In-situ powder XRD experiments with gas adsorption for 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 MCM-41 and MCM-48. 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 or channels, 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.

The changes of the unit cell parameter and the thickness of the gas layer were reported for the MCM-41[2)]. However, the authors observed three peaks at each pressure, and only the first peak had enough intensity for quantitative analysis. It is necessary to improve a quality of observation in order to discuss the gas adsorption procedure quantitatively, we performed a synchrotron in-situ XRD experiment using calcined MCM-41 and

MCM-48 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 observations 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. Four Bragg peaks are clearly observed at each pressure. The dependences of integrated intensities and the unit cell parameter of the MCM-41 on the gas pressure are shown in Fig. 2 and Fig. 3, respectively. Abrupt changes were observed at the pressure where capillary condensation took place. The quantitative analyses are in progress.

References

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

2) P. Albouy and A. Ayral, *Chem. Mater.* **2002**, 14, 3391

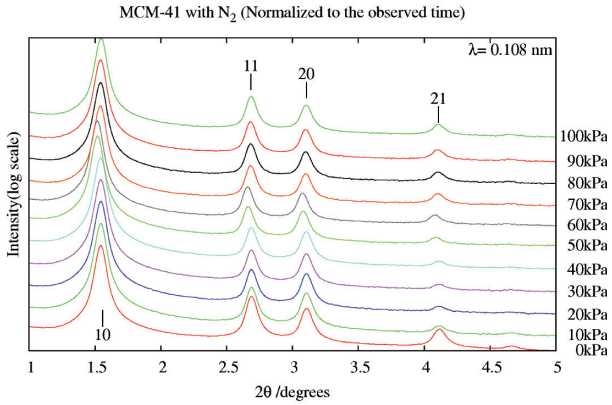

Fig. 1 Observed XRD intensity profiles of MCM-41with N_2 gas loading

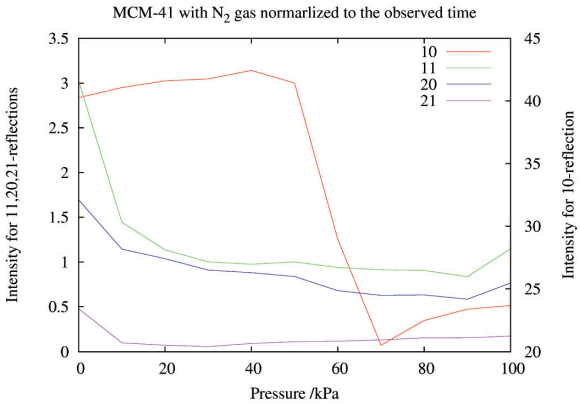

Fig. 2 Observed intensities for each reflection vs. N_2 gas pressure for MCM-41

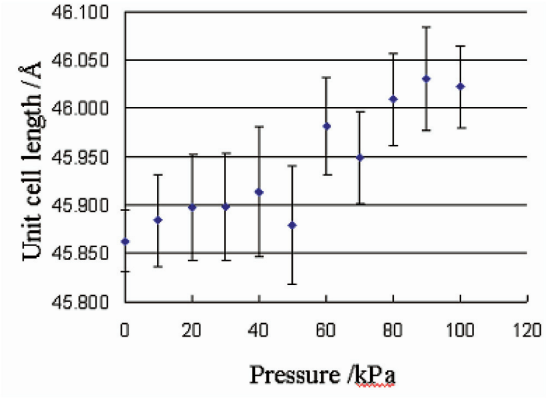

Fig. 3 Dependence of unit cell parameter on the N_2 gas pressure for MCM-41