Carborane-based metal–organic frameworks as highly selective sorbents for CO_2 over methane

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Separation of CO_2/CH_4 mixtures was studied in carborane-based metal–organic framework materials with and without coordinatively unsaturated metal sites; high selectivities for CO_2 over CH_4 (~ 17) are obtained, especially in the material with open metal sites.

The separation of carbon dioxide from methane is an important process in natural gas upgrading because CO_2 reduces the energy content of natural gas and induces pipeline corrosion.[1–3] Compared to the conventional technologies for this separation, adsorption-based processes such as pressure-swing adsorption (PSA) are attractive due to their low cost and high energy efficiency.[1] High CO_2 selectivity and capacity are essential when selecting an adsorbent for a PSA process.[4]

Metal–organic frameworks (MOFs) and coordination polymer materials in general have attracted great interest recently for potential applications in adsorption separations, sensing, gas storage, and catalysis.[5] However, studies on the separation and purification of CO_2/CH_4 mixtures by MOFs are scarce and come mostly from molecular simulations.[6–8] The metal atoms in most MOFs are coordinately saturated by framework components, but in a few materials some metal atoms are partially coordinated by solvent molecules. When these coordinated solvent molecules are removed, open metal sites can be created within the MOF pores.[9–11] These coordinatively unsaturated metal sites have been shown to be useful for attaining high gas uptake, especially for H_2 adsorption.[10–13]

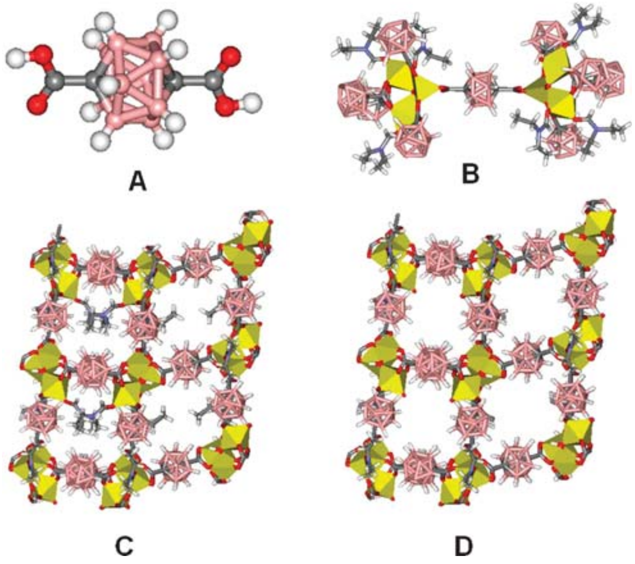

Fig. 1 Crystallographically derived (a) structure of *p*-$CDCH_2$, (b) topology of **1**, (c) extended structure of **1**, (d) extended structure of **1** omitting the coordinated solvents for clarity; see ref. 18.

Recently, Farha *et al*. synthesized a carborane-based MOF $[Zn_3(OH)(p\text{-}CDC)_{2.5}(DEF)_4]_n$ (**1**) [$p\text{-}CDC^{2-}$ = deprotonated form of 1,12-dihydroxydicarbonyl-1,12-dicarba-*closo*-dodecaborane; DEF = diethylformamide] (Fig. 1). This is the first MOF to make use of boron-rich components as building blocks.[12] Carboranes possess several material-favorable properties including rigidity, thermal stability, and chemical stability. Dicarbon carboranes of the form $C_2B_{n-2}H_n$ ($6 \leq n \leq 12$) can be regarded as three-dimensional delocalized aromatic systems without π–π interaction.[14] The absence of this interaction can reduce the chance of material collapse. In addition, carboranes can produce MOFs with smaller pores than phenyl-based MOFs. The X-ray single-crystal structure of **1** shows that two DEF molecules are coordinated to two of the three zinc ions at each corner. For large scale synthesis, dimethylformamide (DMF) was used instead of DEF without substantive structural change, as evidenced by powder X-ray diffraction (PXRD) (Fig. 2). By heating **1′** (**1** prepared by DMF) at 300 °C under vacuum for 24 h, all of the free and coordinated DMF molecules were completely removed, and a DMF-free version, **2**, was obtained, as evidenced by elemental analysis, thermogravimetric analysis (TGA), and infrared (IR)

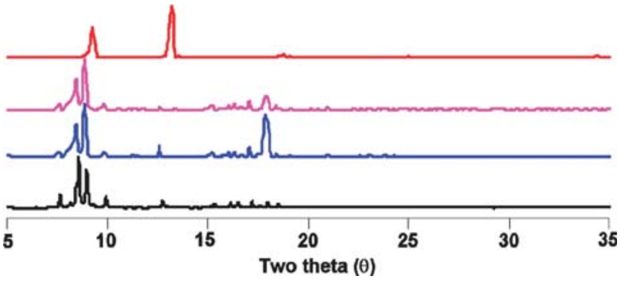

Fig. 2 Simulated PXRD pattern based on single-crystal structure of **1** (black), and experimental PXRD patterns of **1′** (blue), **3** (pink) and **2** (red).

