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Metal–Organic Frameworks

Organosilica-Functionalized Zeolitic Imidazolate Framework ZIF-90 Membrane with High Gas-Separation Performance**

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Membrane-based separation techniques are energy- and cost-intensive in comparison with conventional separation processes like distillation and adsorption.[1] Recently, supported metal-organic framework (MOF) films have attracted intense attention for potential applications as semiconductors, sensors, and molecular sieve membranes because of their highly diversified structures and pore sizes as well as specific adsorption affinities.[2–20] In particular, attributed to their zeolite-like properties such as permanent porosity, uniform pore size, exceptional thermal and chemical stabilities, zeolitic imidazolate frameworks (ZIFs) have emerged as a novel type of crystalline porous material for the preparation of superior molecular sieve membranes.[21–23] So far, a series of supported ZIF membranes, including ZIF-7,[24] ZIF-8,[14,25–27] ZIF-22,[28] ZIF-69,[29] and ZIF-90,[30,31] have been reported for permeation of single gases or separation of mixed gases. Despite much progress in the preparation of MOF membranes, there is still a long road ahead before highly permselective MOF membranes can be developed for practical applications, as highlighted recently.[32] It is often found that the as-prepared MOF layers have a polycrystalline structure containing intercrystalline defects, which are detrimental to the membrane selectivity. Therefore, post-modification of the as-prepared MOF membranes is helpful to minimize the nonselective transport pathways through the intercrystalline gaps.[18,31]

As proposed by Yaghi and co-workers,[33] the free aldehyde groups in the ZIF-90 framework allow the covalent functionalization with amine groups through an imine condensation reaction (see Figure S1 in the Supporting Information).[34–37] Therefore, the hydrogen selectivity of the as-prepared ZIF-90 membrane can be improved through the covalent post-functionalization with ethanolamine.[31] However, the membrane selectivity was enhanced at the expense of the permeance since the small ethanolamine molecules could easily permeate into the ZIF-90 structure, resulting in a lower hydrogen permeance because of a homogeneous constriction of the pore network. In addition, the post-functionalization process using ethanolamine as reactant is rather long (usually over 10 h), leading to some decomposition of the ZIF-90 material. Therefore, the development of a facile and effective post-functionalization route is desirable to prepare ZIF-90 membranes with high selectivity, while maintaining their high permeance. In our previous report,[30] we found that the amine group of the 3-aminopropyltriethoxysilane (APTES) reacts easily with the free aldehyde groups in the ZIF-90 framework, as shown in Figure 1 a. Thus, the organosilica APTES can be expected to modify the ZIF-90 membrane (Figure 1 b). On one hand, the covalent post-functionalization is promising for the reduction of the intercrystalline defects of the polycrystalline ZIF-90 layer, thus enhancing the selectivity of gas separation. On the other hand, the relatively large APTES molecules are restrained from entering the interior of the ZIF-90 layer, thus making possible a high hydrogen permeance of the ZIF-90 membrane. Therefore, the APTES-modified ZIF-90 membranes will display a high gas-separation performance.

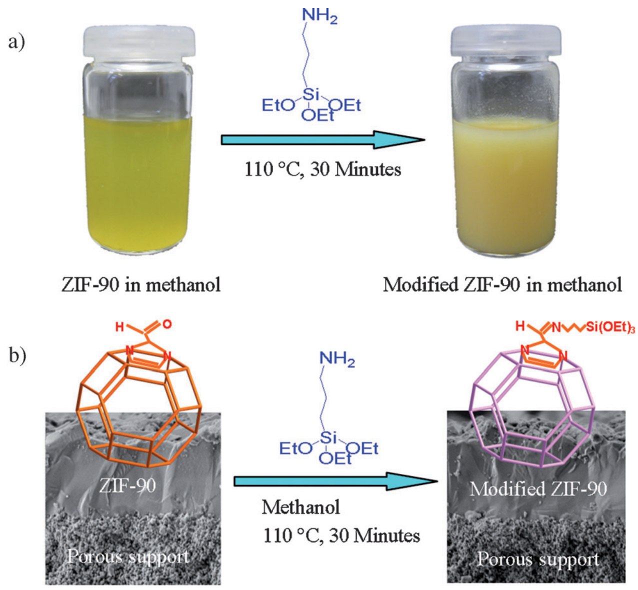

Figure 1. a) Covalent post-functionalization of suspended ZIF-90 crystals in methanol and b) molecular sieve membrane through amine condensation by using organosilica APTES.

