Inclusion Compounds

Direct Observation of Hydrogen Molecules Adsorbed onto a Microporous Coordination Polymer**

Yoshiki Kubota, Masaki Takata, Ryotaro Matsuda,
Ryo Kitaura, Susumu Kitagawa, Kenichi Kato,
Makoto Sakata, and Tatsuo C. Kobayashi*

Hydrogen storage is an important technology and is indispensable for the establishment of clean hydrogen energy systems. Although various materials have been studied as hydrogen-storage materials,[1] there is yet no decisive way to store and release H_2 molecules efficiently. Adsorption of H_2 molecules in metal–organic porous materials[2,3] 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 interactions between H_2 molecules and pore walls is essential. Despite several investigations into novel metal–organic porous materials as hydrogen-storage materials,[4] little is known about the effective interaction mechanism and the fundamental structural characteristics of the adsorbed H_2 molecules. In previous work,[5] we determined the assembled structure of O_2 molecules in nanochannels by

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[*] Dr. Y. Kubota
Department of Environmental Sciences
Faculty of Science, Osaka Women's University
Sakai, Osaka 590-0035 (Japan)
Fax: (+81) 72-222-4791
E-mail: kubotay@center.osaka-wu.ac.jp
Dr. M. Takata, K. Kato
Japan Synchrotron Radiation Research Institute/SPring-8
Sayo-gun, Hyogo 679-5198 (Japan)
and
CREST, Japan Science and Technology Agency
R. Matsuda, Dr. R. Kitaura,[+] Prof. Dr. S. Kitagawa
Department of Synthetic Chemistry and Biological Chemistry
Graduate School of Engineering, Kyoto University
Katsura, Kyoto 615-8510 (Japan)
Prof. Dr. M. Sakata
Department of Applied Physics, Nagoya University
Nagoya 464-8603 (Japan)
Prof. Dr. T. C. Kobayashi
Department of Physics, Okayama University
Okayama 700-8530 (Japan)
[+] Present address: Toyota Central Research and Development
Laboratories, Inc.
Nagakute, Aichi 480-1192 (Japan)

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in situ synchrotron powder diffraction, which allowed a good understanding of the magnetic and adsorption behavior of O_2 molecules. Therefore the structure determination of adsorbed H_2 molecules should also provide us with much information on physicochemical properties to allow a rational design and synthesis of high-performance hydrogen-storage materials. Although the weakest X-ray scattering amplitude of hydrogen made it difficult to determine the structure, the elusive hydrogen can be observed by using a high-brilliance synchrotron light source and MEM (maximum entropy method)/Rietveld charge-density analysis.[6] These techniques are particularly suitable for systems in which the contribution from heavy elements is not dominant. In a recent study on metal hydrides,[7] the position of the hydrogen atoms was determined and the bonding between the hydrogen atom and the metal atom was revealed. Herein we report the first successful direct observation of H_2 molecules adsorbed in the nanochannels of metal–organic porous materials by in-situ synchrotron powder diffraction experiment of gas adsorption and MEM/Rietveld analysis.

The sample used in this study is $[Cu_2(pzdc)_2(pyz)]_n$ (pzdc = pyrazine-2,3-dicarboxylate, pyz = pyrazine), which has a pillared layer structure with uniform nanochannels of 4×6 Å.[2] We call it CPL-1 (coordination polymer 1 with pillared layer structure). Figure 1 shows the variation of the lattice parameters and the cell volume of CPL-1 with hydrogen gas obtained by Rietveld analysis. Significant lattice expansion occurred between 90 and 110 K. This can be considered as the H_2 molecules being adsorbed in the nanochannels of CPL-1. Changes in cell parameters are due to the slight transformation of the CPL framework to accommodate the adsorbed hydrogen molecules. The peak shifts and a slight profile broadening by the H_2 adsorption are also seen in the powder pattern at 90 K. As a reference, the powder diffraction pattern of CPL-1 without hydrogen gas was also collected. The powder patterns of CPL-1 with and without hydrogen gas at 90 K were analyzed (Figure 2).

