Microporous Materials

DOI: 10.1002/ange.200502844

A Microporous Metal–Organic Framework for Gas-Chromatographic Separation of Alkanes**

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Microporous metal–organic frameworks (MOFs),[1] which are new types of zeolite analogues, have been paid extensive attention because of their potential applications in gas storage,[2] separation,[3] and catalysis.[4] The modular construction of MOFs allows their pore size and shape to be systematically tuned by the judicious choice of metal-containing secondary building units (SBUs) and/or bridging linkers, and by making use of framework interpenetration or interweaving.[5] Their selective adsorption and high thermal stability make these microporous materials potentially useful for alkane separation. However, this application has not yet been developed. In the petroleum industry, the separation of alkane isomers is a very important process, and some narrow-pore zeolites have been used to sieve linear from branched alkanes, to boost octane ratings in gasoline.[6] To match the alkane molecule sizes, the microporous compound Zn-

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[**] This work was supported by the University of Texas-Pan American through a Faculty Research Council award to B.C., by the Welch Foundation grant (BG-0017) to the Department of Chemistry at UTPA, by an appointment to the Higher Education Research Experiences (HERE) at the Oak Ridge National Laboratory (ORNL) for faculty (B.C.), which is sponsored by the US Department of Energy and administered by the Oak Ridge Institute for Science and Education, and by the Office of Basic Energy Sciences, US Department of Energy, under contract No. DE-AC05-00OR22725 with UT-Battelle, LLC (S.D.). We thank Dr. Jing-Feng Huang for his help with the GC separation of alkanes.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

(BDC)(4,4′-Bipy)$_{0.5}$ (MOF-508; BDC = 1,4-benzenedicarboxylic acid, 4,4′-Bipy = 4,4′-bipyridine) was designed to have a primitive cubic framework with pores that can be tuned by double interpenetration to have 1D channels of approximately 4.0 × 4.0 Å in cross section. Herein, we report the first example of a microporous MOF that is highly selective in the GC separation of alkanes.

A guest-filled phase, MOF-508a, was synthesized by the solvothermal reaction of H_2BDC, 4,4′-Bipy, and $Zn(NO_3)_2 \cdot 6H_2O$ in DMF/ethanol at 90 °C for 24 h, and isolated as colorless block-shaped crystals. The formula of the compound was determined to be $Zn(BDC)(4,4'\text{-Bipy})_{0.5} \cdot (DMF)(H_2O)_{0.5}$ by elemental microanalysis and single-crystal X-ray diffraction studies,[7] and the phase purity of the bulk material was independently confirmed by both powder X-ray diffraction (PXRD) and thermal gravimetric analysis (TGA). TGA data indicate that MOF-508a releases its guest molecules over the temperature range 25–145 °C to form the guest-free phase Zn(BDC)(4,4′-Bipy)$_{0.5}$ (MOF-508b), which is thermally stable to 360 °C. Interestingly, the PXRD pattern of the guest-free phase MOF-508b is significantly different from that of the as-synthesized MOF-508a (see Supporting Information), indicating the formation of a new phase whose structure was also characterized by single-crystal X-ray crystallography.[7]

As expected, the framework of MOF-508a is composed of paddle-wheel dinuclear zinc carboxylate units $\{Zn_2(COO)_4\}$, which are bridged by the BDC ligands to form a distorted 2D square grid. The 2D square grids are pillared by 4,4′-Bipy molecules, whose nitrogen atoms occupy the axial sites of the $\{Zn_2(COO)_4\}$ paddle wheels, to form a 3D framework with a topology that can be described as an elongated primitive cubic lattice (see Supporting Information). Two of the 3D frameworks interpenetrate in MOF-508a, reducing the pore size. A 1D channel occurs in the direction of the rectangular diagonal of the paddle-wheel clusters (Figure 1 a). This channel has a cross section of approximately 4.0 × 4.0 Å. The X-ray crystal structure of the guest-free phase MOF-508b reveals that the framework retains the overall connectivity, but the $\{Zn_2(COO)_4\}$ paddle-wheel clusters are significantly distorted, and the 4,4′-Bipy linkers are bent. These changes compress the framework considerably: the volume per formula unit decreases from 410.7 (MOF-508a) to 342.3 Å^3 (MOF-508b), a 16.7 % reduction. Thus, a dense doubly interpenetrating 3D framework is formed (Figure 1 b).

