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VIP **Metal–Organic Frameworks**

Selective Adsorption and Separation of Xylene Isomers and Ethylbenzene with the Microporous Vanadium(IV) Terephthalate MIL-47**

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The separation of mixed C_8 alkylaromatic compounds is one of the most challenging issues in the chemical industry because of its direct link with PET manufacture, for example.[1a] Distillation is only feasible for the removal of *o*-xylene; it fails for the other C_8 alkylaromatic compounds because of the similarity of their boiling points (*p*-xylene: 138 °C, *m*-xylene: 138–139 °C, and ethylbenzene: 136 °C).[1a,c] Besides crystallization, which has a poor efficiency, adsorption is widely used to separate C_8 alkylaromatic isomers, for example, in Parex or Ebex units in which simulated moving-bed processes are used for the recovery of *para*-xylene and ethylbenzene.[1b] Zeolites X and Y exchanged with cations such as Na^+, K^+, and Ba^{2+} discriminate very selectively between the different C_8 alkylaromatic isomers and are nowadays used as industrial adsorbents.[1c–k]

Metal–organic frameworks (MOFs) are a new class of microporous crystalline materials and currently receive much attention in regard to adsorption applications.[2a–g] The mainly organic character of the inner surface of MOFs offers unprecedented potential for enhancing and fine-tuning the affinity for aromatic adsorbates. For example, *para*-xylene is selectively included inside a zinc 2,6-naphthalene dicarboxylate during its synthesis.[3a] Different affinities for *para*-xylene and *ortho*-xylene are observed in a zinc terephthalate MOF.[3b] The present study demonstrates the first successful use of MOFs as selective adsorbents for the extremely difficult and industrially relevant separations of *para*-xylene versus *meta*-xylene and *para*-xylene versus ethylbenzene.

From the series of MOFs that were screened for the separation of mixed C_8 alkylaromatic compounds, three materials will be discussed. $[Cu_3(BTC)_2]$ (BTC = 1,3,5-benzenetricarboxylate) has a three-dimensional pore structure with easily accessible Cu^{II} sites and BTC ligands as potential adsorption sites.[2b] The one-dimensional pores of the isotypic materials MIL-53 ht and MIL-47 are lined with terephthalate ligands and hydroxy or oxo groups which are connected by coordinatively saturated Al^{3+}, Cr^{3+} (MIL-53 ht), or V^{4+} ions (MIL-47).[4a,b] Both structures were fully characterized by Férey and co-workers, who disclosed an impressive series of MOFs with new topologies.[4a–g] MIL-53 ht and MIL-47 show high thermal stability and have already been investigated as adsorbents for H_2, CO_2, and CH_4.[4f,g] The lattice constants of MIL-47 undergo clear changes upon adsorption of thiophene, acetone, or aniline.[4h]

First, the competitive adsorption equilibria of liquid mixtures of two C_8 alkylaromatic compounds in hexane were studied with $[Cu_3(BTC)_2]$, MIL-47, and MIL-53(Al) ht as adsorbents (Table 1). The orders of preference strongly vary between the adsorbents. $[Cu_3(BTC)_2]$ displays low

Table 1: Selectivities α_{ij} calculated from the uptake from mixtures of binary C_8 alkylaromatic compounds from hexane by MOF adsorbents in batch experiments.[a]

Adsorbent		*j*			
	i	*ortho*-Xylene	*meta*-Xylene	*para*-Xylene	Ethylbenzene
$[Cu_3(BTC)_2]$	*ortho*-xylene	–	0.4	0.7	0.7
	meta-xylene	2.4	–	1.1	1.4
	para-xylene	1.4	0.9	–	1.2
	ethylbenzene	1.4	0.7	0.8	–
MIL-53(Al) ht	*ortho*-xylene	–	2.7	3.5	10.9
	meta-xylene	0.4	–	1.2	3.8
	para-xylene	0.3	0.8	–	3.1
	ethylbenzene	0.1	0.3	0.3	–
MIL-47	*ortho*-xylene	–	2.0	1.4	10.9
	meta-xylene	0.5	–	0.4	4.2
	para-xylene	0.7	2.9	–	9.7
	ethylbenzene	0.1	0.2	0.1	–

[a] Numbers express the selectivity α_{ij} for the compound *i* in the second column over the compound *j* in the top row; 2 mmol of each C_8 compound (0.028 M in hexane) was offered per gram of adsorbent.

