

# Molecular Sieve Membrane: Supported Metal–Organic Framework with High Hydrogen Selectivity\*\*

Yan-Shuo Li,\* Fang-Yi Liang, Helge Bux, Armin Feldhoff, Wei-Shen Yang, and Jürgen Caro\*

Microporous membranes with pore apertures below the nanolevel can exhibit size selectivity by serving as a molecular sieve, which is promising for overcoming Robeson's "upper-bound" limits in membrane-based gas separation.<sup>[1]</sup> Zeolites, polymers of intrinsic microporosity (PIMs), metal oxides, and active carbon<sup>[2a]</sup> are the typical materials used for this purpose. Metal–organic frameworks (MOFs) have attracted much research interest in recent years, and are emerging as a new family of molecular sieves.<sup>[2b,3–5]</sup> MOFs are novel porous crystalline materials consisting of metal ions or clusters interconnected by a variety of organic linkers. In addition to promising applications in adsorptive gas separation and storage or in catalysis, their unique properties, such as their highly diversified structures, large range in pore sizes, very high surface areas, and specific adsorption affinities, make MOFs excellent candidates for use in the construction of molecular sieve membranes with superior performance.<sup>[6,7]</sup> The preparation of MOF membranes for gas separation is rapidly becoming a research focus. A number of attempts have been made to prepare supported-MOF membranes;<sup>[8–12]</sup> however, progress is very limited and so far there are only very few reports of continuous MOF films on porous supports being used as separating membranes. Recently, Guo et al. reported a copper-net-supported HKUST-1 ( $\text{Cu}_3(\text{BTC})_2$ ; BTC = benzene-1,3,5-tricarboxylate) membrane exhibiting a  $\text{H}_2/\text{N}_2$  selectivity of 7<sup>[13]</sup> (separation factor of  $\text{H}_2$  over  $\text{N}_2$  is calculated as the permeate-to-retentate composition ratio of  $\text{H}_2$ , divided by the same ratio for  $\text{N}_2$  as proposed by IUPAC<sup>[28]</sup>); this is the first MOF membrane to show gas-separation performance beyond Knudsen diffusion behavior.

Very recently, Ranjan and Tsapatsis prepared a microporous metal–organic framework [MMOF,  $\text{Cu}(\text{hfipbb})(\text{H}_2\text{hfipbb})_{0.5}$ ; hfipbb = 4,4'-(hexafluoroisopropylidene)bis(benzoic acid)] membrane by seeded growth on an alumina support.<sup>[14]</sup> The ideal selectivity for  $\text{H}_2/\text{N}_2$ , based on single permeation tests, was 23 at 190 °C. This higher selectivity, compared to the report from Guo et al., might be a result of the smaller effective pore size (ca. 0.32 nm of MMOF versus 0.9 nm of HKUST-1),<sup>[15]</sup> which results in a relatively low  $\text{H}_2$  permeance of this MMOF membrane ( $10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  at 190 °C). The authors attributed this finding to the blockage of the one-dimensional (1D) straight-pore channels in the membrane. Therefore, with regard to  $\text{H}_2$  separation, small-pore MOFs having three-dimensional (3D) channel structures are considered to be ideal membrane materials. Zeolitic imidazolate frameworks (ZIFs), a subfamily of MOFs, consist of transition metals (Zn, Co) and imidazolate linkers which form 3D tetrahedral frameworks and frequently resemble zeolite topologies.<sup>[16–18]</sup> A number of ZIFs exhibit exceptional thermal and chemical stability.<sup>[16]</sup> Another important feature of ZIFs is their hydrophobic surfaces, which give ZIF membranes certain advantages over zeolite membranes and sol-gel-derived silica membranes in the separation of  $\text{H}_2$  in the presence of steam.<sup>[19]</sup>

Very recently we reported the first result from permeation measurements on a ZIF-8 membrane.<sup>[20]</sup> The ZIF-8 membrane showed a  $\text{H}_2/\text{CH}_4$  separation factor greater than 10. Whereas the ZIF-8 pores (0.34 nm) are slightly larger than the kinetic diameter of  $\text{CO}_2$  (0.33 nm), and are very flexible, the  $\text{H}_2/\text{CO}_2$  separation on this ZIF-8 membrane showed Knudsen selectivity. In the current work, we therefore chose ZIF-7 as a promising candidate for the development of a  $\text{H}_2$ -selective membrane to satisfy the above requirements. ZIF-7 ( $\text{Zn}(\text{bim})_2$ ) is formed by bridging benzimidazolate (bim) anions and zinc cations with sodalite (SOD) topology.<sup>[16,18]</sup> The pore size of ZIF-7 (the hexagonal window size in the SOD cage) estimated from crystallographic data is about 0.3 nm, which is just in between the size of  $\text{H}_2$  (0.29 nm) and  $\text{CO}_2$  (0.33 nm). We could therefore expect a ZIF-7 membrane to achieve a high selectivity of  $\text{H}_2$  over  $\text{CO}_2$  and other gases through a molecular sieving effect.

