**Microporous Membranes**

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# Molecular-Sieve Membrane with Hydrogen Permselectivity: ZIF-22 in LTA Topology Prepared with 3-Aminopropyltriethoxysilane as Covalent Linker**

*Aisheng Huang,* Helge Bux, Frank Steinbach, and Jürgen Caro**

Microporous metal–organic frameworks (MOFs) have attracted intense interest due to their potential applications for gas adsorption and storage, molecular separation, and catalysis.[1–6] To date, research has mainly been directed towards the synthesis of novel MOF structures through assembly of molecular building blocks to construct tailored frameworks with tunable sizes, morphologies, structures, and desired properties.[7–10] On the other hand, their highly diverse structures and pore size, as well as large surface areas and specific adsorption affinities, make MOFs candidates for fabrication of superior molecular sieve membranes for gas separation. Therefore, a great deal of research has focused on the preparation of supported MOF membranes.[11–13] However, progress in MOF membranes is rather limited, and synthesis of continuous MOF membranes still remains a challenge. Recently, Guo et al. reported copper-net-supported HKUST-1 ($Cu_3(BTC)_2$, BTC = benzene-1,3,5-tricarboxylate) membrane with a $H_2/N_2$ selectivity of 7, which is the first report of an MOF membrane showing gas separation performance better than Knudsen diffusion behavior.[14] Thereafter, Tsapatsis and co-workers prepared microporous MOF membranes [MMOF, Cu(hfipbb)($H_2$hfipbb)$_{0.5}$, hfipbb = 4,4′-(hexafluoroisopropylidene)bis(benzoic acid)] with a high ideal $H_2/N_2$ selectivity of 23 at 190 °C by the secondary growth method on porous alumina supports.[15]

Zeolitic imidazolate frameworks (ZIFs), a subfamily of MOFs based on transition metals (Zn, Co) and imidazolates as linkers, with exceptional thermal and chemical stability, are very promising for the fabrication of molecular sieve membranes.[16–18] Recently, we prepared sodalite (SOD) topology ZIF-8 and ZIF-7 membranes with molecular sieving performance by microwave-assisted synthesis.[19,20] The ZIF-8 membrane showed $H_2/CH_4$ selectivity higher than 10 but a $H_2/CO_2$ selectivity close to Knudsen diffusion, because ZIF-8 is flexible and its crystallographic pore size of 0.34 nm is slightly larger than the kinetic diameter of $CO_2$ (0.33 nm). The ZIF-7 membrane displayed better performance in the separation of $H_2$ from $CO_2$, with a $H_2/CO_2$ selectivity of 6.5 due to its smaller pore size of 0.30 nm, which is between the molecular sizes of $H_2$ (0.29 nm) and $CO_2$ (0.33 nm). Yaghi and co-workers proposed the synthesis of ZIFs in LTA topology (ZIF-20, ZIF-21, and ZIF-22) with high stability and high porosity.[21] Although LTA aluminosilicate[22] and aluminophosphate[23] membranes have been reported recently for successful gas separation, to the best of our knowledge, so far no ZIF membranes with LTA structure could be prepared. We therefore attempted to make the first molecular-sieve ZIF-22 membrane for gas separation. ZIF-22 has the same pore size as ZIF-7 (about 0.3 nm), so we can expect ZIF-22 membranes to display high molecular-sieving performance for separation of $H_2$ from $CO_2$ and other larger gas molecules.

As reported elsewhere,[15,24,25] it was rather difficult to prepare continuous MOF membranes by a simple in situ synthesis route, since heterogeneous nucleation of MOF crystals on supports was very poor. Therefore, chemical modifications[11,25,26] and seed coating[15,20,27] of the supports turned out to be indispensable for directing nucleation and growth of the MOF layers. Actually, in our first attempt to synthesize a ZIF-22 membrane by in situ synthesis, we failed to obtain a continuous ZIF-22 membrane on bare $TiO_2$ supports (Supporting Information Figure S1). Due to their high organic functionality and flexibility with which the organic linkers can be modified, MOFs have been exemplified as ideal candidates for the fabrication of covalently functionalized materials through host–guest reactions of pendant functional groups pre-installed on the organic components.[28–32] Based on our recent experience in fabricating aluminosilicate LTA zeolite membranes on 3-aminopropyltriethoxysilane (APTES)-functionalized supports,[22] APTES can be expected to act as a covalent linker for facile preparation of ZIF-22 membrane on APTES-functionalized supports. Thus, the influence of surface chemistry is eliminated and the nucleation and growth of the ZIF-22 layer on porous ceramic supports promoted, as shown in Figure 1.