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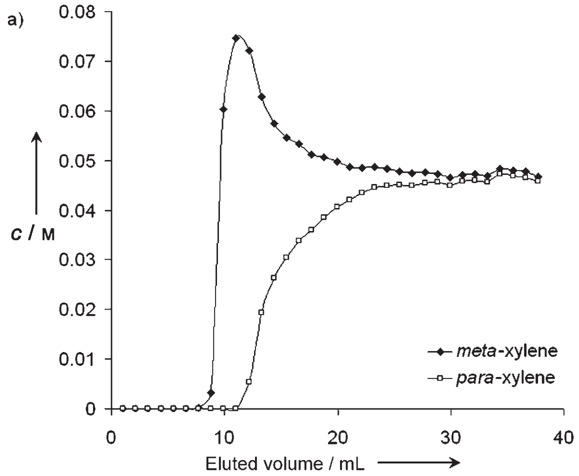
selectivities except for *meta*-xylene versus *ortho*-xylene. This material later serves as a reference adsorbent that provides poor selectivity. By contrast, MIL-53(Al)ht and MIL-47 discriminate much better between C_8 alkylaromatic compounds. Their preference for *para*-xylene over ethylbenzene is striking. Interestingly, MIL-47 also prefers *para*-xylene over *meta*-xylene, with a selectivity of 2.9:1, while MIL-53(Al)ht hardly discriminates between these isomers.

These promising results obtained with MIL-47 inspired us to test the separation of C_8 alkylaromatic compounds in a continuous-flow setup, using a column packed with MIL-47 crystals. In a breakthrough experiment a hexane solution containing equimolar amounts (0.047 M) of *para*-xylene and *meta*-xylene was pumped through the adsorbent bed at a flow rate of 0.5 mL min^{-1}. Figure 1a shows the breakthrough profile of this mixture. After an initial phase during which *para*-xylene and *meta*-xylene are both fully absorbed by MIL-47, a roll-up effect is observed: the displacement of *meta*-xylene by *para*-xylene, which is more strongly adsorbed, results in eluant concentrations of *meta*-xylene temporarily surpassing those of the feed. An analogous roll-up is found when a mixture of *para*-xylene and ethylbenzene is pumped through the column (Figure 1b). The average selectivities calculated from these breakthrough profiles were 2.5:1 for the separation of *para*-xylene and *meta*-xylene, and 7.6:1 for the separation of *para*-xylene and ethylbenzene. Hexane proved to be a suitable desorbent for regeneration of the column between the different experiments. A similar MIL-47 column can also be used in a pulse chromatographic experiment, in which a ternary mixture of ethylbenzene, *meta*-xylene, and *para*-xylene is injected into hexane flowing at 4 mL min^{-1} through the column. Three well-separated peaks are obtained in the chromatogram, with *para*-xylene again being most strongly held by the adsorbent (Figure 2). Selectivities were 3.1:1 for *para*-xylene versus *meta*-xylene, and 9.7:1 for *para*-xylene versus ethylbenzene. These results are in reasonable agreement with results obtained from competitive batch adsorption (Table 1), and remained unchanged over a range of flow rates (2 to 5 mL min^{-1}).



