

Enhancement of CO₂/N₂ selectivity in a metal-organic framework by cavity modification

Youn-Sang Bae,^a Omar K. Farha,^b Joseph T. Hupp^{*b} and Randall Q. Snurr^{*a}

Received 9th January 2009, Accepted 2nd March 2009

First published as an Advance Article on the web 12th March 2009

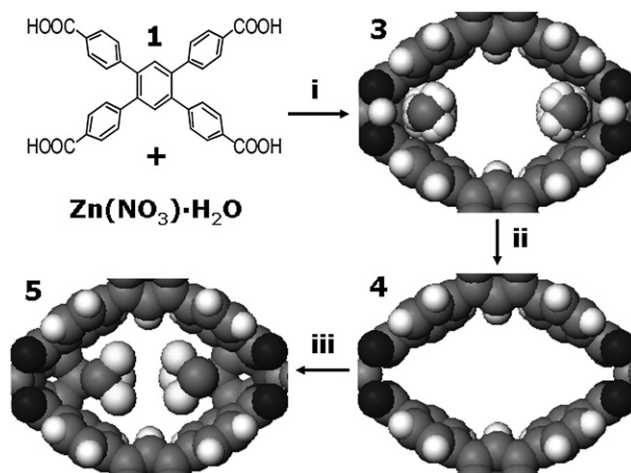
DOI: 10.1039/b900390h

Post-synthesis modification of a MOF by replacing coordinated solvent molecules with highly polar ligands leads to considerable enhancement of CO₂/N₂ selectivity.

Concerns about greenhouse gas concentrations in the atmosphere are a strong motivation to reduce CO₂ emissions from industrial processes. Burning of fossil fuel to generate electricity is a major source of CO₂ in the atmosphere, but the capture and sequestration of CO₂ from flue gas emissions of power plants is a daunting challenge.¹ Flue gases consist of nitrogen (typically more than two-thirds), CO₂, water vapor, oxygen, and minor components such as carbon monoxide, nitrogen oxides, and sulfur oxides. Several technologies have been considered for CO₂ separation from nitrogen-rich streams, including absorption, membranes, and adsorption separations.² Adsorption-based separations such as pressure-swing adsorption (PSA) are attractive due to their low energy requirements. However, an adsorbent with high CO₂ selectivity and capacity is essential in PSA processes for CO₂ separations.³

Recently, metal-organic frameworks (MOFs) have attracted great interest as adsorbents due to their extremely high surface areas, low densities, and uniform, tailorable pore structures. These properties make them promising candidates for adsorption separations, as well as gas storage, catalysis, and sensing.⁴ Efforts to tune the pore size and provide desired surface chemistries in MOFs can be divided into two main strategies: (1) direct assembly of new MOFs from particular metal nodes and organic linkers and (2) post-synthesis modification of pre-constructed robust *precursor* MOFs. In the direct-assembly strategies, certain desirable functional groups may be hard to incorporate into MOFs, either because of thermal instability under MOF synthesis conditions or due to competitive reaction with intended framework components.⁵ Additionally, it is known that both the connectivity and the degree of catenation can be very sensitive to small changes in the organic ligands for the synthesis of MOFs through direct assembly.⁶ Because of these complexities, post-synthesis modification strategies are emerging as an alternative method for tailoring MOFs toward specific applications. Several reports on this strategy have appeared recently.⁷

Recently, Farha *et al.* proposed a new MOF strut (4,4',4'',4'''-benzene-1,2,4,5-tetratyltetrabenzoic acid, **1**, Scheme 1) and used it to synthesize a 3D non-catenated Zn-paddlewheel MOF



Scheme 1 Preparation methods of **3**, **4**, and **5**. i) DMF/80 °C/24 h, followed by evacuation while heating at 100 °C; ii) evacuation while heating at 150 °C; iii) soak in a solution of CHCl₃/4-(trifluoromethyl)pyridine, followed by evacuation while heating at 100 °C.