For covalent post-functionalization, the as-prepared ZIF-90 crystals and membranes were immersed in a solution of

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APTES in methanol, and then refluxed for 30 minutes at 110 °C. As intuitively shown in Figure 1 a, when APTES was added to the green-yellow ZIF-90 clear solution, a beige colloidal solution which scatters the light because of particle aggregation is quickly observed, indicating that the linkages between the free aldehyde groups of the ZIF-90 and the amino group of APTES have been formed. Further, the reaction of ZIF-90 with APTES was confirmed by Fourier Transform infrared spectroscopy (FTIR). As shown in Figure S2 in the Supporting Information, the C=O band of the aldehyde at about 1668 cm^{-1} is replaced by the C=N bond of the imine at 1640 cm^{-1}. The presence of the H−CNR band at 2970 cm^{-1} and the Si−O band at 1080 cm^{-1} after APTES modification also suggests that APTES has been grafted on the surface of the ZIF-90 crystals.

After APTES functionalization, no remarkable differences in the membrane morphology are found between the as-prepared and the APTES-functionalized ZIF-90 membranes. A well intergrown ZIF-90 layer with a thickness of about 20 μm was formed on the porous alumina support, and no visible cracks, pinholes or other defects are observed for both ZIF-90 membranes (Figure S3 in the Supporting Information). The X-ray diffraction (XRD) pattern (Figure S4) shows that the high crystallinity of the ZIF-90 membrane is unchanged after APTES functionalization. All XRD peaks of the APTES-functionalized ZIF-90 membrane match well with those of the as-prepared ZIF-90 membrane.

Before permeation of single gases and separation of mixed gases, the as-prepared and APTES-functionalized ZIF-90 membranes were on-stream activated at 225 °C with a heating rate of 0.2 °C per minute by using an equimolar H_2/CH_4 mixture in the Wicke–Kallenbach permeation apparatus (Figure S5). Figure 2 shows the increase of the H_2 and CH_4 permeances as well as of the H_2/CH_4 selectivity from their binary mixture with increasing temperature during the on-stream activation. Whereas the H_2 permeance remarkably increases with increasing temperature from 25 to 225 °C, the CH_4 permeance only slightly increases, resulting in a remarkable enhancement of H_2/CH_4 selectivity from 8 to 71. Similar to the previous report,[31] the APTES-functionalized ZIF-90 membrane is more easily activated than the as-prepared ZIF-90 membrane since the guest molecule DMF that is difficult to remove has been exchanged by the more volatile methanol during the covalent post-functionalization (Figure S6). After on-stream activation at 225 °C for 60 h, the APTES-functionalized ZIF-90 membrane shows a constant H_2 permeance of about 2.9×10^{-7} $mol\,m^{-2}s^{-1}Pa^{-1}$ and a H_2/CH_4 selectivity of 71.

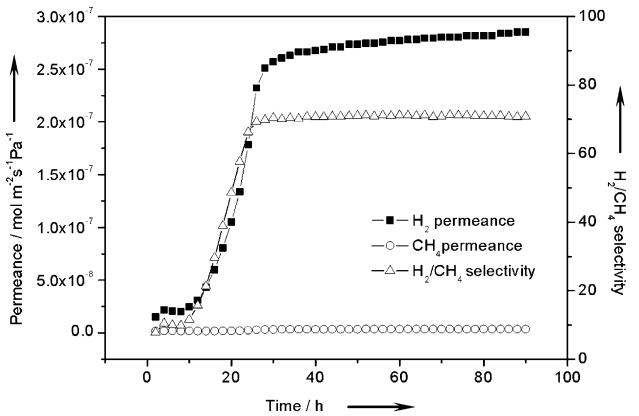

Figure 2. H_2 and CH_4 permeances as well as H_2/CH_4 selectivity of an equimolar H_2/CH_4 mixture of the APTES-functionalized ZIF-90 membrane during the on-stream activation at 225 °C.

