J|A|C|S
COMMUNICATIONS

Zeolitic Imidazolate Framework Membrane with Molecular Sieving Properties by Microwave-Assisted Solvothermal Synthesis

Helge Bux,[†] Fangyi Liang,[†] Yanshuo Li,[†,§] Janosch Cravillon,[‡] Michael Wiebcke,[‡] and Jürgen Caro*,[†]

Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover, Callinstr. 3A,
D-30167 Hannover, Germany, Institute of Inorganic Chemistry, Leibniz University Hannover, Callinstr. 9,
D-30167 Hannover, Germany, and Dalian Institute of Chemical Physics, Chinese Academy of Sciences,
Zhong-Shan Road 457, Dalian 116023, China

Received August 31, 2009; E-mail: juergen.caro@pci.uni-hannover.de

Metal−organic frameworks (MOFs) are new microporous inorganic−organic hybrid materials.[1,2] Their remarkable properties allow their utilization in various applications.[3−9] The large diversity in structures and pore sizes as well as the high surface areas and adsorption affinities make MOFs attractive as advanced separation media.[10] Supported microporous membranes possess significant potential for the development of methods for energy-efficient and environmentally benign separation of gas mixtures. Although there have been attempts to synthesize MOF layers on porous supports,[9,11,12] only a very few have reported dense coatings.[13−17] For membrane synthesis, not only the problems with growing a dense polycrystalline layer on porous ceramic or metal supports but also the thermal and chemical stability of a MOF have to be considered. Among the zeolitic imidazolate frameworks (ZIFs), a new subclass of MOFs, there are ZIFs that exhibit exceptionally high thermal and chemical stability.[18−22] Therefore, we focused on ZIF-8, having the formula $Zn(mim)_2$ (mim = 2-methylimidazolate), which crystallizes with a sodalite-related structure (Figure 1).[18,19] ZIF-8 not only is highly stable but also shows adsorption affinity toward hydrogen and methane.[23−25] Because of the narrow size of the six-membered-ring pores (∼3.4 Å), it can be anticipated that a ZIF-8 membrane should be able to separate H_2 (kinetic diameter ∼2.9 Å) from larger molecules. Another important feature of ZIF-8 is its hydrophobic behavior, whereas ultramicroporous zeolites are usually hydrophilic. This should give a ZIF-8 membrane an advantage over zeolites in the separation of H_2 from a mixture with steam.

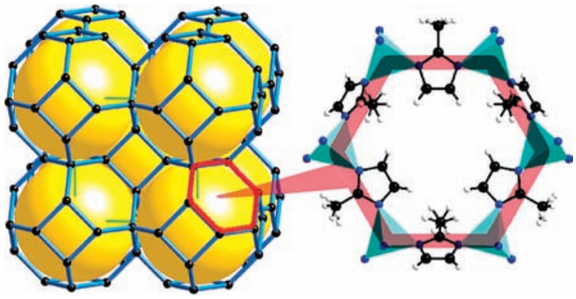

Figure 1. (left) Sodalite topology and (right) narrow six-membered-ring opening through which molecules have to pass.

Recently, we succeeded in preparing ZIF-8 nanocrystals at room temperature by modifying reported synthetic protocols[18,19] in replacing the solvents dimethylformamide (DMF) and aqueous methanol with pure methanol.[26] Methanol has a much smaller kinetic diameter than DMF. The ZIF-8 adsorption isotherm of methanol exhibits an unusual s shape,[19] indicating that polar methanol only weakly interacts with the ZIF-8 framework. Therefore, methanol can be removed much more easily from the pore network than DMF, and importantly for membrane synthesis, the stress to the crystals is strongly reduced. By further modifying the synthesis in adding sodium formate and using solvothermal conditions, we were able to obtain in methanol pure-phase ZIF-8 material containing large crystals with sizes of up to 300 μm (Figure S1 in the Supporting Information). The time of synthesis could be substantially reduced to 4 h by using microwave-assisted heating.

By applying this improved synthetic protocol in membrane preparation (see the Supporting Information), we were able to obtain a crack-free, dense polycrystalline layer of ZIF-8 on a porous titania support (Figure 2). The cross section of the membrane shows a continuous, well-intergrown layer of ZIF-8 crystals on top of the support. Energy-dispersive X-ray spectroscopy (EDXS) revealed that there is a sharp transition between the ZIF-8 layer (Zn signal) and the titania support (Ti signal). A comparsion of the X-ray diffraction (XRD) patterns of the ZIF-8 layer and the corresponding crystal powder sedimented during membrane synthesis indicated that the membrane layer consists of randomly oriented crystallites (Figure S2). In thermogravimetric (TG) analysis of the sedimented powder in air, no mass loss was observed at temperatures up to ∼360 °C, where decomposition of the framework structure starts (Figure S3). This proves that in air, methanol has readily escaped completely from the cavities even at room temperature, yielding guest-free, activated ZIF-8.