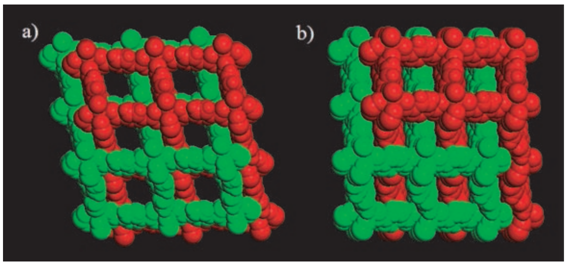

Figure 1. Space-filling representations of the structures of a) the open phase $Zn(BDC)(4,4'\text{-Bipy})_{0.5} \cdot (DMF)(H_2O)_{0.5}$ (MOF-508a), which contains 1D channels of 4.0 × 4.0 Å, and b) the dense phase Zn(BDC)(4,4′-Bipy)$_{0.5}$ (MOF-508b), viewed along the rectangular diagonal of the paddle-wheel clusters. The two interpenetrating frameworks are shown in red and green. The disordered guest molecules in MOF-508a are omitted for clarity.

Soaking the guest-free phase MOF-508b in DMF/ethanol for one day regenerated the guest-filled phase MOF-508a. The PXRD pattern of the product is exactly the same as that of the as-synthesized MOF-508a (see Supporting Information). Therefore, the host framework expands back to its former volume upon guest inclusion. This reversible cycle can be repeated many times without loss of crystallinity. Note that, although some dynamic microporous MOFs are known, MOFs exhibiting reversible open–dense framework transformations in the crystalline state are still very rare.[8] Clearly, this reversible open–dense framework transformation is responsible for the dynamic features and hysteresis of the compound's gas sorption isotherms for N_2 and H_2 at 77 K, and for CO_2 at 195 K (Figure 2). Similar sorption behavior was also observed for the copper analogue of MOF-508a, Cu(BDC)(4,4′-Bipy)$_{0.5}$.[9] The overall Langmuir surface area (A_s), calculated using the Langmuir equation from the N_2 sorption isotherm of the compound, is 946 m^{2}g^{-1}.[10] The material can take up 90 cm^{3}g^{-1} or 0.8 wt. % H_2 at standard temperature and pressure (STP).

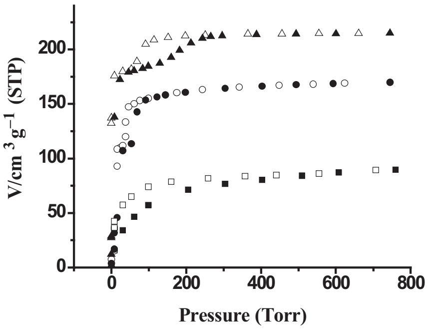

Figure 2. N_2 (△), CO_2 (○), and H_2 (□) sorption isotherms for MOF-508b (N_2 and H_2 at 77 K; CO_2 at 195 K). Adsorption: filled symbols; desorption: open symbols.

The 4.0 × 4.0 Å cross section of the 1D channels in the guest-filled phase MOF-508a is slightly larger than a methane molecule (3.8 × 3.8 Å). Thus, we initially examined the possibility of using MOF-508 phases for the chromatographic separation of natural gas. A chromatographic column of 120 cm was packed with single crystals of MOF-508b with sizes of 25–100 μm (3 g). The GC separation of natural gas was carried out at an inlet pressure of 60 psi with helium as the carrier gas over the temperature range 40–150 °C. Preliminary results indicated that the MOF-508 column can efficiently separate natural gas mixtures (see Supporting Information).

The GC separation was examined in detail for linear and branched isomers of pentane and hexane, because of their availability and industrial relevance in petroleum refining. The MOF-508 column can clearly separate *n*-pentane from *n*-hexane with retention times of 6.39 min and 12.06 min, respectively (Figure 3 a). Branched 2-methylbutane (retention time of 5.31 min) elutes from the column before its linear isomer *n*-pentane (Figure 3 b). Similarly, 2-methylpentane