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spectra. PXRD patterns, BET surface areas, and pore sizes showed that the removal of the coordinated DMF molecules forms a more constricted pore structure having a higher surface area rather than a collapse of the structure.[12] Moreover, a mismatch between the number of coordination sites occupied by DMF in **1′** and the number of coordination sites required for complete coordination of *p*-CDC^{2-} indicates that there are coordinatively unsaturated metal sites in **2**.[15] Due to these open metal sites and/or the constricted pore size, **2** showed substantial H_2 uptake (2.1%) at 77 K and 1 atm, especially in comparison to **1** (0.75%).[12]

In this work, we examine the potential of **2** for separating and purifying mixtures of CO_2 and CH_4 at 298 K. We reasoned that the open metal sites in this material might enhance the selectivity of quadrupolar CO_2 over the essential nonpolar CH_4 (small octupole moment; no dipole or quadrupole moment). For comparison, **3** was prepared by heating **1′** at 100 °C under vacuum for 24 h. In this case, all of the free DMF molecules are removed from **1′**, but the coordinated DMF remains in the pores. Hence, **3** does not possess open metal sites. Our approach was to first compare the experimental single-component isotherms of CO_2 and CH_4 for **2** and **3** at 298 K. Then, from these single-component isotherms, the multi-component isotherms and the selectivities for CO_2/CH_4 mixture adsorption on **2** and **3** can be analyzed using the ideal adsorbed solution theory (IAST).[16] Previous studies have established that the IAST can accurately predict gas mixture adsorption in many zeolites[6,17] and MOF materials.[6,7]

MOF materials were synthesized as follows. Exact amounts of $Zn(NO_3)\cdot6H_2O$ (1.20 g) and 1,12-dihydroxy-dicarbonyl-1,12-dicarba-*closo*-dodecaborane (0.30 g) were dissolved in a large vial using (1 : 1) dimethylformamide (DMF)–ethanol (18 ml : 18 ml). The solution was heated at 80 °C for 24 h. The compound **1′** was obtained by filtration, washed with DMF followed by ethanol and then dried in air. Then, this material was evacuated at two different temperatures: 300 °C (**2**) and 100 °C (**3**) for 24 h.

Adsorption isotherms of CO_2 and CH_4 were measured volumetrically on both evacuated samples (**2** and **3**) at 298 K up to 18 atm (Fig. 3). The detailed procedure can be found elsewhere.[18] All isotherms show type I behavior as expected for materials with micropores (5 and 6 Å for **2** and **3**, respectively[12]). In both samples, CO_2 is more strongly adsorbed than CH_4. We ascribe the difference to the existence of a quadrupolar moment for CO_2, but not for CH_4 (thereby providing framework-partial-charge/quadrupole interactions for CO_2, but not CH_4). Remarkably, **2** shows considerably larger adsorption capacities than **3**, especially for CO_2 (Table 1).

Table 1 The adsorbed amounts (mol kg^{-1}) of CO_2 and CH_4 in **2** and **3** (at 0.5 bar and 298 K)

	CO_2	CH_4
2	0.586	0.0754
3	0.277	0.0682
Ratio **2**/**3**	2.11	1.10

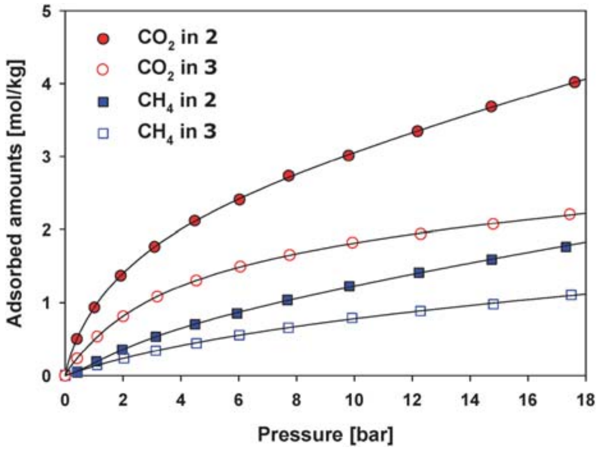

Fig. 3 Single-component isotherms of CO_2 and CH_4 in **2** and **3** at 298 K. Solid lines indicate fits from the dual-site Langmuir–Freundlich model.

