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Selective CO₂ adsorption in a flexible non-interpenetrated metal–organic framework[†]

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We have prepared a flexible metal–organic framework and demonstrated that when activated by supercritical CO_2 it has greater gas sorption capacities than that activated by the heat-evacuation method, and it selectively adsorbs CO_2 over N_2 at room temperature.

Metal-organic frameworks (MOFs) have attracted great attention because of their potential applications in selective molecular adsorption,¹ gas storage,^{2,3} gas separation,^{4,5} ion exchange,⁶ catalysis,⁷ and the fabrication of metal nanoparticles.^{2a,8} Flexible MOFs are of particular interest because of their ability to selectively capture $CO_2^{2b,9}$ and their structural transformations in response to external stimuli.¹⁰ One interesting aspect of these types of MOFs is the effect of the activation method. It has been reported that MOFs activated by the supercritical CO₂ treatment showed an increase in gas sorption capacities compared with those activated by the heat-evacuation method.¹¹ However, it is still unclear in previous reports whether the coordinated solvent molecules were removed together with the guest solvent molecules during each of these processes, which must greatly affect the gas sorption properties.2c,12

Here, we report synthesis, X-ray structure, and gas sorption properties of a flexible MOF constructed of paddle-wheel type Cu(II) dimers and the flexible ligand, tetrakis[4-(carboxyphenyl)oxamethyl]methane acid (H₄TCM). Both the heat-evacuation method and the supercritical CO₂ treatment method afforded [Cu₂(TCM)]_n that lost coordinated solvent molecules as well as guest solvent molecules. The latter method showed an increase in gas sorption capacities as well as isosteric heats of gas adsorption, compared to the former method. We also report that the present MOF has selective and reversible CO₂ capture ability at room temperature.

A bluish-green prismatic crystal of a 3D MOF, $\{[Cu_2(TCM)(H_2O)_2]\cdot 7DMF\cdot 3(1,4-dioxane)\cdot MeOH\}_n$ (SNU-21),



Fig. 1 The X-ray crystal structure of **SNU-21**. (a) A view seen on the *bc* plane. (b) A view seen on the *ac* plane. Colour code: Cu, blue; C, white; O, red.

has been prepared by heating $Cu(NO_3)_2 \cdot 2.5H_2O$ and H_4TCM in DMF/1,4-doxane/MeOH (3 : 3 : 1 v/v) at 80 °C for 24 h.

Previously, we reported two multiply interpenetrated networks prepared from TCM^{4–} and Ni(II) macrocyclic complexes.^{1b,8d} Several Zn(II)–TCM MOFs^{9,13} and a Cu(II)–TCM MOF,¹⁴ which had interpenetrated structures, were also reported. The Cu(II)–TCM MOF in this report is a newly discovered MOF that exhibits a non-interpenetrated 3D structure with large pores and void space.¹⁵

The X-ray crystal structure of SNU-21 (Fig. 1) indicates that $\{Cu_2(O_2CR)_4\}$ assembles in paddle-wheel shaped cluster units, in which each Cu(II) ion coordinates a water molecule at the axial site. A TCM⁴⁻ coordinates eight Cu(II) ions because each carboxylate behaves as a bidentate to coordinate two Cu(II) ions. The connectivity between the square-shaped $\{Cu_2(O_2CR)_4\}$ cluster units and tetrahedral TCM⁴⁻ ligands gives rise to a (4,4)-connected PtS-net type 3D framework. The angles around the central carbon (C1) of TCM^{4-} ($\angle C-C1-C$) are 107.1°-113.9°. The phenyl rings located at the trans positions in a TCM^{4-} are twisted relative to each other with a dihedral angle of 29.31(65)°. The framework is non-interpenetrated and generates 3D channels having rhombic apertures. The effective aperture sizes of the channels on the bc, ac, and ab planes, respectively, are $7.4 \times 7.5 \text{ Å}^2$, $22.8 \times 5.75 \text{ Å}^2$, and $12.1 \times 11.5 \text{ Å}^2$. The guest molecules occupying the channels were identified by IR, EA, and TGA data as well as NMR spectra measured in CDCl₃ where SNU-21 was immersed for 24 h (see ESI[†]). The void volumes of SNU-21 with and without coordinated water molecules are 72.0% and 73.8%, respectively, as estimated by PLATON.¹⁶ Solid SNU-21 is insoluble in water and common organic solvents.

