Metal–Organic Frameworks

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Metal–Organic Framework MIL-101 for High-Resolution Gas-Chromatographic Separation of Xylene Isomers and Ethylbenzene**

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Metal–organic frameworks (MOFs) have received great attention because of their fascinating structures[1] and intriguing applications in hydrogen storage,[2] gas separation,[3] catalysis,[4] chiral separation,[5] sensing,[6] and imaging.[7] Recently, MOFs such as MOF-508,[8] MIL-47,[9] and MIL-53[10] have been shown to be promising as stationary phases for gas chromatography (GC)[3a,8,9b,d] and liquid chromatography.[9a,c,10,11] All these pioneering works on the utilization of MOFs as stationary phases in chromatography were performed on packed columns. However, packed columns usually result in low resolution as a result of peak broadening, which impairs the separation efficiency of MOFs. Moreover, gram-scale MOFs are needed for packed columns, leading to high-cost applications of MOFs as stationary phases in chromatographic separation. In contrast, capillary columns, either wall-coated open tubular (WCOT) columns or porous layer open tube (PLOT) columns,[12] involve a thin film of MOFs coated on their inner walls, and thus improve the resolving power of MOFs and reduce the amount of MOFs required for GC applications. However, to the best of our knowledge, no work on the utilization of MOFs as stationary phases for high-resolution capillary GC separation has been reported so far.

Herein we show the first fabrication of the MOF-coated capillary column for high-resolution GC separation. For a proof-of-concept demonstration, we choose MIL-101 as the stationary phase and xylene isomers and ethylbenzene (EB) as the targets for separation.

Xylene isomers and EB are important raw chemicals in industry; in particular, *p*-xylene is used in the manufacture of terephthalic acid for the polyester industry.[13] The separation and detection of individual xylene isomers and EB are also of environmental concern, and of great practical interest in air monitoring[14] and blood analysis.[15] For these reasons, numerous stationary phases have been developed for GC separation of xylene isomers and EB, for example, 7,8-benzoquinoline,[16] tetrachlorophthalate,[17] 1,8-diaminonaphthalene,[18] modified organo-clays Bentone-34,[19] liquid-crystalline compounds,[20] β-cyclodextrin derivatives,[14,21] poly(ethylene glycol),[15] and MIL-47.[9b] However, long analysis time (27–90 min)[17–19,20a,22] or temperature programming[15,23] is often needed.

MIL-101 is a chromium terephthalate MOF with coordinatively unsaturated sites (CUS).[24] We utilized MIL-101 as the stationary phase because of its high surface area, large pores (2.9–3.4 nm), accessible CUS, and excellent chemical and thermal stability,[25] which make it an attractive candidate for isomer separation. However, MIL-101 has never been explored as the stationary phase for chromatographic separation before, even though the tiny crystal size characteristic of MIL-101 is beneficial to the fabrication of MIL-101 coated capillary columns by a dynamic coating method.[12c–e]

In this work, we prepared the MIL-101 coated capillary column and achieved a baseline separation of *p*-xylene, *o*-xylene, *m*-xylene, and EB on the fabricated MOF coated capillary column by GC within 1.6 min without the need for temperature programming (Figure 1).

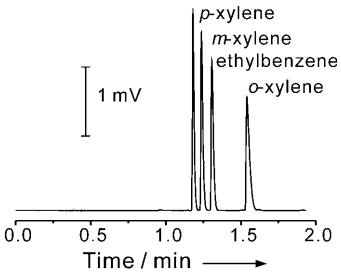

Figure 1. GC separation of xylene isomers and EB on a MIL-101 coated capillary column (15 m long × 0.53 mm i.d.) at 160 °C under a N_2 flow rate of 3 mL min^{-1}. The mass of each isomer is 350 ng.

