Modification of flexible part in Cu^{2+} interdigitated framework for CH_4/CO_2 separation[†]

Yasutaka Inubushi,^a Satoshi Horike,^{*b} Tomohiro Fukushima,^b George Akiyama,^c Ryotaro Matsuda^{cd} and Susumu Kitagawa^{*bcd}

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The structural flexibility of Cu^{2+} interdigitated layer type framework was controlled and the compound represented clear separation property of CH_4/CO_2 at range of 0–1.0 MPa and recovery of adsorbed CO_2 above 0.1 MPa.

Development of materials and technology for selective adsorption of CO₂ gas from CH₄/CO₂ mixture has been a significant challenge in the area of natural-gas processing. Regarding the porous materials for selective CO₂ capture from CH₄/CO₂ mixture, we could employ either kinetic or equilibrium-based separation.¹ Activated carbon or zeolites have been mainly studied as equilibrium-based adsorbents and the main drawbacks are either low selectivity or regenerability. For a porous material design, we have to control gas sorption isotherms and some points are required. First, desorption pressure of CO_2 is related to the energy of CO_2 recovery and it should not be lower than 0.1 MPa, otherwise we need a vacuum to regenerate the CO₂. Second, the separation ability should be observed in a wide range of pressure (~ 1.0 MPa) for various types of pressure-swing processes. Especially the materials are required not to adsorb CH4 at all in the pressure range mentioned above.

Porous coordination polymers (PCPs) or metal–organic framework (MOFs) constructed from metal cations and organic linkers are a new class of microporous materials that show promise for gas separation applications because of their structural versatility.^{2–7} Especially the PCPs whose structures have a flexible nature are attractive due to their potential applications in gas separation with unique mechanisms.^{8,9} They represent a reversible transformation of open/close frameworks accompanied by guest sorption processes and it is often sensitive to the specific guest molecule.^{8,10–12}

Extended frameworks constructed from two-dimensional (2D) layers have been widely studied because they can accommodate various guest molecules in the interlayer spaces.^{13,14} Likewise, 2D PCPs are significant motifs for selective gas adsorption because we can tune the flexibility of the layer–layer interaction and intrinsic flexibility of the coordination bond.^{15,16} Rational design of a PCP framework has encouraged us to optimize the gas separation performance, especially the capture of CO₂ gas from CH₄/CO₂ mixture at ambient condition. Herein we demonstrate a modification of flexibility in a 2D PCP framework by ligand design and control the adsorption isotherms of CO₂ and CH₄ to give idea for the optimization of gas separation property.

Previously we reported a flexible 2D PCP; [Cu(dhbc)₂bpy]. H₂O $(1 \supset H_2O)$, where Hdhbc = 2.5-dihvdroxybenzoic acid and bpy = 4,4'-bipyridyl, which represents various "gate-opening" type gas adsorption profiles.^{17,18} Several gas adsorptions at 298 K were reported and to carefully investigate the adsorption behavior at below 0.1 MPa, the CO₂ and CH₄ adsorption isotherms of 1 at 273 K were measured as shown in Fig. 1c. It starts to adsorb CO_2 at P = 0.04 MPa and CH_4 at 0.65 MPa. Many flexible PCPs including 1 adsorb CO₂ below 0.1 MPa and CH₄ below 1.0 MPa and the compounds are not satisfactory for CH_4/CO_2 separation with a low energetic cycle. To elucidate the structural contribution for the gas adsorption profiles, we characterized the crystal structure of guest-free 1. Careful degas treatment of a single crystal of $1 \supset H_2O$ gave the closed structure of 1 (Fig. 1a and b). Although the coordination environment around the Cu²⁺ ion is not different compared with $1 \supset H_2O$, the benzene rings of the dhbc ligand largely tilt because of the bending of coordination bonds (Cu-O) in carboxylate and hydroxy groups. Two dhbc ligands have trans-type fashion around the Cu^{2+} ion, whereas they have *cis*-type fashion in the original phase $(1 \supset H_2 O)$. The local reorientation affects the stacking of 2D layers and the networks are densely packed resulting in the guest accessible void volume of 2.1%.¹⁹ This means the structural transformation is "porous" $(1 \supset H_2O)$ to "nonporous" (1) and it causes the gate-opening type adsorption behavior for various gasses.^{12,20}