The desolvated solids, SNU-21H and SNU-21S, were prepared by heating SNU-21 at 180 $^\circ$ C under vacuum for 12 h

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[†] Electronic supplementary information (ESI) available: Detailed experimental procedures, ORTEP drawings, ¹H-NMR spectra, TGA/DSC traces, PXRD patterns, tables of X-ray data for SNU-21, tables of gas adsorption data for SNU-21H and SNU-21S. CCDC 779539. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc05199c

Gas	T/\mathbf{K}	P/atm	Adsorption capacity (wt% gas)	
			SNU-21H	SNU-21S
<i>^a P</i> /bar				
N_2	77	0.9	24.9	31.5
$\overline{O_2}$	77	0.2	42.0	48.6
H ₂	77	1.0	1.64	1.95
	87	1.0	1.11	1.46
	77	70^a	4.36 (total, 4.95)	4.37 (total, 5.10)
	298	70^a	0.18 (total, 0.34)	0.26 (total, 0.43)
CO ₂	195	1.0	45.9	50.5
	273	1.0	17.1	18.4
	298	1.0	9.65	11.1
	298	45^a	24.9	27.2
CH ₄	195	1.0	7.62	8.86
	273	1.0	1.87	1.97
	298	1.0	1.07	1.17
	298	50^a	5.32	6.38

and by treating SNU-21 with supercritical CO₂. Both samples lost all guests and coordinated H₂O molecules to form [Cu₂(TCM)]_n, as evidenced by IR, EA, and TGA data. SNU-21H and SNU-21S lost transparency and single-crystallinity. The PXRD patterns of SNU-21H and SNU-21S differ from each other and from the measured- and simulated-patterns of SNU-21 (see ESI†). In particular, the peaks corresponding to (002), (-111), and (220) planes of the pristine SNU-21 shift to a slightly higher angle region in SNU-21H, while they shift to a lower angle region in SNU-21S (see ESI†). This indicates the expansion of the framework during the supercritical CO₂ activation process. Similarly, it was previously reported that freeze dried MOFs showed considerable changes in PXRD patterns, indicating expansion and shrinkage of the unit cell parameters.¹⁷

The gas sorption isotherms of SNU-21H and SNU-21S were measured for N₂, O₂, H₂, CO₂, and CH₄ gases, and the results are summarized in Table 1. As seen in Table 1, SNU-21S that resulted from the supercritical CO₂ drying method adsorbs higher amounts of gases than SNU-21H that resulted from the heat-evacuation method, which is consistent with the expansion of SNU-21S as revealed by the PXRD analysis.

Solids **SNU-21H** and **SNU-21S** adsorb N_2 gas, showing typical Type-I sorption isotherms, characteristic of microporous materials (Fig. 2a). The surface areas and pore volumes, which

are estimated from the N₂ adsorption data by applying the Langmuir and Dubinin–Radushkevich (DR) equations, are 695 m² g⁻¹ and 0.25 cm³ g⁻¹ for **SNU-21H** and 905 m² g⁻¹ and 0.31 cm³ g⁻¹ for **SNU-21S**, respectively. These surface areas are significantly lower than the Connolly surface area (4042 m² g⁻¹) calculated from the X-ray crystal structure of **SNU-21** by using Materials Studio Program with a probe radius of 1.82 Å and a grid interval of 0.25 Å.¹⁸ The pore size distribution derived from the N₂ adsorption isotherms using the Horvath–Kawazoe (HK) method¹⁹ suggests that **SNU-21H** has pore sizes of 6.3 Å and 10.7 Å and **SNU-21S** has pore sizes of 6.6 Å, 9.2 Å, and 11.4 Å (see ESI†).

The O₂ adsorption isotherms at 77 K were measured up to 0.20 atm (147 Torr) since the saturation vapor pressure of O₂ is 147.8 Torr at 77 K. **SNU-21H** and **SNU-21S** adsorb more than 40 wt% of O₂ at 77 K (Table 1). The highest O₂ adsorption data reported is 118 wt% (829 cm³ g⁻¹) in **SNU-50'**.²⁰ Interestingly, the adsorption capacity for O₂ is higher than that of N₂ in both **SNU-21H** and **SNU-21S** at 77 K. This may be attributed to the smaller kinetic diameter and lower critical temperature of O₂ (3.47 Å, 33.2 K) than those of N₂ (3.64 Å, 126.2 K), which allows the O₂ adsorption in the smaller pores and in more condensable manner.