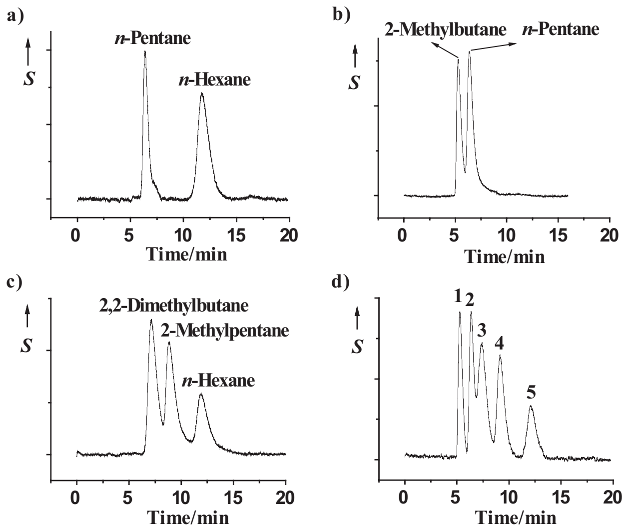

Figure 3. Chromatograms of alkane mixtures separated on a MOF-508 column: a) separation of *n*-pentane and *n*-hexane, b) separation of 2-methylbutane and *n*-pentane, c) separation of 2,2-dimethylbutane, 2-methylpentane, and *n*-hexane, and d) separation of an alkane mixture containing 2-methylbutane (**1**), *n*-pentane (**2**), 2,2-dimethylbutane (**3**), 2-methylpentane (**4**), and *n*-hexane (**5**). S = thermal conductivity detector response.

(retention time of 9.16 min) runs through the column faster than its linear isomer *n*-hexane, while 2,2-dimethylbutane, the isomer of hexane with the shortest linear chain, elutes even faster at a time of 7.40 min (Figure 3c). Thus, mixtures of 2-methylbutane, *n*-pentane, 2,2-dimethylbutane, 2-methylpentane, and *n*-hexane can be easily separated with this new type of microporous MOF column (Figure 3d). The potential applications of this microporous MOF column in the efficient GC separation of natural gas and alkane mixtures are remarkable and foreseeable: the column could be used to identify the impurities in natural gas, and to monitor the amounts of mono- and multibranched alkanes formed in cracking reactions.

The selective GC separation of alkanes on the MOF-508 column is the result of their different van der Waals interactions with the microporous MOF-508 walls, which arise from the subtle matching of the size and shape of the alkanes with the MOF-508 micropores.[11] The 4.0 × 4.0 Å channels of in the open phases of MOF-508 are accessible to the linear chains, but not to the branched parts of the alkanes. Thus, the retention of alkanes on the column mainly depends on the length of the linear part of the alkane, which contributes to its van der Waals interactions with the microporous MOF walls. The 2-methylbutane molecule, with its shorter linear chain of two carbon atoms, has a weaker van der Waals interaction and elutes faster than its linear isomer *n*-pentane. The same trend is observed for 2,2-dimethylbutane, 2-methylpentane, and *n*-hexane. This behavior is analogous to the pore and pore-mouth adsorption effect observed in mordenite and ZSM-22, which have small 1D channels.[12]

In conclusion, we present a rare example of a MOF exhibiting a reversible open–dense framework transformation in the crystalline state. This transformation is attributed to the rigid and flexible nature of the 4,4′-Bipy linkers and the variable distortion of the paddle-wheel clusters. Most importantly, for the first time, we demonstrated the application of a microporous MOF in the GC separation of alkanes based on their different van der Waals interactions arising from subtle size- and shape-selective matching. The unique features of MOF-508 are its 1D pores of 4.0 × 4.0 Å, which selectively accommodate linear alkanes and discriminate branched alkanes. Thus, its good GC separation capability is a result of its differential interactions with the alkane isomers. Compared with inorganic zeolite analogues, the specific interactions between the analytes and the organic moieties of MOFs might further enhance their separation capabilities. Further studies on related microporous MOFs and their applications in highly selective separation are in progress.

Experimental Section

MOF-508a: A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (1.407 g, 4.73 mmol), H_2BDC (0.786 g, 4.73 mmol), and 4,4′-Bipy (0.369 g, 2.36 mmol) was suspended in DMF/ethanol (1:1, 400 mL), and heated in a teflon vessel (500 mL) at 90 °C for 24 h. The colorless block-shaped crystals formed were collected, washed with DMF and hexane, and dried in air (1.82 g, 95 %). Elemental analysis (%) calcd for $Zn(BDC)(4,4'\text{-}Bipy)_{0.5}\cdot(DMF)(H_2O)_{0.5}$ ($C_{16}H_{16}N_2O_{5.5}Zn$): C 47.37, H 3.98, N 6.90, Zn 16.12; found: C 47.60, H 3.97, N 6.40, Zn 16.80; TGA data, calcd weight loss (%) for $1\,DMF + 0.5\,H_2O$: 15.1; found: 15.1. MOF-508b: A sample of MOF-508a was heated at 120 °C under vacuum for 24 h to produce MOF-508b. TGA indicated that there was no further weight loss.