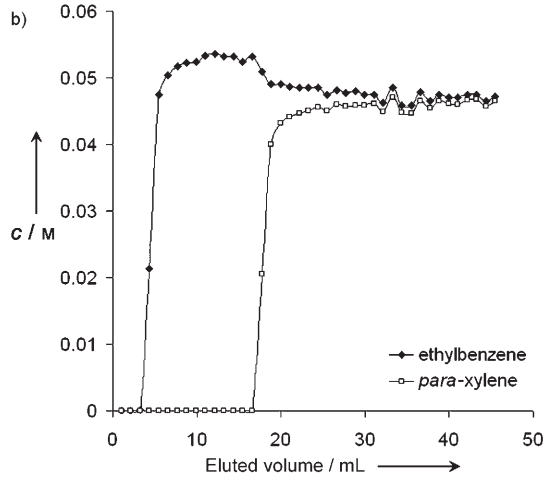


Figure 1. Breakthrough experiments with binary 0.047 M solutions of C_8 alkylaromatic compounds in hexane on a 5-cm column filled with MIL-47 at 298 K: effluent concentrations *C* of: a) *para*-xylene and *meta*-xylene and b) *para*-xylene and ethylbenzene as a function of the eluted volume.

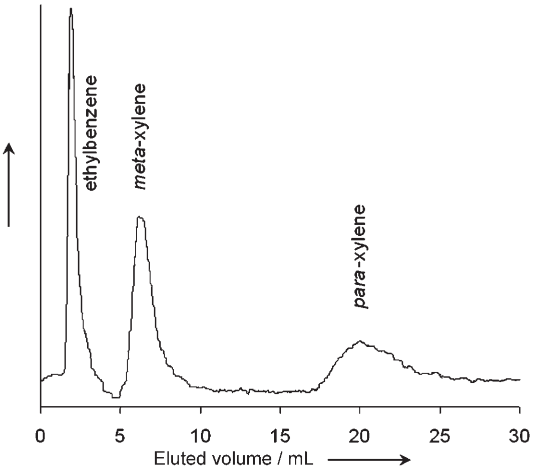


Figure 2. Chromatographic separation of a mixture of ethylbenzene, *meta*-xylene, and *para*-xylene on a column packed with MIL-47 in the liquid phase, with hexane as the desorbent at 298 K. The signal intensity of the refractive index detector is shown versus the eluted volume.

The zero coverage adsorption enthalpies measured in the gas phase are nearly identical for all C_8 alkylaromatic compounds (see the Supporting Information). The observed selectivities in the liquid phase therefore cannot be a consequence of different interaction energies between the MIL-47 framework and the adsorbed molecules, but rather result from molecular packing effects inside the sterically confining environment of the MIL-47 pore system.[5a–c] The critical role of adsorbate packing was confirmed by measuring room-temperature isotherms for the adsorption of the individual C_8 alkylaromatic compounds from a hexane solution (Figure 3). The isotherms for *para*-xylene and *ortho*-xylene reach a plateau of 35–37 wt %, which shows that *para*-xylene is packed more easily and efficiently inside the MIL-47 pores than is *meta*-xylene or ethylbenzene. This finding is also reflected in competitive batch adsorption

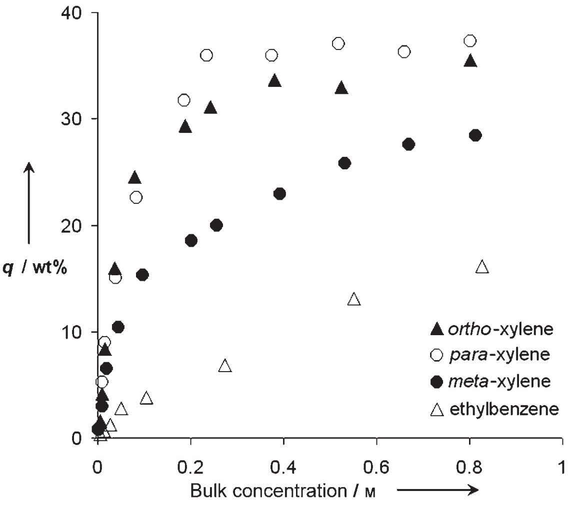


Figure 3. Single-compound adsorption on MIL-47 in batch mode at 298 K: uptake *q* of C_8 alkylaromatic compounds from hexane as a function of the bulk phase concentration.

