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Communication

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Dense Coordination Network Capable of Selective CO_2 Capture from C1 and C2 Hydrocarbons

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Supporting Information

ABSTRACT: We elucidated the specific adsorption property of CO_2 for a densely interpenetrated coordination polymer which was a nonporous structure and observed gas separation properties of CO_2 over CH_4, C_2H_4, and C_2H_6, studied under both equilibrium and kinetic conditions of gases at ambient temperature and pressure.

Crystalline porous materials have been intensively studied because of their functions, such as gas storage, separation, and heterogeneous catalysis. Regarding the gas separation, porous coordination polymers (PCPs) or metal−organic frameworks (MOFs) have been highlighted in the past decade.[1] These are constructed from metal cations and organic ligands and versatile porous structures for gas separation are feasible.

In general, pores of PCP/MOFs are filled with synthetic solvents or water molecules from the air as templates, and we need a pretreatment (activation) by heating under vacuum condition for the use of gas storage and separation.[2] We have not focused on densely packed coordination polymers for gas adsorption because they are apparently nonporous. If we could find gas adsorption/separation properties by dense coordination polymers, then it gives a new insight for design of adsorbent. To develop such unique materials, herein we employed a dense, nonporous coordination polymer with a triply interpenetrated system. The mutual interpenetration avoids inclusion of synthetic solvents and water molecules during the synthesis. We elucidated the intrinsic structure flexibility of the dense framework, and it exhibited an efficient CO_2 separation property over several hydrocarbons, such as methane (CH_4), ethylene (C_2H_4), and ethane (C_2H_6). Note some ionic crystals and organic hosts show guest accommodation behavior in the nonporous phase.[3] However, a neutral and nonporous coordination polymer has scarcely been observed in gas separation. It is because dense coordination networks should be thermodynamically stable and networks have only a small interaction with gas molecules.

$Zn(NO_3)_2\cdot 6H_2O$, 5-nitroisophthalic acid (H_2-5NO_2-ip), and 1,2-di(4-pyridyl)ethylene (dpe) were reacted with *N*,*N*′-dimethylformamide under N_2 atmosphere, and a white microcrystalline compound [Zn(5NO_2-ip)(dpe)] (**1**) was obtained. The formula of **1** was determined by single X-ray diffraction analysis and elemental analysis. Crystal structure of **1** is shown in Figure 1. The asymmetric unit of **1** contains one of each: Zn^{2+} ion, 5NO_2-ip, and dpe ligand. The Zn^{2+} center is coordinated by two oxygen atoms from two carboxylate groups of 5NO_2-ip and two nitrogen atoms from dpe to form a ZnO2N2 tetrahedral geometry. Further linkages of Zn^{2+} and ligands extend to form a 3D reticular network with high void spaces. Then each network is interpenetrated with a three-fold fashion to stabilize the assembled structure of **1**. The compound is four-connected 3D (6^5.8)-**dmp** topology, which is identified by TOPOS software.[4] Based on a recent analysis of the CCDC crystal database,[4a] we found several isostructures

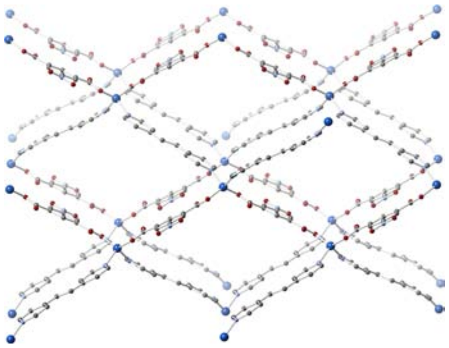

Figure 1. Crystal structure of a single reticular network of **1**. Actual crystal structure of **1** is a three-fold interpenetrated dense structure. H atoms are omitted. Zn, blue; C, gray; O, red; and N, sky blue, respectively.

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with the same topology.[5] Their gas sorption properties are also described later.

