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Highly Selective Carbon Dioxide Sorption in an Organic Molecular Porous Material

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Abstract: The organic molecular porous material **1** obtained by recrystallization of cucurbit[6]uril (CB[6]) from HCl shows a high CO_2 sorption capacity at 298 K, 1 bar. Most interestingly, **1** showed the highest selectivity of CO_2 over CO among the known porous materials so far. The remarkable selectivity of CO_2 may be attributed to the exceptionally high enthalpy of adsorption (33.0 kJ/mol). X-ray crystal structure analysis of CO_2 adsorbed **1** revealed three independent CO_2 sorption sites: two in the 1D channels (**A** and **B**) and one in the molecular cavities (**C**). The CO_2 molecules adsorbed at sorption site **A** near the wall of the 1D channels interact with **1** through hydrogen bonding and at the same time interact with those at site **B** mainly through quadrupole−quadrupole interaction in a T-shaped arrangement. Interestingly, two CO_2 molecules are included in the CB[6] cavity (site **C**), interacting not only with the carbonyl groups of CB[6] but also with each other in a slipped-parallel geometry. The exceptionally selective CO_2 sorption properties of **1** may find useful applications in the pressure swing adsorption (PSA) process for CO_2 separation not only in the steel industry but also in other industries such as natural gas mining.

The removal of CO_2 generated by power plants and steel mills has drawn a great amount of attention because 40−50% of total CO_2 emission causing global warming is coming out of such stationary sources.[1] Especially, in the process of steelmaking, a large amount of CO_2 is generated, as CO gas is used as a reducing agent and converted into CO_2 gas. Capturing CO_2 selectively in flue gases and recycling unreacted CO is thus an important issue in the steel industry.[2] Various amine solutions have been commonly used to capture CO_2 selectively from the flue gases through a chemical reaction between the amines and CO_2 molecules.[3] In addition to the toxicity and corrosion problems, however, this process requires substantial energy to recover the amines for recycling, leading to low energy efficiency and high cost.[4]

The search for new materials for selective separation of CO_2 from flue gases is thus critically important. Recently, metal−organic frameworks (MOFs), emerging absorbents made of metal ions and organic building blocks, with an exceptionally high surface area and easily modifiable functional groups showed a remarkable CO_2 sorption capacity and selectivity.[5] However, no MOF has met stringent industrial requirements, as they are generally too expensive, sensitive to moisture, etc. Organic molecular porous materials assembled from cheap, robust, and readily available organic molecules may be good candidates for such adsorbents, but only a few organic molecular porous materials have been investigated for this purpose.[6] Herein we report the highly selective sorption of CO_2 over CO and CH_4 in an organic molecular porous material (**1**) based on cucurbit[6]uril (CB[6]) with high thermal and chemical stability and permanent porosity. Single-crystal X-ray structure of CO_2 adsorbed **1** revealed three CO_2 sorption sites located in 1D channels and molecular cavities.

Cucurbit[6]uril is a hollowed-out pumpkin-shaped macrocycle with a hydrophobic cavity accessible through two identical carbonyl-fringed portals.[7] The molecule with high thermal and chemical stability is readily synthesized in high yield from cheap starting materials, glycoluril and formaldehyde. The organic molecular porous material (**1**) obtained by recrystallization of CB[6] from HCl showed a honeycomb-like structure with 1D channels along the *c* axis (Figure S1).[8] The interesting structure, high thermal and chemical stability,[9] and gas sorption properties of **1** prompted us to tackle the challenging issue of selective CO_2 separation and storage.

Gas (CO_2, CH_4, and CO) sorption isotherms for **1** were measured up to 1 bar at 273 and 298 K (Figures 1 and S4). Interestingly, **1** showed an unusually high CO_2 sorption capacity with little hysteresis (45 cm^3/g, 2.2 mmol/g at 298 K, 1 bar), which is much higher than those of any known organic molecular porous materials.[6,10] In particular, CO_2 uptake (32 mg/g) of **1** at 0.1 bar, a typical partial pressure of CO_2 in flue gases from power plants and steel mills, is comparable or even superior to that of many MOFs (Table S1).[5e,f] The maximum sorption capacity for CO_2 at 1 bar, 196 K is 97 cm^3/g (4.4 mmol/g), which corresponds to 4.5 CO_2 molecules per CB[6]. Unlike CO_2, however, CO gas was minimally absorbed in **1** up to 1 bar at 298 K. It should be noted that the selectivity of CO_2 over CO estimated by Henry's constants at 298 K is 46.4, which is the highest

