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Hydrogen-adsorption Properties of a Novel Lantern-type Dinuclear Co(BDC)(DABCO)$_{1/2}$

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A three-dimensional (3-D) cobalt coordination polymer Co(BDC)(DABCO)$_{1/2}$ (BDC = 1,4-benzenedicarboxylate; DABCO = 1,4-diazabicyclo[2.2.2]octane), which has a novel lantern-type structure, was synthesized and characterized by X-ray powder diffraction patterns and elemental analysis. In addition, hydrogen-adsorption characteristics were evaluated at 77 K. The highest measured hydrogen uptake was 2.28 wt% at 77 K and 0.1 MPa for Co(BDC)(DABCO)$_{1/2}$.

Porous metal–organic frameworks (MOFs) have become competitors to other porous materials such as zeolite[1] and carbon materials.[2] Recent studies have confirmed that these frameworks can store considerable quantities of hydrogen at 77 K.[3] The U.S. Department of Energy (DOE), in its guidelines leading up to 2010, has set performance targets for on-board automobile storage systems to have densities of 60 mg H_2/g (gravimetric) and 45 g H_2/L (volumetric).[4] Recently, Yaghi and co-workers reported on the considerable potential for hydrogen storage in microporous coordination solids with robust 3-D frameworks and high surface areas.[3a–3c]

Previously, we reported that copper(II) dicarboxylates,[5] molybdenum(II) dicarboxylates,[6] and ruthenium(II,III) dicarboxylates,[7] which have lantern-type structures, reversibly occluded large amounts of gases such as N_2, Ar, O_2, CH_4, and Xe. The uniform linear micropores of these adsorbents were assumed as having been constructed by the stacking or bonding of two-dimensional (2-D) lattices of dinuclear transition-metal dicarboxylates. It is well known that cobalt with carboxylate forms a chelating bis-bidentate coordinate,[8] but there are no reports of a lantern-type cobalt(II) dicarboxylate complex. Recently, it has been found that mononuclear copper(II) BDC-pyridine,[9] which has a regular one-dimensional (1-D) structure, occludes large amounts of gases. In this paper, we report the synthesis and characterization of new lantern-type coordination polymers with 3-D network structures formed by linking original 2-D layer frameworks of mononuclear cobalt(II) BDC-pyridine with pillar ligands such as DABCO. This 3-D polymer is expected to have superior porosities and higher stabilities than those of the original 2-D polymers. In addition, hydrogen adsorption, which is a very important factor in the application of these porous materials, is evaluated at 77 K.

An aqueous solution (100 mL) of cobalt(II) acetate tetrahydrate (0.25 g) was added to a pyridine solution (400 mL) of terephthalic acid (0.2 g). After mixing, the solution was allowed to stand for several days at room temperature leaving a pink, plate-like crystal precipitate. $[Co^{II}(O_2CC_6H_4CO_2)(py)_2(H_2O)_2]\cdot py\cdot H_2O$ Anal. Calcd for $C_{23}H_{25}CoN_3O_7$: C, 53.70; H, 4.90; N, 8.17%. Found: C, 53.92; H, 5.06; N, 8.47%. A methanol solution (100 mL) of DABCO (0.1 g) was added to the pink, plate-like crystal precipitate (0.1 g), and the mixture was stirred for about 24 h at 338 K. A purplish-red powder capable of adsorbing gases was collected, washed with methanol, and dried at 373 K under vacuum for 4 h (yield: 67%). $[Co^{II}(O_2CC_6H_4CO_2)(N_2C_6H_{12})_{0.5}]$ Anal. Calcd for $C_{11}H_{10}CoN_1O_4$: C, 47.33; H, 3.61; N, 4.95%. Found: C, 47.27; H, 3.58; N, 4.91%.

Figure 1a shows that the observed X-ray powder diffraction patterns (XRPD) are in good accordance with the simulated patterns of the optimized Cu(BDC)(DABCO)$_{1/2}$[10] structure by using Cerius2 software, confirming that the structures of the obtained compounds are plausible. From these results and elemental analyses, the structure is thought to be lantern-type and 3-D in which 2-D layers bridging the cobalt(II) ions with the dicarboxylate ions are linked with DABCO as a pillar ligand, as shown in Figure 1b. Thermogravimetric analysis of Co(BDC)(DABCO)$_{1/2}$ was performed under atmospheric conditions. The result showed that Co(BDC)(DABCO)$_{1/2}$ has high thermal stability, with no chemical decomposition between room temperature and ca. 600 K. This high thermal stability is similar to that of Cu(BDC)(DABCO)$_{1/2}$ and Zn(BDC)(DABCO)$_{1/2}$[3d] with an isostructure.