Porous $TiO_2$ disks were treated with APTES (0.2 mM in 10 mL toluene) at 110 °C for 1 h under argon to deposit an APTES monolayer on the $TiO_2$ support surface.[22] The ZIF-22 membrane was prepared by a solvothermal reaction of zinc nitrate hexahydrate (0.136 g) and 5-azabenzimidazole (0.5 g) in *N,N*-dimethylformamide (DMF, 8 mL). The APTES-treated $TiO_2$ support was placed horizontally in a Teflon-lined stainless steel autoclave and heated in air at 423 K for

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[*] Dr. A. Huang, H. Bux, F. Steinbach, Prof. Dr. J. Caro
Institute of Physical Chemistry and Electrochemistry
Leibniz University Hannover
Callinstrasse 3A, 30167 Hannover (Germany)
Fax: (+49) 511-7621-9121
E-mail: aisheng.huang@pci.uni-hannover.de
juergen.caro@pci.uni-hannover.de

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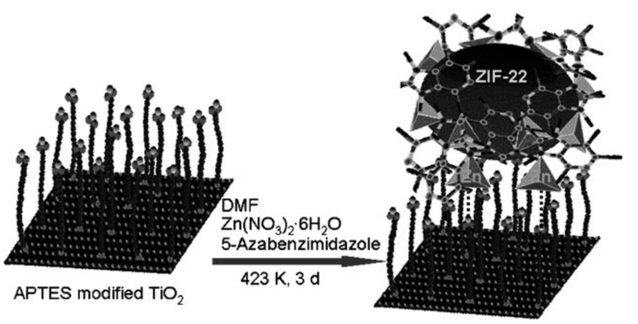

***Figure 1.*** Preparation of a ZIF-22 membrane by using 3-aminopropyltriethoxysilane (APTES) as covalent linker between the ZIF-22 membrane and the titania support.

3 d. After solvothermal reaction, polycrystalline ZIF-22 had grown as a compact layer on the APTES-modified $TiO_2$. The SEM top view (Figure 2 a) and cross section (Figure 2 b) show that the ZIF-22 membrane has a thickness of about 40 µm and is well intergrown; no cracks, pinholes, or other defects are visible. On the contrary, separate ZIF-22 crystals and crystal islands rather than a continuous layer formed if the support surface was not treated with APTES before ZIF-22 crystallization (Supporting Information Figure S1). It is possible that the 3-aminopropylsilyl groups of APTES can coordinate to the free $Zn^{2+}$ centers and bind the growing nanocrystals directly. Therefore, a covalent linker between the growing ZIF-22 layer and the support is formed to anchor the ZIF-22 crystals for membrane formation. Energy-dispersive X-ray spectroscopy (EDXS, Figure 2 c and d) reveals sharp transition between the ZIF-22 layer (Zn signal) and the titania support (Ti signal). A typical X-ray diffraction (XRD) pattern of ZIF-22 layer (Supporting Information Figure S2) shows a high degree of crystallinity, and all peaks match well with those of ZIF-22.[21]

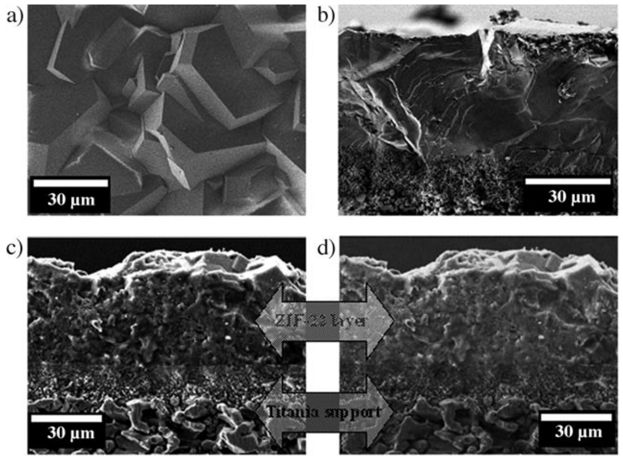

***Figure 2.*** a) Top-view and b) cross-section SEM images of the ZIF-22 membrane. c,d) EDXS mapping of the sawn and polished ZIF-22 membrane.

