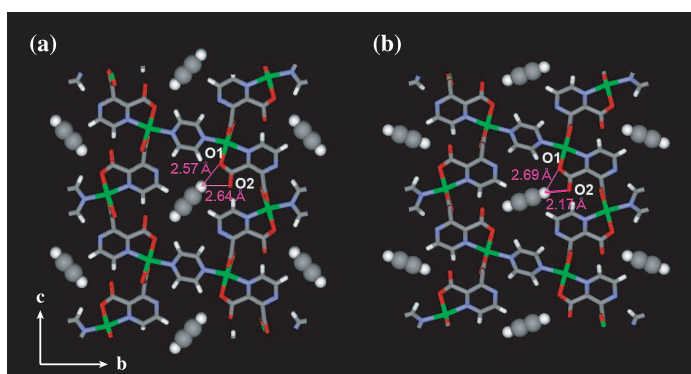


## OBSERVATION OF GAS ADSORPTION PROCESS ON POROUS COORDINATION POLYMER BY X-RAY DIFFRACTION

Metal-organic microporous materials (MOMMs) [1] have attracted the attention of scientists for a number of reasons including the creation of nanometer-sized spaces and the discovery of novel phenomena as well as commercial interests such as their application in gas separation, gas storage and heterogeneous catalysis. Recent activities in crystal engineering have provided several examples of MOMMs that have rigid open frameworks, and therefore have the potential to be functionally related to zeolites. MOMMs often have a much more dynamic framework than is generally believed, and the characteristic of metal-organic species. The structural rearrangement of the host framework responding to guest molecules proceeds from the “open” phase to the “close” phase. MOMMs could also be used as a unique class of materials, with unique characteristic unlike rigid porous materials. Although the sorption profiles of MOMMs with saturated amounts of guest molecules have been well characterized so far [2,3], their intermediate profiles are still unknown. It is important to determine how guest molecules are recognized, and finally confined by nanopores. An in-depth understanding of the intermediate state provides us with a feasible design for a porous framework, which changes its structure into one well suited for the desired guest molecules and results in an efficient accommodation system. Therefore, fundamental structural information on not only the host framework but also the guest molecules is required throughout adsorption phenomena. X-ray diffraction is one of the most powerful methods that

can directly provide structural information for adsorbed molecules. Herein, we report the structure analysis of an intermediate phase during gas adsorption in the nanochannels of a MOMM using *in situ* synchrotron powder diffraction at beamline **BL02B2** [4].

In our previous work [3], we reported acetylene gas adsorption on CPL-1 (coordination polymer 1 with pillared-layer structure:  $\text{Cu}_2(\text{pzdc})_2(\text{pyz})$ , where pzdc is pyrazine-2,3-dicarboxylate and pyz is pyrazine). From accurate structural analysis, acetylene molecules were found to be trapped by the non-coordinated oxygen atoms of carboxylate forming double hydrogen bonds. The *in situ* powder diffraction patterns of gas adsorption between the anhydrous hollow phase (phase I) and the saturated adsorbed phase (phase S) revealed another phase mixed with the saturated phase. In an acetylene adsorption isotherm, a step is recognized at about 0.7 molecules per unit pore during a steep rise at a low pressure region. These data suggest the existence of an intermediate phase (phase M) of adsorption. By carefully adjusting both the temperature and the gas pressure, we succeeded in obtaining phase M as a single phase at a pressure of 150 kPa at 360 K. A structure analysis was carried out using the MEM (maximum entropy method)/Rietveld method [5]. **Figure 1** shows the crystal structures of phases M and S. Acetylene molecules are located at the center of the nanochannel with one molecular site per unit pore. The refined occupancy factor of the acetylene molecule in phase M was 0.70(2) and shows very



**Fig. 1.** Crystal structures of CPL-1 with adsorption of acetylene viewed in nanochannel directions. (a) intermediate adsorbed phase M and (b) saturated adsorbed phase S. These figures show around one unit pore. Acetylene molecules are shown as balls. Other atoms are connected by lines. Acetylene molecules occupy the sites with a probability of 0.7 in (a).

good agreement with the step position in the adsorption isotherm. In phase M, the molecular axis of acetylene is perpendicular to the nanochannel direction and is on the line connecting the two oxygen (O1) atoms of carboxylate bonded to a Cu ion. This orientation is different from that in phase S in which the molecular axis is on the line connecting the non-coordinated oxygen (O2) atoms of carboxylate. The interatomic distance between the hydrogen atom of acetylene and the neighboring O1 atom is 2.57 Å, while the distance to the O2 atom is 2.64 Å. These values are approximately equal to the sum of the van der Waals radii of hydrogen (1.2 Å) and oxygen (1.4 Å), 2.6 Å. **Figure 2** shows the section MEM charge densities containing the molecular axis of acetylene. In phase M, few electron densities were observed

between the adsorbed acetylene molecules and the O1 atoms on the pore wall. In phase S, the acetylene molecules were trapped by hydrogen bonds between the acetylene molecules and the O2 atoms. From these results, the interaction of acetylene molecules with the oxygen atom site is much weaker in phase M than in phase S.