The porosity and specific surface areas of the metal–organic porous material Co(BDC)(DABCO)$_{1/2}$ were estimated by measuring argon gas sorption isotherms at 87.3 K in a relative pressure range from 10^{-6} to 1. Analyses of the Ar isotherm gave a Langmuir surface area of 1965 m^2/g, BET surface area of 1639 m^2/g, maximum micropore volume of 0.659 cm^3/g, and effective pore size of 6.0 Å (using DR methods[11] and Horvath–Kawazoe (HK) methods[12]). The argon gas sorption isotherms and effective pore diameter are shown in Figure 2. In this case, the sorption of argon reaches near saturation at low relative pres-

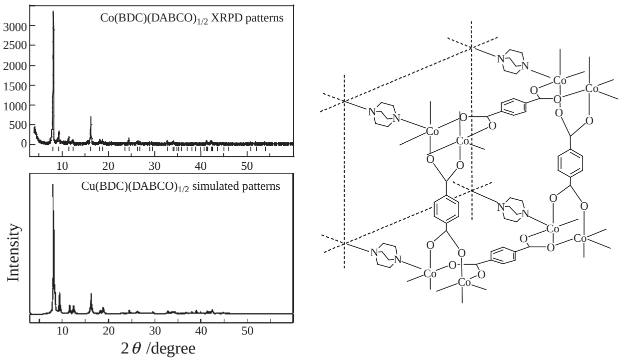

Figure 1. (a) XRPD pattern for Co(BDC)(DABCO)$_{1/2}$ (top). Simulated XRPD pattern for Cu(BDC)(DABCO)$_{1/2}$[10] (bottom). (b) Plausible three-dimensional structure for Co(BDC)(DABCO)$_{1/2}$.

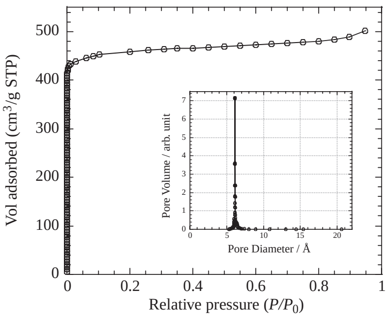

Figure 2. Adsorption isotherm of Co(BDC)(DABCO)$_{1/2}$ obtained with argon gas in the relative pressure range of 10^{-6} to 1 at the temperature of liquid argon. The pore size distribution is shown in the inset.

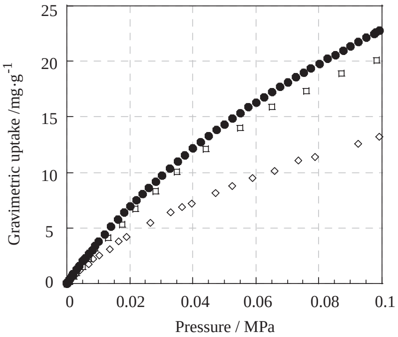

Figure 3. Hydrogen-adsorption isotherms for Co(BDC)(DABCO)$_{1/2}$ measured at 77 K in gravimetric units. Adsorption data is indicated by closed circles, Yaghi's IRMOF-1 adsorption data[3b] by open diamonds, and Kim's Zn(BDC)(DABCO)$_{1/2}$ adsorption data[3d] by open squares.

sures ($P/P_0 < 0.05$), and thereafter increases very slowly up to 1 atm. The adsorption isotherms of argon for Co(BDC)(DABCO)$_{1/2}$ can be interpreted as Type-1 of the Langmuir type adsorption isotherm, implying that the cavities in this material consist of micropores but have no large cavities that may be classified as mesopores. The sharp rising of argon adsorption at low relative pressures indicates that the micropores are uniform. The rising of argon adsorption at high relative pressures depends on the condensation into interparticle voids.

As expected from their high level of porosity, the materials adsorbed considerable amounts of hydrogen. Figure 3 shows the resulting hydrogen-adsorption isotherms up to 0.1 MPa at 77 K in gravimetric units (mg/g). This material displays approximately a Type-1 isotherm, and saturation was not reached under this condition. The maximum amount of hydrogen gas storage was 22.8 mg/g (2.28 wt %). This value is higher in terms of the quantity of hydrogen adsorption than that of Yaghi's IRMOF-1($Zn_4O(BDC)_3$)[3b] and Kim's Zn(BDC)(DABCO)$_{1/2}$[3d] under the same conditions.

This study has demonstrated that coordination polymers having a lantern-type, 3-D network structure bridging the 2-D layer of cobalt(II) dicarboxylates by DABCO as a pillar ligand have uniform micropores. In addition, the reactions are reproducible and can be readily scaled up. The cobalt coordination polymer exhibits hydrogen-adsorption characteristics and has a microporous structure that changes in response to external stimuli such as pressure. The highest measured hydrogen uptake of Co(BDC)(DABCO)$_{1/2}$ was 2.28 wt % at 77 K and 0.1 MPa. The result of the present work is the possibility of achieving a DOE goal of an even higher pressure.