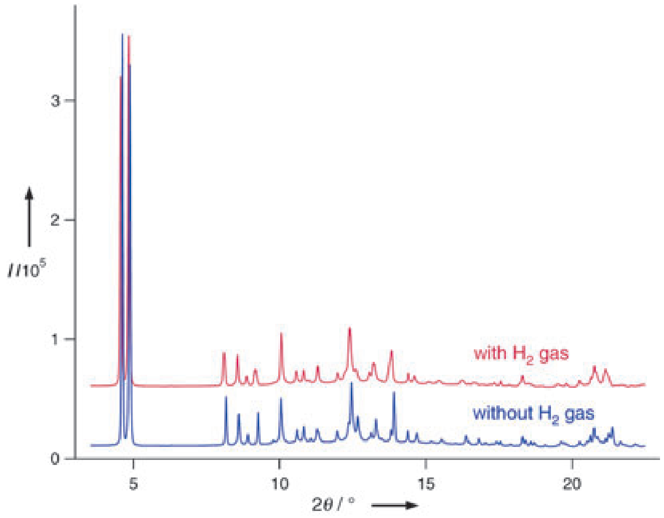

Figure 2. Synchrotron X-ray powder diffraction patterns of CPL-1 (90 K) with hydrogen gas (102 kPa) and without hydrogen gas.

The structure was analyzed by using the MEM/Rietveld method.[6] 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 measurement of the hydrogen-adsorption isotherm. Thus, the atomic occupancy parameter of a hydro-

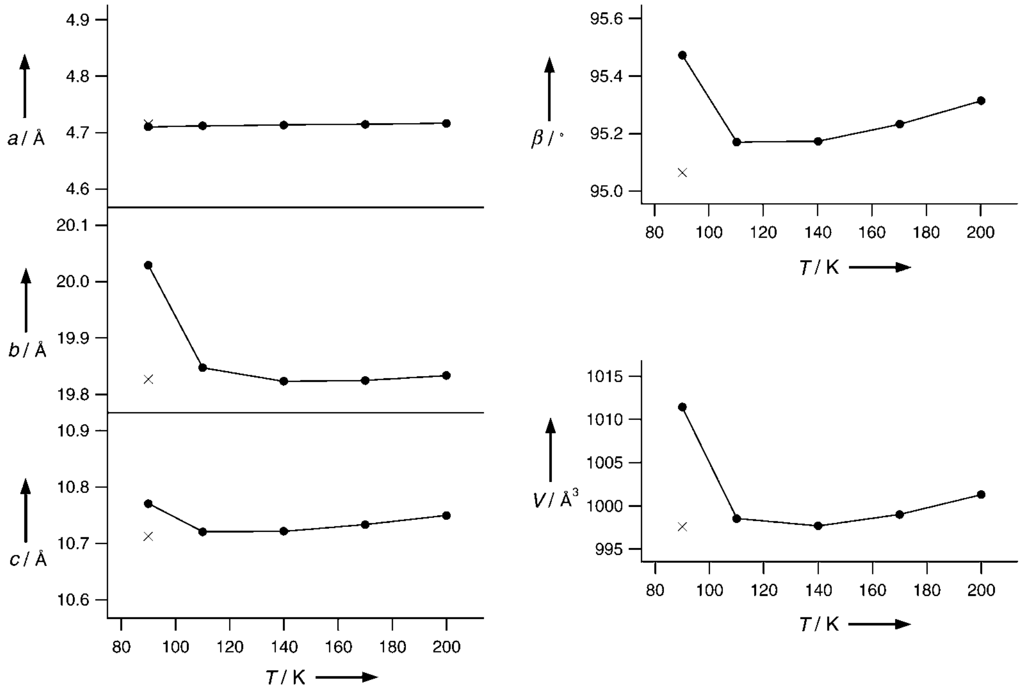

Figure 1. Variation of the lattice parameters and the cell volume of CPL-1 in hydrogen-gas adsorption. The black circles show the data with hydrogen gas and the crosses show the data without hydrogen gas.

gen atom of a H_2 molecule was fixed as 0.3 in the Rietveld analysis. The MEM calculation was carried out by the computer program ENIGMA.[8] The reliability (R) factors based on the powder profile R_{WP} and the Bragg integrated intensities R_I for the final Rietveld analysis of CPL-1 with H_2 gas were 2.45 % and 3.33 %, respectively. The R factor based on the structure factors in the final MEM analysis R_F was 1.86 %. The R_{WP}, R_I, and R_F for CPL-1 without H_2 gas were 2.21 %, 3.89 %, and 2.50 %, respectively.

