In-situ gas adsorption powder X-ray diffraction measurement for 3D large cage-like mesoporous crystal SBA-16

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Through measurements of powder X-ray diffraction intensities as a function of nitrogen gas pressure, the gas adsorption process onto a large cage-like mesoporous silica SBA-16 material was studied using a beam line BL02B2 at SPring-8 in Japan. The changes of the intensities were clearly observed during the nitrogen adsorption process. The observed profiles were analyzed to refine the parameters, such as, the pore diameter, the thickness of the adsorbed gas layer, and the density ratio of silica and nitrogen. It can be seen that there is a clear correspondence between the gas adsorption data and our analyses, which will provide us information about the gas adsorption procedure within the periodic mesopores of SBA-16 mesoporous crystal.

Key word: Silica mesoporous material, in-situ powder X-ray diffraction, gas adsorption process

Introduction :

Silica mesoporous materials have attracted a lot of attention since the first reported preparation in the early 1990s,[1] because of the advancements from a synthetic, characterization, and applications perspective, which have given rise to a rapidly developing field centered on the co-assembly of surfactant molecules with silica and non-siliceous precursors. For example, the use of polymer surfactants has allowed expansion of the pore size to larger sizes, while applications in chemical sensing, photocatalysis, and optics are currently being investigated. The use of silica mesoporous solids as hard templates for carbon replicas and polymer-carbon composites is also attracting a lot of interest as the resultant materials exhibit surface properties of the polymer as well as the electric conductivity of the carbon network, which could provide new possibilities for advanced applications.

An ordered silica mesoporous material, SBA-16, is a member of SBA-n family prepared using non-ionic triblock copolymers as the structure-directing agents. SBA-16 comprises large cage-like mesopores that are placed at the body-centered cubic lattice points, and shows well-defined pore size distribution along with high surface area and good thermal stability. SBA-16 possesses random micropores and periodic mesopores where the individual mesopore is surrounded by the micropores. The gas adsorption process in such a confined geometry is of interest, and attempt in this study is to provide information about the mesopore structure and gas adsorbed onto the cage-like geometry with the changing gas pressure.

Experiment :

In-situ synchrotron powder X-ray diffraction profiles were observed at 90K as a function of nitrogen gas pressure, at BL02B2 line in SPring-8, Japan. The observed intensities at different loadings were rescaled by (i)duration of the observations and (ii)diffraction intensities from a small amount of the internal standard of α-Al_2O_3.

Result and Discussion :

Seven reflections have been detected during the measurement: a strong peak of 110, and six weaker reflections of 200, 211, 220, 310, 222 and 321. Their integrated intensities have been extracted using Le-Bail analysis implemented by YK, and the cell parameter determined through the process was 15.3 nm. Figure 1 shows, with the changing pressures, the transition of the observed intensities for (a)100, (b)200 and 211 reflections. Intensities of these reflections show sudden changes. The adsorption and desorption branches seemingly show no hysteresis loop.

By extending our previous modelling for 2D hexagonal mesostructure MCM-41,[2] a structure for the simplified large cage-like mesopore of SBA-16 and the film of gas adsorbed at a pressure was modelled as the nitrogen gas with a constant electron density piles up, maintaining the spheroidal symmetry, on the solid approximated as an electron density distribution binarized from the mesopore.[3] Moreover, a Gaussian term was introduced to represent possible structural fluctuations. In this setup the form factor will be given by

$$-\exp\left[-2\pi^2\mu^2a^2{q_{hkl}}^2\right]\times$$
$$\left[(1-\rho)\cdot\frac{\sin(\pi q_{hkl}ca)-(\pi q_{hkl}ca)\cos(\pi q_{hkl}ca)}{2\pi^2{q_{hkl}}^3}\right.$$
$$\left.+\rho\cdot\frac{\sin(\pi q_{hkl}ca(1-t))-(\pi q_{hkl}ca(1-t))\cos(\pi q_{hkl}ca(1-t))}{2\pi^2{q_{hkl}}^3}\right]$$

where $q_{hkl}=\sqrt{h^2+k^2+l^2}/a$. Here a, c, μ, ρ and t represents the cell parameter, the mesopore diameter, the fluctuation parameter, the nitrogen fluid density and the nitrogen film thickness, respectively. Values of c and μ are denoted by the relative fractions to a. t is a fraction to the mesopore radius $ca/2$, and ρ is designated as a relative value to the presumed electron density of amorphous silica (~ 661 nm^{-3}).