There is no guest molecule observed in the structure. Powder X-ray diffraction of as-synthesized **1** matches the simulated pattern of **1** from single crystal structure. As the crystal structure does not contain any guest molecule, no void volume is observed by PLATON program[6] when we set probe molecule as 3.3 Å which is a kinetic diameter of CO_2. When we use 2.8 Å for probe diameter, eventually observe 6.3% of void volume. This is much smaller than the kinetic diameters of almost all the gases and comparable to hydrogen (H_2, 2.89 Å). **1** adsorbs negligible amount of H_2O from adsorption isotherms at 298 K. TGA profile of as-synthesized **1** does not show clear weight loss over 400 °C and it supports no guest molecules are included in the framework of **1** and the framework has high thermal stability under N_2 atmosphere. As a result, we regard **1** as nonporous, dense coordination polymer for gas molecules such as CO_2.

To estimate the gas adsorption property of **1** without an initial activation process, we employed a powder sample of as-synthesized **1** and measured the CO_2, CH_4, C_2H_4, and C_2H_6 gas adsorption isotherms. Physical properties of these gases are comparable, and separations of these gases, such as CO_2/CH_4, CO_2/C_2H_4, C_2H_4/C_2H_6, under ambient temperature and pressure have been a significant challenge. Figure 2a shows adsorption isotherms of CO_2 and CH_4 at 273 K. We observe a Type-I isotherm for CO_2 and the total uptake amount reaches 50 mL g^{-1}. Type-I profile is representative for a gas adsorption of microporous compounds.[7] Although the kinetic diameter of CO_2 is clearly larger than the interstices in **1**, we observed over 40 mL g^{-1} of adsorption below 101 kPa, and we assume that the dense structure of **1** shows rearrangement with the accommodation of CO_2 molecules. On the other hand, **1** adsorbs less than 3 mL g^{-1} of CH_4 across the entire pressure range studied. The selectivity is probably because of a molecular sieving effect since **1** possesses very restricted void spaces even after the structural rearrangement and CH_4 could not enter the structure. CO_2/CH_4 separation has been studied by the use of various porous materials to purify CH_4 from biogas, and the framework is also interesting with regard to the application.[8] The adsorption property on ethane (C_2H_6) was also studied (Figure 2a). C_2H_6 is larger than CO_2 and CH_4, and the boiling point is close to that of CO_2. If boiling points of gases were the major factor for adsorption in **1**, we could observe similar isotherms for CO_2 and C_2H_6. If the kinetic diameters of the gases were the major factor, then distinct adsorption behavior would be observed. CO_2 and C_2H_6 are both adsorbed when we employ porous compounds with a pore diameter above 0.6 nm. However, as shown in Figure 2a, the observed C_2H_6 adsorption amount of **1** was negligible (less than 10 mL g^{-1} at 800 kPa), and the clear separation behavior of CO_2 and C_2H_6 is observed from single component gas adsorption studies.

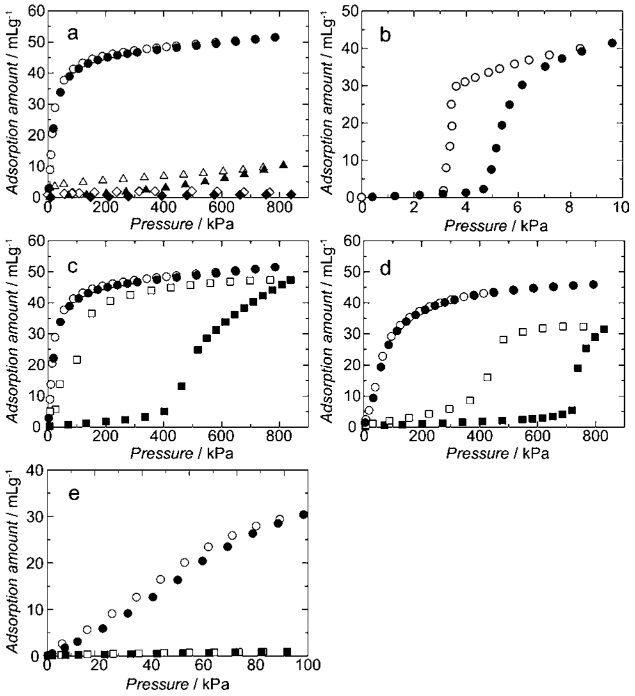

Figure 2. Adsorption/desorption isotherms of **1** for (a) CO_2 (circle), CH_4 (diamond), and C_2H_6 (triangle) at 273 K; (b) methanol at 298 K; (c) CO_2 (circle) and C_2H_4 (square) at 273 K; (d) CO_2 (circle) and C_2H_4 (square) at 298 K; (e) CO_2 (circle)and C_2H_4 (square) at 298 K in the range of 0−101 kPa. Close characters are adsorption, and open characters are desorption.