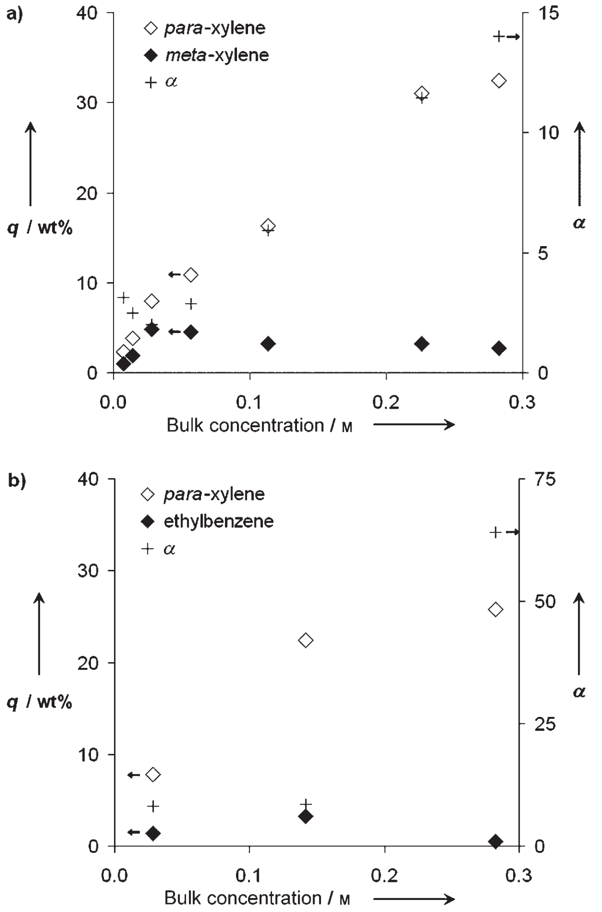


Figure 4. Competitive adsorption on MIL-47 in batch mode: uptake *q* from: a) a mixture of *para*-xylene and *meta*-xylene and b) a mixture of *para*-xylene and ethylbenzene in hexane as a function of the bulk phase concentration. Selectivities α calculated from the data points are given on the right axis.

experiments using 1:1 mixtures of *para*-xylene and *meta*-xylene over a range of bulk concentrations (Figure 4a). Selectivities are already significant at low bulk phase concentrations of *para*-xylene and *meta*-xylene and steadily increase up to values higher than 10:1 at higher concentrations. A similar exclusion is observed in the co-adsorption of *para*-xylene and ethylbenzene: the dominant adsorption of *para*-xylene practically inhibits uptake of ethylbenzene (Figure 4b). These results are fully in line with the roll-up effects seen in the breakthrough experiments (Figure 1).

The adsorbates were located inside the MIL-47 host by Rietveld refinements of the X-ray powder diffraction patterns of MIL-47 samples saturated with each of the aromatic compounds (Figure 5). While changes in the lattice constants of MIL-47 upon adsorption of guests have been observed before,[4b,h] the adsorption of *para*-, *ortho*-, or *meta*-xylene induces hardly any changes in the lattice constants compared with the calcined and relaxed material. Structure refinement of the xylene-loaded samples (Figure 5a–c) shows that the molecules fill the structure pairwise. Moving down the channels in the *a* direction of a theoretically fully loaded structure, one encounters a xylene pair in every unit cell, that is, every 6.81 Å. Four different positions are available for each pair within one channel; these positions are symmetrically equivalent. However, they cannot be simultaneously occupied because of steric effects (see the Supporting Information). The major difference between the molecular arrangements of the three xylene isomers is the relative alignment of the aromatic planes of the molecules within a pair. For *para*-xylene, the benzene rings in a pair are almost perfectly parallel, with staggered methyl groups (Figure 5a). This parallel orientation is indicative of a strong π–π interaction between the *para*-xylene molecules. The interaction of adsorbed *para*-xylene molecules with the terephthalate ligands in the pore walls seems much weaker. This weak interaction is in line with the negligible changes in the lattice constants upon filling of the pores with *para*-xylene. No evidence for long-range order has been found, either along the channels or between the channels. Structure refinement of MIL-47 crystals loaded with *ortho*-xylene reveals that the stacking of these isomers is analogous to that found for *para*-xylene, but ring alignment is slightly less effective (Figure 5b). However, when the pores are filled with pairs of *meta*-xylene molecules, a steric interaction arises between an aromatic ring of one molecule and a methyl group of a molecule in the neighboring unit cell in the *a* direction. This interaction causes a tilt and a turn of the aromatic molecules (Figure 5c). To achieve a similar dense packing as observed for *para*-xylene, the small value of the lattice constant *a* forces the two aromatic rings within the *meta*-xylene pair away from the mutually most favorable alignment for π–π interactions. This arrangement readily explains the less-efficient packing of *meta*-xylene in comparison to *para*-xylene sorption.