After on-stream activation, the volumetric flow rates of the single gases H_2, CO_2, CH_4, C_2H_6, and C_3H_8 as well as of their equimolar binary mixtures of H_2 with CO_2, CH_4, C_2H_6, and C_3H_8 have been measured through the as-prepared and APTES-functionalized ZIF-90 membranes by using the Wicke–Kallenbach technique. The single-gas permeances and ideal separation factors are summarized in Table S1. Figure 3 shows the permeances of the single gases through the as-prepared and APTES-functionalized ZIF-90 membranes at 225 °C and 1 bar as a function of the kinetic diameters of the permeating molecules. As shown in Figure 3 and Table S1, for the APTES-functionalized ZIF-90 membrane, the H_2 permeance of 3.0×10^{-7} $mol\,m^{-2}s^{-1}Pa^{-1}$ is much higher than those of the other gases, and a cut-off is observed between H_2 and the other more bulky gases. Compared with the as-prepared ZIF-90 membrane, the H_2 permeance of the APTES-functionalized ZIF-90 membrane keeps almost unchanged although all other gas permeances decrease. In our previous report,[31] a remarkable reduction of the H_2 permeance has been reported since the small ethanolamine molecules can easily enter the pore volume of the ZIF-90 layer, thus resulting in a severe constriction of the pore apertures in the whole bulk phase. In the present work, the bulky APTES molecules are restricted to enter the interior of the ZIF-90 layer in a short time, thus avoiding remarkable reduction of the H_2 permeance. At 225 °C and 1 bar, the ideal separation factors of H_2 from CO_2, CH_4, C_2H_6, and C_3H_8 are 22, 74, 261, and 473, which by far exceed the corresponding Knudsen coefficients (4.7, 2.8, 3.9, and 4.7) and those of the

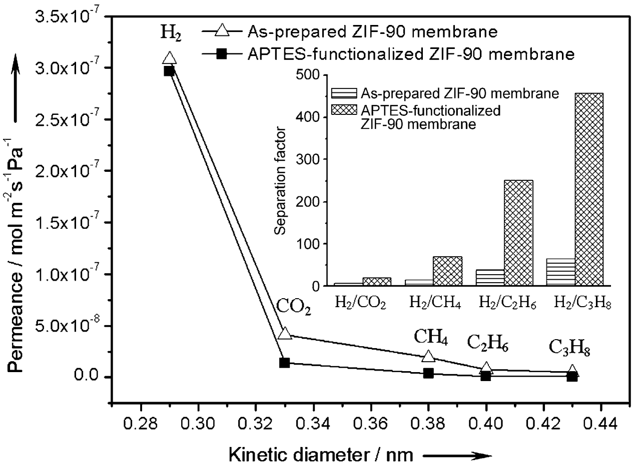

Figure 3. Permeances of single gases for the as-prepared and APTES-functionalized ZIF-90 membranes as a function of the kinetic diameter at 225 °C and 1 bar using the Wicke–Kallenbach technique. The inset shows the separation factors for equimolar mixtures of H_2 and other gases as determined by gas chromatography.

as-prepared ZIF-90 membrane (7.5, 16, 41, and 67). These results are in good agreement with our supposition that the hydrogen selectivity of the modified ZIF-90 membrane can be enhanced through APTES functionalization by eliminating the intercrystalline defects.