1 has high flexibility in the part of the dhbc because of the coordination bond with hydroxy group and the size of ligand and it promoted the overall transformation. The structural transformation had a low activation energy and afforded the favorable adsorptions of CO_2 and CH_4 at low pressure at 273 K. To shift the gate-opening pressure of CO_2 above 0.1 MPa and

^a Synthesis Research Laboratory, Kurashiki Research Center, Kuraray Co. Ltd., 2045-1, Sakazu, Kurashiki, Okayama 710-0801, Japan

^b Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

^c Kitagawa Integrated Pores Project, Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Agency (JST), Kyoto Research Park, Bldg#3, Chudoji, Awata-cho, Shimogyo-ku, Kyoto 600-8815, Japan

^d Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan. E-mail: kitagawa@icems.kyoto-u.ac.jp; Fax: +81-75-383-2732; Tel: +81-75-383-2733

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Fig. 1 Representations of crystal structure transformation of **1** and $1 \supset H_2O$ (a) environment around the Cu²⁺ ions and (b) 2D layer stacking motif with/without guest molecules. Guests are omitted. (c) Adsorption and desorption isotherms of CO₂ (open and closed circles) and CH₄ (open and closed triangles) for **1** at 273 K.

avoid CH₄ adsorption in the pressure range of zero to 1 MPa, we prepared an interdigitated framework by employing 4,4'-dihydroxybiphenyl-3-carboxylic acid (H₂dhbpc) as a ligand.²¹ The H₃dhbpc can be regarded as an elongated version of the dhbc ligand in **1** and the enlargement of the ligand could promote a lower flexibility in the 2D layers because of an increase of activation energy for structural transformation. The H₃dhbpc was synthesized according to the literature method.²¹ Slow diffusion of Cu(NO₃)₂·3H₂O and H₃dhbpc with bpy in acetone and water solution formed green

single crystals of $[Cu(H_2dhbpc)_2bpy]$ 2Acetone (2 \supset Acetone) and the crystal structure is shown in Fig. 2a and 2b. The framework has a similar motif with $1 \supset H_2O$ and the dhbpc replace the positions of dhbc to form an interdigitated framework. The coordination environment around the Cu²⁺ center is octahedrally coordinated to dhbpc and bpy, and the dihedral angle of benzene rings in dhbpc is 34.0°. The Cu²⁺ and dhbpc and bpy form 2D layers and each layer is stacked with interdigitated fashion containing two acetone molecules as guests. The void volume of the framework of $2 \supset$ Acetone is 20% and it is comparable to the $1 \supset H_2O$. We have not determined the crystal structure of degassed 2 because of the large transformation confirmed by powder X-ray measurement but clearly it showed reversible transformation via guest accommodation and release. We refined the cell parameters of guest-free 2 from XRD pattern by LeBail fitting and the refined values are different from that of 2 - Acetone which indicates the large structural transformation. We could expect higher activation energy from close to open phase than 1 if 2 has a similar reorientation around the Cu^{2+} atoms with 1 because of the size of the dhbpc ligand. Thermogravimetric analysis of guest-free 2 supported a thermal stability of the framework until 500 K.