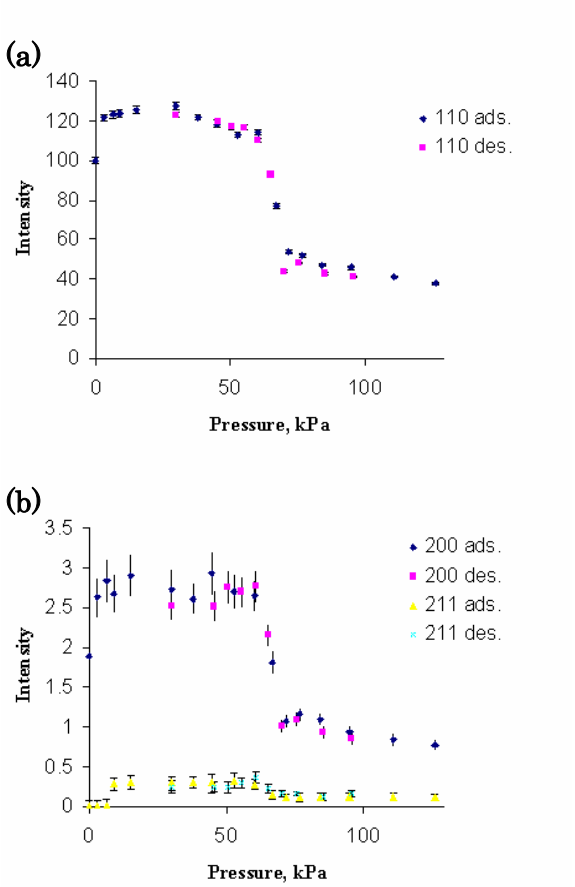

Figure 1. Integrated intensities during the nitrogen gas adsorption / desorption on SBA-16 as a function of pressure at 90K. (a)100 reflection (b)200 and 211 reflections.

The model has been fitted to the intensity transition in the adsorption branch by least-square minimization using R-factor. Current result for the structural parameters gives the mesopore diameter = 13 nm and the fluctuation ~ 4 nm. The evaluated nitrogen fluid density was 0.81 g/cm^3. Transition of the nitrogen film thickness is shown in Figure 2(a), and therefrom the electron density profiles at various pressures are reconstructed as shown in Figure 2(b). From this picture, the capillary condensation is expected to take place between pressures of 60 kPa and 72 kPa. We will further analyze the result in combination with the quenched solid density functional analysis designed for spherical mesopore geometry.

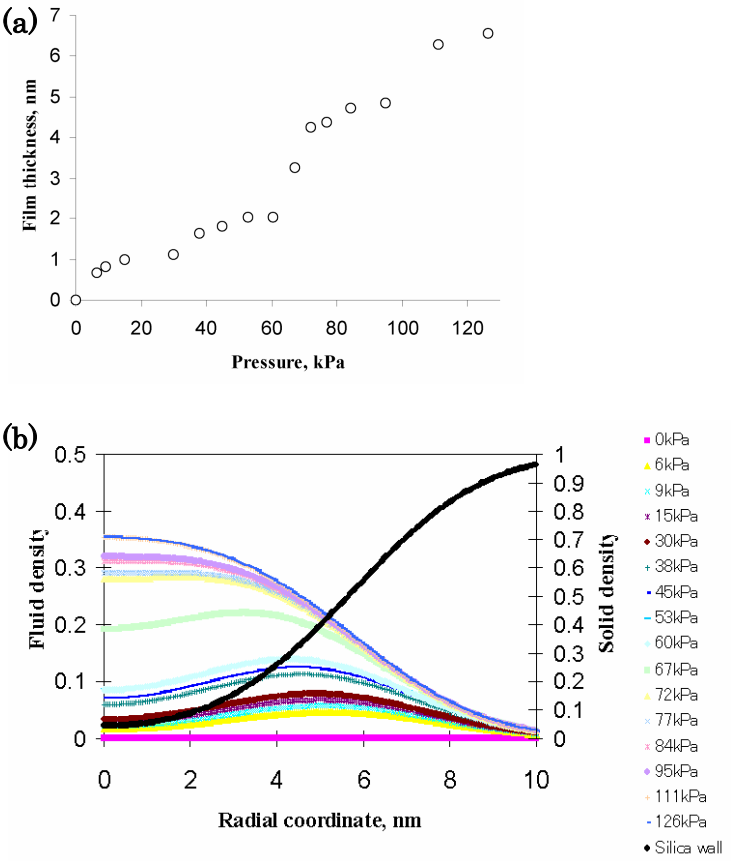

Figure 2. Film thickness of nitrogen gas as a function of pressure at 90K. (b)Reconstructed electron density profiles with the increasing pressures.

Conclusion :

By in-situ powder X-ray diffraction measured at various pressures, transition of the nitrogen film thickness is able to be traced as a function of the gas pressure in addition to the information about the mesopore structure of a large cage-like mesoporous silica SBA-16.

References :

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