In many cases, it was reported that the heterogeneous nucleation density of MOF crystals on ceramic supports is very low,<sup>[8,9,14]</sup> which makes it extremely difficult to prepare supported-MOF membranes by an in situ synthesis route. Chemical modifications of substrate surfaces have been proposed to direct the nucleation and orientation of the deposited MOF layers.<sup>[21,22]</sup> Based on our knowledge in the development of zeolite membranes,<sup>[23,24]</sup> we adopted a seeded secondary growth method for the ZIF-7 membrane prepara-

[\*] Prof. Dr. Y.-S. Li, F.-Y. Liang, H. Bux, A. Feldhoff, Prof. Dr. J. Caro  
Institute of Physical Chemistry and Electrochemistry  
and the Laboratory for Nano and Quantum Engineering (LNQE)  
in cooperation with the Center for Solid State Research and New  
Materials, Leibniz Universität Hannover  
Callinstrasse 3A, 30167 Hannover (Germany)  
Fax: (+49) 511-762-19121  
E-mail: yanshuo.li@pci.uni-hannover.de  
juergen.caro@pci.uni-hannover.de

Prof. Dr. Y.-S. Li, Prof. Dr. W.-S. Yang  
State Key Laboratory of Catalysis  
Dalian Institute of Chemical Physics  
Chinese Academy of Sciences  
Zhong-Shan Road 457, 116023 Dalian (China)

[\*\*] Y.-S. Li is grateful for the financial support from the Alexander von Humboldt Foundation. DFG Priority Program 1362 "Porous Metal–Organic Frameworks" is acknowledged for financial support. The authors thank F. Steinbach for support in electron microscopy and K. Efimov for TGA measurements.

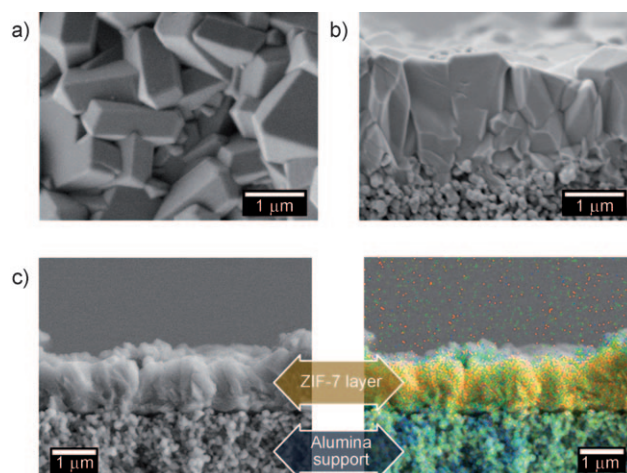
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.200905645>.

tion to eliminate the influence of the surface chemistry and to promote the growth of ZIF-7 on the supports; this approach has been well-established in the research of zeolite membranes.<sup>[25]</sup> To this end, an effective seeding method is necessary.<sup>[10]</sup> In addition, we used a microwave dielectric heating technique to shorten the secondary growth time so as to reduce the thickness of the crystallized ZIF-7 layer, which is essential to ensure a high flux, especially for the ultra-microporous ZIF-7 membranes.

ZIF-7 nanoseeds were synthesized at room temperature using a modified synthetic protocol according to a report from Yaghi and co-workers,<sup>[16]</sup> in which the linker (bim) to zinc ratio was increased from 0.74 to 6.5. Similar to the case of the room-temperature synthesis of ZIF-8 nanocrystals,<sup>[26]</sup> it was speculated that the excess bim could act both as a linker in its deprotonated form and as a growth terminator and stabilizing agent in its neutral form. Compared with reported structural data, the obtained product is pure ZIF-7 according to the powder X-ray diffraction (PXRD; see Figure S1 in the Supporting Information). The average particle size of the ZIF-7 is 30 nm as estimated from the broadening of the XRD peaks (calculated based on Scherrer's equation), which is in agreement with the direct determination of the particle size by transmission electron microscopy (TEM; see Figure S2 in the Supporting Information).

