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Significantly Enhanced CO_2/CH_4 Separation Selectivity within a 3D Prototype Metal–Organic Framework Functionalized with OH Groups on Pore Surfaces at Room Temperature

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A new three-dimensional microporous metal–organic framework (MOF) $Zn(BDC\text{-}OH)(DABCO)_{0.5}\cdot(DMF)_2(H_2O)$ (UTSA-25; $H_2BDC\text{-}OH$ = 2-hydroxybenzenedicarboxylic acid, DABCO = 1,4-diazabicyclo[2.2.2]octane) with functional –OH groups on the pore surfaces was solvothermally synthesized and structurally characterized. UTSA-25 features a three-dimensional structure with 3D intercrossed channels of about 7.5×7.5, 3.2×4.7, and 3.2×4.7 Å^2, respectively. The small pores and the functional –OH groups on the pore surfaces within the activated UTSA-25a have enabled their strong interactions with CO_2 of adsorption enthalpy of 22.5 kJ mol^{-1}, which is higher than that of 17.5 kJ mol^{-1} in the original MOF $Zn(BDC)(DABCO)_{0.5}$ without the functionalized –OH groups. Accordingly, CO_2/CH_4 separation selectivities in UTSA-25a of 17.2 and 12.5 at 273 and 296 K, respectively, are much higher than those of 4.4 and 3.7 in $Zn(BDC)(DABCO)_{0.5}$, thus highlighting UTSA-25a as a very promising porous material for industrially important CO_2/CH_4 separation.

Introduction

Carbon dioxide removal is industrially important for air purification and environmentally significant for minimization of its effect on global warming.[1,2] On the other hand, removal of carbon dioxide from methane is critical for methane transportation and usage in which corrosion of equipment and pipelines need to be prevented. Among the diverse technologies for such separation purposes, physical adsorption by microporous materials is a very promising cost-efficient technology,[3] particularly for low- to medium-volume production by methods such as pressure-swing adsorption.[4,5]

Among the diverse microporous materials, emerging microporous metal–organic framework (MOF) materials are very promising for the capture and separation of carbon dioxide from methane.[6–8] The carbon dioxide uptake capacities of such porous MOFs are apparently much higher than traditional porous materials because of their extraordinary pore surface areas.[9–37] Furthermore, by immobilization of functional sites to induce their stronger interactions with carbon dioxide and control/tune the pore size/curvature to maximize the size-exclusive effects in which smaller molecules can go through the microporous channels while larger substrates are blocked, the CO_2/CH_4 separation selectivities can be readily tuned and improved for their potential usage.[35–37] The realization of a few porous MOFs for the enlarged scale separation of CO_2/CH_4 by fixed-bed adsorption further enforced the notion that porous MOFs are very promising materials for carbon dioxide capture and separation.

Over the past several years, we have initiated and established a research program on metal–organic frameworks with functional pores for recognition of small molecules, and targeted a series of microporous MOFs for their diverse functions on gas storage, separation, and sensing.[12,36] In terms of porous MOFs for their gas separation, our previous efforts have been mainly focused on the tuning/control of pore size/curvature to realize gas separation. The immobilization of some functional sites within porous MOFs to induce their strong interactions with carbon dioxide is another equally important approach to realize porous MOFs for their carbon dioxide capture and separation abilities. Herein we report a 3D prototype MOF $Zn(BDC\text{-}OH)(DABCO)_{0.5}\cdot(DMF)_2(H_2O)$ (UTSA-25a; BDC-OH = 2-hydroxy-1,4-benzenedicarboxylate, DABCO = 1,4-diazabicyclo[2.2.2]octane) functionalized with OH groups on pore surfaces for a significantly enhanced CO_2/CH_4 separation selectivity of 12.5, which is three times higher than that of 3.7 within the original MOF $Zn(BDC)(DABCO)_{0.5}$ at room temperature.

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Results and Discussion

Compound UTSA-25 was synthesized by the solvothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$, H_2BDC-OH, and DABCO in DMF at 110 °C for 24 h as colorless column single crystals. The structure was characterized by single-crystal X-ray diffraction studies, and the phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD) (see Figure S1 in the Supporting Information) and thermogravimetric analysis (TGA) (Figure S2).