[Zn₂(**1**)(DMF)₂](DMF)_m (**2**) [DMF = dimethylformamide].⁵ The single-crystal X-ray structure of **2** indicates that two DMF molecules are coordinated to the axial sites of the Zn(II)₂ units. Farha *et al.* showed that by heating **2** at 100 °C under vacuum for 24 h, free non-coordinated DMF molecules (designated (DMF)_m) were removed and a partially evacuated MOF, **3**, was prepared. In **3**, the coordinated DMF molecules remain in the pores. A DMF-free version, **4**, was obtained by heating **2** at 150 °C under vacuum for 24 h. In this case, all free and coordinated DMF molecules were removed and open metal sites were formed. By immersing **4** in CHCl₃ solutions of each of several pyridine derivatives (py-R), a collection of py-R-modified MOFs was obtained. ¹H NMR and TGA results showed the formation of highly porous cavity-modified MOFs, [Zn₂(**1**)(py-R)₂]_n, as well as the coordinative binding of the py-R ligands.⁵

In this work, we compare adsorption in MOFs **3**, **4**, and **5**, where **5** is the py-CF₃ modified version of **4**, *i.e.* [Zn₂(**1**)(py-CF₃)₂]_n. Single-component adsorption isotherms for CO₂, N₂, and CH₄ were measured experimentally in all three MOFs. Then from the pure-component isotherms, the selectivities for CO₂/N₂ and CO₂/CH₄ mixtures were calculated using ideal adsorbed solution theory (IAST).⁸ Many studies have shown that IAST can be used to successfully predict gas mixture adsorption in zeolites,^{9–11} and recently the theory has been tested in MOFs using molecular simulations.^{9,12,13}

MOFs **3**, **4**, and **5** form an interesting series for elucidating the effects of different framework features on adsorption capacity and selectivity. MOF **4** has open-metal sites, which are expected to enhance adsorption, especially for CO₂ and N₂, which are

^aDepartment of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois, 60208, USA. E-mail: snurr@northwestern.edu; Fax: +1-847-467-1018; Tel: +1-847-467-2977

^bDepartment of Chemistry and International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois, 60208, USA. E-mail: j-hupp@northwestern.edu

quadrupolar molecules. Similarly, the highly polar $-\text{CF}_3$ functional group was introduced into **5** with the intention of increasing CO_2 sorption. Finally, the pore sizes and surface areas of the three MOFs are different due to the cavity modification. These factors may also have a strong effect on adsorption and selectivity of CO_2 , N_2 , and CH_4 . By comparing adsorption in the three MOFs, we can obtain information on the relative importance of open-metal sites, polar surface groups, pore size, and surface area.

The parent MOF material (**2**) was synthesized from a solvothermal reaction of **1** and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in DMF solution at 80°C for 24 h. Then, **3** and **4** were obtained by heating this material at 100°C and 150°C , respectively. The py- CF_3 modified MOF (**5**) was prepared by immersing **4** in a CHCl_3 solution of the py- CF_3 ligand for 24 h (Scheme 1). The details are described elsewhere.⁵ Surface areas were obtained from CO_2 isotherms measured at 273 K using the BET theory (Fig. 1 and Table 1). We also calculated the surface areas of **3**, **4**, and **5** geometrically¹⁴ assuming that they all have the same framework structure as **2**. The excellent agreement between the BET and geometric surface areas provides indirect evidence that all three MOFs have essentially the same structure as **2**, with the main difference being the presence or absence of DMF or py- CF_3 at the open-metal sites.

Fig. 2 shows the adsorption isotherms of CO_2 , N_2 , and CH_4 at 298 K up to 18 bar, measured volumetrically on evacuated samples of **3**, **4**, and **5**. The detailed procedure can be found elsewhere.¹³ In each sample, CO_2 is the most strongly adsorbed molecule due to its large quadrupolar moment. Also, CH_4 shows stronger adsorption than N_2 as already reported in all known sorbents. This is attributed to the higher polarizability of CH_4 ($26 \times 10^{-25} \text{ cm}^3$) vs. N_2 ($17.6 \times 10^{-25} \text{ cm}^3$).³ Interestingly, it was impossible to measure N_2 isotherms for any of the three MOFs at 77 K, but the materials do take up N_2 at

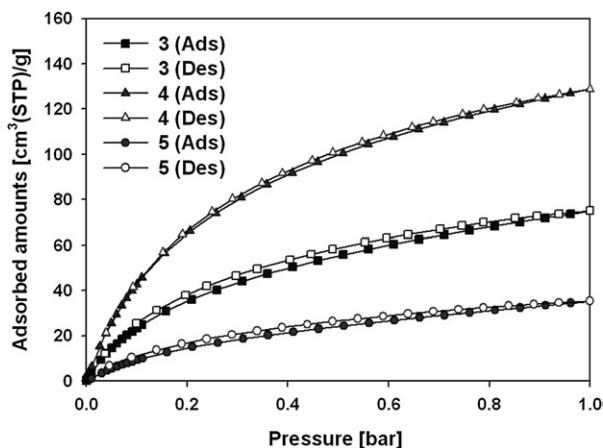


Fig. 1 Adsorption and desorption isotherms of CO_2 in **3**, **4**, and **5** at 273 K.

