(※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。)

TOKAI CROSS Experimental Report J-PARC	承認日 Date of Approval 2013.7.5 承認者 Approver Takashi Ohhara 提出日 Date of Report 2013.7. 1
課題番号 Project No. 2012B0112 実験課題名 Title of experiment Direct Observation of Deuterium Gas Adsorbed on Porous Coordination Polymers with Viologen Surface 実験責任者名 Name of principal investigator Masakazu HIGUCHI 所属 Affiliation Kyoto University	装置責任者 Name of responsible person Takashi OHHARA 装置名 Name of Instrument/(BL No.) SENJU (BL18) 実施日時 Date and time of Experiment Feb. 14, 2013, 9:00 ～ Feb. 18, 2013, 9:00

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

When we made the proposal of the application, we have proposed that we would synthesize a porous coordination polymers with viologen surface (reported in Angew. Chem. Int. Ed. 2012, 51, 8369.) to elucidate the position of hydrogen molecules on its surface. However we could not successfully synthesized its single crystal suitable for experiments in SENJU(BL18). Therefore, for experiments in in SENJU(BL18), we synthesized single crystal of Ca(C4O4)(H2O), which has an adequate size, 0.7 mm x 0.7 mm x 1.0 mm, of the single crystal. In this proposal, we carried out a single crystal neutron diffraction measurement of this single crystal to observe hydrogen atom of H2O in Ca(C4O4)(H2O) and hydrogen molecules in the pore.

2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。)
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

Method

A 0.7 mm x 0.7 mm x 1.0 mm single crystal of Ca(C4O4)(H2O) in the quarts capillary with hydrogen molecule as gas was attached to an aluminum stick using epoxy glue and mounted to the goniometer at the end of 4K-cryostat.

Neutron diffraction intensities were collected on the following conditions.

Crystal orientation: 8

Exposure time: 8 hrs. / orientation

Temperature: 77 K

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2. 実験方法及び結果（つづき） Experimental method and results (continued)

Result

In this experiment, low temperature diffraction measurement by using the 77K-cryostat at was performed to detect hydrogen molecules in the pore. We could not success to find hydrogen molecule in the pore by the analysis, but hydrogen atom of H2O in Ca(C4O4)(H2O) was observed, which is fundamentally of importance when we discuss adsorption phenomena. Figure 1 shows the single crystal structure of Ca(C4O4)(H2O) with hydrogen molecules (unfortunately hydrogen molecules were not detected) and Table 1 shows the crystallographic parameters of Ca(C4O4)(H2O) obtained. Data processing was performed by software STARGazer. Obtained cell parameters were a = 13.71770 Å, c = 7.6987 Å, (tetragonal). These values well agreed with those of X-rays.

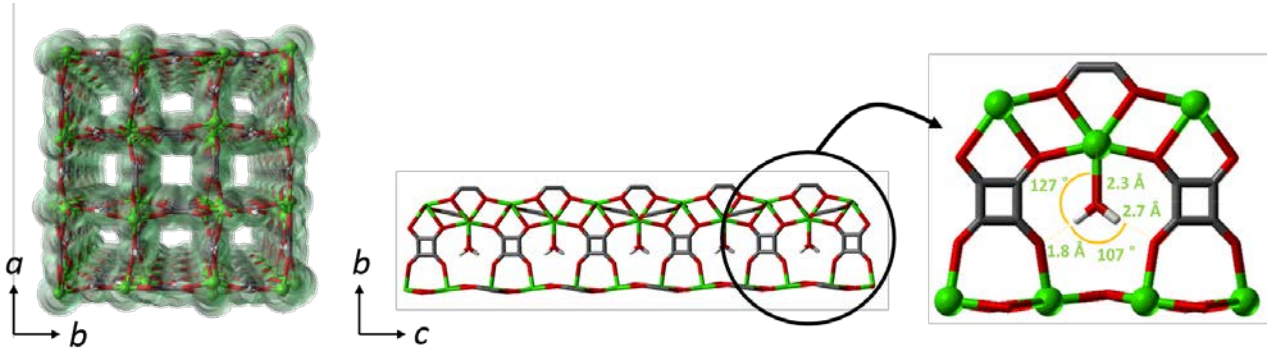

Figure 1. the single crystal structure of Ca(C4O4)(H2O).

Table 1. the crystallographic parameters of Ca(C4O4)(H2O)

Compounds	$Ca(C_4O_4)(H_2O)$
Crystal system	Tetragonal
Formula	$C_4H_2Ca_1O_5$
a, Å	13.71770
c, Å	7.6987
V, Å^3	1448.705
Space group	*I-42d*
Z	8
Temp, K	77

The hydrogen atom of H2O in Ca(C4O4)(H2O) was observed in this experiment, which is not detected by X-ray single crystal measurement. As a result, we obtained the detailed information of the framework of Ca(C4O4)(H2O). Hydrogen atom in H2O coordinated to oxygen atom of C4O4 with the distance of 2.7 Å, which is the typical distance of hydrogen bond. This measurement revealed that water molecules play the key role in constructing the framework of Ca(C4O4)(H2O) to show slightly zigzag 1-dimansional channel. Unfortunately although we dosed hydrogen gas in the capillary with the single crystal of Ca(C4O4)(H2O), we could not detected hydrogen molecules in the pore. We guess that there are two issues to detect hydrogen molecules. One is that there is not enough hydrogen molecules to detect. Another is that hydrogen molecules come out from the capillary inside because of high vacuum in the cryostat.