Single-crystal X-ray diffraction analysis reveals that UTSA-25 crystallizes in the tetragonal space group of *I*4/*mcm*, which is isostructural to $Zn(BDC)(DABCO)_{0.5} \cdot (G)_x$. The $Zn_2(COO)_4$ paddlewheel secondary building units (SBUs) are bridged by BDC-OH to form 2D (4,4) square sheets, which are further connected by the bridging DABCO linkers to construct a 3D distorted cubic network. There exist three-dimensional intercrossed pores of about 7.5×7.5 Å^2 along the *c* axis (Figure 1, a) and 3.2×4.7 Å^2 along the *a* and *b* axes (Figure 1, b) if one takes into account the van der Waals radii. The pores along the *c* axis of 7.5×7.5 Å^2 in UTSA-25 are basically same as those found in $Zn(BDC)(DABCO)_{0.5} \cdot (G)_x$. However, immobilization of –OH functional groups on the pore surfaces does decrease the pore sizes from the original 3.8×4.7 Å^2 in $Zn(BDC)(DABCO)_{0.5}$ to 3.2×4.7 Å^2 in UTSA-25 in which some of the pore space has been occupied by OH groups. The effective free volume in UTSA-25 is 54.3% as calculated by the PLATON program.[38]

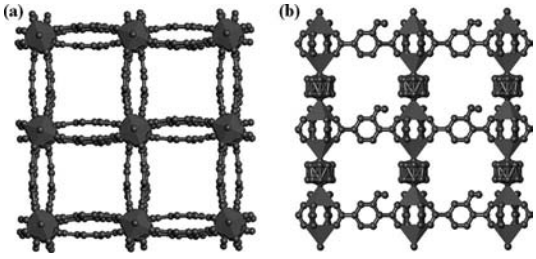

Figure 1. The crystal structure of UTSA-25 indicating the 3D intercrossed pores of about (a) 7.5×7.5 Å^2 along the *c* axis and (b) 3.2×4.7 Å^2 along the *a* axis (Zn, polyhedral. Only hydroxy hydrogen atoms are showed for the clarity).

Thermogravimetric analysis (TGA) of UTSA-25 showed that approximately 29.15% weight loss occurred from 23 to 250 °C, which is attributed to the release of solvent molecules (Figure S2 in the Supporting Information). The solvent molecules within the as-synthesized UTSA-25 can be readily removed at 100 °C under high vacuum overnight to form desolvated $Zn_2(BDC\text{-}OH)_2(DABCO)$ (UTSA-25a) for gas uptake. The N_2 sorption isotherm at 77 K shows that UTSA-25a displays typical Type I but two-step hysteresis sorption behavior (Figure 2). Such unique sorption behaviors have been also realized in $Zn(BDC)(4,4'\text{-Bipy})_{0.5}$ (Bipy = 2,2′-bipyridine) and vapor sorption of the isostructural MOFs $Zn(BDC\text{-X})(DABCO)_{0.5}$ (X = H, Br, NO_2), which are attributed to the phase transitions and the existence of the metastable intermediate phases. The phase transitions are mainly determined by the robustness or flexibility of the frameworks, which are dominated by the rigidity of the metal-containing secondary building units and the organic linkers. They can also be affected by the interactions among the frameworks themselves through the framework interweaving and/or interpenetration, and between the host framework and the guest solvent/gas molecules, as exemplified here the different N_2 sorption isotherm in UTSA-25a from those in the isostructural MOFs $Zn(BDC\text{-X})(DABCO)_{0.5}$ (X = H, Br, NO_2).[39] UTSA-25a has a Brunauer–Emmett–Teller (BET) surface area of 994 m^2 g^{-1} (Langmuir surface area, 1461 m^2 g^{-1}), which is slightly lower than 1216 m^2 g^{-1} in $Zn(BDC)(DABCO)_{0.5}$ (Langmuir surface area, 1804 m^2 g^{-1}) because of the smaller accessible pore volume in UTSA-25a.

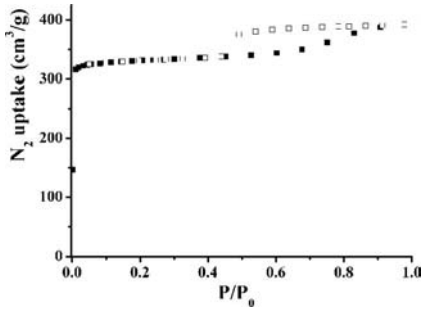

Figure 2. N_2 adsorption isotherm of UTSA-25a at 77 K (solid square, adsorption; empty square, desorption).

To examine the effect of the –OH groups on the framework interactions with gas molecules of CO_2 and CH_4, and the potential application of UTSA-25a on the selective CO_2/CH_4 gas separation, CO_2 and CH_4 adsorption isotherms have been carried out for $Zn(BDC)(DABCO)_{0.5}$ and UTSA-25a at 273 and 296 K. As shown in Figure 3, $Zn(BDC)(DABCO)_{0.5}$ and UTSA-25a take up comparable moderate amount of CH_4 both at 273 and 296 K; however,

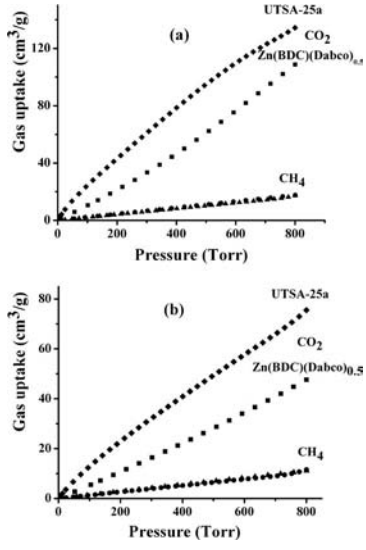

Figure 3. The CO_2 and CH_4 gas sorption isotherms for $Zn(BDC)(DABCO)_{0.5}$ and UTSA-25a at (a) 273 K and (b) 296 K.

