Direct Observation of Hydrogen Molecules Adsorbed in Microporous Coordination Polymer

Hydrogen storage is an important technology and is indispensable for the establishment of clean hydrogen energy systems. Although various kinds of materials have been studied as hydrogen-storage materials, there is as yet no decisive way to store and release H_2 molecules efficiently. The adsorption of H_2 molecules in metal-organic porous materials [1] is one of the most promising candidates. To develop a rational synthetic strategy for novel metal-organic porous materials that can adsorb large amounts of H_2 molecules, the elucidation of the intermolecular interaction between H_2 molecules and pore walls is essential. Despite several investigations into novel metal-organic porous materials for hydrogen storage [2], little is known about the effective interaction mechanism and the fundamental structural characteristics of the adsorbed H_2 molecules. In our previous work [3], we determined the assembled structure of O_2 molecules in nano-channels by *in situ* synchrotron powder diffraction, which allowed a good understanding of the magnetic and adsorption behaviors of O_2 molecules. Therefore, the structure determination of adsorbed H_2 molecules should also provide us with much information on their physicochemical properties to enable the rational design and synthesis of high-performance hydrogen-storage materials. Although the weakest X-ray scattering amplitude of hydrogen made it difficult to determine their structure, we have succeeded in the first direct observation of elusive H_2 molecules adsorbed in the nano-channels of a metal-organic porous material by the *in situ* synchrotron powder diffraction experiment of gas adsorption and by MEM (maximum entropy method)/Rietveld charge-density analysis [4].

The sample used in this study is microporous coordination polymer 1 with a pillared layer structure (CPL-1) with uniform ordered nano-channels of 4 Å × 6 Å. The *in situ* synchrotron powder diffraction experiment for hydrogen gas adsorption was carried out using the large Debye-Scherrer camera installed at beamline **BL02B2**. The hydrogen gas was dosed into the capillary sample through a stainless steel tube connected to the gas-handling system. The amount of adsorbed gas was controlled by adjusting the sample temperature under a constant hydrogen gas pressure of 102 kPa.

The structure was investigated by MEM/Rietveld analysis [5]. The amount of H_2 molecules adsorbed in CPL-1 at 90 K at 102 kPa was determined to be 0.3 molecules per Cu atom from the hydrogen adsorption isotherm. The reliability (R) factors based on the powder profile R_{WP} and the Bragg integrated intensities R_I were 2.45% and 3.33%, respectively. The cell parameters for CPL-1 with H_2 gas were determined as a = 4.7101(1) Å, b = 20.0289(2) Å, c = 10.7704(1) Å, and β = 95.472(2)° (space group $P2_1/c$). The R factor based on the structure factors in the final MEM analysis R_F was 1.86%.

In the MEM charge density of CPL-1 without H_2 molecules shown in Fig. 1(a), only the nano-channel structure was clearly seen and no electron density was observed in the nano-channels, even at lower electron-density levels. On the other hand, in the MEM charge density of CPL-1 with H_2 molecules (Fig. 1(b)), the small peak maxima of the electron densities with an elongated shape distribution, which are due to the adsorbed H_2 molecules, were observed in the nano-channels. It should be noted that the position and orientation of the H_2 molecules are mean values obtained by statistical analysis. The