The synthesized ZIF-7 nanoseeds can be dispersed in methanol or *N,N*-dimethylformamide (DMF) to form stable colloidal dispersions. When these colloidal dispersions are used to seed alumina supports, however, the seed layer can easily peel away from the supports. To address this problem, we dispersed the ZIF-7 nanoseeds in a polyethyleneimine (PEI) solution to obtain a viscous seeding solution (containing 4 wt % ZIF-7 and 2 wt % PEI). Although ZIF-7 cannot be dispersed in the aqueous phase because of its hydrophobic property, it can be homogeneously dispersed in an aqueous PEI solution by using ultrasonic treatment. This dispersion may possibly arise because PEI can coordinate with the zinc atoms at the surface of the nanoseeds, thereby making them compatible with the aqueous solution.<sup>[27]</sup> Furthermore, PEI can effectively enhance the linkage between the seeds and the support through H-bonding interactions. A dip-coating technique was used for the surface seeding of the alumina support (20 s). No obvious ZIF-7 phase can be detected by XRD (see Figure S3 in the Supporting Information), indicating that the seed layer is very thin and, consequently, does not alter the permeation patterns of the seeded support. The seeded alumina support showed a high flux of H<sub>2</sub> and a low H<sub>2</sub>/N<sub>2</sub> selectivity of 2.8, indicating that the seed layer does not act as a gas-transport barrier and shows no gas separation.

Microwave-assisted solvothermal synthesis was carried out to perform the secondary (seeded) growth. The seeded support was placed vertically in a clear synthesis solution with a molar composition of Zn<sup>2+</sup>/bim/DMF = 0.75:1:150, and then heated by a microwave at 100 °C for three hours. After secondary growth, a large-scale ordered polycrystalline ZIF-7 layer without any pinholes or cracks formed on the alumina support. The SEM top view (Figure 1 a) shows that the ZIF-7 grains are 1–2 μm in size and intergrown. Owing to the very thin seed layer and the short seeded secondary growth time by

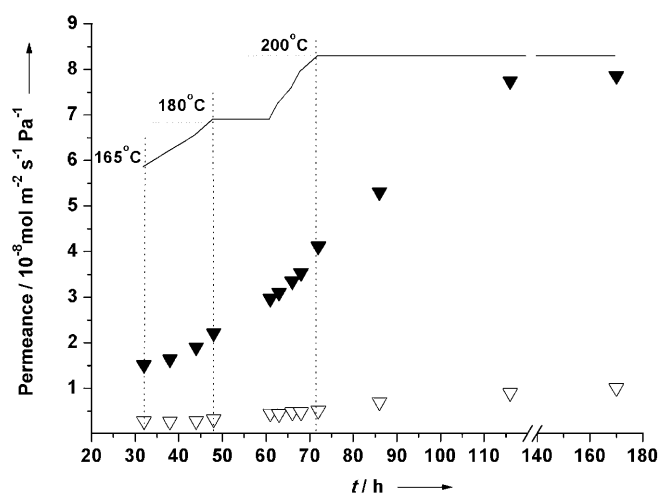


**Figure 1.** a) Top view and b) cross-section SEM images of the ZIF-7 membrane; c) EDXS mapping of the ZIF-7 membrane; orange Zn, cyan Al.

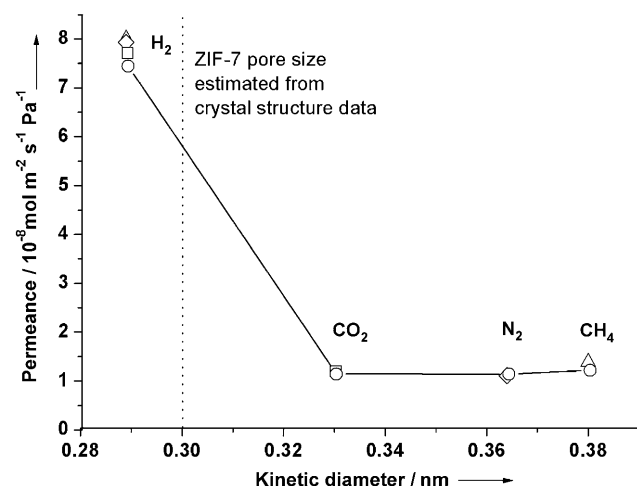
microwave heating, the ZIF-7 top layer is about 1.5 μm thick (Figure 1 b), which is much thinner than the MOF layers reported thus far.<sup>[8,10–12]</sup> Energy-dispersive X-ray spectroscopy (EDXS) reveals that there is a sharp transition between the ZIF-7 layer (Zn signal) and the alumina support (Al signal; Figure 1 c). The XRD pattern of the ZIF-7 membrane shows that the ZIF-7 layer consists of randomly oriented grains and is free of impurity phases (see Figure S3 in the Supporting Information).