The volumetric flow rates of the single gases H_2, CO_2, O_2, N_2, and CH_4 and of a 1:1 mixture of H_2 and CH_4 through the membrane were measured using the Wicke−Kallenbach technique (Figure S4). The permeation measurements were performed both with and without activation of the ZIF-8 membrane in fine vacuum. Nearly the same flow rates were observed in those two cases, confirming the TG results that methanol readily escapes from the pores and clearly demonstrating the advantage of replacing the DMF solvent by methanol in the synthesis.

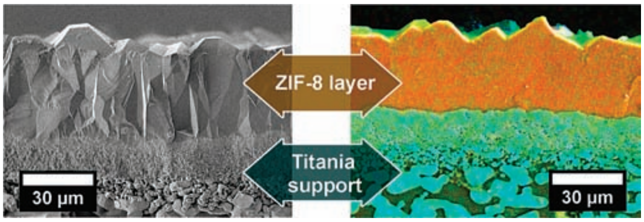

Figure 2. (left) SEM image of the cross section of a simply broken ZIF-8 membrane. (right) EDXS mapping of the sawn and polished ZIF-8 membrane (color code: orange, Zn; cyan, Ti).

[†] Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover.
[‡] Institute of Inorganic Chemistry, Leibniz University Hannover.
[§] Dalian Institute of Chemical Physics.

10.1021/ja907359t CCC: $40.75

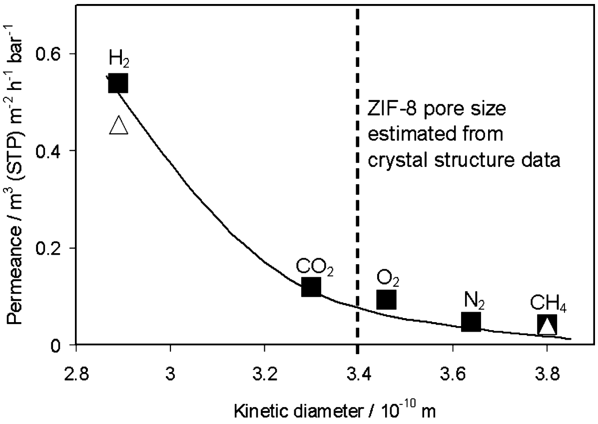

Figure 3. Single (squares) and mixed (triangles) gas permeances for a ZIF-8 membrane vs kinetic diameters.

The permeances calculated from the volumetric flow rates through the ZIF-8 membrane are presented in Figure 3 and Table S1. From both it can be seen that the permeances clearly depend on the molecular size of the gases. Although the pore size of ZIF-8 is estimated from crystallographic data to be ~3.4 Å, even larger molecules like CH_4 (kinetic diameter ~3.8 Å) can (only slowly) pass through the pore network, and consequently, there exists no sharp cutoff at 3.4 Å. This indicates that the framework structure of ZIF-8 is in fact more flexible rather than static in its nature, in accordance with recent findings by inelastic neutron scattering.[27]

Comparison of the H_2 single-gas permeance with the H_2/CH_4 mixed-gas one revealed only a small difference, meaning that the larger CH_4 only slightly influences the permeation of the mobile H_2. This experimental finding is different from the results for mixture diffusion in zeolites, where an immobile component usually reduces the mobility of a coadsorbed, more mobile component. As an example, the presence of isobutane reduces the self-diffusivity of *n*-butane in MFI zeolites by orders of magnitude.[28] Our observation can be understood by considering that the pore size of ZIF-8 is narrow but the cages are large (~11.4 Å in diameter). Thus, although a CH_4 molecule can block the pore entrance for an H_2 molecule, as soon as it has entered the cage, it does not restrict the H_2 diffusion any more.

The separation factor $\alpha_{i,j}$ of a binary mixture is defined as the molar ratio of the components i and j in the permeate divided by the molar ratio of i and j in the retentate.[29] From the Wicke–Kallenbach permeation studies with gas-chromatographic control of a 1:1 H_2/CH_4 mixture, the value of α at 298 K and 1 bar was determined to be 11.2, which considerably exceeds the Knudsen separation factor for H_2/CH_4 (~2.8). In comparison, Guo et al.[16] reported a H_2/CH_4 separation factor of ~6 for a supported $Cu_3(btc)_2$ membrane (btc = benzene-1,3,5-tricarboxylate). Very recently, Ranjan and Tsapatsis[17] reported a high ideal H_2/N_2 selectivity (~23) but relatively low fluxes for a $Cu(hfipbb)(H_2hfipbb)_{0.5}$ membrane [H_2hfipbb = 4,4′-(hexafluoroisopropylidene)bis(benzoic acid)].