The lattice constants undergo a major change upon adsorption of ethylbenzene (Figure 5d). The ethyl group prevents a similar planar alignment of two ethylbenzene molecules within the confinement of the channel. Surprisingly, the methyl groups of the alkyl chains are found in proximity to three lattice oxygen atoms in the corners of the

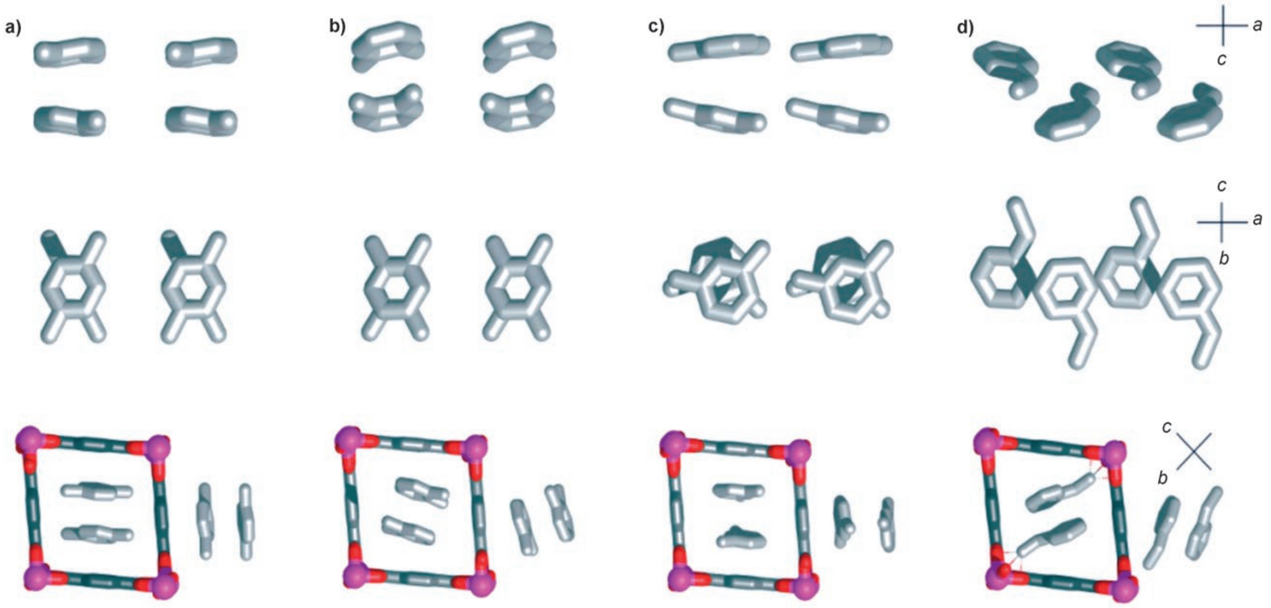


Figure 5. Structure refinements of MIL-47 crystals loaded with different C_8 alkylaromatic compounds: packing in the pores of a) *para*-xylene; b) *ortho*-xylene; c) *meta*-xylene; d) ethylbenzene (gray = carbon, red = oxygen, pink = vanadium; hydrogen atoms have been omitted for clarity). All refinements were made in Pnma; note that only one of the symmetry-generated molecule positions is shown (see the Supporting Information).