References

1 a) H. W. Langmi, A. Walton, M. M. Al-Mamouri, S. R. Johnson, D. Book, J. D. Speight, P. P. Edwards, I. Gameson, P. A. Anderson, I. R. Harris, *J. Alloys Compd.* **2003**, *356–357*, 710. b) A. Zecchina, S. Bordiga, J. G. Vitillo, G. Ricchiardi, C. Lamberti, G. Spoto, M. Bjorgen, K. P. Lillerud, *J. Am. Chem. Soc.* **2005**, *127*, 6361. c) J. Eckert, J. M. Nicol, J. Howard, F. R. Trouw, *J. Phys. Chem.* **1996**, *100*, 10646.

2 a) B. Panella, M. Hirscher, S. Roth, *Carbon* **2005**, *43*, 2209. b) H. G. Schimmel, G. J. Kearley, M. G. Nijkamp, C. T. Visser, K. P. de Jong, F. M. Mulder, *Chem. Eur. J.* **2003**, *9*, 4764. c) G. Gundiah, A. Govindaraj, N. Rajalakshmi, K. S. Dhathathreyan, C. N. R. Rao, *J. Mater. Chem.* **2003**, *13*, 209. d) M. Becher, M. Haluska, M. Hirsher, A. Quintel, V. Skakalova, U. Dettlaff-Weglikovska, X. Chen, M. Hulman, Y. Choi, S. Roth, V. Meregalli, M. Parrinello, R. Ströbel, L. Jörissen, M. M. Kappes, J. Fink, A. Züttel, I. Stepanek, P. Bernier, *C. R. Phys.* **2003**, *4*, 1055.

3 a) N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, *Science* **2003**, *300*, 1127. b) J. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, *128*, 1304. c) A. G. Wong-Foy, A. J. Matzger, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, *128*, 3494. d) D. N. Dybtsev, H. Chun, K. Kim, *Angew. Chem., Int. Ed.* **2004**, *43*, 5033. e) H. Chun, D. N. Dybtsev, H. Kim, K. Kim, *Chem. Eur. J.* **2005**, *11*, 3521. f) D. Sun, S. Ma, Y. Ke, D. J. Coollins, H.-C. Zhou, *J. Am. Chem. Soc.* **2006**, *128*, 3896. g) J. Jia, X. Lin, C. Wilson, A. J. Blake, N. R. Champness, P. Hubberstey, G. Walker, E. J. Cussen, M. Schröder, *Chem. Commun.* **2007**, 840.

4 a) *Hydrogen, Fuel Cells, & Infrastructure Technorogies Program: Multiyear Research, Development, and Demonstration Plan*; U.S. Department of Energy, February 2005, Chapter 3, http://www.eere.energy.gov/hydrogenandfuelcells/mypp/. b) *Basic Research Needs for the Hydrogen Economy*, report of the Basic Energy Sciences Workshop on Hydrogen Production, Storage, and Use, U.S. Department of Energy, May 13–15, 2005, http://www.sc.doe.gov/bes/.

5 W. Mori, F. Inoue, K. Yoshida, H. Nakayama, S. Takamizawa, M. Kishita, *Chem. Lett.* **1997**, 1219.

6 S. Takamizawa, W. Mori, M. Furihata, S. Takeda, K. Yamaguchi, *Inorg. Chim. Acta* **1998**, *283*, 268.

7 a) S. Takamizawa, K. Yamaguchi, W. Mori, *Inorg. Chem. Commun.* **1998**, *1*, 177. b) S. Takamizawa, T. Ohmura, K. Yamaguchi, W. Mori, *Mol. Cryst. Liq. Cryst.* **2000**, *342*, 199.

8 a) L.-J. Zhang, X.-L. Zhao, P. Cheng, J.-Q. Xu, X. Tang, X.-B. Cui, W. Xu, T.-G. Wang, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1179. b) J. Cano, G. D. Munno, J. L. Sanz, R. Ruiz, J. Faus, F. Lloret, M. Julve, A. Caneschi, *J. Chem. Soc., Dalton Trans.*, **1997**, 1915.

9 a) T. Ohmura, W. Mori, M. Hasegawa, T. Takei, A. Yoshizawa, *Chem. Lett.* **2003**, *32*, 34. b) T. Ohmura, W. Mori, M. Hasegawa, T. Takei, T. Ikeda, E. Hasegawa, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1387.

10 K. Seki, S. Takamizawa, W. Mori, *Chem. Lett.* **2001**, 332.

11 S. J. Gregg, K. S. W. Sing, in *Adsorption, Surface Area, Porosity*, 2nd ed., Academic Press, London, UK **1982**.

12 G. Horvath, K. Kawazoe, *J. Chem. Eng. Jpn.* **1983**, *16*, 470.