The MIL-101 coated capillary column was fabricated by a dynamic coating method.[12c–e] First, MIL-101 was synthesized according to the method of Férey et al. (see the Supporting Information).[24] Then, a suspension of MIL-101 in ethanol was filled into a fused silica capillary column under gas pressure to dynamically coat the MIL-101 on the inner wall of the capillary column, as described in experimental section. Figure 2 shows scanning electron microscopy (SEM) images of the cross section of the fabricated capillary column (15 m long × 0.53 mm i.d.; i.d. = internal diameter) and the coated MIL-101 films on the inner wall of the capillary column. The fabricated capillary column had an approximately 0.4 μm thick MIL-101 coating on the inner wall (Figure 2a, inset) and showed high resolution and selectivity for the separation of xylene isomers and EB (Figure 1). All the targets in the

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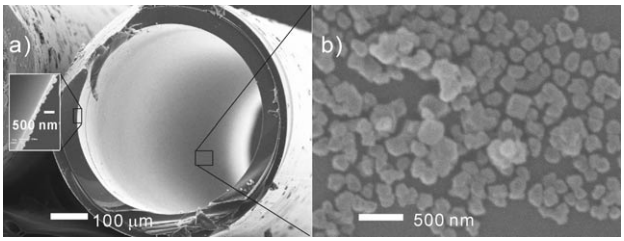

Figure 2. SEM images of a) the cross section of MIL-101 coated capillary column (inset shows the thickness of the MIL-101 coating); and b) MIL-101 deposited on the inner wall of the capillary column.

mixture were well resolved and baseline separated from each other in less than 1.6 min, which had not been achieved on packed columns of MIL-47 or MIL-53.[9a,b,10] The number of theoretical plates calculated from *p*-xylene was up to 3800 plates m^{-1} for the MIL-101 coated capillary column (Figure 3d), which is much larger than that of the packed columns. The present MIL-101 coated capillary column even efficiently separated *p*-xylene and *m*-xylene, even though such separation is challenging in the chemical industry because of the similarity of their boiling points. Moreover, only 1 mg MIL-101 was needed for the fabrication of a capillary column, which substantially improves the cost efficiency of MOFs in chromatographic separation.

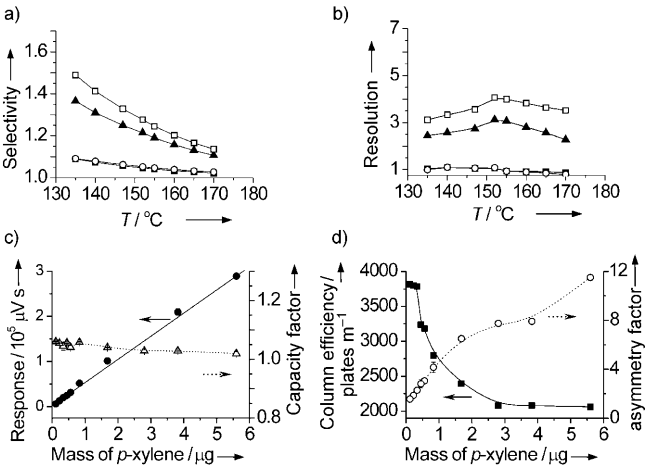

Figure 3. Parameters affecting the separation of xylene isomers and EB: a) effect of temperature on selectivity; □ *o*-xylene/*m*-xylene, ▲ *o*-xylene/ethylbenzene, ○ ethylbenzene/*m*-xylene, ■ *m*-xylene/*p*-xylene; b) effect of temperature on resolution, symbols see panel (a); c) effect of analyte mass on the peak area response (●) and capacity factor (△); and d) effect of analyte mass on column efficiency (■) and asymmetry factor (○). The asymmetry factor is defined as the distance from the center line of the peak to the back slope divided by the distance from the center line of the peak to the front slope, with all measurements made at 10% of the maximum peak height. All experiments were performed at a N_2 flow rate of 2.3 mL min^{-1}.

The resolution and selectivity for the separation of xylene isomers and EB on the MIL-101 coated capillary column were affected by temperature and the mass of isomers. Increasing the temperature from 135 °C to 170 °C decreased the selectivity (Figure 3a), but substantially improved the column efficiency (Figure S1 in the Supporting Information). As a result, the resolution of xylene isomers and EB on the MIL-101 coated capillary column was stable over a broad temperature range, thus facilitating the choice of temperature for effective separation (Figure 3b). Moreover, the separation of xylene isomers and EB mixture on the MIL-101 coated capillary column did not require temperature-programmed control, which was essential for some other stationary phases, such as poly(ethylene glycol), for separation of the same mixture.[15]

Increasing the injected analyte mass resulted in a linear increase of chromatographic peak area, but no change in retention time, and thereby a stable capacity factor (Figure 3c). This feature of the present MIL-101 coated capillary column is favorable for its application to both qualitative and quantitative analysis. However, the column efficiency decreased as the injected analyte mass was increased (Figure 3d). More analyte mass injected also led to larger asymmetric factors, suggesting peak tailing to a greater extent.