Table 1 Comparisons between the experimental surface areas and the calculated surface areas of **3**, **4**, and **5** (all units are m^2/g)

	Experimental surface area	Calculated surface area
3	800	769
4	1370	1805
5	390	454

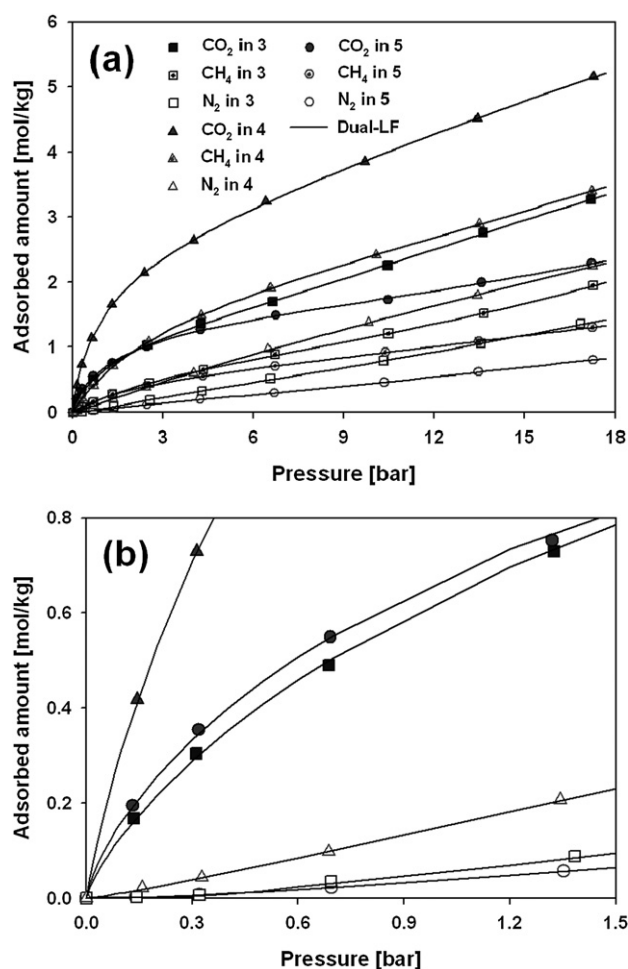


Fig. 2 Adsorption isotherms of CO_2 , N_2 , and CH_4 in **3**, **4**, **5** at 298 K: (a) full pressure range, (b) low pressure range (CH_4 isotherms are omitted for clarity). Lines are fits to a dual-site Langmuir–Freundlich (Dual-LF) equation.¹³

298 K. This suggests that the pores of **3**, **4**, and **5** may be close to the kinetic diameter of N_2 ($3.64 \text{ \AA}$).¹⁵ For such tightly constricted pores, a likely explanation is that N_2 molecules cannot enter the pores at 77 K due to large diffusional resistances, but at 298 K the additional thermal energy allows the molecules to overcome these resistances. Similar behavior has been reported in other studies.¹⁶

None of the isotherms in Fig. 2 show saturation at 18 bar. For all gases, the order of the adsorbed amounts around 18 bar is as follows: **4** > **3** > **5** (Fig. 2a). This coincides with the order of the surface areas, in agreement with the notion that at intermediate loadings the amount adsorbed should correlate with the surface area.¹⁷ At low pressures, adsorption is not expected to correlate with the surface area. Instead, adsorption should correlate with the strength of binding.¹⁷ Here, we again find that **4** shows the highest adsorption of the three MOFs for all three gases (Fig. 2b), but this is presumably due to strong adsorption on the open-metal sites rather than the larger surface area of **4**. At low loading, the py- CF_3 -modified MOF **5** adsorbs more CO_2 than **3** at 298 K, but less N_2 and CH_4 . This selectivity difference is discussed below.

