Direct Observation of O_2 Molecules Adsorbed in a Nanoporous Metal-Organic Solid

One-dimensional regular assembly of dioxygen molecules, which cannot be realized under normal conditions, has long been one of the most fascinating targets in chemistry and physics because of the keen interest in its magnetic and photophysical properties that are characteristic of low dimensionality [1]. One approach to the formation of a one-dimensional specific assembly of dioxygen molecules is to use a uniform nano-sized channel in a microporous compound. Molecules tend to be condensed in a nano-sized channel by a type of confinement effect resulting from dispersion-type attractive interactions of contiguous pore walls, which eventually form an ordered assembly well suited to regulated pore geometry. A clue to a regular one-dimensional assembly is the creation of well-regulated channel structures. Crystalline microporous coordination polymers possessing uniform low-dimensional channels are relevant for a host framework where guest molecules are confined in their channels [2-4]. Here we report the first direct observation of dioxygen molecules physisorbed in nano-channels of a microporous copper coordination polymer by the MEM (Maximum Entropy Method)/Rietveld Method using *in situ* high-resolution synchrotron X-ray powder diffraction measurements on beamline **BL02B2** [5].

For this purpose, we employed a microporous copper coordination polymer with pillared layer structure (**CPL-1**), which possesses one-dimensional nano-channels with a cross section of 4 × 6 Å^2. Figure 1 shows *in situ* powder X-ray diffraction patterns of as-synthesized **CPL-1** and anhydrous **CPL-1** with oxygen at 80 KPa over a temperature range of 300 to 90 K. The powder diffraction pattern changes significantly (i) after heating under reduced pressure to remove water molecules, (ii) during the cooling process between 130 K and 150 K, and (iii) during the reheating

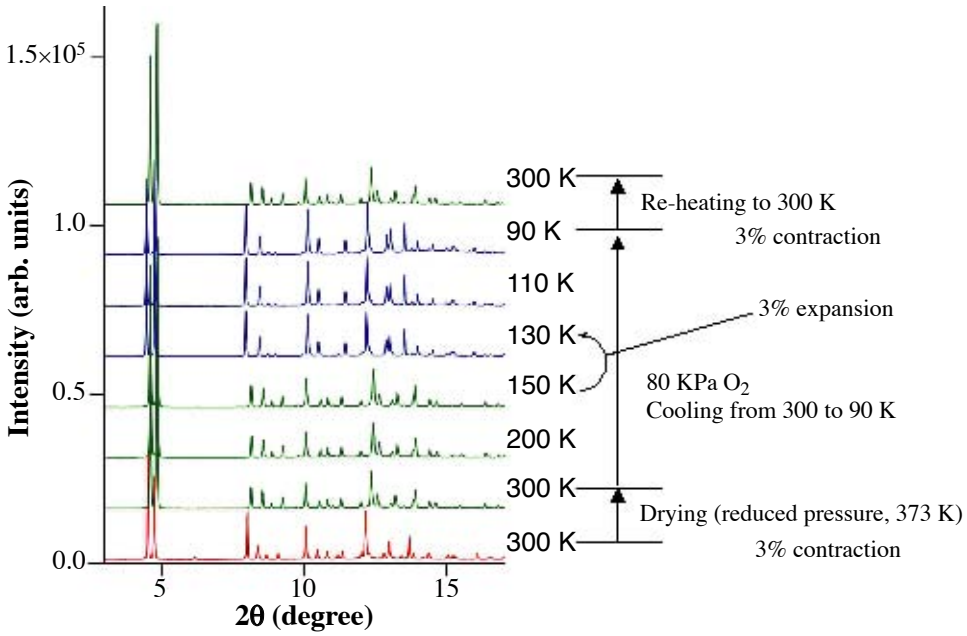

Fig. 1. Temperature-dependence of synchrotron XRD patterns of CPL-1 at 80 KPa of O_2.

process from 90 K to 300 K. No change was observed without any oxygen molecules over the whole temperature range studied.

Crystal structure of anhydrous **CPL-1** at 90 K without O_2 molecules determined by Rietveld analysis revealed that the porous structure was identical to as-synthesized **CPL-1** with slight structure distortion. MEM/Rietveld analysis proved significantly that no water molecule exists in the nano-channel (Fig. 2(a)).

Cell parameters of the anhydrous **CPL-1** with O_2 of 80 KPa at 90 K (space group $P2_1/c$) were determined by Rietveld analysis as follows: a is 4.68759(4) Å, b 20.4373(2) Å, c 10.9484(1) Å, and β 96.9480(6)°.

The reliability (R) factor based on the Bragg intensities R_I and the weighted profile R factor R_{wp} of the final Rietveld fitting were 3.9% and 2.1%, respectively. The final electron densities, obtained by the maximum-entropy method with reliability factor R_F of 1.5%, clearly reveal the 3-D pillared-layer structure, which is consistent with single-crystal data. Figure 2(b) shows the perspective view of the electron density distribution map along the a-axis; front view and side view. The earthnut-shaped electron densities, which are presumably due to O_2 molecules, are clearly recognized in the mid of channels. The relatively small value of isotropic displacement parameter (B 4.1(2)) and no disorder of O_2 molecules indicate that O_2 molecules adsorbed in the nano-channel is like solid state rather than liquid state at 90K which is much higher than the freezing point of O_2, 54.4 K at atmospheric pressure. Interestingly, two O_2 molecules align parallel with each other along the a-axis with intermolecular distance of 3.28(4) Å which is much smaller than the one corresponding to the minimum of the Lennard-Jones potential (Re = 3.9 Å). This intermolecular distance is comparable to the distance between the two nearest molecules in solid α-O_2, which is stable below 24 K at atmospheric pressure. This indicates that O_2 molecules adsorbed in the nano-channel form van der Waals dimers ($(O_2)_2$), whose successful structural characterization has not been reported yet. Each dimer aligns along the a-axis to form 1-D ladder-like structure.

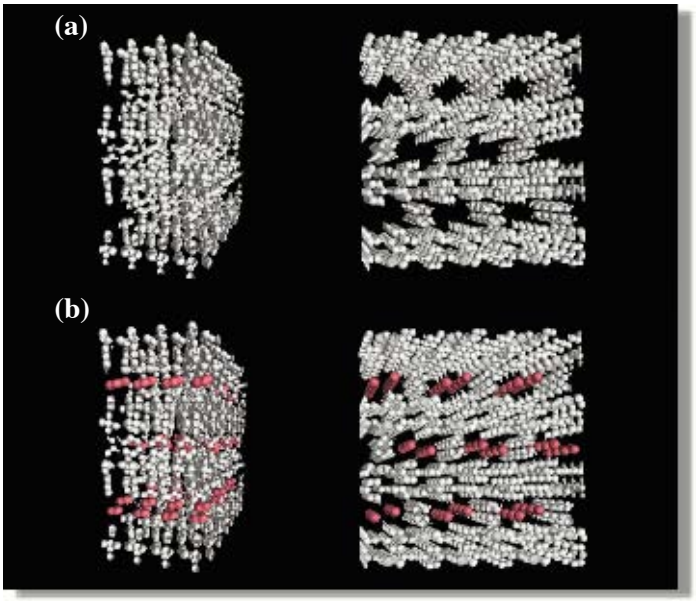

Fig. 2. MEM electron density maps of ***(a)*** *anhydrous CPL-1 without O_2 molecules at 90 K and* ***(b)*** *CPL-1 with adsorbed O_2 at 90 K as an equal –density contour surface. The equicontour level is 1.0 e Å^{-3}.*

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