Compared with the permeance of H_2 as a single component, the H_2 permeance in the mixtures shows only a slight reduction with a H_2 permeance of about 2.9×10^{-7} mol m^{-2} s^{-1} Pa^{-1}, suggesting that no competitive adsorption between the species plays a significant role at a high temperature, and the larger molecules (CO_2, CH_4, C_2H_6, and C_3H_8) only slightly hinder the permeation of the highly mobile H_2. For the 1:1 binary mixtures, the separation factors of H_2/CO_2, H_2/CH_4, H_2/C_2H_6, and H_2/C_3H_8 mixtures are 20, 71, 250, and 458, respectively, which are higher than those on the as-prepared ZIF-90 membrane (7.2, 15, 39, and 65), as shown in the inset of Figure 3 and Table S2. As usual, with longer modification time, the permeances decrease parallel to the selectivity increase. As shown in Table S3, extending the modification time to 1 h, the H_2 permeance decreases to 6.8×10^{-8} mol m^{-2} s^{-1} Pa^{-1} while the H_2/CH_4 selectivity increases to 146 since the covalent docking of APTES restricts the adsorption rate. Compared with literature data for permeation of mixed gases on MOF and zeolite membranes (Table S4),[16–20,24–31,38–44] the APTES-functionalized ZIF-90 membrane developed in this study shows higher gas separation performances. The obtained high H_2 selectivity of the ZIF-90 membrane is attributed to the narrowing of the pore mouth and minimizing of intercrystalline defects by APTES post-functionalization, and thus enhancing the reproducibility of the membrane preparation (Table S5).

To investigate the thermal stability of the APTES-functionalized ZIF-90 membrane, the operating temperature for the separation of the H_2/CH_4 mixture was increased from 25 to 225 °C. It can be seen that the H_2 permeance increases from 8.3×10^{-8} to 2.9×10^{-7} mol m^{-2} s^{-1} Pa^{-1}, while the CH_4 permeance only slightly increases from 3.0×10^{-9} to 4.0×10^{-9} mol m^{-2} s^{-1} Pa^{-1}, thus the separation factor of the H_2/CH_4 mixture rises from 27 to 71 (Figure S7). This phenomenon can also be explained by an adsorption–diffusion model. At low temperature, ZIF-90 adsorbs CH_4 more strongly than H_2, thus blocking the diffusion paths of the rarely adsorbed but highly mobile H_2. When the temperature increases, less CH_4 becomes adsorbed, and more H_2 can diffuse through the resulting free volume,[45] leading to an enhancement of the H_2 permeance. Furthermore, the APTES-functionalized ZIF-90 membrane shows a completely reversible separation behavior between 25 and 225 °C. In addition, the ZIF-90 membrane can keep its high H_2/CH_4 selectivity when the CH_4 partial pressure increases from 0.5 to 2.0 bar corresponding to total feed pressures of 1.0 to 4.0 bar while the permeate pressure was 1 bar constant. The slight reduction of the H_2/CH_4 selectivity with increasing feed pressure is due to an increased CH_4 loading of the membrane which reduces the H_2 diffusivity (Figure S8).

As reported previously,[30,31] the as-prepared and imine-functionalized ZIF-90 membranes show a high hydrothermal stability. Also the APTES-functionalized ZIF-90 membranes consistently exhibit a high stability in the presence of steam, and both H_2 permeance and H_2/CH_4 selectivity are unchanged for at least 48 h (Figure 4), which shows that the ZIF-90 pore volume is not blocked by the adsorbed water. The slight reduction of the H_2 permeance can be attributed to the parallel permeation of H_2O and H_2 through the ZIF-90 membrane since the kinetic diameter of H_2O is only 0.26 nm,

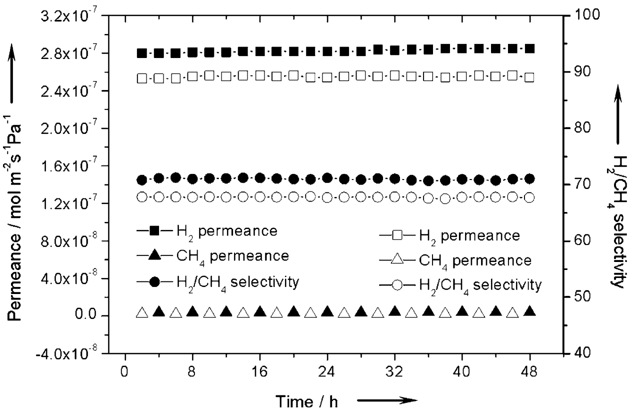

Figure 4. Hydrothermal stability measurement of the APTES-functionalized ZIF-90 membrane for the separation of an equimolar H_2/CH_4 mixture and addition of 3 mol% steam at 225 °C. Filled symbols (■▲●): without steam, and open symbols (□△○): with steam.

