In-situ gas adsorption powder XRD measurement for 3D bimodal cage type silica mesoporous crystal AMS-8

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By a precise measurement of X-ray powder diffraction intensities as a function of amount of gas adsorption and desorption, the gas adsorption process was studied at SPring-8 in Japan, on the silica mesoporous crystals of the AMS-8 material. The changes of the intensities were clearly observed during gas adsorption process. The observed profiles were analyzed 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. It can be seen that there is a clear correspondence between the gas adsorption data and our analyses, which will provide us a new insight for gas adsorption procedure in periodic mesopores of mesoporous crystals.

Introduction: Silica mesoporous crystals have been synthesised through cooperative self-assembly of surfactants and silicas in water. The crystals characteristically show periodic arrangement of mesopores, supported by amorphous silica wall. The size distribution of mesopore is normally evaluated by gas adsorption experiment assuming a certain geometry of the mesopores: slit, cylinder, or cage types. By X-ray diffraction (XRD) measurements, the structure is studied through the Fourier components of the electron density distribution of matter. Besides the cell parameters, the geometry of mesopores can be evaluated.[1] Combined with the gas adsorption data, it is possible to trace changes of fluid film during the gas adsorption and discuss the gas adsorption process within periodic pores of the mesoporous crystals.[2] AMS-8 is a silica mesoporous crystal composed of bimodal interconnected cages arranging with space group *Fd*-3*m*. This structure refers to a minimal D-surface of which the surface divides space into two distinct subspaces. Each subspace is occupied by large(L) and small(S) cages, respectively. From the result of TEM observation along with electron crystallography, we found that a sequence of L cages can be regarded as bumped cylinders rather than cages, while S cages are allocated as spheroidal cavities.[3] The gas adsorption process in such geometry is of interest. The attempt in this study was to perceive information about the gas adsorption process by extending our previous study to the geometry of AMS-8.

Experiment: In-situ synchrotron powder X-ray diffraction profiles were observed at 90K as a function of N_2 gas loading at BL02B2 line in SPring-8, Japan. The observed intensities at different loadings were scaled by (i)duration of observations and (ii)diffraction intensities from a

small amount of internal standard of α-Al_2O_3.

Result and Discussions: We have observed two strong peaks of 220 and 311, and a few broad peaks involving reflections up to 440. The cell parameter was 15.2 nm. ***Figure*** shows the integrated intensities of (a)111 and (b)220 and 311 reflections at different pressures. The adsorption and desorption branches seemingly show a slight hysteresis. The intensity dependence of 111 reflection on N_2 gas pressure suggests that N_2 adheres onto S cages rather than L cages in the first stage with the increasing pressure. We roughly confirmed that the simulated intensity change in 111 reflection agreed with the observed one, where a 3D structure model obtained from electron crystallographic result was used for AMS-8 mesostructure. We are currently in progress for further quantitative analysis combined with the quenched solid density functional theory[4] for spherical pore geometry, which has been under development recently.

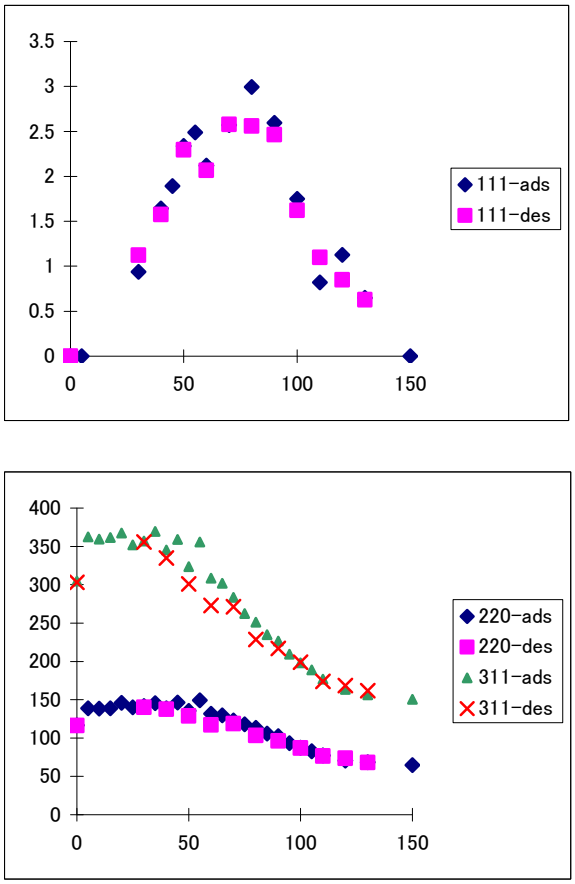

Figure: Absolute intensity of N_2/AMS-8 as a function of pressure at 90K. (a)111 reflection. (b)220 and 311 reflections.

References

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