Considering the molecular size of xylene isomers and EB (0.58 to 0.68 nm), the size selectivity of the MIL-101 coated capillary column could not be rationalized because of the large pore window diameter (1.4 and 1.6 nm) of MIL-101.[25] The typical elution sequence of xylene isomers and EB commonly observed in ordinary stationary phases such as (5%-phenyl)-methylpolysiloxane,[26] which usually follows the order of boiling points (EB (136 °C) < *p*-xylene (138 °C) ≈ *m*-xylene (139 °C) < *o*-xylene (144 °C)), was not observed on the MIL-101 coated capillary column (Figure 1). In particular, EB eluted after *p*-xylene and *m*-xylene, and before *o*-xylene on the MIL-101 coated capillary column. The same elution order was also observed on MIL-47[9b] and a β-cyclodextrin column[14,21a] because of the pore-filling effect[9b] and guest–host interactions.[9b,21a]

The excellent selectivity of the MIL-101 coated capillary column for the separation of xylene isomers and EB originated not only from the host–guest interactions, but also from the CUS and suitable polarity of MIL-101.

Numerous CUS in MIL-101 enabled the surface functionalization to modify the characteristics of the pore.[25,27] To demonstrate the effect of CUS on the separation of xylene isomers and EB, we grafted pyridine to the CUS of MIL-101 by postsynthetic modification (see the Supporting Information). The successful modification of MIL-101 to form pyridine-grafted MIL-101 was confirmed by thermal gravimetric analysis (TGA), X-ray diffraction (XRD) spectrometry, Fourier transform infrared (FTIR) spectroscopy, N_2 adsorption, and SEM experiments (Supporting Information, Figures S2–S5). The pyridine-grafted MIL-101 coated capillary column obtained by using the same dynamic method did not offer baseline separation of *p*-xylene from *m*-xylene in the mixture of xylene isomers and EB (Figure S6) because the occupation of the CUS by the pyridine would decrease the electron donor and acceptor interactions between the MIL-101 stationary phase and isomers, and thus impair the selectivity.

Polarity is an important factor affecting the selectivity for the separation of xylene isomers and EB. To investigate its effect, McReynolds constants were measured to evaluate the polarity of the MIL-101 and pyridine-grafted MIL-101 stationary phases (see the Supporting Information).[28] The McReynolds constants show weak polarity for MIL-101, which is comparable to that of dioctyl phthalate (Table 1).

Table 1: McReynolds constants of the MIL-101 and pyridine-grafted MIL-101 stationary phases.

Column	X[c]	Y[c]	Z[c]	U[c]	S[c]
dioctyl phthalate[a]	92	186	150	236	157
MIL-101[b]	102	182	–	270	–
pyridine-grafted MIL-101[b]	39	135	–	88	–

[a] Data from Ref. [28a]; [b] measured at 160 °C; [c] X, Y, Z, U, and S refer to benzene, butanol, 2-pentanone, nitropropane, and pyridine, respectively.

The suitable polarity of MIL-101 is of benefit to the separation of xylene isomers and EB because of the difference in the polarity of these isomers. 2-Pentanone and pyridine were not eluted on the MIL-101 coated capillary column because of the strong electron acceptor and donor interactions offered by the CUS. Postsynthetic modification of MIL-101 by pyridine also affected the polarity of the MOF. The McReynolds constants of pyridine-grafted MIL-101 were much smaller than those of MIL-101. It was demonstrated that the McReynolds test solutes were more likely to retain on the MIL-101 with CUS.

The capability of the MIL-101 coated capillary column was further demonstrated by high-resolution GC separation of two other isomer mixtures of substituted benzene derivatives (*o*-, *m*-, and *p*-chlorotoluene; and 1,3,5-trimethylbenzene, *n*-propylbenzene, and isopropylbenzene), as well as a mixture of *n*-alkanes with a broad range of boiling points (Figure 4).

In summary, we have fabricated the first MOF-coated capillary column using MIL-101 as the stationary phase for high-resolution GC separation of isomers. The results reported herein are very promising for the application of MOFs for high-resolution capillary GC. Further research should focus on the potential of other MOFs for high-resolution separation, even for high-resolution enantioseparation of chiral compounds.

