Supporting Information

Enhanced Selectivity of CO_2 from a Ternary Gas Mixture in an Interdigitated Porous Framework

Keiji Nakagawa,[a] Daisuke Tanaka,[a] Satoshi Horike,[a] Satoru Shimomura,[a] Masakazu Higuchi,[a] and Susumu Kitagawa*[a,b,c]

[a] Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan. E-mail: kitagawa@sbchem.kyoto-u.ac.jp; Fax: +81-75-383-2732; Tel: +81-75-383-2733. [b] Kitagawa Integrated Pore Project, Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Agency (JST) Kyoto Research Park, 134, Chudoji Minami - machi, Shimogyo-ku, Kyoto 600-8813, Japan. [c] Institute for Integrated Cell-Material Sciences, Kyoto University Katsura, Nishikyo-ku, Kyoto 615-8510, Japan.

E-mail: kitagawa@sbchem.kyoto-u.ac.jp

General Information.

$Zn(NO_3)_2 \cdot 6H_2O$ were purchased from Wako and dimethylnaphthalene-2,7-dicarboxylate and 4,4'-bipyridyl (bpy) were purchased from TCI. All chemicals and solvents used in the syntheses were of reagent grade and used without further purification. NaX zeolite F-9 (100 mesh) was purchased by Wako Pure Chemical Industries, Ltd. The carbon dioxide, oxygen, nitrogen and helium gases were supplied by Japan Air Gases Co. with a purity of 99.9999 %. The water content in each gas is less than 10 ppm.

Synthesis of Naphthalene-2,7-dicarboxylic acid (H_2ndca).

Dimethylnaphthalene-2,7-dicarboxylate (5.2 g, 21 mmol) and sodium hydroxide (7.0 g, 180 mmol) was refluxed with methanol / water 1:1 solution (300 mL) for 22 h. After acidified with hydrochloric acid to pH = 1, precipitation was filtered, washed with water (200 mL), ethanol (200 mL), and chloroform (200 mL) respectively, to yield white powder; yield: 4.4 g (96%). ^{1}H NMR(DMSO): δ = 8.76 (s, 1H), 8.09 (s, 2H) ppm.

Synthesis of {[Zn(ndca)(bpy)]·DMF}$_n$ (CID-3⊃DMF).

A single crystal of CID-3⊃DMF was prepared by treating $Zn(NO_3)_2 \cdot 6H_2O$ (0.30 g, 1 mmol), H_2ndca (0.22 g, 1 mmol) and bpy (0.16 g, 1 mmol) in DMF (10 ml) by the hydrothermal technique in a Teflon-lined autoclave. The autoclave was heated under autogenous pressure to 120 ˚C for 2 days and then cooled to RT over 24h. Upon cooling the mixture to RT, the desired compound appeared as colourless rectangular crystal in ca. 70 % yield. Elemental analysis (%) calcd for $C_{22}H_{14}N_2O_4Zn$ (435.77):C 60.6, H 3.24, N 6.43 %; found : C 59.9, H 3.31, N 6.36 %.

Single Crystal X-ray Diffraction.

X-ray structure determination was made on Rigaku Mercury CCD system with $Mo_{K\alpha}$ radiation. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 (SHELXL-97). All non-hydrogen atoms were anisotropically refined, while all hydrogen atoms were placed geometrically and refined with a riding model with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom. Crystal data for CID-3⊃DMF, $C_{25}H_{21}N_3O_5Zn$, $M_r = 508.82$, monoclinic, space group $C2/c$, (#15), $a = 16.14(4)$ Å, $b = 11.35(3)$ Å, $c = 24.67(9)$ Å, $\beta = 102.11(7)$, $V = 4419(23)$ Å^3, $Z = 8$, $T = 223(2)$ K. $\rho_{calcd} = 1.530$ g/cm^3, $\mu(Mo_{K\alpha}) = 1.155$ cm^{-1}, $2\theta_{max} = 55.4$˚, $\lambda(MoK\alpha) = 0.71070$ Å, 19572 reflections measured, 5102 unique, $3851 > 2\sigma(I)$ were used to refine 307 parameters, no restraints, $R_{int} = 0.0495$. The final R_1 values were 0.0777 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2335 ($I > 2\sigma(I)$). GOF = 1.656. CCDC number CCDC 745860.