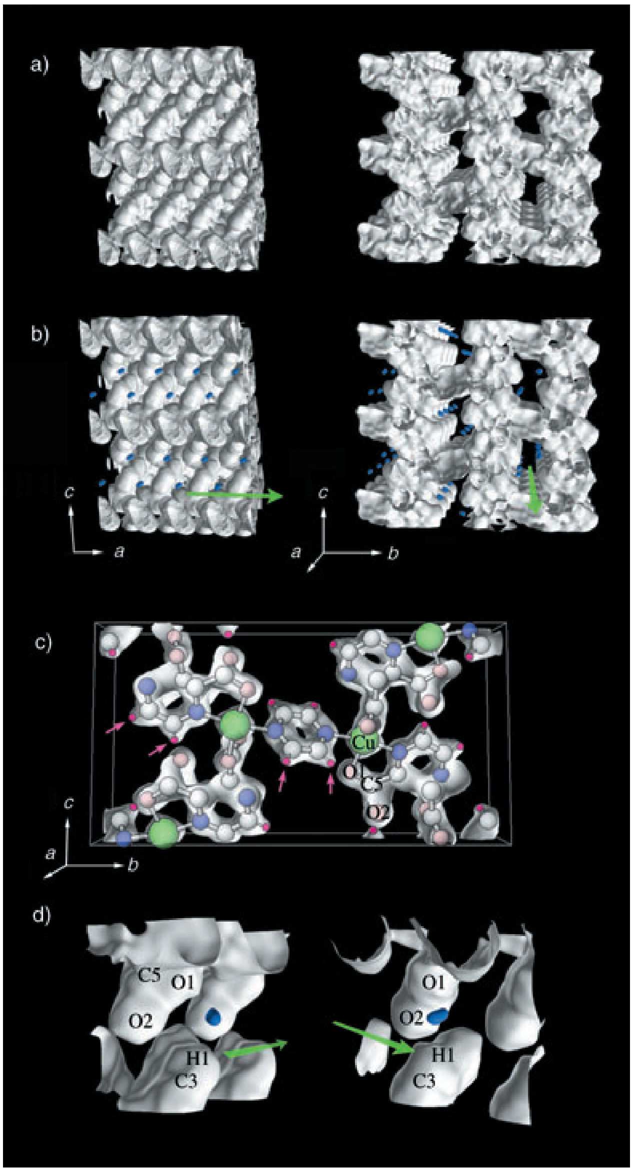

Figure 3. MEM charge-density distributions of CPL-1 at 90 K as an equidensity contour surface: a) without H_2 molecules, b) and c) with adsorbed H_2 molecules, and d) close-up views around the adsorbed H_2 molecule. The equidensity contour level is $0.11\ e\text{A}^{-3}$ in a), b), and d) and $0.80\ e\text{A}^{-3}$ in c). Charge densities of adsorbed H_2 molecules are colored in blue. The green arrows indicate the direction of the nanochannel of CPL-1. In c), the charge density within the unit cell is drawn and the structural model is superimposed. Arrows indicate the hydrogen atoms of pyrazine in the CPL framework. The charge density of adsorbed H_2 molecules is not seen at this level.

The MEM charge density distributions of CPL-1 with and without H_2 molecules are shown in Figure 3 as an equidensity contour surface. In the MEM charge density of CPL-1 without H_2 molecules (Figure 3 a), only the nanochannel structure was clearly seen and no electron density was observed in the nanochannels, even at lower electron-density levels. On the other hand, in the MEM charge density of CPL-1 with H_2 molecules (Figure 3 b), the small peak maxima of the electron densities with elongated shape distribution were observed in the nanochannels. The number of electrons around the density areas was calculated to be 0.6(1) e, which virtually agrees with the initial estimated amount of adsorbed H_2 molecules ($0.3\,e \times 2 = 0.6\,e$). Thus, we considered those to be the densities of adsorbed H_2 molecules. It should be noted that the position and the orientation of the H_2 molecules are mean values obtained by statistical analysis. The charge-density distribution of the adsorbed H_2 molecule is broader than that of the hydrogen atoms of pyrazine in the CPL framework (see Figure 3 c) as a result of the large thermal motion. The position of the H_2 molecule is found to be displaced from the center of the nanochannel and is near the corner of the rectangular nanochannels. They align in a zigzag pattern to form a one-dimensional array along the nanochannels. The H_2 molecule is positioned closely to the oxygen atom (O1) of the carboxylate group (Figure 3 d). The H_2 molecules seem to be trapped in the concave spaces formed by the O1 atoms and the hydrogen atoms H1 of the pyrazine molecules of the CPL framework. The determined crystal structure of CPL-1 with the adsorbed H_2 molecules is shown in Figure 4.