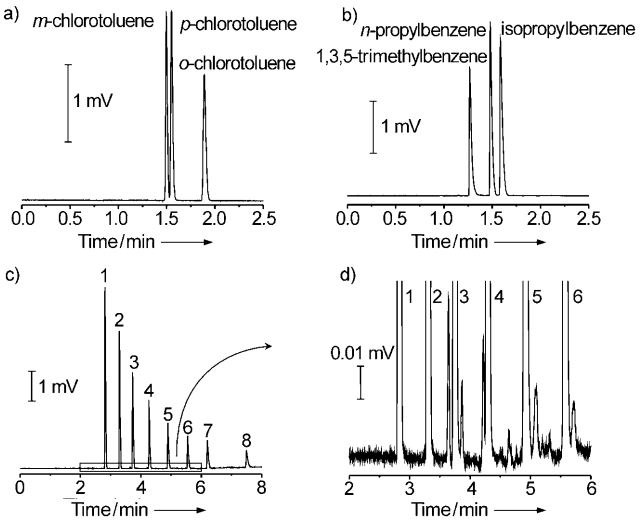

Figure 4. GC chromatograms on the MIL-101 coated capillary column (15 m long × 0.53 mm i.d.) for the separation of a) *m*-, *p*-, and *o*-chlorotoluene (890 ng each) at a N_2 flow rate of 3 mL min^{-1} under 160 °C; b) 1,3,5-trimethylbenzene, *n*-propylbenzene, and isopropylbenzene (1.0 μg each) at a N_2 flow rate of 3 mL min^{-1} under 160 °C; and c) *n*-alkanes (1: hexane; 2: heptane; 3: octane; 4: nonane; 5: decane; 6: undecane; 7: dodecane; 8: tetradecane) using a three-step temperature program: 60 °C for 0.2 min, then 20 °C min^{-1} to 200 °C, and finally 200 °C for the remainder of the measurement; d) expanded view of (c) showing the high-resolution separation of the impurities in the *n*-alkanes mixture.

Experimental Section

MIL-101 was synthesized according to the method of Férey et al.[24] Details for the synthesis of MIL-101, the postsynthetic modification of MIL-101, and the pretreatment of the capillary column are described in the Supporting Information. MIL-101 and pyridine-grafted MIL-101 were coated onto the pretreated capillary column by a dynamic coating method as follows.[12e] A 0.5 mL suspension of MIL-101 or pyridine-grafted MIL-101 (2 mg mL^{-1}) in ethanol was first filled as a plug into the capillary column under gas pressure, and then pushed through the column at a rate of 40 cm min^{-1} to leave a wet coating layer on the inner wall of the capillary column. To avoid acceleration of the solution plug near the end of the column, a 1 m long buffer tube was attached to the end of the capillary column as a restrictor. After coating, the capillary column settled for 2 h for conditioning under nitrogen. Further conditioning of the capillary column was carried out using a temperature program including three steps: 25 °C for 10 min, ramp from 25 °C to 240 °C at a rate of 2 °C min^{-1}, and 240 °C for 30 min.

GC measurements were performed on a Trace GC Ultra system (Thermo Scientific, Waltham, MA, USA) with a flame ionization detector (FID). Nitrogen (99.999 %) was used as the carrier gas. A split ratio of 20:1 was used for all experiments. Data acquisition and processing were controlled by Thermo Chrom-Card software.

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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) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334; c) G. Férey, *Chem. Soc. Rev.* **2008**, *37*, 191; d) J. R. Long, O. M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1213.

[2] a) S. S. Kaye, A. Dailly, O. M. Yaghi, J. R. Long, *J. Am. Chem. Soc.* **2007**, *129*, 14176; b) J. G. Vitillo, L. Regli, S. Chavan, G. Ricchiardi, G. Spoto, P. D. C. Dietzel, S. Bordiga, A. Zecchina, *J. Am. Chem. Soc.* **2008**, *130*, 8386; c) L. J. Murray, M. Dinca, J. R. Long, *Chem. Soc. Rev.* **2009**, *38*, 1294.