Figure 3 shows the acetylene adsorption isotherm and crystal structures of phases I, M and S. By acetylene adsorption, the pillar-ligands, i.e., the pyrazine-rings, slightly rotated and the crystal lattice sheared in the direction of the *a*-axis, indicating a flexible transformation for efficient guest accommodation in phase M. Subsequently, phase M changes to phase S with a slight rotation of acetylene molecules and then hydrogen bonds are formed with two non-coordinated oxygen atoms. With this change, there is now sufficient space for the pyrazine ring to rotate. The shearing of the lattice also occurs again to permit more efficient guest accommodation. In the change from phases M to S, unit cell volume decreases, where the lattice parameter *c* contracts with the change of the orientation of the acetylene molecule forming double hydrogen bonds with two oxygen atoms on the pore wall. However, the rotation of the pillar-ligand creates a space without changing pore volume significantly. At the same time, the change in the size and shape of the nanochannel causes more acetylene load to reach the saturation of adsorption.

Using X-ray structure analysis, we have succeeded in visualizing the rearrangement of guest molecules and the transformation of the framework during adsorption. These findings will contribute to the development of novel functional MOMMs responsive to guest molecules. More structural studies on gas adsorption process should be promoted to attain an in-depth understanding of adsorption phenomena.

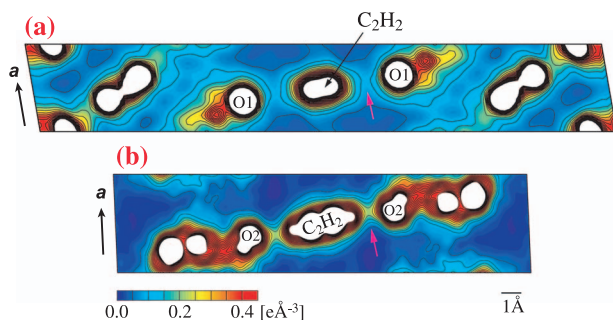


Fig. 2. Section MEM charge densities of CPL-1 with adsorption of acetylene containing molecular axis of acetylene and *a*-axis. (a) intermediate adsorbed phase M and (b) saturated adsorbed phase S. Contour lines are drawn from 0.00 to 1.00 eÅ<sup>-3</sup> with intervals of 0.05 eÅ<sup>-3</sup>. Higher density regions are omitted in the figure.

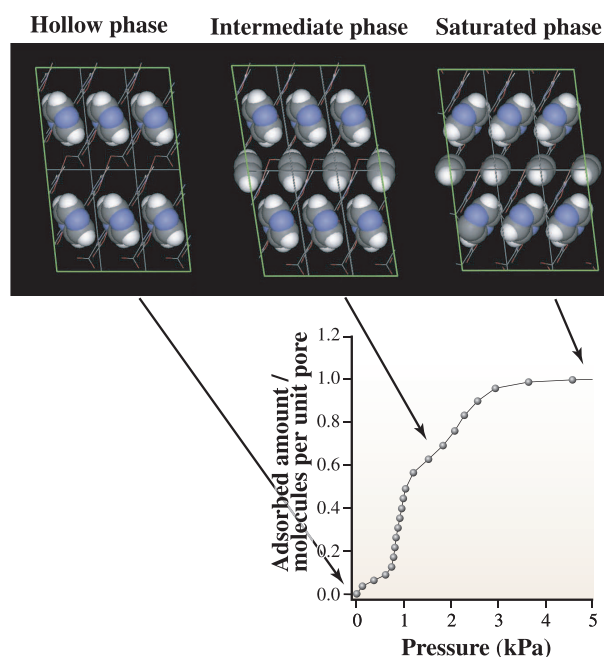


Fig. 3. Acetylene adsorption isotherm and crystal structures of CPL-1 with adsorption of acetylene corresponding to the amount of adsorbed gas. These figures are viewed from the side of the nanochannels. Pillar-molecules (pyrazine) and adsorbed acetylene molecules are shown by the space filling model. Other molecules are shown by connecting lines.

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