The synthesized ZIF-7 membrane is impermeable to all gases, including H<sub>2</sub>, since it still contains the guest molecules within its cavities. An on-stream activation was carried out to open the pores and to monitor the activation process simultaneously by using a Wicke–Kallenbach permeation cell with a 1:1 mixture of H<sub>2</sub> and N<sub>2</sub> on the feed side (see Figure S4 in the Supporting Information). Figure 2 represents the variation of the H<sub>2</sub> and the N<sub>2</sub> permeances from their binary mixture during the on-stream activation process. Coinciding with the thermogravimetric (TG) analysis (see Figure S5 in the Supporting Information), the guest molecules began to leave the cavities when the cell was heated up to 100 °C, at which point the ZIF-7 membrane became gas permeable. At 165 °C this partially activated ZIF-7 membrane showed a H<sub>2</sub> permeance of about  $7 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and a H<sub>2</sub>/N<sub>2</sub> separation factor of 8. The complete activation was accomplished after the temperature had been maintained at 200 °C for around 40 hours, and the H<sub>2</sub> permeance reached a plateau value of approximately to  $8 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and the H<sub>2</sub>/N<sub>2</sub> separation factor was 7.7.

For applications at elevated temperature, the activated ZIF-7 membrane was tested in single-gas and mixed-gas permeation at 200 °C using the Wicke–Kallenbach technique (see Figure S4 in the Supporting Information). Figure 3 (also see Table S1 in the Supporting Information) gives the permeances of H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> as single gases as well as from their 1:1 mixtures through the ZIF-7 membrane as a function of the kinetic diameter of the gas molecules. For both single- and mixed-gas permeation, there is a clear cut-off between H<sub>2</sub> and CO<sub>2</sub>. The H<sub>2</sub>/CO<sub>2</sub> ideal selectivity (calculated



**Figure 2.** H<sub>2</sub> (solid triangles) and N<sub>2</sub> (triangles) permeances from the 1:1 mixture through the ZIF-7 membrane during the on-stream activation process with increasing temperature.



**Figure 3.** Permeances of single gases (circles) and from 1:1 mixtures (squares: H<sub>2</sub>/CO<sub>2</sub> mixture, rhombuses: H<sub>2</sub>/N<sub>2</sub> mixture, triangles: H<sub>2</sub>/CH<sub>4</sub> mixture) of the ZIF-7 membrane at 200°C as a function of molecular kinetic diameters.

as the ratio of single-gas permeances) and separation factor are 6.7 and 6.5, respectively, which exceed the Knudsen separation factor (ca. 4.7). This result is consistent with our previous speculation that separation H<sub>2</sub>/CO<sub>2</sub> by molecular sieves can be fulfilled by using ultramicroporous ZIF-7 membranes. For the 1:1 binary mixtures, the H<sub>2</sub>/N<sub>2</sub> and H<sub>2</sub>/CH<sub>4</sub> separation factors determined by the Wicke–Kallenbach method are 7.7 and 5.9, respectively (at 200°C and 1 bar), both are higher than the corresponding Knudsen separation factors (3.7 and 2.8, respectively). It follows from Figure 3 that the permeances are almost the same for H<sub>2</sub> as single gases and H<sub>2</sub> in the 1:1 binary mixtures. This experimental finding indicates a rather independent transport mechanism for the components of a mixture which can be correlated with ZIF-7 structure. ZIF-7 crystallizes in the sodalite structure with a hexagonal arrangement of the cavities octahedrally intercon-

nected by narrow windows interconnecting the cavities, which are responsible for the molecular sieving effect. The non-zero permeances of CO<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> can be attributed to a certain influence of the non-size-selective mass transport through the imperfect sealing or through the grain boundaries of the polycrystalline ZIF-7 layer. Nevertheless, the H<sub>2</sub>/CO<sub>2</sub> separation factor of the ZIF-7 membrane in the current work is by far the highest value reported for a MOF membrane, and the membrane performance had already exceeded the latest Robeson's "upper-bound" line (see Figure S6 in the Supporting Information).<sup>[29]</sup> Notably, in the present study the same ZIF-7 membrane had been tested for more than one week at 200°C and showed no degradation. This indicates that the ZIF-7 membrane has a good thermal stability.