Table 1. Data for virial graph analyses of UTSA-25 and $Zn_2(BDC)_2(DABCO)$ for their CO_2/CH_4 separation selectivities at 273 and 296 K.

	Adsorbate	T [K]	K_H[a] [mol g^{-1} Pa^{-1}]	A_0[b] [ln (mol g^{-1} Pa^{-1})]	A_1[c] [g mol^{-1}]	R^2	S_{ij}[d]	Q_{st}[e] [kJ mol^{-1}]
UTSA-25	CH_4	273	7.062×10^{-9}	-18.769 ± 0.001	-53.635 ± 1.976	0.983		13.3
		296	4.479×10^{-9}	-19.224 ± 0.001	-129.967 ± 7.205	0.970		
	CO_2	273	1.212×10^{-7}	-15.926 ± 0.004	-439.445 ± 11.760	0.996	17.2	22.5
		296	5.607×10^{-8}	-16.697 ± 0.003	-568.967 ± 16.069	0.997	12.5	
$Zn_2(BDC)_2(DABCO)$	CH_4	273	7.547×10^{-9}	-18.702 ± 0.001	-88.662 ± 2.672	0.997		13.0
		296	4.665×10^{-9}	-19.183 ± 0.001	-25.589 ± 1.401	0.979		
	CO_2	273	3.317×10^{-8}	-17.222 ± 0.002	75.319 ± 0.853	0.999	4.4	17.5
		296	1.735×10^{-8}	-17.870 ± 0.001	66.646 ± 0.575	0.999	3.7	

[a] K_H is the Henry's Law constant, equal to $\exp(A_0)$. [b] A_0 is related to adsorbate–adsorbent interactions. [c] A_1 describes adsorbate–adsorbate interactions. [d] Henry's Law selectivity for gas component CO_2 over CH_4 at the speculated temperature is calculated based on $S(CO_2/CH_4) = K_H(CO_2)/K_H(CH_4)$. [e] Q_{st} is the enthalpy at zero coverage.

at 1 atm they adsorb quite different amounts of CO_2: 102 and 129 cm^3 g^{-1} at 273 K, and 45 and 71 cm^3 g^{-1} at 296 K, respectively. The increased amount of CO_2 uptake in UTSA-25a indicates that UTSA-25a exhibits higher selective separation of CO_2/CH_4 than $Zn(BDC)(DABCO)_{0.5}$ at ambient temperature.

The coverage-dependent adsorption enthalpies of $Zn(BDC)(DABCO)_{0.5}$ and UTSA-25a toward CO_2 and CH_4, were calculated based on a virial method, a well-established and reliable methodology from fits of their adsorption isotherms at 273 and 296 K (Table 1).[37] The enthalpies at zero coverage for $Zn(BDC)(DABCO)_{0.5}$ are 17.5 and 13.0 kJ mol^{-1} for CO_2 and CH_4, respectively, whereas those for UTSA-25a are 22.5 and 13.3 kJ mol^{-1} for CO_2 and CH_4, respectively. These values are moderate, which indicates that the interactions between the frameworks and these two gas molecules are not strong, mainly because of the large pores in $Zn(BDC)(DABCO)_{0.5}$ and UTSA-25a. The most interesting feature is that the immobilization of –OH functional groups in UTSA-25a do enhance their stronger interaction with CO_2, as shown in the larger adsorption enthalpy of 22.5 kJ mol^{-1} compared with that of 17.5 kJ mol^{-1} in $Zn(BDC)(DABCO)_{0.5}$. Such higher interactions might be attributed to the electrostatic interactions between the functionalized –OH groups on the pore surface of UTSA-25a and CO_2. As a result, UTSA-25a exhibits higher CO_2/CH_4 separation with a Henry's Law selectivity of 17.2 and 12.5 at 273 and 296 K, respectively, which are much larger values than those of 4.4 and 3.7 for $Zn(BDC)(DABCO)_{0.5}$. The significantly enhanced CO_2/CH_4 separation selectivity demonstrates the promise of this new microporous MOF UTSA-25a for practical CO_2/CH_4 separation at room temperature.