[3] a) J. W. Yoon, S. H. Jhung, Y. K. Hwang, S. M. Humphrey, P. T. Wood, J. S. Chang, *Adv. Mater.* **2007**, *19*, 1830; b) L. Bastin, P. S. Bárcia, E. J. Hurtado, J. A. C. Silva, A. E. Rodrigues, B. Chen, *J.*

Phys. Chem. C **2008**, *112*, 1575; c) J.-R. Li, R. J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477.
[4] a) C. D. Wu, W. B. Lin, *Angew. Chem.* **2007**, *119*, 1093; *Angew. Chem. Int. Ed.* **2007**, *46*, 1075; b) M. H. Alkordi, Y. Liu, R. W. Larsen, J. F. Eubank, M. Eddaoudi, *J. Am. Chem. Soc.* **2008**, *130*, 12639; c) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* **2009**, *38*, 1450.
[5] a) B. Kesanli, W. B. Lin, *Coord. Chem. Rev.* **2003**, *246*, 305; b) W. B. Lin, *J. Solid State Chem.* **2005**, *178*, 2486.
[6] a) B. Chen, L. Wang, F. Zapata, G. Qian, E. B. Lobkovsky, *J. Am. Chem. Soc.* **2008**, *130*, 6718; b) A. Lan, K. Li, H. Wu, D. H. Olson, T. J. Emge, W. Ki, M. Hong, J. Li, *Angew. Chem.* **2009**, *121*, 2370; *Angew. Chem. Int. Ed.* **2009**, *48*, 2334; c) M. D. Allendorf, C. A. Bauer, R. K. Bhakta, R. J. T. Houk, *Chem. Soc. Rev.* **2009**, *38*, 1330.
[7] a) K. M. L. Taylor, A. Jin, W. Lin, *Angew. Chem.* **2008**, *120*, 7836; *Angew. Chem. Int. Ed.* **2008**, *47*, 7722; b) K. M. L. Taylor, W. J. Rieter, W. Lin, *J. Am. Chem. Soc.* **2008**, *130*, 14358.
[8] B. Chen, C. Liang, J. Yang, D. S. Contreras, Y. L. Clancy, E. B. Lobkovsky, O. M. Yaghi, S. Dai, *Angew. Chem.* **2006**, *118*, 1418; *Angew. Chem. Int. Ed.* **2006**, *45*, 1390.
[9] a) L. Alaerts, C. E. A. Kirschhock, M. Maes, M. A. van der Veen, V. Finsy, A. Depla, J. A. Martens, G. V. Baron, P. A. Jacobs, J. E. M. Denayer, D. E. De Vos, *Angew. Chem.* **2007**, *119*, 4371; *Angew. Chem. Int. Ed.* **2007**, *46*, 4293; b) V. Finsy, H. Verelst, L. Alaerts, D. De Vos, P. A. Jacobs, G. V. Baron, J. F. M. Denayer, *J. Am. Chem. Soc.* **2008**, *130*, 7110; c) L. Alaerts, M. Maes, P. A. Jacobs, J. F. M. Denayer, D. E. De Vos, *Phys. Chem. Chem. Phys.* **2008**, *10*, 2979; d) V. Finsy, S. Calero, E. García-Pérez, P. J. Merkling, G. Vedts, D. E. D. Vos, G. V. Baron, J. F. M. Denayer, *Phys. Chem. Chem. Phys.* **2009**, *11*, 3515.
[10] L. Alaerts, M. Maes, L. Giebeler, P. A. Jacobs, J. A. Martens, J. F. M. Denayer, C. E. A. Kirschhock, D. E. De Vos, *J. Am. Chem. Soc.* **2008**, *130*, 14170.
[11] a) A. L. Nuzhdin, D. N. Dybtsev, K. P. Bryliakov, E. P. Talsi, V. P. Fedin, *J. Am. Chem. Soc.* **2007**, *129*, 12958; b) R. Ahmad, A. G. Wong-Foy, A. J. Matzger, *Langmuir* **2009**, *25*, 11977.
[12] a) J. C. Giddings, R. A. Keller, in *Advances in Chromatography, Vol. 10*, Marcel Dekker, New York, **1974**, p. 2; b) T. Welsch, W. Engewald, J. Poerschmann, *J. Chromatogr.* **1978**, *148*, 143; c) J. G. Nikelly, *Anal. Chem.* **1972**, *44*, 623; d) J. G. Nikelly, *Anal. Chem.* **1972**, *44*, 625; e) Z. H. Ji, R. E. Majors, E. J. Guthrie, *J. Chromatogr. A* **1999**, *842*, 115.