Physical Measurements.

Thermogravimetric analysis (TGA) were performed using a Rigaku Thermo plus TG 8120 apparatus in the temperature range between 298 and 723 K in a N_2 atmosphere and at a heating rate of 5 Kmin^{-1}. X-ray powder diffraction (XRPD) data were collected on a Rigaku RINT-2200HF (Ultima) diffractometer with CuKα radiation. The adsorption isotherms for CO_2 at 195 K and N_2 and O_2 at 77 K were measured with Quantachrome AUTOSORB-1. High pressure single component adsorption experiments and ternary adsorption experiments were carried out with BELSORP-VC volumetric adsorption equipment from BEL Japan, Inc. The break through curve was measured by BELSORP-DYNA from BEL Japan, Inc. The carrier gas (Helium) was purged into the sample column filled by the 2 g CID-3. The gas mixture (1 MPa, $CO_2:O_2:N_2 = 1:21:78$) was injected into the column at 298 K and the relative amounts of the gases passing through the column were monitored by using gas chromatograph technique. The flows of CO_2, O_2, N_2, and He were set to 0.1, 2.1, 7.8, and 10 sccm, respectively, and the total gas pressure was 1.0 MPa. The sample was activated

under high vacuum at 393 K for 8 h to remove the adsorbed small molecules in the pore before the adsorption measurements.

Adsorption Experiments by BELSORP-VC volumetric adsorption equipment.

The experimental method is based on a masss balance principle, which employs precise measurments of pressures, volumes and temperatures. The experimental setup for volumetric-chromatographic measurements of pure and mixed gas adsorption equilibria is schimatically shown in Figure S1. Pressures are measured using high precision pressure transducers (GC Druck PMP4000, $\Delta P = \pm 0.0008 \cdot P_{max}$). Temperatures are measured and controlled by peltier-type temperature controller (Yamatake C35TV0UA3200). The sample was activated under high vacuum at 393 K for 8 h to remove the adsorbed small molecules in the pore before the adsorption measurements.

Analysis of single component adsorption isotherms measured at 298 K

The saturated adsorption amounts of each gas on CIDs are calculated by Langmuir equation

$$\theta = \frac{A}{A_{sat}} = \frac{BP}{1+BP} \qquad (1)$$

where, θ is the fractional coverage, A is the adsorption amount, $A_{sat.}$ is the saturated adsorption amount, B is Langmuir constant and P is pressure. These parameters are listed in Table S1. Henry's law constant, which is calculated by Equation. 2, is useful in predicting the equilibrium separation factor to estimate separation conditions.

$$b = BA_{sat} \qquad (2)$$

where, b is Henry's law constant. The primary requirement for an economic separation process is an adsorbent with sufficiently high selectivity. Generally, a good indicator of the ability for separation equilibrium process is the selectivity S, defined by

$$S = \frac{x_A/x_B}{y_A/y_B} \qquad (3)$$

where, x_A, x_B, y_A, and y_B are the mole fractions of components A and B in adsorbed and fluid phases at equilibrium. For favorable Langmuir type adsorption isotherms, this separation factor is constant and is given by the ratio of the Henry's law constants which is defined as follows;