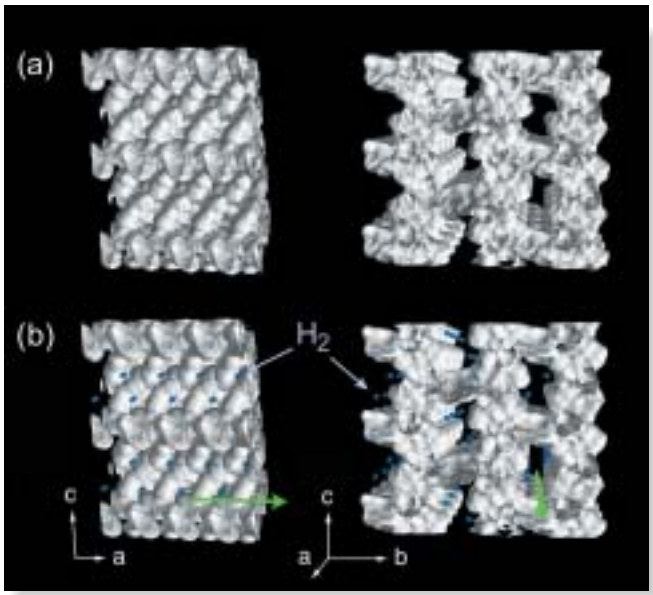

Fig. 1. MEM charge density maps of CPL-1 at 90K as equi-density contour surfaces **(a)** without H_2 molecules and **(b)** with adsorbed H_2 molecules. The equi-contour level is 0.11 eÅ^{-3}. The charge densities of the adsorbed H_2 molecules are colored blue. The green arrows indicate the nano-channel direction.

charge density distribution of the adsorbed H_2 molecules is broader than that of hydrogen atoms of pyrazine in CPL framework as a result of the large thermal motion. The H_2 molecules align in a zigzag pattern to form a one-dimensional array along the nano-channels. The position of each H_2 molecule is found to be displaced from the center of the nano-channel and is near a corner of the rectangular nano-channels. The H_2 molecule is positioned closely to the oxygen atom (O1) of the carboxylate group (Fig. 2). The O1 atom forms a coordination bond with the Cu^{II} ion and is slightly negatively charged. The Cu-OOC moiety is associated with an attractive interaction site for H_2 molecules. Interestingly, most metal-organic porous compounds reported to date that behave as hydrogen- gas-storage materials have similar metal-oxygen (M-O) bonded units. The possibility that the interaction between the hydrogen molecules and the M-O units is essential for H_2 adsorption will be examined in the next stage of this work. Moreover, the H_2 molecule seems to be trapped in the concave space formed by the O1 atom and the hydrogen atom H1 of the pyrazine molecules of the CPL framework. The pocket of the cavity formed by the carboxylate group and the pyrazine unit is suited to the size of adsorbed H_2 molecules in CPL-1.

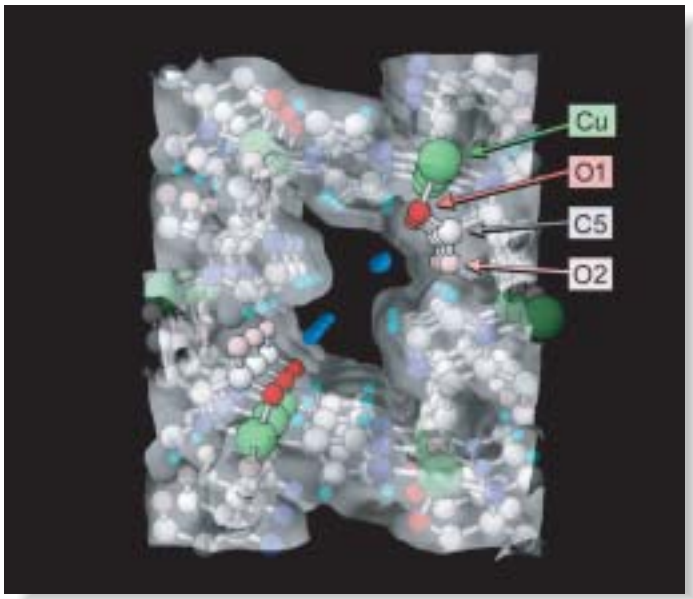

Fig. 2. Close-up view of MEM charge density map around an adsorbed H_2 molecule. The equi-contour level is 0.11 $eÅ^{-3}$. The structural model of the CPL framework is superimposed on the charge density map.

At a lower temperature and/or a higher gas pressure, more H_2 molecules are expected to be adsorbed into CPL-1. In the case of the adsorption of dilute hydrogen gas, it is interesting and important to know where the first adsorbed H_2 molecule is located in the nano-channel, because that will provide us with structural information on the initial stage of adsorption in this system. A pocket that is well suited to the size of the adsorbed molecule *and* a functional site from the Cu-OOC moiety could have an effect on H_2 adsorption in this system. The first direct observation of H_2 molecules adsorbed in the nano-channels of CPL-1 could give us promising guidelines for designing hydrogen-gas-storage materials.

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