[13] a) M. Minceva, A. E. Rodrigues, *AIChE J.* **2007**, *53*, 138; b) H. A. Mohameed, B. A. Jdayil, K. Takrouri, *Chem. Eng. Process.* **2007**, *46*, 25; c) V. Cottier, J.-P. Bellat, M.-H. Simonot-Grange, A. Methivier, *J. Phys. Chem. B* **1997**, *101*, 4798; d) R. Meyers in *Handbook of Petroleum Refining Processes*, 3th ed., McGraw-Hill, New York, **2003**, pp. 2.47–2.53; e) D. Ruthven in *Principles of Adsorption and Adsorption Processes*, Wiley, New York, **1984**, pp. 401–405.
[14] N. Yassaa, E. Brancaleoni, M. Frattoni, P. Ciccioli, *Chemosphere* **2006**, *63*, 502.
[15] H. Hattori, M. Iwai, S. Kurono, T. Yamada, K. Watanabe-Suzuki, A. Ishii, H. Seno, O. Suzuki, *J. Chromatogr. B* **1998**, *718*, 285.
[16] D. H. Desty, A. Goldup, W. T. Swanton, *Nature* **1959**, *183*, 107.
[17] S. H. Langer, C. Zahn, G. Pantazoplos, *J. Chromatogr.* **1960**, *3*, 154.
[18] L. C. Case, *J. Chromatogr.* **1961**, *6*, 381.
[19] a) J. V. Mortimer, P. L. Gent, *Nature* **1963**, *197*, 789; b) G.-C. Lin, C. A. Chang, *J. Chromatogr.* **1987**, *409*, 371.
[20] a) Z. Witkiewicz, Z. Suprynowicz, J. Wójcik, R. Dabrowski, *J. Chromatogr.* **1978**, *152*, 323; b) G. K. M. Schierhorn, *J. High Resolut. Chromatogr.* **1981**, *4*, 123; c) L. Soják, I. Ostrovský, *J. Chromatogr.* **1988**, *446*, 339; d) Z. Witkiewicz, *J. Chromatogr.* **1989**, *466*, 37.
[21] a) D. Sybliska, T. Kościelski, *J. Chromatogr.* **1983**, *261*, 357; b) N. Yassaa, B. Y. Meklati, A. Cecinato, *J. Chromatogr. A* **1999**, *846*, 287; c) X. Y. Shi, H. C. Guo, M. Wang, S. R. Jiang, *Chromatographia* **2002**, *55*, 755; d) X. Y. Shi, P. Liang, X. W. Gao, *Anal. Chim. Acta* **2005**, *548*, 86.
[22] A. Zlatkis, L. O'Brien, P. R. Scholly, *Nature* **1958**, *181*, 1794.
[23] P. E. Joos, A. F. L. Godoi, R. De Jong, J. de Zeeuw, R. Van Grieken, *J. Chromatogr. A* **2003**, *985*, 191.
[24] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surble, I. Margiolaki, *Science* **2005**, *309*, 2040.
[25] D.-Y. Hong, Y. K. Hwang, C. Serre, G. Férey, J.-S. Chang, *Adv. Funct. Mater.* **2009**, *19*, 1537.
[26] a) F. A. Esteve-Turrillas, S. Armenta, S. Garrigues, A. Pastor, M. de La Guardia, *Anal. Chim. Acta* **2007**, *587*, 89; b) E. Aguilera-Herrador, R. Lucena, S. Cárdenas, M. Valcárcel, *J. Chromatogr. A* **2008**, *1201*, 106.
[27] a) Y. K. Hwang, D.-Y. Hong, J.-S. Chang, Sung H. Jhung, Y.-K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Férey, *Angew. Chem.* **2008**, *120*, 4212; *Angew. Chem. Int. Ed.* **2008**, *47*, 4144; b) M. Banerjee, S. Das, M. Yoon, H. J. Choi, M. H. Hyun, S. M. Park, G. Seo, K. Kim, *J. Am. Chem. Soc.* **2009**, *131*, 7524.
[28] a) W. O. McReynolds, *J. Chromatogr. Sci.* **1970**, *8*, 685; b) A. Berthod, E. Y. Zhou, K. Le, D. W. Armstrong, *Anal. Chem.* **1995**, *67*, 849.