In conclusion, an ultramicroporous zeolitic imidazolate framework, ZIF-7, was tested for its gas-separation properties in membrane applications by synthesizing it on a porous alumina support using a microwave-assisted secondary growth technique. In terms of H<sub>2</sub> separation, the ZIF-7 membrane has several advantages: 1) its pore dimension approaches the size of H<sub>2</sub>, therefore a high H<sub>2</sub> selectivity could be obtained without any sophisticated pore-size engineering as is essential for zeolite membranes targeting H<sub>2</sub>/CO<sub>2</sub> separation;<sup>[30,31]</sup> 2) it is thermally stable for use at elevated temperatures (ZIF-7 is stable at least to 500°C in air according to the TG analysis, see Figure S5 in the Supporting Information); and 3) its hydrophobic property endows it with very good hydrothermal stability. Apart from exploring promising membrane materials, the present work also demonstrates a general approach towards the fabrication of high-quality MOF membranes on ceramic supports, namely polymers with coordination abilities (such as PEI in current work) which can be used to aid the seeding procedure, and the fast microwave synthesis is superior for reducing the membrane thickness. As shown in this work, and considering the very versatile structures and the development on the rational design of MOFs,<sup>[32]</sup> as well as the recent advances in molecular simulation studies,<sup>[33]</sup> MOF membranes might be able to revolutionize gas separations by using molecular sieves.

## Experimental Section

Asymmetric alumina disks (Inoceramic) were used as supports in current work. The disk has a diameter of 18 mm and thickness of 1 mm. The pore size of the top layer is 70 nm.

ZIF-7 nanoseeds were synthesized at room temperature. A typical synthesis procedure is as follows: 100 mL DMF (>99.8%, Arcos) was added to a solid mixture of 0.302 g Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (>99%, Aldrich) and 0.769 g benzimidazole (>99%, Aldrich) with stirring (molar composition of the synthesis solution: Zn<sup>2+</sup>/bim/DMF=0.154:1:200). After the reaction mixture had been kept at room temperature for 48 h, the product was separated using a centrifuge, and then washed with DMF.

The solution used for seeding was prepared by dispersing ZIF-7 nanoseeds into polyethyleneimine (PEI) solution. In a typical synthesis 0.2 g PEI (50 wt % in water, Aldrich) was dissolved in 4 mL NaHCO<sub>3</sub> solution (50 mM), and then 0.18 g of the as-synthesized ZIF-7 nanocrystals was added to the mixture, which was then treated under ultrasonic conditions for 20 min. The obtained seeding solution can be stored in a glass bottle for the later use.

An alumina support was dip-coated in the above seeding solution for 20 s. After briefly drying at room temperature for 2 h, the seeded support was dried in an oven (80°C) overnight before secondary growth.

For the microwave-assisted secondary growth, 30 mL DMF was added into a solid mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.57 g) and bim (0.31 g) with stirring (molar composition of the synthesis solution:  $\text{Zn}^{2+}/\text{bim}/\text{DMF} = 0.75:1:150$ ). This clear solution was transferred into a Teflon autoclave in which a seeded support was placed vertically. Afterwards the autoclave was heated in a microwave oven (Ethos 1, MLS) at a power of 300 W to 100°C in 10 min, and then kept at 100°C for 3 h. After cooling, the membrane was washed with methanol and dried at 50°C overnight.

The experimental characterization techniques, including XRD, TEM, SEM, EDXS and TGA methods, as well as permeation measurements are described in detail in the Supporting Information.