The selectivities of CO_2/N_2 and CO_2/CH_4 binary mixtures were predicted from the experimental single-component isotherms using IAST. Fig. 3a and b present the predicted selectivities for equimolar

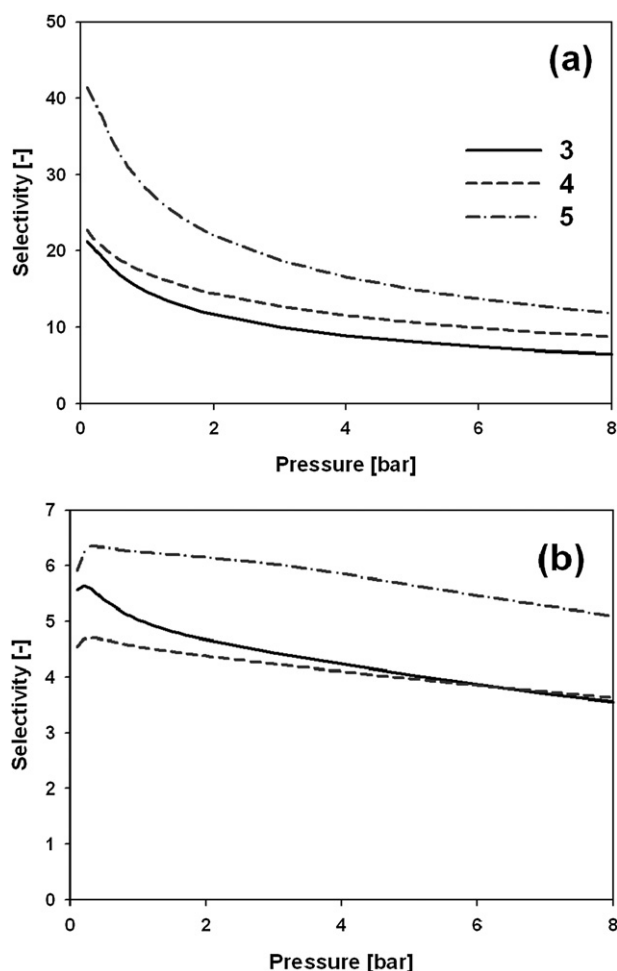


Fig. 3 IAST selectivities of (a) CO₂ over N₂, and (b) CO₂ over CH₄ for equimolar binary mixtures in **3**, **4**, **5** at 298 K.

CO₂/N₂ and CO₂/CH₄ mixtures in **3**, **4**, and **5** as a function of total bulk pressure. The most remarkable point of Fig. 3 is the high CO₂/N₂ selectivity (~42) of **5** at low pressure. Throughout the entire pressure range, **5** exhibits larger CO₂/N₂ and CO₂/CH₄ selectivities than **3** and **4**. This can be explained by the following factors. First, the highly polar -CF₃ groups in **5** should be more attractive to CO₂ (large quadrupole moment, 13.4 C m²) than N₂ (smaller quadrupole moment, 4.7 C m²) or CH₄ (nonpolar).¹⁸ Second, the more constricted pores of **5** should enhance the selectivity of the more strongly adsorbed CO₂ over N₂ and CH₄ due to the increased potential.¹⁹

Fig. 4 shows the CO₂/N₂ selectivities in **5** at different pressures and different mixture compositions predicted by IAST. The selectivity increases with decreasing pressure. Also, the selectivity increases as y_{N_2} approaches unity, but at zero coverage it does not depend on the gas composition. For the case of $y_{N_2} = 0.85$, which is a typical composition for flue gas from power plants,² the selectivity is in the range of 25–45. In addition, the selectivity is high (30–37) at or slightly above atmospheric pressure, which is the pressure regime of interest for removing CO₂ from flue gas. For these conditions, the selectivity of **5** is higher than that of Cu-BTC (20–22 as predicted by molecular simulation), to our knowledge the largest previously reported for MOFs.²⁰ Even for equimolar mixtures of N₂ and CO₂, the selectivity

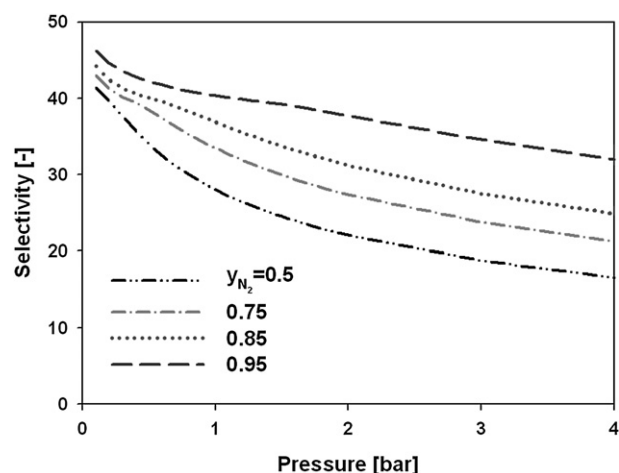


Fig. 4 IAST selectivities of CO₂ over N₂ in **5** at different pressures and mixture compositions.