We also synthesized two reported coordination compounds which possess the same structural topology ((6^5.8)-**dmp**) and evaluated the gas sorption properties. [Zn(isophthalate)(1,2-bis(4-pyridyl)ethane)][5a] adsorbs both CO_2 and C_2H_4 with Type-I isotherms at 273 K, whereas [Zn(5-methylisophthalate)(1,2-bis(4-pyridyl)ethane)][9] does not adsorb any gas molecule representing its nonporosity. These results tell that the gas separation property of **1** originates from not only the structural topology but also the substituent groups of ligands and the degree of packing.

To investigate the structural rearrangement of **1**, we studied the mechanism by use of methanol as an adsorbate. Adsorption/desorption isotherms of methanol at 298 K are shown in Figure 2b. We observed a sigmoid-type adsorption isotherm, and the adsorption behavior is regarded as a "gate-opening" phenomenon.[10] The gate-opening behavior is representative for PCP/MOF frameworks with flexible characteristics, and the phenomena are observed for structure transformation from nonporous to porous phase during the gas sorption processes.[11] Then it is different from that in the robust porous compounds, and the pressure of a gate opening usually depends not only on the fluid−solid interaction but also fluid−fluid interaction, in other words, the boiling point of the gas. XRD pattern of **1** with fully loaded methanol at 298 K was measured. The overall crystal structure of **1** changes as it adsorbs methanol, indicating the dense framework of **1** has flexibility, and the structure returns to an initial phase as it releases methanol. Interestingly, the rate of methanol release of **1** in the air is quite fast, and the transformation to the original, dense structure is completed less than 5 min. This suggests the as-synthesized **1** is thermodynamically much more stable than with methanol in a wide range of methanol vapor pressure. We tried characterizing the crystal structure of **1** with methanol; however, we have not succeeded because of the loss of single crystallinity.

Since we observed gas accommodation into **1** via flexible behavior, we tried to detect a local dynamic motion of the framework of **1** by solid-state NMR.[12] Narrow interspace of **1** is surrounded with aromatic rings of two kinds of organic ligands, 5-NO_2-ip and dpe. To detect the dynamics of organic moiety, protons in the framework were partially deuterated by use of dpe-d4 (1,2-di(4-pyridyl-d2)ethylene) ligand. Successful synthesis of deuterated **1** was confirmed by XRD, and the solid-state ^{2}H NMR spectrum was measured at 298 K (see Supporting Information (SI)). The obtained spectrum shows typical Pake-doublet-type pattern with a quadrupole coupling constant (Qcc) = 173 kHz. This value is close to that of Qcc for a deuteron on a rigid aromatic ring.[13] This line shape indicates that the fast rotational jumps of the pyridyl rings of dpe ligand in **1** do not occur at the temperature, and we assume that the dynamic rearrangement is observed only when gas molecules are accessing the framework.