$$S_{i,A/B} = \frac{b_A}{b_B} \qquad (4)$$

where $S_{i,A/B}$ is the initial equilibrium separation factor calculated according to this equation. The obtained $S_{i,A/B}$ are listed in Table 1.
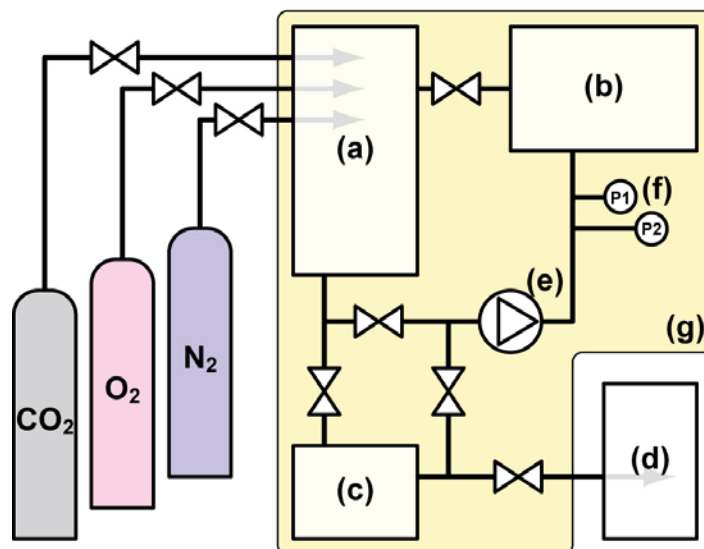
Figure S1. The experimental setup for volumetric-chromatographic measurements of pure and mixed gas adsorption equilibria (BELSORP-VC volumetric adsorption equipment). (a) the storage vessel, (b) the adsorptive vessel, (c) the micro vessel, (d) micro GC, (e) circulation pump, and (f) absolute pressure transducers operating in two different pressure ranges, and (g) constant temperature bath.
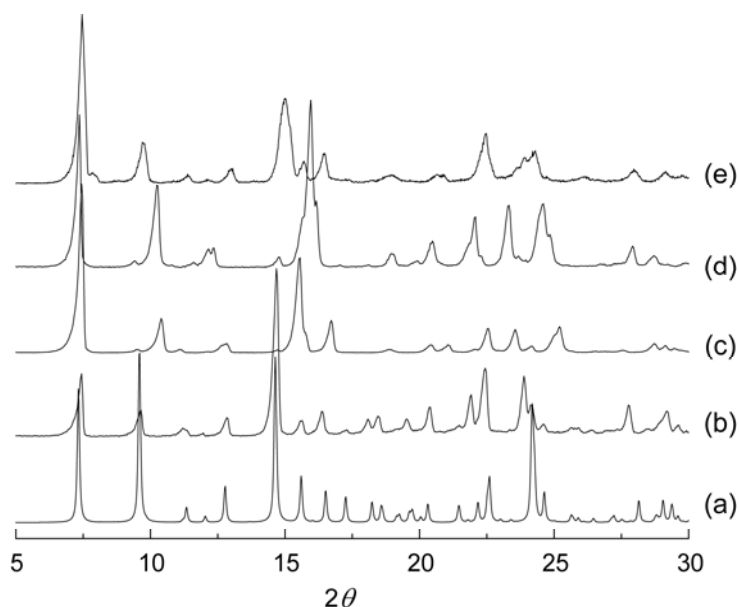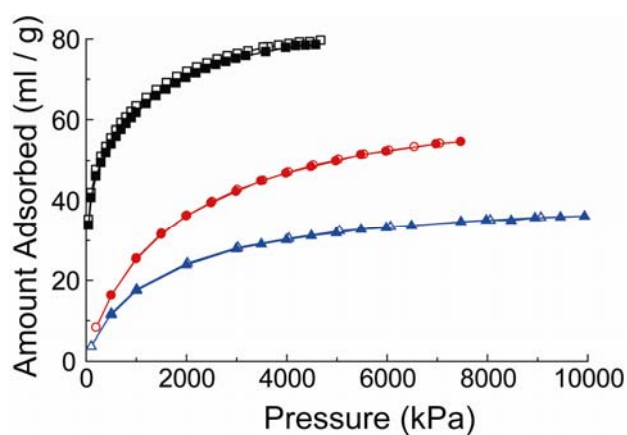