is fairly high (17–41) compared to reports for other MOFs: Cu-BTC (20–25)²⁰ and MOF-508b (4–6).²¹ Moreover, these selectivities are considerably higher than the experimental CO₂/N₂ selectivities reported for zeolite and carbon adsorbents under similar conditions: zeolite 4A (19),²² zeolite 13X (18),²² activated carbon (15).²³ While the selectivity of **5** is high, the adsorption capacity for CO₂ is not as high as some other MOFs such as Cu-BTC, MOF-508b, MIL-101 and MIL-53.^{20,21,24,25}

For PSA processes, the kinetics and reversibility of adsorption are also important. Adsorption of CO₂ was found to be completely reversible in **5** (Fig. 1), and a graph of the time evolution for CO₂ and N₂ adsorption in **5** at the first point of the isotherms (0.2 atm and 298 K) shows that the adsorption rate of CO₂ is much faster than that of N₂ (Fig. 5). This means that the selectivity of CO₂ over N₂ would increase even more if we considered the adsorption kinetics in addition to the adsorption equilibria. The fast and reversible adsorption of CO₂ in **5**, along with the high selectivity, indicate that this material is an attractive candidate for the adsorptive separation of CO₂ from N₂.

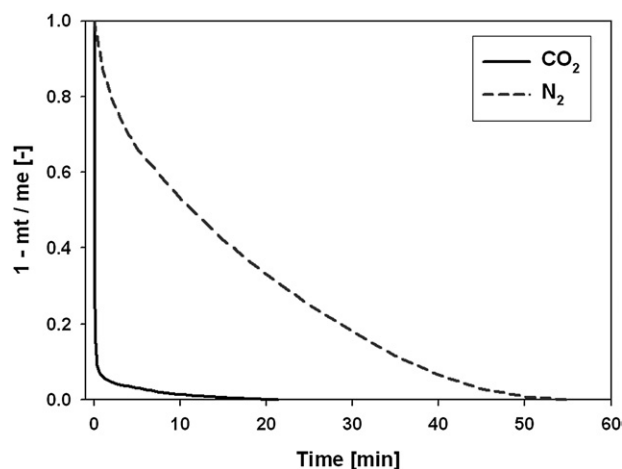


Fig. 5 Adsorption rates of CO₂ and N₂ in **5** at 298 K (at the 1st adsorption points). mt is the amount adsorbed at time t , and me is the equilibrium amount adsorbed.

In summary, experimental isotherms and IAST calculations have shown that **5** is a promising material for CO₂/N₂ separations. In addition, they provide preliminary insight into the factors of most importance for adsorption selectivity of CO₂, N₂, and CH₄ mixtures in MOFs. Post-synthesis modification of MOFs by replacing coordinated solvent molecules with highly polar ligands or ligands featuring other chemical functionalities may be a powerful method for generating new sorbents for other difficult separations.

Acknowledgements

We gratefully acknowledge the U.S. Dept. of Energy Office of Science (Grant No. DE-FG02-01ER15244) and the Northwestern Nanoscale Science and Engineering Center.