which is smaller than the pore size of ZIF-90.[45] In the presence of steam, the aminopropyl groups are hydrolytically stable and will not split from the surface of the ZIF-90 layer. Although the ethoxy bonds of APTES are hydrolyzed, the transient silanol groups will condense with other silanol groups to form stable linkages. This covalent attachment of APTES to the linker could prevent or at least reduce the so called "gate opening" effect by a linker flip-flop movement as observed for ZIF-8.[46] This minimized framework flexibility could also be a reason for the increase of the separation factor for mixed gases as shown in Table S2.

In conclusion, in the present work we have developed a facile post-functionalization road for the preparation of highly permselective ZIF-90 molecular sieve membranes through an imine condensation reaction by using the organosilica APTES. By covalent linkages between the free aldehyde groups of the ZIF-90 and the amino group of APTES, both narrowing of the pore mouth and sealing of intercrystalline defects of the polycrystalline ZIF-90 layer are achieved, and thus the selectivity for gas separation was enhanced. For binary mixtures at 225 °C and 1 bar, the separation factors of H_2/CO_2, H_2/CH_4, H_2/C_2H_6, and H_2/C_3H_8 mixtures were found to be 20, 71, 250, and 458, and a relatively high H_2 permeance of about 2.9×10^{-7} mol m^{-2} s^{-1} Pa^{-1} can be obtained to avoid pore blocking. Further, the APTES-functionalized ZIF-90 molecular sieve membranes display a high thermal and hydrothermal stability. These properties recommend APTES-functionalized ZIF-90 membranes as a promising candidate for industrial hydrogen separation.

Experimental Section

All chemicals were used as received: zinc nitrate tetrahydrate (> 99%, Merck), imidazolate-2-carboxyaldehyde (ICA, > 99%, Alfa Aesar), 3-aminopropyltriethoxysilane (APTES, 98%, Abcr), toluene (Acros), and *N,N*-dimethylformamide (DMF, water < 50 ppm, Acros). Porous α-Al_2O_3 disks (Fraunhofer Institute IKTS, former HITK/Inocermic, Hermsdorf, Germany: 18 mm in diameter, 1.0 mm in thickness, 70 nm particles in the top layer) were used as support materials.

Synthesis of ZIF-90 crystals and membranes: The ZIF-90 crystals and membranes were prepared as reported previously.[30,34] The APTES-treated α-Al_2O_3 support materials[47,48] were placed horizontally in a Teflon-lined stainless steel autoclave which was filled with synthesis solution, and heated at 100 °C in an air-circulating oven for 18 h. After solvothermal reaction, the ZIF-90 crystals and membranes were washed with DMF several times, and then dried in air at 60 °C over night.

Covalent functionalization of ZIF-90 crystals and membranes: The as-prepared ZIF-90 crystals and membranes were immersed in methanol and APTES solution, and refluxed at 110 °C for 0–1.0 h. After the reaction, the modified ZIF-90 crystals and membranes were washed with methanol several times and then dried in air at room temperature over night before characterization and permeation measurements.

Characterization of ZIF-90 crystals and membranes: The as-prepared and APTES-functionalized ZIF-90 crystals were measured by FTIR spectroscopy and XRD. The as-prepared and APTES-functionalized ZIF-90 mebranes were measured by SEM and XRD. FTIR spectra were recorded with a Tensor 27 instrument (Bruker) through KBr pellets using an Ar/Xe laser line at 633 nm. SEM micrographs were taken on a JEOL JSM-6700F with a cold field emission gun operating at 2 kV and 10 μA. The XRD patterns were recorded at room temperature under ambient conditions with a Bruker D8 ADVANCE X-ray diffractometer with CuKα radiation at 40 kV and 40 mA.