Figure S2. XRPD patterns of (a) simulated CID-3⊃DMF from singlecrystal analysis, (b) experimental CID-3⊃DMF (as synthesized), (c) dried CID-3 (d) CID-3⊃MeOH, and (e) CID-3⊃EtOH.
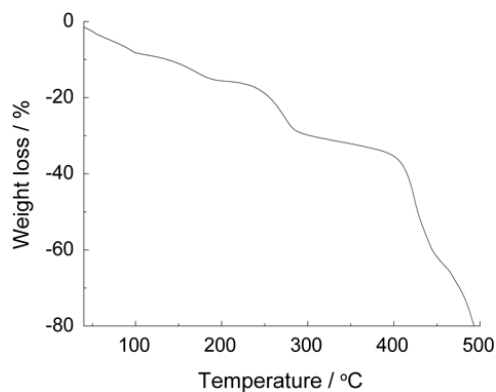
Figure S3. TGA showing the weight loss of CID-3⊃DMF.
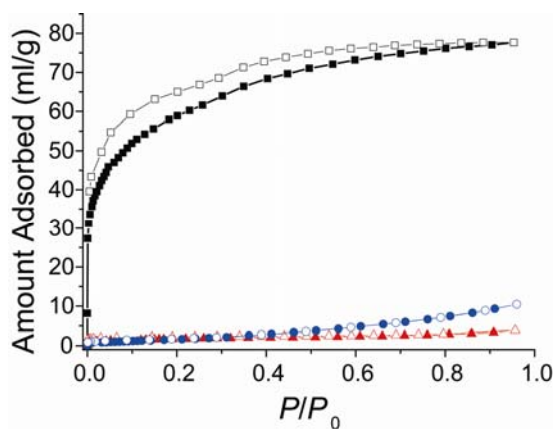
Figure S4. Sorption isotherms of N_2 (blue circles) and O_2 (red circles) at 77 K and CO_2 (black circles) at 195 K in CID-3. (Filled symbol: adsorption. Open symbol: desorption).

Figure S5. Sorption isotherms of N_2 (blue circles), O_2 (red circles) and CO_2 (black circles) at 298 K. (Filled symbol: adsorption. Open symbol: desorption).

Table S1. The Henry's law constants (b) and the selectivity for CO_2 over N_2 ($S_{CO2/N2}$) and O_2 ($S_{CO2/O2}$) on CID-3 and NaX zeolite estimated from Langmuir analysis.

Compound	b (CO_2)	b (N_2)	b (O_2)	$S_{CO2/N2}$	$S_{CO2/O2}$
CID-3	381.6	30.0	33.0	12.7	11.6
NaX	12665.9	93.8	33.3	135.0	380.4

Table S2. The experimental data of mixed gas on CID-3 at 3 MPa, $CO_2:O_2:N_2 = 1:21:78$.

Time	Mole fraction (%)			Adsorption amount (ml(STP) g^{-1})			S
(h)	CO_2	O_2	N_2	CO_2	O_2	N_2	
0.1	0.96	21.42	77.63	0.79	10.39	24.92	2.3
3	0.75	21.35	77.89	7.06	14.26	17.7	29.2
6	0.7	21.37	77.93	8.59	14.2	16.89	39.2

Table S3. The experimental data of mixed gas on NaX zeolite at 3 MPa, $CO_2:O_2:N_2 = 1:21:78$.

Time	Mole fraction (%)			Adsorption amount (ml(STP) g^{-1})			S
(h)	CO_2	O_2	N_2	CO_2	O_2	N_2	
0.1	0.85	21.82	77.34	5.74	42.29	184.85	2.9
3	0.43	22.2	77.37	18.09	31.32	188.67	19.0
6	0.27	22.23	77.5	22.94	30.3	185.34	39.3