Notes and references

- 1 R. F. Service, *Science*, 2004, **305**, 962.
- 2 L. Liu, A. Chakma and X. Feng, *Ind. Eng. Chem. Res.*, 2005, **44**, 6874.
- 3 R. T. Yang, *Adsorbents: Fundamentals and Applications*, John Wiley & Sons, Inc., Hoboken, 2003.
- 4 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. Férey, *Chem. Soc. Rev.*, 2008, **37**, 191.
- 5 O. K. Farha, K. L. Mulfort and J. T. Hupp, *Inorg. Chem.*, 2008, **47**, 10223.
- 6 T. Gadzikwa, B.-S. Zeng, J. T. Hupp and S. T. Nguyen, *Chem. Commun.*, 2008, 3672.
- 7 C.-D. Wu, A. Hu, L. Zhang and W. Lin, *J. Am. Chem. Soc.*, 2005, **127**, 8940; K. L. Mulfort and J. T. Hupp, *J. Am. Chem. Soc.*, 2007, **129**, 9604; Z. Wang and S. M. Cohen, *J. Am. Chem. Soc.*, 2007, **129**, 12368; Z. Wang and S. M. Cohen, *Angew. Chem. Int. Ed.*, 2008, **47**, 4699; K. K. Tanabe, Z. Wang and S. M. Cohen, *J. Am. Chem. Soc.*, 2008, **130**, 8508; J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon and K. Kim, *Nature*, 2000, **404**, 982; S. S. Kaye and J. R. Long, *J. Am. Chem. Soc.*, 2008, **130**, 806; K. L. Mulfort and J. T. Hupp, *Inorg. Chem.*, 2008, **47**, 7936; S. S. Y. Chui, S. M. F. Lo, J. P. H. Chartmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148; A. Ö. Yazaydin, A. I. Benin, S. A. Faheem, P. Jakubczak, J. J. Low, R. R. Willis and R. Q. Snurr, *Chem. Mater.*, 2008, DOI: 10.1021/cm900049x.
- 8 A. L. Myers and J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121.
- 9 R. Babarao, Z. Q. Hu, J. W. Jiang, S. Chempath and S. I. Sandler, *Langmuir*, 2007, **23**, 659.
- 10 S. R. Challa, D. S. Sholl and J. K. Johnson, *J. Chem. Phys.*, 2002, **116**, 814.
- 11 A. Goj, D. S. Sholl, E. D. Akten and D. Kohen, *J. Phys. Chem. B*, 2002, **106**, 8367.
- 12 Q. Y. Yang and C. L. Zhong, *J. Phys. Chem. B*, 2006, **110**, 17776.
- 13 Y.-S. Bae, K. L. Mulfort, H. Frost, P. Ryan, S. Punnathanam, L. J. Broadbelt, J. T. Hupp and R. Q. Snurr, *Langmuir*, 2008, **24**, 8592.
- 14 T. Düren, F. Millange, G. Férey, K. S. Walton and R. Q. Snurr, *J. Phys. Chem. C*, 2007, **111**, 15350.
- 15 J.-H. Moon, Y.-S. Bae, S.-H. Hyun and C.-H. Lee, *J. Membr. Sci.*, 2006, **285**, 343.
- 16 J. Garrido, A. Linares-Solano, J. M. Martin-Martinez, M. Molina-Sabio, F. Rodriguez-Reinoso and R. Torregrosa, *Langmuir*, 1987, **3**, 76; D. Lozano-Castello, D. Cazorla-Amoros and A. Linares-Solano, *Carbon*, 2004, **42**, 1233; T. X. Nguyen and S. K. Bhatia, *J. Phys. Chem. C*, 2007, **111**, 2212.
- 17 H. Frost, T. Düren and R. Q. Snurr, *J. Phys. Chem. B*, 2006, **110**, 9565.
- 18 Y.-S. Bae and C.-H. Lee, *Carbon*, 2005, **43**, 95.
- 19 T. Düren and R. Q. Snurr, *J. Phys. Chem. B*, 2004, **108**, 15703; B. Liu, Q. Yang, C. Xue, C. Zhong, B. Chen and B. Smit, *J. Phys. Chem. C*, 2008, **112**, 9854.
- 20 Q. Yang, C. Xue, C. Zhong and J.-F. Chen, *AIChE J.*, 2007, **53**, 2832.
- 21 L. Bastin, P. S. Barcia, E. J. Hurtado, J. A. C. Silva, A. E. Rodrigues and B. Chen, *J. Phys. Chem. C*, 2008, **112**, 1575.
- 22 R. V. Siriwardane, M.-S. Shen, E. P. Fisher and J. A. Poston, *Energy Fuels*, 2001, **15**, 279.
- 23 F. Dreisbach, R. Staudt and J. U. Keller, *Adsorption*, 1999, **5**, 215.
- 24 P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. D. Weireld, J.-S. Chang, D.-Y. Hong, Y. K. Hwang, S. H. Jung and G. Férey, *Langmuir*, 2008, **24**, 7245.
- 25 S. Bourrelly, P. L. Llewellyn, C. Serre, F. Millange, T. Loiseau and G. Férey, *J. Am. Chem. Soc.*, 2005, **127**, 13519.