GC separation of natural gas: GC measurements were performed with a Buck Scientific 910 GC system. The instrument control and data acquisition were carried out by the software Peakwin, which runs on a laptop with the Windows XP operating system. A thermal conductivity detector was used for data collection. Helium was used as the carrier gas and was driven at the inlet pressure of 60 psi. Fresh columns of MOF-508b were conditioned at 160 °C overnight before injection. The GC measurements were conducted with a temperature program consisting of two steps: 40 °C for the first 4 min, and 150 °C for the remainder of the measurement. For a typical run, 1 mL of natural gas was manually injected through the injection port. Each run ended after 20 min.

GC separation of linear and branched pentane and hexane isomers: The GC measurement was conducted with a temperature program consisting of three steps: 120 °C for 2 min, ramp from 120–160 °C over 2 min, and 160 °C for the remainder of the measurement. For a typical run, 1 (two components) to 2 μL (five components) of the alkane mixture was manually injected through the injection port. Each run ended after 20 min.

Received: August 10, 2005
Revised: November 15, 2005
Published online: January 20, 2006

Keywords: alkanes · gas chromatography · metal–organic frameworks · microporous materials · sorption

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[1] a) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705; b) C. Janiak, *Dalton Trans.* **2003**, 2781; c) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334; d) C. N. R. Rao, S. Natarajan, R. Vaidhyanathan, *Angew. Chem.*

2004, *116*, 1490; *Angew. Chem. Int. Ed.* **2004**, *43*, 1466; e) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior, M. J. Rosseinsky, *Acc. Chem. Res.* **2005**, *38*, 273; f) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, *Acc. Chem. Res.* **2005**, *38*, 217.

[2] a) J. L. C. Rowsell, A. R. Millward, K. S. Park, O. M. Yaghi, *J. Am. Chem. Soc.* **2004**, *126*, 5666; b) D. N. Dybstev, H. Chun, K. Kim, *Angew. Chem.* **2004**, *116*, 5143; *Angew. Chem. Int. Ed.* **2004**, *43*, 5033; c) L. Pan, M. B. Sander, X. Huang, J. Li, M. Smith, E. Bittner, B. Bockrath, J. K. Johnson, *J. Am. Chem. Soc.* **2004**, *126*, 1308; d) X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *Science* **2004**, *306*, 1012; e) B. Chen, N. W. Ockwig, A. R. Millward, D. S. Contreras, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4823; *Angew. Chem. Int. Ed.* **2005**, *44*, 4745; f) J. L. C. Rowsell, O. M. Yaghi, *Angew. Chem.* **2005**, 117, 4748; *Angew. Chem. Int. Ed.* **2005**, *44*, 4670.

[3] a) O. M. Yaghi, C. E. Davis, G. Li, H. Li, *J. Am. Chem. Soc.* **1997**, *119*, 2861; b) H. J. Choi, T. S. Lee, M. P. Suh, *Angew. Chem.* **1999**, *111*, 1490; *Angew. Chem. Int. Ed.* **1999**, *38*, 1405; c) R. Kitaura, K. Fujimoto, S. Noro, M. Kondo, S. Kitagawa, *Angew. Chem.* **2002**, *114*, 141; *Angew. Chem. Int. Ed.* **2002**, *41*, 133; d) T. K. Maji, K. Uemura, H.-C. Chang, R. Matsuda, S. Kitagawa, *Angew. Chem.* **2004**, *116*, 3331; *Angew. Chem. Int. Ed.* **2004**, *43*, 3269; e) E. Y. Lee, M. P. Suh, *Angew. Chem.* **2004**, *116*, 2858; *Angew. Chem. Int. Ed.* **2004**, *43*, 2798.