As evidenced by the binding ability of CO_2 for **1**, we next tried to observe the separation ability for CO_2 and ethylene (C_2H_4). C_2H_4 has comparable physical properties with CO_2. Recently a few olefin/paraffin separations have been investigated on PCP/MOFs,[14] but the separation of CO_2 over C_2H_4 has not been studied regardless of its significance.[15] For instance, oxidation reaction processes using C_2H_4 gas have side reactions and produce CO_2 as a byproduct. Figure 2c,d shows CO_2 and C_2H_4 gas adsorption isotherms at 273 and 298 K. At 273 K, different from that of CH_4 and C_2H_6, an adsorption isotherm of C_2H_4 represents the gate-opening behavior, like a methanol adsorption at 298 K. There is almost no adsorption in the pressure range from 0 to 400 kPa, and at this point, sudden adsorption occurs, and the adsorption amount of C_2H_4 reaches to 48 mL g^{-1} at 800 kPa. At 298 K, the total adsorption amount of C_2H_4 is smaller than that of 273 K (32 mL g^{-1} at 800 kPa), and the pressure point to start adsorbing is 720 kPa. The decrease of adsorption amount and shift of adsorption pressure point are because of a weaker interaction of C_2H_4 and the framework of **1** as measurement temperature increases. At 298 K and 101 kPa, as shown in Figure 2e, distinguishable adsorption profiles of CO_2 and C_2H_4 remain and 31 mL g^{-1} of CO_2 is adsorbed, whereas a negligible amount of C_2H_4 is adsorbed. Linear adsorption profile is an advantage for separation by a pressure swing adsorption (PSA) process regarding the regeneration energy, and further optimization of the steepness of CO_2 isotherm by use of solid solution systems of **1** could be possible.[16] According to the gas adsorption measurements under equilibrium conditions, dense coordination network **1** possesses promising property for separation of CO_2 over C_2H_4 at ambient temperature and pressure. Conventional porous materials, such as zeolites and a molecular sieve, and π-complexation sorbents exhibit Type-I adsorption isotherm for both CO_2 and C_2H_4 or preferable adsorption for C_2H_4 over CO_2 with chemical interaction,[8a,17] and the preferential CO_2 adsorption of **1** over C_2H_4 is an unique character.

To evaluate the gas separation ability for solid adsorbents, not only the study under an equilibrium condition for a single gas component but also the study under flowing (kinetic) conditions for mixed gas is important. Then we measured breakthrough curve of **1** under the mixture of C_2H_4 and CO_2 (C_2H_4/CO_2 = 80:20 (vol)) at 298 K (Figure 3). Total pressure of the gas mixture was 0.74 MPa, space velocity was 1.2 min^{-1}, and consequently relative pressures of CO_2 and C_2H_4 were 0.59 and 0.15 MPa, respectively. The breakthrough curve suggests a clear separation property of CO_2 over C_2H_4 under kinetic conditions. Composition of gas in outlet is almost 100% of C_2H_4 and no detection of CO_2. After 60 min of retention time, it reaches breakpoint and goes back to the original gas fraction in the mixture. Note the recovery profile is gradual indicating that the CO_2 is effectively bound to **1**. The relative pressure of C_2H_4 at 298 K is below the gate-opening pressure to promote the structure transformation of **1**.

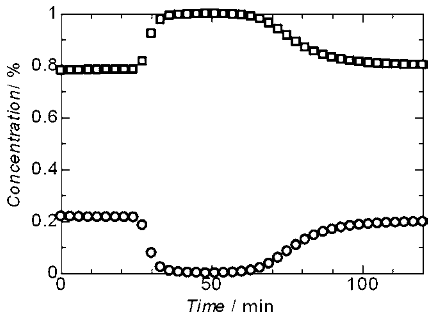

Figure 3. Breakthrough curves of C_2H_4/CO_2 mixture (80:20 (vol)) for **1**. Open circle is CO_2, and open square is C_2H_4. Measured at 298 K, the total pressure was 0.74 MPa, and the space velocity was 1.2 min^{-1}.

In conclusion, we demonstrated a significant potential of dense coordination frameworks for the gas separation. The densely interpenetrated compound **1** showed intrinsic structure flexibility and effective C_2H_4/CO_2 gas separation under both equilibrium conditions by single gas components and mixed-gas flowing conditions at ambient temperature and pressure. Gas separation property of the dense coordination networks contributes to the decrease in the total energy consumption, especially for the PSA process. Structure nonporosity for gases allows a skip in the initial activation process, and the structure flexibility affords a low-energy requirement for regeneration of adsorbents. The result would highlight a various densely packed coordination framework so far and in the future as potential adsorbents for the gas separation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Sample preparation, procedures of measurements, TGA, XRD, H_2O sorption, solid-state ^{2}H NMR. CCDC deposition number of **1** is 862 167. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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