In-situ powder XRD experiments with gas adsorption for 3D cage type silica mesoporous crystals

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By a precise measurement of X-ray powder diffraction intensities as a function of amount of gas adsorption, the procedure of gas adsorption was studied at SPring-8, Japan, for the silica mesoporous crystals of the SBA-16. The changes of the intensities were clearly observed during gas adsorption process. The observed profiles were studied analytically in order to refine the parameters, such as, the pore shape, the thickness of adsorption-gas layer, and the density ratio of silica and gas. We can see clear correspondence between the gas adsorption data and our analyses, which will provide us a new insight for gas adsorption procedure.

Introduction: Various silica mesoporous crystals have been synthesised using self-organisation mechanism in surfactants, silica and water system. The crystals contain periodically arranged cages (e.g. SBA-16) or channels (e.g. MCM-41, MCM-48), called mesopore, supported by amorphous silica wall. The size of mesopore is normally estimated by a gas adsorption experiment, however the analysis contains a few assumptions. In the X-ray diffraction, structure is studied through the Fourier components of the electron distribution of the object. Not only unit cell length but also the pore geometries (pore shape and diameter) of the MCM-41 have been studied by an analytical approach[1)]. It is possible to study the gas adsorption process in the mesoporous crystals directly by diffraction process and to give a new insight to the gas adsorption process by comparing with the gas adsorption data. In the previous study, the gas adsorption process of MCM-41 (2D, *p6mm*) was done. In this study, the result of XRD is correspondent with the result of gas adsorption analysis[2)].

SBA-16 has a body centred cubic structure with spherical cages. SBA-16 shows a big hysteresis in gas adsorption-desorption process while MCM-41 doesn't. The difference in gas adsorption characterisc can be explained by the differences in pore shapes and their geometries. From gas adsorption analysis, however, it is hard to obtain the information of the pore shape and pore arrangement. Here we have measured powder XRD intensities precisely of SBA-16 as a function of gas pressure in order to understand basic gas-adsorption process in silica mesoporous crystals.

Experiment: In-situ synchrotron powder X-ray diffraction profiles were observed at 90K as a function of N_2 or Ar gas loading at BL02B2 line

in SPring-8, Japan. The observed intensities at different loadings were normalised by (i) duration of exposure times and (ii) diffraction intensities from a small amount of internal standard of α-Al_2O_3.

Result and Discussions: The observed XRD patterns are shown Fig.1. Two Bragg peaks are clearly observed at each pressure. The dependences of 110-reflection intensities of the SBA-16 on the gas pressure are shown in Fig. 2. These intensities are normalised by the exposure times. Abrupt changes were observed at the pressure where capillary condensation took place, and clear hysteresis in adsorption-desorption was clearly observed. The quantitative analyses are in progress.

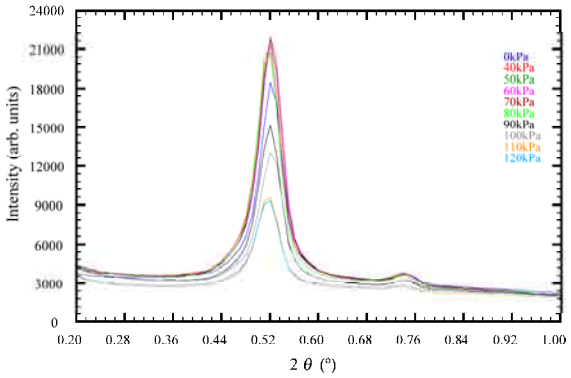

Fig. 1: Observed XRD intensity profiles of SBA-16 with N_2 gas adsorption process.

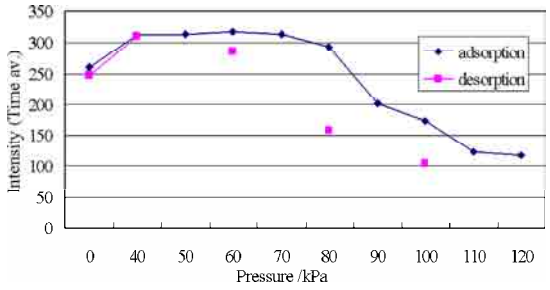

Fig. 2: Observed intensities for 110-reflection vs. N_2 gas pressure for SBA-16

References

[1] N.Muroyama et al., *J. Phys. Chem. B* **2006**, *110*, 10630

[2] N.Muroyama et al., *in preparation*