In conclusion, we have obtained by a novel microwave-assisted solvothermal process a gas-separating ZIF membrane with selectivity for H_2 with respect to other gases. The membrane achieves a fine balance between flux and selectivity relative to other MOF membranes reported to date.[16,17] The hydrogen permeance of our still relatively thick ZIF-8 membrane is ~50% of the hydrogen permeances of zeolite membranes of the same selectivity.[30] It is expected that the membrane permeance can be improved by reducing the membrane thickness through further optimization of the synthesis parameters. Our ZIF-8 membrane has the additional advantage of high thermal and chemical stability, which provides the possibility of increasing the permeance at high temperature. Our work demonstrates that it is generally possible to prepare highly gas-selective MOF membranes on ceramic supports by in situ crystallization. There is some optimism that MOF membranes can represent a new generation of advanced molecular sieving membranes for gas separation.

Acknowledgment. We thank O. M. Yaghi and B. Wang for permission to use their ZIF-8 structure drawing. We thank A. Feldhoff and F. Steinbach for support in electron microscopy and F. Brieler for adsorption measurements. Y.L. thanks the Alexander von Humboldt Foundation. This work is part of DFG Priority Program 1362 (Porous Metal–Organic Frameworks).

Supporting Information Available: Synthesis protocol, measured flow rates, permeance calculation, numeric permeance data, XRD patterns of the ZIF-8 membrane and ZIF-8 crystal powder, and TG and Ar physisorption data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.
(2) Ferèy, G. *Chem. Soc. Rev.* **2008**, *37*, 191.
(3) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.
(4) Murray, L. J.; Dincâ, M.; Long, J. R. *Chem. Soc. Rev.* **2009**, *38*, 1294.
(5) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450.
(6) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* **2009**, *38*, 1248.
(7) Czaja, A. U.; Trukhan, N.; Müller, U. *Chem. Soc. Rev.* **2009**, *38*, 1284.
(8) Spokoyny, A. M.; Kim, D.; Sumrein, A.; Mirkin, C. A. *Chem. Soc. Rev.* **2009**, *38*, 1218.
(9) Zacher, D.; Shekhah, O.; Wöll, C.; Fischer, R. A. *Chem. Soc. Rev.* **2009**, *38*, 1418.
(10) Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. *Chem. Soc. Rev.* **2009**, *38*, 1477.
(11) Arnold, M.; Kortunov, P.; Jones, D. J.; Nedellec, Y.; Kärger, J.; Caro, J. *Eur. J. Inorg. Chem.* **2007**, 60.
(12) Yoo, Y.; Jeong, H.-K. *Chem. Commun.* **2008**, 2441.
(13) Gascon, J.; Aguado, S.; Kapteijn, F. *Microporous Mesoporous Mater.* **2008**, *113*, 132.
(14) Liu, Y.; Ng, Z.; Khan, E. A.; Jeong, H.-K.; Ching, C.; Lai, Z. *Microporous Mesoporous Mater.* **2009**, *118*, 296.
(15) Yoo, Y.; Lai, Z.; Jeong, H.-K. *Microporous Mesoporous Mater.* **2009**, *123*, 100.
(16) Guo, H.; Zhu, G.; Hewitt, I. J.; Qiu, S. *J. Am. Chem. Soc.* **2009**, *131*, 1646.
(17) Ranjan, R.; Tsapatsis, M. *Chem. Mater.* [Online early access]. DOI: 10.1021/cm902032y. Published Online: Sept 1, 2009.
(18) Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 10186.
(19) Huang, X.-C.; Lin, Y.-Y.; Zhang, J.-P.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1557.
(20) Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. *Science* **2008**, *319*, 939.
(21) Banerjee, R.; Furukawa, H.; Britt, D.; Knobler, C.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2009**, *131*, 3875.
(22) Wu, T.; Zhang, J.; Zhou, C.; Wang, L.; Bu, X.; Feng, P. *J. Am. Chem. Soc.* **2009**, *131*, 6111.
(23) Wu, H.; Zhou, W.; Yildirim, T. *J. Am. Chem. Soc.* **2007**, *129*, 5314.
(24) Zhou, W.; Wu, H.; Hartman, M. R.; Yildirim, T. *J. Phys. Chem. C* **2007**, *111*, 16131.
(25) Wu, H.; Zhou, W.; Yildirim, T. *J. Phys. Chem. C* **2009**, *113*, 3029.
(26) Cravillon, J.; Münzer, S.; Lohmeier, S.-J.; Feldhoff, A.; Huber, K.; Wiebcke, M. *Chem. Mater.* **2009**, *21*, 1410.
(27) Zhou, W.; Wu, H.; Udovic, T. J.; Rush, J. J.; Yildirim, T. *J. Phys. Chem. A* **2008**, *112*, 12602.
(28) Fernandez, M.; Kärger, J.; Freude, D.; Pampel, A.; van Baten, J. M.; Krishna, R. *Microporous Mesoporous Mater.* **2007**, *105*, 124.
(29) Koros, W. J.; Ma, Y. H.; Shimidzu, T. *Pure Appl. Chem.* **1996**, *68*, 1479.
(30) Caro, J.; Noack, M. *Microporous Mesoporous Mater.* **2008**, *115*, 215.

JA907359T