In situ powder X-ray diffraction for argon adsorption on mesoporous carbon CMK-5

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Through measurements of powder X-ray diffraction (XRD) intensities as a function of the gas pressure, argon sorption into a mesoporous carbon material having the dual pore system, CMK-5, is studied using a beam line BL02B2 at SPring-8 in Japan. The change in intensities of the Bragg reflections was clearly observed during the adsorption processes. This is correlated to the alteration of the density contrast within the dual mesopores of CMK-5 mesostructure due to uptake of argon onto the two kinds of mesopores (inside and intermediate of the carbon rods) that are arranged in a manner of two-dimensional *p6mm* symmetry.

Key word: Carbon mesoporous crystals, in-situ powder X-ray diffraction, gas adsorption process, adsorption deformation

INTRODUCTION

Since the first advent of ordered mesoporous materials, they have attracted a lot of attention due to their potential to various applications: energy gas storages, separation and purification of molecules, catalysis, drug delivery system, etc. A mesoporous carbon material named CMK-5 has been synthesized by loading carbon on the silica mesoporous crystalline template or by carbonization process of ordered polymers within two dimensional channels with p6mm symmetry like MCM-41. After removal of hard silica template, CMK-5 consequently has two types of pore channels (dual mesopore system, *i.e.* internal and external pores of carbon rods) partitioned by the carbon wall. For chemical and medical applications of these materials, the accurate information about the mesopore structure and the adsorption process is essential.

In the present study, combining with the gas adsorption data, we investigate argon gas adsorption process in CMK-5 with *p6mm* plane group symmetry using *in situ* synchrotron powder X-ray diffraction (XRD). On the basis of the mesopore structure already established, we are able to observe structural change directly under the gas adsorption, which enables discussion about the gas adsorption process in the mesoporous carbon crystals.

EXPERIMENTAL

In situ synchrotron powder X-ray diffraction profiles were observed at 83K as a function of argon gas pressure, at BL02B2 line in SPring-8, Japan. It should be noted that the thermometer used was calibrated using the melting point of argon gas, which allowed more precise temperature indication compared to previous similar measurements.[1] The observed intensities at different loadings of argon were rescaled using a small amount of the internal standard of α-Al_2O_3. Le Bail analyses for the internal standard and CMK-5 were carried out using a program RIETAN-2000.

RESULTS AND DISCUSSION

Figure 1 shows the rescaled XRD profiles as a function of Ar pressure. Four Bragg reflections (10, 11, 20 and 21) were observed showing a definitive change in intensities. This change stems from the alteration of the mean electron density distribution in the carbon wall, internal and external mesopores caused by the adhesion of argon molecules onto the mesopores. Since two different kinds of channels exist (inside and intermediate of the carbon walls), it is expected that CMK-5 shows two-step pore condensation in the volumetric adsorption isotherm unless their pore sizes are identical. The corresponding change in XRD intensity, however, shows the gradual transition of the diffraction profiles. It suggests that the size distribution of the narrower mesopore is broad. The complete pore condensation occurs in between 57 kPa and 60 kPa, which can be noted by the eminent attenuation of diffraction intensities in the profile. Figure 2 shows the plots of the integrated intensities of all the observed reflections at various gas pressures. The integrated intensities were calculated by Le Bail method with the use of split-type Pearson VII profile function. All reflections increase their integrated intensities in the early stage of Ar adsorption. This phenomenon can be ascribed to the increase of the

electron density contrast between the carbon wall and the empty mesopore caused by the adsorption within the carbon wall.
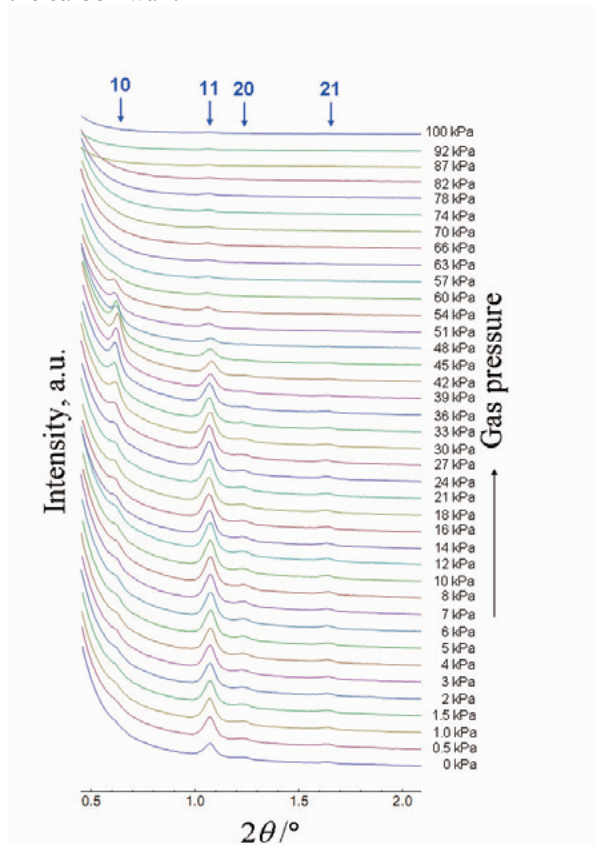