Received: October 8, 2009

Published online: November 26, 2009

**Keywords:** gas separation · membranes · metal–organic frameworks · microwave chemistry · supported structures

- [1] L. M. Robeson, *J. Membr. Sci.* **1991**, 62, 165.
- [2] a) Y. S. Lin, I. Kumakiri, B. N. Nair, H. Alsyouri, *Sep. Purif. Methods*, **2002**, 31, 229; b) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem.* **2004**, 116, 2388; *Angew. Chem. Int. Ed.* **2004**, 43, 2334.
- [3] M. Yaghi, M. O’Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, 423, 705.
- [4] G. Férey, *Chem. Soc. Rev.* **2008**, 37, 191.
- [5] S. L. James, *Chem. Soc. Rev.* **2003**, 32, 276.
- [6] J.-R. Li, R. J. Kuppler, H.-C. Zhou, *Chem. Soc. Rev.* **2009**, 38, 1477.
- [7] D. Zacher, O. Shekhah, C. Wöll, R. A. Fischer, *Chem. Soc. Rev.* **2009**, 38, 1418.
- [8] M. Arnold, P. Kortunov, D. J. Jones, Y. Nedellec, J. Kärger, J. Caro, *Eur. J. Inorg. Chem.* **2007**, 1, 60.
- [9] Y. Yoo, H. K. Jeong, *Chem. Commun.* **2008**, 2441.
- [10] J. Gascon, S. Aguado, F. Kapteijn, *Microporous Mesoporous Mater.* **2008**, 113, 132.
- [11] Y. Liu, Z. Ng, E. A. Khan, H. K. Jeong, C. Ching, Z. P. Lai, *Microporous Mesoporous Mater.* **2009**, 118, 296.
- [12] Y. Yoo, Z.-P. Lai, H. K. Jeong, *Microporous Mesoporous Mater.* **2009**, 123, 100.
- [13] H. Guo, G. Zhu, I. J. Hewitt, S. L. Qiu, *J. Am. Chem. Soc.* **2009**, 131, 1646.
- [14] R. Ranjan, M. Tsapatsis, *Chem. Mater.* **2009**, 21, 4920.
- [15] L. Pan, D. H. Olson, L. R. Ciemmolonski, R. Heddy, J. Li, *Angew. Chem.* **2006**, 118, 632; *Angew. Chem. Int. Ed.* **2006**, 45, 616.
- [16] K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O’Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* **2006**, 103, 10186.
- [17] X.-C. Huang, Y.-Y. Lin, J.-P. Zhang, X.-M. Chen, *Angew. Chem.* **2006**, 118, 1587; *Angew. Chem. Int. Ed.* **2006**, 45, 1557.
- [18] X.-C. Huang, J.-P. Zhang, X.-M. Chen, *Chin. Sci. Bull.* **2003**, 48, 1531.
- [19] P. Küsgens, M. Rose, I. Senkovska, H. Fröde, A. Henschel, S. Siegle, S. Kaskel, *Microporous Mesoporous Mater.* **2009**, 123, 100.
- [20] H. Bux, F.-Y. Liang, Y.-S. Li, J. Cravillon, M. Wiebcke, J. Caro, *J. Am. Chem. Soc.*, DOI: 10.1021/ja907359t.
- [21] S. Hermes, F. Schröder, R. Chelmoski, C. Wöll, R. A. Fischer, *J. Am. Chem. Soc.* **2005**, 127, 13744.
- [22] E. Biemmi, C. Scherb, T. Bein, *J. Am. Chem. Soc.* **2007**, 129, 8054.
- [23] J. Caro, M. Noack, *Microporous Mesoporous Mater.* **2008**, 115, 215.
- [24] Y.-S. Li, W.-S. Yang, *J. Membr. Sci.* **2008**, 316, 3.
- [25] M. A. Snyder, M. Tsapatsis, *Angew. Chem.* **2007**, 119, 7704; *Angew. Chem. Int. Ed.* **2007**, 46, 7560.
- [26] J. Cravillon, S. Münzer, S. J. Lohmeier, A. Feldhoff, K. Huber, M. Wiebcke, *Chem. Mater.* **2009**, 21, 1410.
- [27] V. N. Kislenko, L. P. Oliynyk, *J. Polym. Sci. Part A* **2002**, 40, 914.
- [28] W. J. Koros, Y. H. Ma, T. Shimidzu, *Pure Appl. Chem.* **1996**, 68, 1479.
- [29] L. M. Robeson, *J. Membr. Sci.* **2008**, 320, 390.
- [30] M. Hong, J. L. Falconer, R. D. Noble, *Ind. Eng. Chem. Res.* **2005**, 44, 4035.
- [31] M. Kanezashi, J. O’Brien-Abraham, Y. S. Lin, *AIChE J.* **2008**, 54, 1478.
- [32] M. O’Keeffe, *Chem. Soc. Rev.* **2009**, 38, 1215.
- [33] M. Zhou, Q. Wang, L. Zhang, Y.-C. Liu, Y. Kang, *J. Phys. Chem. B* **2009**, 113, 11049.