A dual-site Langmuir–Freundlich model was used to fit the pure isotherms, and the fits are nearly perfect ($R^2 > 0.9995$) as shown in Fig. 3. The fitted isotherm parameters were used to predict the mixture adsorption in **2** and **3** by the IAST. In our previous work, the IAST model was verified for CO_2/CH_4 mixture adsorption in a mixed-ligand Zn-paddle-wheel MOF by grand canonical Monte Carlo (GCMC) simulations.[18] The predicted adsorption isotherms and selectivities for equimolar CO_2/CH_4 mixtures in **2** and **3** as a function of total bulk pressure are presented in Fig. 4(a) and (b), respectively. Compared to the pure isotherms at the same (partial) pressure,

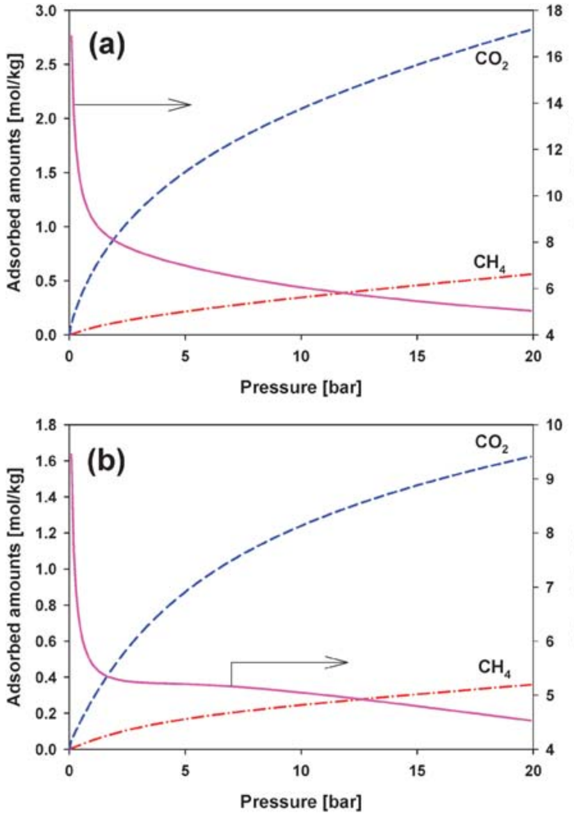

Fig. 4 Mixture isotherms and selectivity of CO_2 over CH_4 in (a) **2** and (b) **3** predicted by IAST for equimolar mixtures of CO_2 and CH_4 at 298 K.

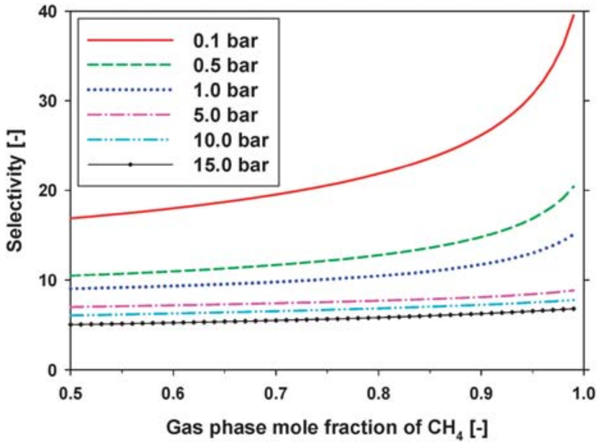

Fig. 5 IAST predicted selectivities of CO_2 over CH_4 in **2** at different compositions and pressures.

CH_4 adsorption is suppressed in the mixtures as a result of competitive adsorption with CO_2. The most striking feature of Fig. 4 is the high selectivity for CO_2 at low pressures. Throughout most of the pressure range, **2** shows much larger selectivities than **3**, as well as larger adsorption capacities. In the high pressure regime, the selectivities of **2** and **3** approach one another. These differences in selectivity between **2** and **3** can likely be explained by the open metal sites, which are most important at low loadings and become less important as the pores are filled with molecules.

Fig. 5 shows the predicted selectivities from IAST at different mixture compositions and different pressures for **2**. The selectivity increases rapidly as the gas-phase mole fraction of CH_4 approaches unity. In the case of $y_{CH_4} = 0.95$, which is a typical feed composition for natural gas purification, the selectivity is in the range of 7–31. Even at $y_{CH_4} = 0.5$, fairly high selectivities (5–17) are obtained compared to reports for other MOFs from GCMC simulations: Cu-BTC (6–10)[7,8] and MOF-5 (2–3).[6,7] Our results are close to the CO_2/CH_4 selectivities reported for zeolites 13X (2–24)[19] and β (28)[2] at similar conditions. However, compared to zeolites, MOFs such as **2** can be regenerated under milder conditions, thus requiring less expenditure of energy.[20] These results indicate that **2** is an excellent candidate for the separation and purification of CO_2 from various CO_2/CH_4 mixtures such as natural gas and landfill gas by adsorptive processes.