rhombic channel. This arrangement suggests an interaction between the protons of the CH_3 group and the terephthalate ligands, thus causing the change in the lattice constants by widening the corresponding channel angle. No π–π interaction between ethylbenzene molecules or between ethylbenzene molecules and the framework is apparent from the structure, which together with the lattice distortion, readily explains the lower uptake observed in the isotherm (Figure 3).

We have described the adsorption and separation of a mixture of C_8 alkylaromatic compounds on $[Cu_3(BTC)_2]$, MIL-53(Al) ht, and MIL-47 in the liquid phase. Of these materials, MIL-47 is clearly the most promising adsorbent and displays high selectivities. The potential of MIL-47 for real separations of C_8 alkylaromatic compounds was demonstrated by breakthrough and chromatographic experiments. In comparison with the currently used zeolites, the remarkable properties of MIL-47 are its high uptake capacity and its hydrophobic nature, which are advantageous for its future application in adsorption processes.

Experimental Section

$[Cu_3(BTC)_2]$ and MIL-53(Al) ht were synthesized according to literature procedures.[4a,6] MIL-47 was hydrothermally synthesized based on a literature procedure[4b] and calcined in a shallow bed in air at 300 °C for 21.5 h; the obtained material has a pore volume of $0.32\,mL\,g^{-1}$ and a specific surface of $800\,m^2\,g^{-1}$. Orthorhombic crystals ranging from 0.25 to 2.0 μm were observed by scanning electron microscopy (SEM). Batch experiments were performed in small vials loaded with adsorbent. A 5-cm stainless-steel column placed in an HPLC apparatus was used for pulse and breakthrough experiments. Gas-phase adsorption at low degrees of pore filling was studied using the pulse chromatographic technique with a 15-cm column packed with pellets of MIL-47.[7] Further details about procedures and calculations of selectivities, Henry adsorption constants, and adsorption enthalpies are given in the Supporting Information. Rietveld refinements were performed using the GSAS software[8] and are described in more detail in the Supporting Information. CCDC-632101–632104 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.

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[1] a) *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed., **2000** electronic release; b) R. Meyers, *Handbook of Petroleum Refining Processes*, 3th ed., McGraw-Hill, New York, **2003**, pp. 2.47–2.53; c) A. Méthivier in *Zeolites for Cleaner Technologies, Catalytic Science Series, Vol. 3* (Eds.: M. Guisnet, J. P. Gilson), Imperial College Press, London, **2002**, pp. 209–221; d) R. Hulme, R. Rosensweig, D. Ruthven, *Ind. Eng. Chem. Res.* **1991**, *30*, 752; e) D. Ruthven, M. Goddard, *Zeolites* **1986**, *6*, 275; f) M. Goddard, D. Ruthven, *Zeolites* **1986**, *6*, 283; g) J. Kaerger, D. Ruthven in *Handbook of Porous Solids* (Eds.: F. Schüth, K. Sing, J. Weitkamp), Wiley-VCH, Weinheim, **2002**, pp. 2089–2173; h) S. Kulprathipanja, J. Johnson in *Handbook of Porous Solids* (Eds.: F. Schüth, K. Sing, J. Weitkamp), Wiley-VCH, Weinheim, **2002**, pp. 2568–2612; i) D. Ruthven, *Principles of Adsorption and Adsorption Processes*, Wiley, New York, **1984**, p. 332 and pp. 401–405; j) J. Kaerger, D. Ruthven, *Diffusion in Zeolites*, Wiley, New York, **1992**; k) V. Cottier, J.-P. Bellat, M.-H. Simonot-Grange, *J. Phys. Chem. B* **1997**, *101*, 4798.
[2] a) H. Li, M. Eddaoudi, M. O'Keeffe, O. Yaghi, *Nature* **1999**, *402*, 276; b) S. Chui, S. Lo, J. Charmant, A. Orpen, I. Williams, *Science* **1999**, *283*, 1148; c) N. Rosi, J. Eckert, M. Eddaoudi, D. Vodak, J.