At lower temperature and/or higher gas pressure, more H_2 molecules are expected to be adsorbed in CPL-1. In the case of the adsorption of dilute hydrogen gas, it is interesting and

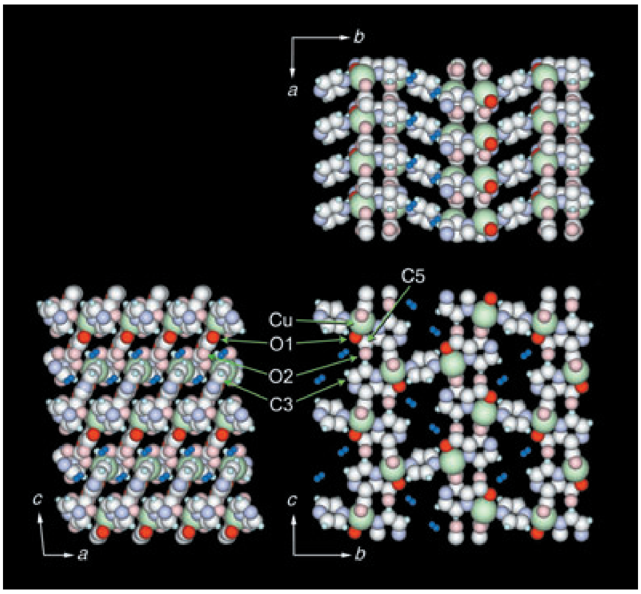

Figure 4. Crystal structure of CPL-1 with adsorbed H_2 molecules. The adsorbed H_2 molecules and the oxygen atoms (O1) of the carboxylate group in the framework are presented as blue dumbbells and red balls, respectively. The adsorbed H_2 molecules randomly occupy the site with a probability of 0.3.

important to know where the first adsorbed H_2 molecule is located in the nanochannel, because that will give us structural information at the beginning stage of adsorption phenomena in this system. The O1 atom to which the H_2 molecule is close forms a coordination bond to the Cu^{II} ion and is slightly negatively charged. The Cu-OOC moiety is associated with an attractive interaction site for H_2 molecules.[9] Interestingly, most metal–organic porous compounds reported to date that behave as hydrogen-gas-storage materials[4] 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 should be examined in the next stage of this work. Moreover 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. 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 the H_2 adsorption in this system. The first direct observation of the H_2 molecules adsorbed in the nanochannels of CPL-1 could give us promising guidelines for designing hydrogen-gas-storage materials.

Experimental Section

The synthesis and crystal structure of CPL-1 are shown in the previous paper.[2] The in situ synchrotron powder diffraction experiment of hydrogen-gas adsorption was performed on the large Debye-Scherrer camera installed at SPring-8 BL02B2,[10] by using an imaging plate as a detector. The wavelength of an incident X-ray was 0.800 Å. The amount of the adsorbed gas was controlled by changing the temperature of the sample under a constant pressure of hydrogen gas (102 kPa).

The space group was assigned as $P2_1/c$. The cell parameters for CPL-1 with H_2 gas determined by the Rietveld refinement were $a = 4.7101(1)$ Å, $b = 20.0289(2)$ Å, $c = 10.7704(1)$ Å, $\beta = 95.472(2)°$. The cell parameters for CPL-1 without H_2 gas were determined as $a = 4.7154(1)$ Å, $b = 19.8268(2)$ Å, $c = 10.7124(2)$ Å, $\beta = 95.065(2)°$. CCDC-249301 (CPL-1 with adsorbed hydrogen) and CCDC-249302 (CPL-1 without adsorbed hydrogen) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[9] When H_2 was introduced below its boiling point (20.3 K) to the sample, the liquid H_2 filled up in the cavity and no information on the attractive sites was obtained. In the structural determination described herein, a low pressure and high temperature allowed a H_2 loading per unit that was low enough to explore a specific attractive site among the functional groups in the cavity.

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