Permeation of single gases and separation of mixed gases: For the permeation of single gases and separation of mixed gases, the as-prepared and APTES-functionalized ZIF-90 membranes were sealed in a permeation module with silicone O-rings. The sweep gas N_2 was fed on the permeate side to keep the concentration of permeating gas as low as possible thus providing a driving force for permeation. The total pressure on each side of the membrane was atmospheric. The fluxes of feed and sweep gases were determined with mass-flow controllers, and a calibrated gas chromotograph (HP6890) was used to measure the gas concentrations (Figure S6). The separation factor $\alpha_{i,j}$ of a binary mixture after permeation is defined as the quotient of the molar ratios of the components (i,j) in the permeate, divided by the quotient of the molar ratio of the components (i,j) in the retentate.

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[1] N. W. Ockwig, T. M. Nenoff, *Chem. Rev.* **2007**, *107*, 4078–4110.
[2] H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276–279.
[3] J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982–986.
[4] O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705–714.
[5] M. Dincâ, A. F. Yu, J. R. Long, *J. Am. Chem. Soc.* **2006**, *128*, 8904–8913.
[6] L. J. Murray, M. Dincâ, J. R. Long, *Chem. Soc. Rev.* **2009**, *38*, 1294–1314.
[7] C. G. Silva, A. Corma, H. García, *J. Mater. Chem.* **2010**, *20*, 3141–3156.
[8] E. Biemmi, C. Scherb, T. Bein, *J. Am. Chem. Soc.* **2007**, *129*, 8054–8055.
[9] S. Hermes, F. Schroder, R. Chelmowski, C. Woll, R. A. Fischer, *J. Am. Chem. Soc.* **2005**, *127*, 13744–13745.
[10] L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.* **2012**, *112*, 1105–1125.
[11] A. Bétard, R. A. Fischer, *Chem. Rev.* **2012**, *112*, 1055–1083.
[12] R. Ranjan, M. Tsapatsis, *Chem. Mater.* **2009**, *21*, 4920–4924.
[13] A. Bétard, H. Bux, S. Henke, D. Zacher, J. Caro, R. A. Fischer, *Microporous Mesoporous Mater.* **2012**, *150*, 76–82.
[14] S. R. Venna, M. A. Carreon, *J. Am. Chem. Soc.* **2010**, *132*, 76–78.
[15] Y. Yoo, Z. Lai, H. K. Jeong, *Microporous Mesoporous Mater.* **2009**, *123*, 100–106.
[16] H. Guo, G. Zhu, I. J. Hewitt, S. Qiu, *J. Am. Chem. Soc.* **2009**, *131*, 1646–1647.
[17] J. Nan, X. Dong, W. Wang, W. Jin, N. Xu, *Langmuir* **2011**, *27*, 4309–4312.
[18] Y. Yoo, V. Varela-Guerrero, H.-K. Jeong, *Langmuir* **2011**, *27*, 2652–2657.
[19] Y. Hu, X. Dong, J. Nan, W. Jin, X. Ren, N. Xu, Y. M. Lee, *Chem. Commun.* **2011**, *47*, 737–739.
[20] S. Aguado, C. H. Nicolas, V. Moizan-Baslé, C. Nieto, H. Amrouche, N. Bats, N. Audebrandd, D. Farrusseng, *New J. Chem.* **2011**, *35*, 41–44.
[21] 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*, 10186–10191.
[22] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Science* **2008**, *319*, 939–943.
[23] A. Phan, C. J. Doonan, F. J. Uribe-romo, C. B. Knobler, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2010**, *43*, 58–67.
[24] Y. Li, F. Liang, H. Bux, A. Feldhoff, W. Yang, J. Caro, *Angew. Chem.* **2010**, *122*, 558–561; *Angew. Chem. Int. Ed.* **2010**, *49*, 548–551.
[25] H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke, J. Caro, *J. Am. Chem. Soc.* **2009**, *131*, 16000–16001.
[26] H. Bux, A. Feldhoff, J. Cravillon, M. Wiebcke, Y. Li, J. Caro, *Chem. Mater.* **2011**, *23*, 2262–2269.
[27] Y. Pan, Z. Lai, *Chem. Commun.* **2011**, *47*, 10275–10277.
[28] A. Huang, H. Bux, F. Steinbach, J. Caro, *Angew. Chem.* **2010**, *122*, 5078–5081; *Angew. Chem. Int. Ed.* **2010**, *49*, 4958–4961.
[29] Y. Liu, E. Hu, E. A. Khan, Z. Lai, *J. Membr. Sci.* **2010**, *353*, 36–40.
[30] A. Huang, W. Dou, J. Caro, *J. Am. Chem. Soc.* **2010**, *132*, 15562–15564.
[31] A. Huang, J. Caro, *Angew. Chem.* **2011**, *123*, 5083–5086; *Angew. Chem. Int. Ed.* **2011**, *50*, 4979–4982.
[32] J. Gascon, F. Kapteijn, *Angew. Chem.* **2010**, *122*, 1572–1574; *Angew. Chem. Int. Ed.* **2010**, *49*, 1530–1532.
[33] W. Morris, C. J. Doonan, H. Furukawa, R. Banerjee, O. M. Yaghi, *J. Am. Chem. Soc.* **2008**, *130*, 12626–12627.
[34] Z. Wang, S. M. Cohen, *Angew. Chem.* **2008**, *120*, 4777–4780; *Angew. Chem. Int. Ed.* **2008**, *47*, 4699–4702.
[35] S. M. Cohen, *Chem. Rev.* **2012**, *112*, 970–1000.
[36] T. Haneda, M. Kawano, T. Kawamichi, M. Fujita, *J. Am. Chem. Soc.* **2008**, *130*, 1578–1579.
[37] A. D. Burrows, C. G. Frost, M. F. Mahon, C. Richardson, *Angew. Chem.* **2008**, *120*, 8610–8614; *Angew. Chem. Int. Ed.* **2008**, *47*, 8482–8486.
[38] M. Kanezashi, J. O'Brien-Abraham, Y. S. Lin, *AIChE J.* **2008**, *54*, 1478–1486.
[39] G. Guan, T. Tanaka, K. Kusakabe, K. Sotowa, S. Morooka, *J. Membr. Sci.* **2003**, *214*, 191–198.

