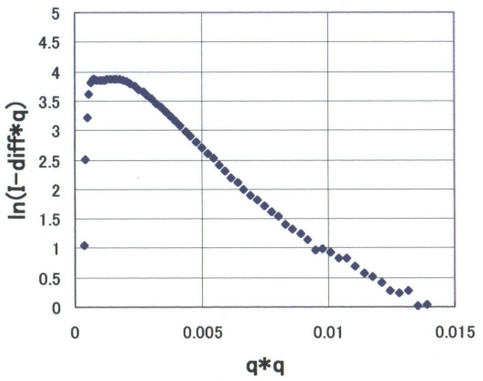

Figure 2. Guinier type plot for cylinder formation of the result obtained at 3 sec.

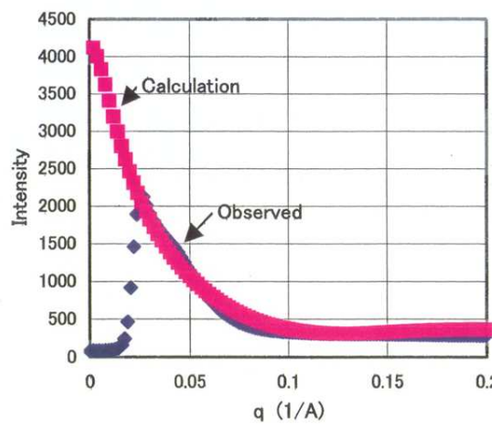

Figure 3. Comparison of observed intensity with the calculated one.

References

(1) Motonari Adachi et al. Langmuir, vol.15, 7097-7100(1999)
(2) Motonari Adachi et al. Langmuir, vol.16, 2376-2384(2000)
(3) Motonari Adachi et al. Transactions of Materials Research Society of Japan, vol. 25, 461-464(2000)