

## ***In situ* powder X-ray diffraction study for argon adsorption on mesoporous carbon FDU-15**

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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 FDU-15 was studied using a beam line BL02B2 at SPring-8 in Japan. The change in intensities of the Bragg reflections was clearly observed during the argon adsorption and desorption processes. This is correlated to the alteration of the density contrast within the FDU-15 mesostructure due to uptake of argon onto the carbon tubular mesopores that are arranged in two-dimensional  $p6mm$  symmetry.

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

### **INTRODUCTION:**

Ordered mesoporous materials have attracted a lot of attention since the first reported preparation in the early 1990s,<sup>1)</sup> 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. As an 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 properties of the polymer on the surfaces as well as the electric conductivity of the carbon network, which could provide new possibilities for advanced applications.

The first successful attempt of generating mesoporous carbon crystals was by a method using silica as the hard template and then etching it away with HF or NaOH to create a replica of the silica template. Today the materials can be made by an organic-organic self assembly process. The extraction of the template is much easier in the latter method. The pore wall consists of amorphous carbon but the arrangement of the mesopores forms several different structures ( $Ia-3d$ ,  $p6mm$ ,  $Im-3m$ ,  $Fd-3m$  and  $Fm-3m$ ) with a pore diameters in the range from 2 to 40 nm.<sup>2)</sup>

In the present study, we investigate the mesoporous carbon FDU-15 with  $p6mm$  plane group symmetry by *in situ* synchrotron powder X-ray diffraction (XRD) profiles as a function of the amount of argon loading. In the XRD, structure is studied through the Fourier components of the electron density distribution of the object. Not only unit cell length but also the pore geometries can be obtained. By combining it with the gas adsorption data, we are able to observe structural change directly under the gas adsorption and discuss the gas adsorption process in the mesoporous carbon crystals.<sup>3-5)</sup>

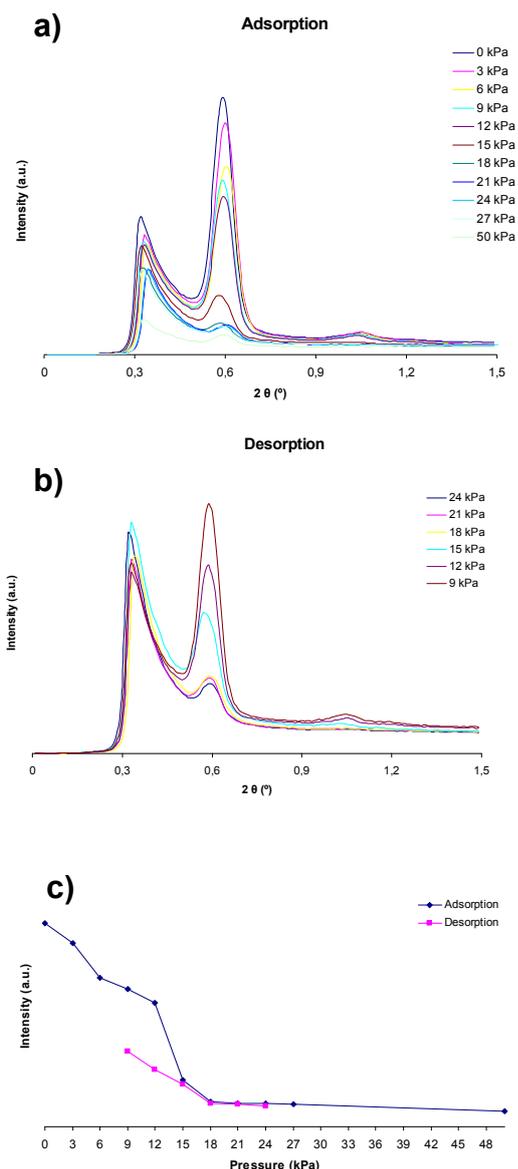
### **EXPERIMENTAL:**

*In situ* synchrotron powder X-ray diffraction profiles were observed at 90K as a function of argon gas pressure, at BL02B2 line in SPring-8, Japan. The observed intensities at different loadings of argon were rescaled using a small amount of the internal standard of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

### **RESULTS AND DISCUSSION:**

The scale factor for normalizing *in situ* XRD data collected at different pressures is estimated by Rietveld analysis on diffractions from the internal standard. Fig.1 shows the XRD profiles, of which the intensities are rescaled by the factor extracted, during argon adsorption and desorption at different pressures measured. Therein, 10 and 11 reflections were observable throughout the measurement. The intensities observed exhibits the clear change with

the argon gas pressure. The peak position seems also to be dependent on the argon gas pressure.

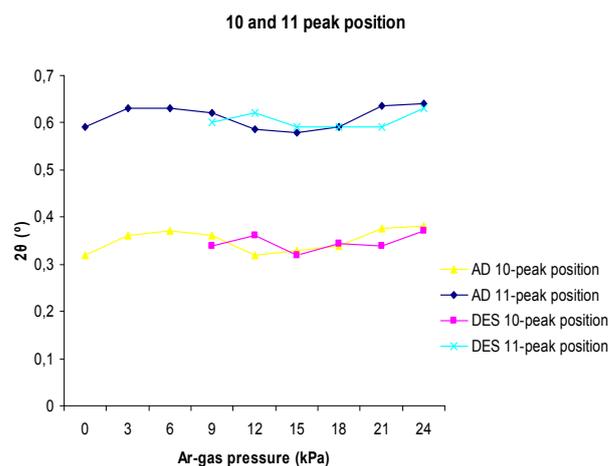


**Fig.1.** Observed XRD profiles (normalized) of FDU-15 during argon sorption. (a) adsorption and (b) desorption branches. (c) Plot of the integrated intensities vs. the pressure of argon gas.

The peak shift at different pressures is refined in terms of Bragg reflections from the internal standard. When looking more closely at the peak shift presented in Fig.2, a systematic trend can be seen, especially from 6 to 18 kPa that are considered as the capillary condensation / desorption pressures from the plot in Fig.1 (c). In the adsorption branch, the peaks are shift to higher angle suggesting the lattice contraction, followed by the swelling of the unit cell that makes the peak

position lower around 15 kPa. This observation can be explained by the adsorption-induced deformation of mesopores, and the trend we observed is consistent with the previous report.<sup>6)</sup>

We further intend to study the integrated intensity data extracted by the profile fitting toward the evaluation of the geometrical parameters of both the pore structure of FDU-15 and the fluid film structure of argon. An analysis for the fluid state confined in the regular mesopores is currently in progress.



**Fig.2.** Plot of the peak position ( $2\theta$ ) as a function of argon gas pressure at 90 K.

## CONCLUSIONS:

By *in situ* powder X-ray diffraction measured at various pressures, transition of the Bragg peak positions are able to be traced as a function of the gas pressure. The systematic change suggests that the change in the pore structure takes place during at least the adsorption branch, in particular in the vicinity of the capillary condensation expected, which is in accordance with the recent report in terms of the adsorption-induced deformation.

## REFERENCES:

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