Figure 1. In situ powder XRD patterns at various pressures during argon adsorption on CMK-5 material. Peak shift was corrected using the internal standard.
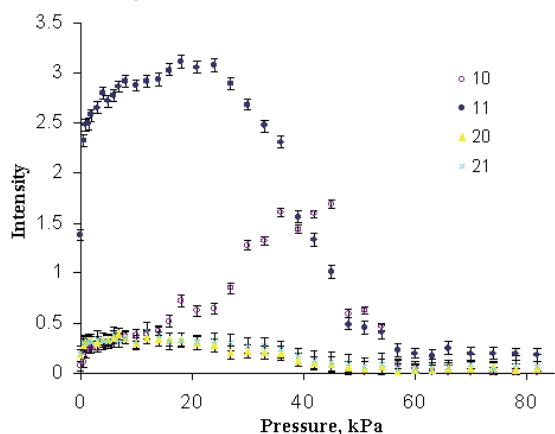

Figure 2. Change in integrated intensities with increasing pressure, where integrated intensities were extracted by Le Bail method with Pearson VII model.

For further analysis of gas adsorption in CMK-5, we first model the mesopore architecture as well as the structure of the fluid film adsorbed. By extending our previous modelling for 2D hexagonal mesostructure MCM-41[1], a structure for the dual mesopore system of CMK-5 and the film of gas adsorbed at a pressure was modelled as the argon fluid with a constant electron density maintaining 2D circular symmetry with a certain thickness for internal pores, and as an averaged electron density of fluid in external pores.

Moreover, a Gaussian term is introduced to represent possible structural fluctuations. In this setup, the form factor will be given by

$$-\exp\left[-2\pi^2\mu^2 a^2 q_{hk}{}^2\right]\times\{-\rho_{ex}F[0,\gamma_2 a/2](q_{hk})$$
$$+F[\gamma_1 a/2,\gamma_2 a/2](q_{hk})+\rho_{in}F[\gamma_1 a(1-t)/2,\gamma_1 a/2](q_{hk})\}$$

where $F[r_1,r_2]$ denotes Fourier transform from r_1 to r_2 for a uniformly distributed cylindrical object:

$$F[r_1,r_2](q_{hk})\equiv 2\pi\int_{r1}^{r2}J_0(2\pi q_{hk}r)rdr$$

Here, $q_{hk}=2\sqrt{h^2+k^2+hk}\big/(\sqrt{3}a)$. Parameters a, γ_1, γ_2, μ, ρ_{in}, ρ_{ex} and t represent the cell dimension, the internal mesopore diameter, the external mesopore (inter-rod pore), the fluctuation degree, the constant argon fluid density within internal pores, the average argon density within external pores and the argon film thickness in internal pores, respectively. All parameters are normalized in a relevant way described elsewhere[1]. Figure 3 shows the transition of the relative film thickness (internal) and of the averaged density (external pores). It is suggested that the external pore filling predominantly occurs at early stage of adsorption, and then the capillary pore condensation takes place simultaneously in both pores. Further refinement by this model with higher accuracy is in progress.
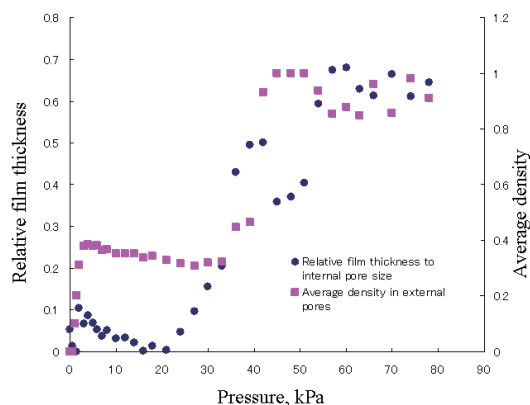

Figure 3. Transition of internal film thickness (left axis) and average density in external pore (right axis).

CONCLUSIONS

Using *in situ* powder XRD, diffraction intensities of the reflections from dual mesopore system CMK-5 were measured as a function of the argon gas pressure. Change in intensities of the Bragg reflections was clearly observed. It is suggested as argon adsorption process that the external intermediate mesopores of CMK-5 are first filled up, followed by the simultaneous mesopore condensation in both channels.

REFERENCES
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