[40] M. Yu, H. H. Funke, R. D. Noble, J. L. Falconer, *J. Am. Chem. Soc.* **2011**, *133*, 1748 – 1750.
[41] A. Huang, F. Liang, F. Steinbach, T. M. Gesing, J. Caro, *J. Am. Chem. Soc.* **2010**, *132*, 2140 – 2141.
[42] A. Huang, J. Caro, *J. Mater. Chem.* **2011**, *21*, 11424 – 11429.
[43] A. Huang, J. Caro, *Chem. Commun.* **2010**, *46*, 7748 – 7750.
[44] U. Illgen, R. Schäfer, M. Noack, P. Kölsch, A. Kühnle, J. Caro, *Catal. Commun.* **2001**, *2*, 339 – 345.
[45] Y. Li, F. Liang, H. Bux, W. Yang, J. Caro, *J. Membr. Sci.* **2010**, *354*, 48 – 54.
[46] D. Fairen-Jimenez, S. A. Moggach, M. T. Wharmby, P. A. Wright, S. Parsons, T. Düren, *J. Am. Chem. Soc.* **2011**, *133*, 8900 – 8902.
[47] A. Huang, F. Liang, F. Steinbach, J. Caro, *J. Membr. Sci.* **2010**, *350*, 5 – 9.
[48] A. Kulak, Y. Lee, Y. S. Park, K. B. Yoon, *Angew. Chem.* **2000**, *112*, 980 – 983; *Angew. Chem. Int. Ed.* **2000**, *39*, 950 – 953.