In summary, our experiments and IAST calculations have shown that **2** is a promising material for the separation and purification of CO_2 from CO_2/CH_4 mixtures. In addition, the comparisons of CO_2/CH_4 selectivities between the MOFs with and without open metal sites strongly suggest that open metal sites in a MOF can aid in the separation of (quadru)polar/nonpolar pairs such as CO_2/CH_4.

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Notes and references

1 S. Cavenati, C. A. Grande and A. E. Rodrigues, *Energy Fuels*, 2006, **20**, 2648.
2 P. Y. Li and F. H. Tezel, *Microporous Mesoporous Mater.*, 2007, **98**, 94.
3 Y. Li, T. S. Chung and S. Kulprathipanja, *AIChE J.*, 2007, **53**, 610.
4 R. T. Yang, *Adsorbents: Fundamentals and Applications*, John Wiley & Sons Inc., Hoboken, 2003.
5 R. Q. Snurr, J. T. Hupp and S. T. Nguyen, *AIChE J.*, 2004, **50**, 1090; J. L. C. Rowsell and O. M. Yaghi, *Microporous Mesoporous Mater.*, 2004, **73**, 3; S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt and J. Pastre, *J. Mater. Chem.*, 2006, **16**, 626; G. Ferey, *Chem. Soc. Rev.*, 2008, **37**, 191; Y. M. Jeon, J. Heo and C. A. Mirkin, *J. Am. Chem. Soc.*, 2007, **129**, 7480; M. Oh and C. A. Mirkin, *Nature*, 2005, **438**, 651; M. Oh and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2006, **45**, 5492.
6 R. Babarao, Z. Q. Hu, J. W. Jiang, S. Chempath and S. I. Sandler, *Langmuir*, 2007, **23**, 659.
7 Q. Y. Yang and C. L. Zhong, *J. Phys. Chem. B*, 2006, **110**, 17776.
8 Q. Y. Yang and C. L. Zhong, *ChemPhysChem*, 2006, **7**, 1417.
9 B. L. Chen, M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 11559; C. Prestipino, L. Regli, J. G. Vitillo, F. Bonino, A. Damin, C. Lamberti, A. Zecchina, P. L. Solari, K. O. Kongshaug and S. Bordiga, *Chem. Mater.*, 2006, **18**, 1337; A. Vimont, J. M. Goupil, J. C. Lavalley, M. Daturi, S. Surble, C. Serre, F. Millange, G. Ferey and N. Audebrand, *J. Am. Chem. Soc.*, 2006, **128**, 3218; P. M. Forster, J. Eckert, B. D. Heiken, J. B. Parise, J. W. Yoon, S. H. Jhung, J. S. Chang and A. K. Cheetham, *J. Am. Chem. Soc.*, 2006, **128**, 16846; R. Q. Zou, H. Sakurai, S. Han, R. Q. Zhong and Q. Xu, *J. Am. Chem. Soc.*, 2007, **129**, 8402.
10 B. L. Chen, N. W. Ockwig, A. R. Millward, D. S. Contreras and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4745.
11 M. Dinca, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann and J. R. Long, *J. Am. Chem. Soc.*, 2006, **128**, 16876.
12 O. K. Farha, A. M. Spokoyny, K. L. Mulfort, M. F. Hawthorne, C. A. Mirkin and J. T. Hupp, *J. Am. Chem. Soc.*, 2007, **129**, 12680.
13 B. Xiao, P. S. Wheatley, X. B. Zhao, A. J. Fletcher, S. Fox, A. G. Rossi, I. L. Megson, S. Bordiga, L. Regli, K. M. Thomas and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 1203.
14 M. F. Hawthorne, *Advances in Boron Chemistry*, Special Publication No. 201, Royal Society of Chemistry, London, 1997, vol. 82, p. 261.
15 H. R. Moon, N. Kobayashi and M. P. Suh, *Inorg. Chem.*, 2006, **45**, 8672.
16 A. L. Myers and J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121.
17 S. R. Challa, D. S. Sholl and J. K. Johnson, *J. Chem. Phys.*, 2002, **116**, 814; A. Goj, D. S. Sholl, E. D. Akten and D. Kohen, *J. Phys. Chem. B*, 2002, **106**, 8367.
18 Y.-S. Bae, K. L. Mulfort, H. Frost, P. Ryan, S. Punnathanam, L. J. Broadbelt, J. T. Hupp and R. Q. Snurr, *Langmuir*, 2008, DOI: 10.1021/la800555x.
19 S. Cavenati, C. A. Grande and A. E. Rodrigues, *J. Chem. Eng. Data*, 2004, **49**, 1095.
20 S. Surble, F. Millange, C. Serre, T. Düren, M. Latroche, S. Bourrelly, P. L. Llewellyn and G. Ferey, *J. Am. Chem. Soc.*, 2006, **128**, 14889.