The volumetric flow rates of the single gases $H_2$, $CO_2$, $O_2$, $N_2$, and $CH_4$ as well as 1:1 binary mixtures of $H_2$ with $CO_2$, $O_2$, $N_2$, and $CH_4$ were measured by the Wicke–Kallenbach technique (Supporting Information Figure S3). The permeances and separation factors are summarized in Table S1 of the Supporting Information. Figure 3 shows the permeances of the single gases through the ZIF-22 membrane as a function of the kinetic diameters of the permeating molecules. As shown in Figure 3 and Table S1 of the Supporting Information, the permeance of $H_2$ is much higher than those of the other gases, and there is a clear cut-off between $H_2$ and $CO_2$, in accordance with the previous report on ZIF-7 membrane, which has the same pore size as ZIF-22,[20] and this suggests that the ZIF-22 membrane shows molecular sieve performance. The ideal separation factors of $H_2$ from $CO_2$, $O_2$, $N_2$ and $CH_4$, determined as the ratio of the single component permeances,[33] are 8.5, 7.2, 7.1, and 6.7, respectively, that is, the ZIF-22 membrane is expected to display hydrogen selectivity in mixed-gas permeation.

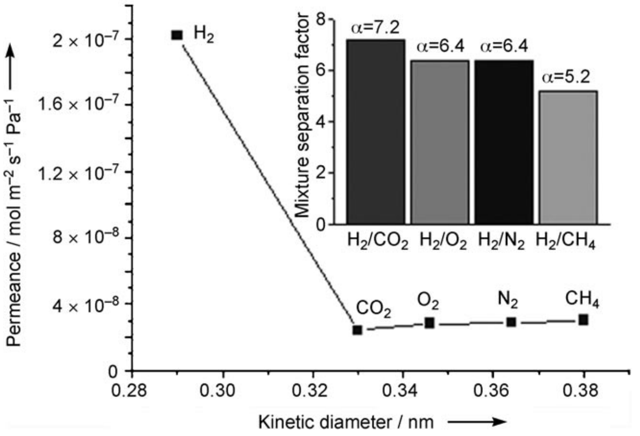

***Figure 3.*** Single-gas permeances of different gases on the ZIF-22 membrane at 323 K as a function of the kinetic diameter. The inset shows the mixture separation factor for $H_2$ over other gases, determined by gas chromatography.

The molecular-sieve performance of the ZIF-22 membrane was confirmed by separation of binary mixtures of $H_2$ with $CO_2$, $O_2$, $N_2$, and $CH_4$. As shown in the inset of Figure 3 and Table S1 of the Supporting Information, the mixture separation factors of $H_2/CO_2$, $H_2/O_2$, $H_2/N_2$ and $H_2/CH_4$, determined as the molar ratios in permeate and retentate,[33] are 7.2, 6.4, 6.4 and 5.2, respectively. All these mixture-separation factors exceed the corresponding Knudsen constants, with $H_2$ permeances higher than $1.6 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$. Compared with literature data on mixed-gas separation performances of MOF and zeolite membranes, the ZIF-22 membranes developed in this study are among those withs high separation performance (Table 1).

To investigate the thermal stability of the ZIF-22 membrane, the permeation temperature was increased from 323 to 423 K. The $H_2$ permeance increased from $1.7 \times 10^{-7}$ to $3.6 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ (Supporting Information Figure S4) while the $H_2/CO_2$ selectivity was slightly reduced from 7.2 to 6.5, which still exceeds the Knudsen constant, which suggests that the ZIF-22 membrane has high thermal stability. The ZIF-22 membrane was tested for more than one week at

***Table 1:*** Comparison of the gas-separation performances of the ZIF-22 membrane in this study with other membranes from the literature.