Kim, M. O'Keeffe, O. Yaghi, *Science* **2003**, *300*, 1127; d) U. Müller, M. Schubert, F. Teich, H. Pütter, K. Schierle-Arndt, J. Pastré, *J. Mater. Chem.* **2006**, *16*, 626; e) Q. Wang, D. Shen, M. Bülow, M. Lau, S. Deng, F. Fitch, N. Lemcoff, J. Semanscin, *Microporous Mesoporous Mater.* **2002**, *55*, 217; f) L. Pan, D. Olson, L. Ciemnolonski, R. Heddy, J. Li, *Angew. Chem.* **2006**, *118*, 632; *Angew. Chem. Int. Ed.* **2006**, *45*, 616; g) B. Chen, C. Liang, J. Yang, D. Contreras, Y. Clancy, E. Lobkovsky, O. Yaghi, S. Dai, *Angew. Chem.* **2006**, *118*, 1418–1421; *Angew. Chem. Int. Ed.* **2006**, *45*, 1390.

[3] a) R. Nandini Devi, M. Edgar, J. Gonzalez, A. M. Z. Slawin, D. P. Tunstall, P. Grewal, P. A. Cox, P. A. Wright, *J. Phys. Chem. B* **2004**, *108*, 535; b) L. Huang, H. Wang, J. Chen, Z. , Wang, J. Sun, D. Zhao, Y. Yan, *Microporous Mesoporous Mater.* **2003**, *58*, 105.

[4] a) T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Férey, *Chem. Eur. J.* **2004**, *10*, 1373; b) K. Barthelet, J. Marrot, D. Riou, G. Férey, *Angew. Chem.* **2002**, *114*, 291; *Angew. Chem. Int. Ed.* **2002**, *41*, 281; c) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* **2005**, *309*, 2040; d) S. Miller, P. Wright, C. Serre, T. Loiseau, J. Marrot, G. Férey, *Chem. Commun.* **2005**, 3850; e) K. Barthelet, J. Marrot, G. Férey, D. Riou, *Chem. Commun.* **2004**, 520; f) G. Férey, M. Latroche, C. Serre, F. Millange, T. Loiseau, A. Percheron-Guégan, *Chem. Commun.* **2003**, 2976; g) S. Bourrelly, P. L. Llewellyn, C. Serre, F. Millange, T. Loiseau, G. Férey, *J. Am. Chem. Soc.* **2005**, *127*, 13519; h) X. Wang, L. Liu, A. J. Jacobson, *Angew. Chem.* **2006**, *118*, 6649; *Angew. Chem. Int. Ed.* **2006**, *45*, 6499.

[5] a) I. Daems, P. Leflaive, A. Méthivier, G. Baron, J. Denayer, *Microporous Mesoporous Mater.* **2006**, *96*, 149; b) M. Schenk, S. Calero, T. Maesen, L. Van Benthem, M. Verbeek, B. Smit, *Angew. Chem.* **2002**, *114*, 2609; *Angew. Chem. Int. Ed.* **2002**, *41*, 2499; c) J. Denayer, K. De Meyer, J. Martens, G. Baron, *Angew. Chem.* **2003**, *115*, 2880; *Angew. Chem. Int. Ed.* **2003**, *42*, 2774.

[6] L. Alaerts, E. Séguin, H. Poelman, F. Thibault-Starzyk, P. Jacobs, D. De Vos, *Chem. Eur. J.* **2006**, *12*, 7353.

[7] R. A. Ocakoglu, J. Denayer, G. Marin, J. Martens, G. Baron, *J. Phys. Chem. B* **2003**, *107*, 398.

[8] A. Larson, R. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR **2004**, 86–748.