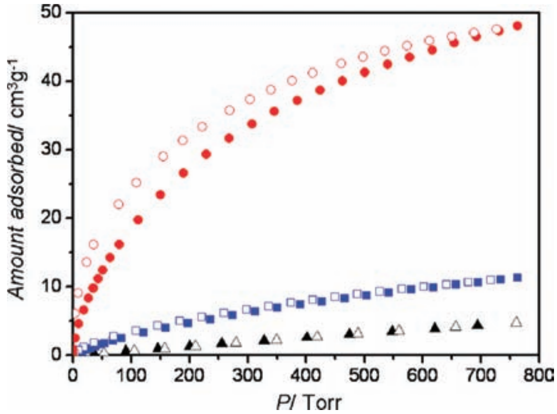

Figure 1. CO_2 (red circles), CH_4 (blue squares), and CO (black triangles) sorption isotherms for **1** at 298 K (filled symbols: adsorption; open symbols: desorption).

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value among those of known porous materials so far (see Supporting Information (SI) for details).[5a,b] Moreover, **1** also showed remarkable CO_2 selectivity (14.8) over CH_4, which suggests that it may be useful in the removal of CO_2 from natural gas.[5b,c]

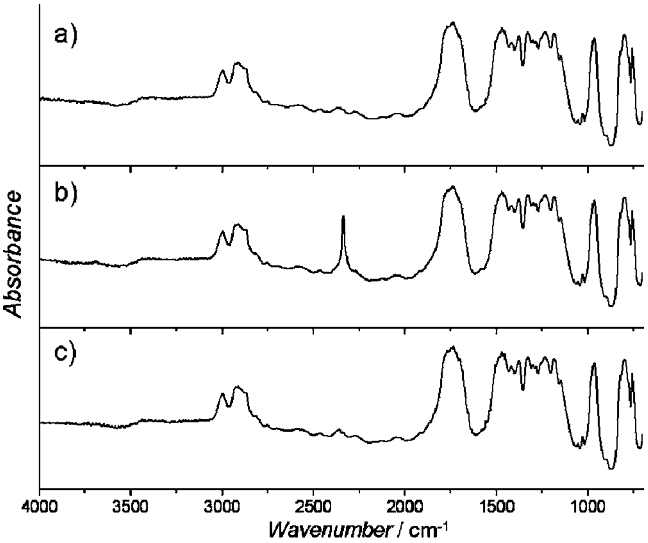

Figure 2. *In situ* FT-IR spectra of (a) **1** after activation at 150 °C, (b) CO_2 loaded **1** at 30 Torr, and (c) CO loaded **1** at 30 Torr.

To confirm the selective sorption of CO_2, we then carried out an *in situ* FT-IR spectroscopic study. The IR spectrum of **1** taken after exposure to CO_2 gas at 30 Torr followed by removal of free CO_2 gas under vacuum at 50 °C showed a characteristic CO_2 peak at 2336 cm^{-1} confirming the strong sorption of CO_2. On the other hand, when the same experiment was repeated with CO, no CO peak was observed, indicating no sorption of CO gas (Figure 2). In addition, the temperature-dependent FT-IR spectra (Figure S9) of CO_2 adsorbed **1** showed that strongly adsorbed CO_2 molecules were slowly removed as the temperature increased from 50 to 100 °C.

The enthalpy of CO_2 adsorption for **1** was estimated from the sorption isotherms at 273 and 298 K using the virial equation to understand the strong affinity of **1** toward CO_2. At zero coverage, the enthalpy of CO_2 adsorption is 33.0 kJ/mol, which is comparable to those of MOFs with organic ammonium ions in the pores for strong CO_2 binding (Figure S10).[5g] The exceptionally high enthalpy of CO_2 adsorption in the organic molecular porous material led us to study the CO_2 sorption sites in **1**.

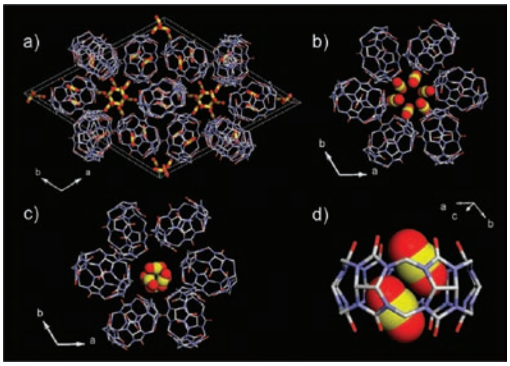

Figure 3. (a) X-ray crystal structure of CO_2 adsorbed **1**, (b) sorption site **A**, (c) sorption site **B**, and (d) sorption site **C**.