2 represented a different type of gas adsorption profile from 1. For CO₂ adsorption at 273 K, the 2 represented double stepwise adsorption (Fig. 2c). Initial gas uptake was at 0.04 MPa and first uptake occurred to reach saturation (34 mL g^{-1}) . The plateau appears in the range of 0.20-0.55 MPa and moved to next uptake to the second saturation point (115 mLg⁻¹). To obtain structural information, we studied simultaneous measurements of CO₂ adsorption and powder X-ray diffraction at 195 K to investigate the structural information via adsorption at each plateau. The XRD pattern at P = 3.9 kPa was slightly different from degassed 2 indicating the presence of metastable phase of structure. As the pressure increased, the second step occurred and was attributed by the transformation to reach the stable structure which was similar with $2 \supset$ Acetone.¹⁵ From the measurement, we could pursue the stepwise transformations of structure of 2. The bulkiness of dhbpc ligand would not permit to give perfect nonporous stacking of layer structure like 1 and it resulted in the initial microporosity. In desorption process, the adsorbed CO₂ at the



Fig. 2 Representation of crystal structures of **2** (a) around the Cu^{2+} ion and (b) 2D layer stacking. Guests are omitted. (c) Adsorption and desorption isotherms of CO₂ (open and closed circles) and CH₄ (open and closed triangles) for **2** at 273 K.

second step (total 81 mL g⁻¹) was released at P = 0.4 MPa which was higher than 0.1 MPa and that of **1**. It is desirable for the regeneration of CO₂ from adsorbed phase.

The stepwise adsorption behavior was also observed in H₂O adsorption at 298 K. Although 1 represented single gate-opening type adsorption at 2.2 kPa, 2 gave gradual uptake until P = 2.2 kPa and a second jump was observed. Both compounds had large hysteresis in desorption curves which was indicative of stabilization of water molecule in the pores. The final adsorption amount of CO_2 for 2 was 1.5 times larger than that of 1 and comparable to the other adsorbents.²²⁻²⁴ The low flexibility in 2 also affected an isotherm of CH_4 . The 2 provided negligible amount of uptake for CH₄ even at pressure of 1.0 MPa at 273 K. Although 1 gradually adsorbed CH_4 until P = 0.65 MPa (10 mLg⁻ Fig. 1c) and showed abrupt uptake to reach 58 mL g^{-1} at 0.95 MPa, **2** adsorbed only 4 mL g^{-1} at 1.0 MPa, resulting in the better selectivity on CH_4/CO_2 . The low flexibility of 2 for CH₄ is unique for creation of repulsive property against the CH₄ molecule at wide pressure range. It provides another idea of PCPs/MOFs for CH₄/CO₂ separation with other metalorganic frameworks having rigid porous scaffold and preferable binding character for CO₂ gas.²⁵⁻²⁷

We checked the separation ability of CO2 over CH4 from CH₄/CO₂ mixture gas and executed the co-adsorption measurement by use of our hand-made instrument. We dosed mixture gas $(CH_4: CO_2 = 1: 1(vol))$ for **2** under the condition of total pressure 0.1 MPa and 273 K then waited three hours for the equilibrium co-adsorption process and detected the adsorbed gas species by gas chromatography. Although the total adsorbed amount of gas was low (17 mL g^{-1}) because of the low total pressure in this measurement, we hardly observed the trace of CH₄ which indicated that all the adsorbed gas was CO_2 , and we observed clear separation property for CO_2 from mixture gas. The adsorption is corresponding to the first uptake of CO_2 for **2** in Fig. 2c. Taking the single adsorption isotherms of CO_2 and CH_4 into consideration, the compound 2 is expected to show high separation ability in a wide range of pressure, especially above 0.1 MPa. Evaluation of separation performance from mixture gas at higher pressure and temperature is under investigation.

Based on the crystallographic information of 1, we enlarged the size of the flexible ligand for tuning of activation energy of structural transformation and gave suitable flexibility for CH_4/CO_2 separation at the total pressure of zero to 1.0 MPa. 2 releases adsorbed CO_2 above 0.1 MPa and it allows gas recovery without vacuum. The flexibility herein is the combination of a layer–layer interaction and local flexibility of coordination bonds in the layer and the approach is feasible only if we employ the 2D porous coordination layer.

In conclusion, we demonstrated that the minor modification of the ligand moiety in the layer framework causes a remarkable change in the gas adsorption properties, which is relevant for appropriate gas separation condition with low energy consumption process.

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