The H₂ adsorption capacities of SNU-21S are also higher than SNU-21H (Fig. 2b). In particular, the H₂ adsorption capacity of SNU-21S at 77 K and 1 atm is quite high, 1.95 wt% (216 cm³ g⁻¹ at STP, 9.66 mmol g⁻¹). The highest value reported so far measured under the same conditions is 2.87 wt%.^{2c} The zero coverage isosteric heat of H_2 adsorption, which is estimated from the adsorption data at 77 K and 87 K by using the virial equation,²¹ is 6.09 kJ mol^{-1} for SNU-21H and 6.65 kJ mol⁻¹ for SNU-21S (see ESI^{\dagger}). These values are lower than the previously reported data for MOFs containing accessible metal sites, such as Cu₆O(TZI)₃(NO₃) (9.5 kJ mol⁻¹),^{3e} HCu[(Cu₄Cl)₃(btt)₈]·3.5HCl (9.5 kJ mol⁻¹),^{3f} and SNU-5 $(11.60 \text{ kJ mol}^{-1})$.^{2c} At 77 K and high pressures, the H₂ adsorption increases linearly as the pressure increases (see ESI[†]). At 298 K and 70 bar, the H₂ adsorption capacity drops down to less than 10% of the values at 77 K, which is commonly observed in many other MOFs.

The CO_2 and CH_4 adsorption isotherms were measured at 195 K, 273 K, and 298 K (Table 1). The surface areas estimated from the CO_2 sorption isotherms at 195 K by using the



Fig. 2 Gas sorption isotherms of **SNU-21H** (blue) and **SNU-21S** (black). (a) N_2 (square) and O_2 (circle) at 77 K, (b) H_2 at 77 K (circle) and 87 K (triangle), (c) CO_2 (square) and N_2 (diamond) at 298 K.

DR equation are 934 m² g⁻¹ for SNU-21H and 1908 m² g⁻¹ for SNU-21S. They are significantly higher than those (695 m² g⁻¹ and 905 m² g⁻¹) estimated from the N₂ adsorption isotherms. This can be explained by the quadrupole moment of CO₂ $(1.43 \times 10^{-39} \text{ Cm}^2)$, which induces stronger interactions with the framework along with the expansion of the framework at 195 K compared to 77 K.²² The DR pore volumes estimated from the CO₂ sorption isotherms at 195 K are 0.33 cm³ g⁻¹ for SNU-21H and 0.68 cm³ g⁻¹ for SNU-21S. The zero coverage isosteric heats of CO₂ adsorption calculated from the adsorption data at 195 K, 273 K, and 298 K by using Clausius–Clapeyron equation are 29.7 kJ mol⁻¹ for SNU-21H and 36.1 kJ mol⁻¹ for SNU-21S (see ESI†). The zero coverage isosteric heats (Q_{st}) of the CH₄ gas adsorption are 23.6 kJ mol⁻¹ for SNU-21H and 25.7 kJ mol⁻¹ for SNU-21S (see ESI†).

Most significantly, SNU-21H and SNU-21S adsorb CO2 gas selectively at 298 K while they do not adsorb N₂ gas (Fig. 2c). Their adsorption capacities at 1 atm are 9.65 wt% and 11.1 wt%, respectively, and the isotherms show almost no hysteresis. The CO₂/N₂ selectivities at 298 K and 1 atm are 14.2 for SNU-21H and 19.7 for SNU-21S as calculated from the uptake ratio by weight for CO_2 over N_2 . These values are comparable to the selectivity value of H₃[(Cu₄Cl)₃(BTTri)₈] (21.0).²³ Typically, the CO₂ concentration of the industry flue gas streams ranges from 3 to 15 v/v% with N_2 gas as a main component. The effective selectivities obtained at a partial pressure of 0.15 atm for CO₂ and 0.85 atm for N₂ are 1.87 for SNU-21H and 2.73 for SNU-21S. The selective CO₂ adsorption over N₂ at 298 K in SNU-21H and SNU-21S is attributed to the fact that at this temperature CO_2 is subcritical and is much more condensable than N_2 that is supercritical. In addition, higher quadrupole moment and polarizability of CO₂ induce better interaction with the accessible Cu(II) centers of the framework.²⁴

In conclusion, we have prepared a flexible non-interpenetrated MOF that coordinates water molecules at the Cu(II) centers. By using two different activation methods, the heating-evacuation and the supercritical CO₂ treatment, respectively, we prepared **SNU-21H** and **SNU-21S**, which lost the coordinated solvent molecules as well as guest solvent molecules. The N₂, O₂, H₂, CO₂, and CH₄ gas adsorption studies in **SNU-21H** and **SNU-21S** indicate that the sample activated by the supercritical CO₂ treatment method adsorbs much higher amounts of gases than samples activated by the heating-evacuation method due to the structural differences. Interestingly, **SNU-21H** and **SNU-21S** show selective and reversible CO₂ adsorption over N₂ gas at room temperature, indicating that the present material can be applied in a CO₂ capture process.

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