To investigate the CO_2 sorption sites in **1**, the structure of CO_2 adsorbed **1** was determined by single-crystal X-ray crystallography. A single-crystal of **1** was sealed in a thick walled glass capillary under a CO_2 atmosphere (see SI for details), and X-ray diffraction data were collected at 90 K with synchrotron radiation.[11] X-ray crystal structure analysis of CO_2 adsorbed **1** revealed that (1) CB[6] molecules are disordered over two positions and (2) there are three independent CO_2 sorption sites, two in the 1D channels (**A** and **B**) and one in the CB[6] cavities (**C**) (Figure 3). The CO_2 molecules adsorbed on sorption site **A** near the wall of the 1D channels interact with **1** through hydrogen bonding ($CH\cdots O{=}C{=}O$; 2.575 Å on average) (Figures 3b and S11). Sorption sites **B** located near the center of the channels along the *c* axis and disordered over three positions (occupancy, 0.33) are the secondary sorption sites (Figure 3c).[12] The CO_2 molecules occupying site **B** interact with those at site **A** mainly through quadrupole−quadrupole interaction in a T-shaped arrangement ($O_2C\cdots O_2C$; 3.00 Å) (Figures S12).[12] From a static structural point of view, the molecular cavities of the CB[6] molecules in **1** are not accessible because both portals of a CB[6] molecule are blocked by neighboring CB[6] molecules. Surprisingly, however, two CO_2 molecules are included in the CB[6] cavity (site **C**; occupancy, 0.89), interacting not only with the carbonyl groups of CB[6] but also with each other in a slipped-parallel geometry (shortest distance; 3.21 and 3.20 Å, respectively) (Figures 3d and S13).[13] This observation clearly indicated that **1** is in dynamic motion to open the portals in the presence of CO_2 gas even in the solid state. The amount of adsorbed CO_2 revealed by the X-ray structure of CO_2 adsorbed **1** (3.72 CO_2 per CB[6]) is slightly smaller than that from the sorption isotherm at 196 K (4.5 CO_2 per CB[6]), presumably owing to the slightly low occupancy at the sorption sites.

In summary, an organic molecular porous material based on CB[6] recrystallized from HCl conditions shows a high CO_2 sorption capacity at 298 K, 1 bar. Most interestingly, **1** showed the highest selectivity of CO_2 over CO among those of any known porous materials so far. The remarkable selectivity of CO_2 may be attributed to the high enthalpy of CO_2 adsorption. Single-crystal X-ray analysis revealed three CO_2 sorption sites including the molecular cavity of CB[6] and adsorbed CO_2 interacting with **1** through hydrogen bonding and/or dipole−quadrupole interactions, which may be responsible for the high enthalpy of CO_2 adsorption. The exceptionally selective CO_2 sorption properties of **1** may find useful applications in the pressure swing adsorption (PSA) process for CO_2 separation not only in the steel industry but also in other industries such as natural gas mining.

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Supporting Information Available: Experimental details for PXRD, gas sorption isotherm, IR, and enthalpy of adsorption. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) **1** soaked in 0.1 M HCl, MeOH, DMSO, and benzene and exposed to moisture in open air maintains its crystallinity at least for several days (Figure S3).

(10) The CO_2 sorption capacity of **1** at 22 bar, RT is measured to be 14.8 wt % (3.36 mmol/g). See SI for details.

(11) X-ray data for CB[6]·3.72CO_2: $C_{39.72}H_{36}N_{24}O_{19.44}$, $M = 1160.61$, trigonal, $R\bar{3}$ (No. 148), $a = 31.782(5)$ Å, $c = 12.388(3)$ Å, $V = 10836(3)$ Å^3, $Z = 9$, $T = 90$ K, μ(synchrotron) $= 0.147$ mm^{-1}, $\rho_{calc} = 1.601$ g·cm^{-3}, R_1 ($I > 2\sigma(I)$) $= 0.0821$, wR_2 (all data) $= 0.2466$ (all data), GOF = 1.094.

(12) Note that the CO_2 molecules at site **B** are significantly bent with an OCO angle of 159(4)°, whereas those at sites **A** and **C** have an almost linear geometry (176.3(9)° and 179.1(8)°, respectively). Similar bending of CO_2 after adsorption in an MOF has been observed: Dietzel, P. D. C.; Johnsen, R. E.; Fjellvag, H.; Bordiga, S.; Groppo, E.; Chavan, S.; Blom, R. *Chem. Commun.* **2008**, 5125.

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