[4] a) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151; b) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982; c) L. Pan, H. Liu, X. Lei, X. Huang, D. H. Olson, N. J. Turro, J. Li, *Angew. Chem.* **2003**, *115*, 560; *Angew. Chem. Int. Ed.* **2003**, *42*, 542; d) A. Hu, H. L. Ngo, W. Lin, *J. Am. Chem. Soc.* **2003**, *125*, 11490; e) A. Hu, H. L. Ngo, W. Lin, *Angew. Chem.* **2003**, *115*, 6182; *Angew. Chem. Int. Ed.* **2003**, *42*, 6000.

[5] a) B. Chen, M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 11559; b) B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe, O. M. Yaghi, *Science* **2001**, *291*, 1021; c) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319; d) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469.

[6] S. Kulprathipanja, R. W. Neuzil, US Patent 4445444, **1984**, UOP; [*Chem. Abs. 101*, 75824].

[7] Single-crystal X-ray diffraction data were collected on a Bruker X8 APEX II diffractometer at 173 K. The data sets were corrected for absorption with the SADABS program (G. M. Sheldrick, SADABS). The structures were solved by direct methods and refined by full-matrix least-squares methods with the SHELXTL-97 program package. For MOF-508a, the electron density contribution of the diffuse scattering of the disordered guest molecules (DMF and H_2O) was handled using the SQUEEZE procedure in the PLATON software suite. Crystal data for MOF-508a ($C_{13}H_8NO_4Zn$; the contribution of the disordered guest molecules is not included in the derived data): triclinic, $P\bar{1}$, $a = 10.880(3)$, $b = 10.918(3)$, $c = 14.122(4)$ Å, $\alpha = 89.335(16)$, $\beta = 89.171(17)$, $\gamma = 78.380(16)°$, $V = 1643.0(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.243\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 1.501\ mm^{-1}$; $2\theta_{max} = 49.42°$, total number of reflections 5144 ($R_{int} = 0.0729$), 417 parameters, $R_1 = 0.0655$ (3426 reflections with $I > 2\sigma(I)$), $wR_2 = 0.1826$ (all data), GOF = 0.933. Crystal data for MOF-508b ($C_{13}H_8NO_4Zn$): triclinic, $P\bar{1}$, $a = 7.7911(18)$, $b = 9.2984(18)$, $c = 10.6284(19)$ Å, $\alpha = 65.320(7)$, $\beta = 86.199(7)$, $\gamma = 78.145(7)°$, $V = 684.6(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.492\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 1.801\ mm^{-1}$; $2\theta_{max} = 51.28°$, total number of reflections 2507 ($R_{int} = 0.0301$), 207 parameters, $R_1 = 0.0325$ (2225 reflections with $I > 2\sigma(I)$), $wR_2 = 0.0930$ (all data), GOF = 1.037. CCDC-265850 (MOF-508a) and CCDC-265851 (MOF-508b) contain 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. The structure of MOF-508a was also published by other groups while this paper was being written and revised (H. Chun, D. N. Dybstev, H. Kim, K. Kim, *Chem. Eur. J.* **2005**, *11*, 3521; B. Ma, K. L. Mulfort, J. T. Hupp, *Inorg. Chem.* **2005**, *44*, 4912).

[8] D. V. Soldatov, J. A. Ripmeester, S. I. Shergina, I. E. Sokolov, A. S. Zanina, S. A. Gromilov, Yu. A. Dyadin, *J. Am. Chem. Soc.* **1999**, *121*, 4179.

[9] a) K. Seki, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1968; b) R. Kitaura, K. Seki, G. Akiyama, S. Kitagawa, *Angew. Chem.* **2003**, *115*, 444; *Angew. Chem. Int. Ed.* **2003**, *42*, 428.

[10] F. Rouquerol, J. Rouqerol, K. Sing, *Absorption by Porous Solids*, Academic Press, London, UK, **1999**.

[11] N. Y. Chen, W. E. Garwood, F. G. Dwyer, *Shape-Selective Catalysis in Industrial Applications*, Marcel Dekker, New York, **1989**.

[12] J. F. M. Denayer, R. A. Ocakoglu, I. C. Arik, C. E. A. Kirschhock, J. A. Martens, G. V. Baron, *Angew. Chem.* **2005**, *117*, 404; *Angew. Chem. Int. Ed.* **2005**, *44*, 400; R. A. Ocakoglu, J. F. M. Denayer, G. B. Marin, J. A. Martens, G. V. Baron, *J. Phys. Chem. B* **2003**, *107*, 398.