Conclusion

We have successfully synthesized one new microporous metal–organic framework $Zn(BDC\text{-}OH)(DABCO)_{0.5}$ (UTSA-25a) with functionalized –OH groups on the pore surfaces. Such functional –OH groups induce their much stronger interactions with CO_2 than CH_4, which demonstrate the potential for UTSA-25a to be a highly selective microporous MOF for the industrially important separation of CO_2/CH_4. The uniqueness of the MOF approach to systematically tune the micropores and immobilize functional groups to induce their different interactions with gas molecules has positioned MOFs as the most promising microporous materials for the adsorptive separation of gas molecules. It is expected that some such microporous MOFs will be eventually implemented in the industrial separation of gas molecules in the future.

Experimental Section

General: All reagents and solvents were used as received from commercial suppliers without further purification. $Zn(BDC)(DABCO)_{0.5}\cdot(G)_x$ was synthesized according to the literature. Thermogravimetric analyses (TGA) were performed with a Mettler Toledo TGA/SDTA851 analyzer in air with a heating rate of 5 K min^{-1}, from 30 to 800 °C. X-ray powder diffraction (XRD) patterns were measured with a Bruker D4 powder diffractometer at 40 kV, 40 mA for Cu-K_α radiation (λ = 1.5418 Å), with a scan speed of 0.2 s per step and a step size of 0.02° (2θ). The elemental analyses were performed with Perkin–Elmer 240 CHN Analyzers.

Synthesis: A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.2900 g, 1.0 mmol) and H_2BDC-OH (0.1840 g, 1.0 mmol) was dissolved in DMF (10 mL) solvent. Then DABCO (0.0584 g, 0.5 mmol) was added, and the mixture was transferred to a screw-capped vial. The vial was capped and placed in an oven at 110 °C for 24 h. The colorless column single crystals were washed with DMF several times to give UTSA-25 [$Zn(BDC\text{-}OH)(DABCO)_{0.5}\cdot(DMF)_2(H_2O)$; 0.298 g; yield based on $Zn(NO_3)_2\cdot 6H_2O$: 66.9%]. Elemental analysis: calcd. C 43.85, H 5.58, N 9.02; found C 43.79, H 5.23; N 9.02.

Single-Crystal X-ray Structure Determination: Intensity data for the reported MOF were collected at 293 K with a Rigaku Saturn724 diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) using an ω-scan technique. The structure was solved by direct methods and subsequent difference Fourier syntheses, and refined using the SHELXTL software package. The OH group on the ligand was disordered in four positions with an occupancy factor of 0.25. The hydrogen atoms on the ligand and water molecules could not be located but are included in the formula. Detailed crystallographic data are shown in Table 2.

Table 2. Crystal data and structure refinement for UTSA-25.

Empirical formula	$C_{17}H_{25}N_3O_{7.50}Zn$
M_r	456.77
T [K]	98.15
λ [Å]	0.71073
Crystal system	tetragonal
Space group	*I*4/*mcm*
a [Å]	15.035(3)
b [Å]	15.035(3)
c [Å]	19.294(4)
V [Å^3]	1910.1(6)
Z	8
$\rho_{calcd.}$ [Mg m^{-3}]	1.391
Absorption coefficient [mm^{-1}]	1.169
F(000)	1904
Crystal size [mm]	0.20 × 0.20 × 0.20
θ range [°]	2.71 to 24.99
Limiting indices	$-17 \le h \le 17$, $-17 \le k \le 17$, $-22 \le l \le 22$
Reflections collected/unique	10144/1046 [R(int) = 0.0746]
Completeness to θ = 25.09 [%]	99.2
Absorption correction	semiempirical from equivalents
Max./min. transmission	0.7998/0.7998
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	1046/0/93
GoF on F^2	1.079
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0816, $wR2$ = 0.1886
R indices (all data)	R_1 = 0.0833, $wR2$ = 0.1899
Largest diff. peak/hole [e Å^{-3}]	0.787/–0.362

CCDC-804572 (for UTSA-25) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Gas Sorption Measurements: A Micrometrics ASAP 2020 instrument was used to measure gas adsorption. To remove guest solvent molecules in the framework, the fresh as-synthesized $Zn(BDC)(DABCO)_{0.5}\cdot(G)_x$ and UTSA-25 were filtered and activated at a temperature of 100 °C under high vacuum overnight to form desolvated $Zn_2(BDC)_2(DABCO)$ and $Zn_2(BDC\text{-}OH)_2(DABCO)$ (UTSA-25a). A sample of 60.0–100.0 mg was used for sorption measurement. It was maintained at 77 K with liquid nitrogen, at 273 K with water/ice bath, and at 296 K with water bath, respectively.

Supporting Information (see footnote on the first page of this article): Powder XRD and TGA data.

Acknowledgments

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