| Membrane | Pore size [nm] | Gas separation performance Selectivity | | | | | Reference |
|---|---|---|---|---|---|---|---|
| | | $H_2/CO_2$ | $H_2/O_2$ | $H_2/N_2$ | $H_2/CH_4$ | $H_2$ permeance [$mol\,m^{-2}\,s^{-1}\,Pa^{-1}$] | |
| zeolite X | 0.74 | 4.5 | – | – | – | $1.4\times10^{-7}$ | [34] |
| silicate-1 | 0.55 | 1.84 | – | 1.23 | – | $7.9\times10^{-6}$ | [35] |
| ZSM-5 | 0.55 | – | – | 15.5 | – | $9.3\times10^{-13}$ | [36] |
| matrix $AlPO_4$ | – | 9.7 | – | – | – | $1.1\times10^{-7}$ | [37] |
| SAPO-34 | 0.38 | 1.3 | – | 25 | – | $3.0\times10^{-8}$ | [38] |
| LTA $AlPO_4$ | 0.4 | 7.6 | 6.1 | – | 4.3 | $2.1–2.5\times10^{-7}$ | [23] |
| NaA | 0.4 | 5.3 | 4.4 | 4.2 | 3.6 | $2.5–3.6\times10^{-7}$ | [22] |
| MOF-5 | 1.56 | KD[b] | KD[b] | KD[b] | KD[b] | $4.7\times10^{-6}$ | [13] |
| MMOF | 0.32 | – | – | 23[a] | – | $1.2\times10^{-7}$ | [15] |
| HKUST-1 | 0.9 | 6.8 | – | 7.0 | 6 | $1\times10^{-6}$ | [14] |
| ZIF-8 | 0.34 | 4.5[a] | 5.8[a] | 11.6[a] | 11.3 | $5.1\times10^{-8}$ | [19] |
| ZIF-7 | 0.3 | 6.5 | – | 7.7 | 5.9 | $7.7–8.0\times10^{-8}$ | [20] |
| ZIF-22 | 0.3 | 7.2 | 6.4 | 6.4 | 5.2 | $1.6–1.9\times10^{-7}$ | this work |

[a] Ideal separation factor. [b] Knudsen diffusion.

323 K, and its separation performance was unchanged (Supporting Information Figure S5). The permeance of the ZIF-22 membrane as function of $H_2$ partial pressure is presented in Figure S6 (Supporting Information). With increasing partial pressure, the $H_2$ permeance slightly decreases, while the $CO_2$ permeance increases, and hence the $H_2/CO_2$ selectivity decreases from 7.2 to 5.1 when the partial pressure increased from 0.5 to 1.0 bar.

We found that APTES also supports the formation of other ZIF membranes such as ZIF-8 and ZIF-7. Similar to the preparation of ZIF-22 membrane, dense ZIF-8 and ZIF-7 membranes can be formed easily on APTES-modified $Al_2O_3$ supports, while no continuous ZIF membranes can be prepared on APTES-free supports (Supporting Information Figures S7–10). Further work is in progress to extend this synthetic approach to other ZIF membranes.

In conclusion, we have developed a universal seeding-free route to prepare ZIF molecular sieve membranes on porous ceramic supports by using 3-aminopropyltriethoxysilane as covalent linker to promote nucleation and growth of ZIFs. For ZIF-22 membrane at 323 K, the mixture separation factors of $H_2/CO_2$, $H_2/O_2$, $H_2/N_2$, and $H_2/CH_4$ are 7.2, 6.4, 6.4, and 5.2, respectively, with $H_2$ permeances higher than $1.6\times10^{-7}\,mol\,m^{-2}\,s^{-1}\,Pa^{-1}$. The ZIF-22 membrane displayed high thermal stability, and thus has potential applications in gas separation.

## Experimental Section

Chemicals were used as received: zinc nitrate hexahydrate (> 99%, Merck), zinc chloride (> 99%, Merck), 5-azabenzimidazole (> 99%, Aldrich), 2-methylimidazole (> 99%, Aldrich), benzimidazole (> 99%, Aldrich), 3-aminopropyltriethoxysilane (98%, Abcr), sodium formate (> 99%, Aldrich), toluene (Acros), *N*,*N*-dimethylformamide (Acros), methanol (99.9%, Roth). Porous $TiO_2$ and $\alpha$-$Al_2O_3$ disks (Fraunhofer IKTS, Inocermic GmbH, Hermsdorf, Germany: 18 mm in diameter, 1.0 mm in thickness, 100 nm particles in the top layer) were used as supports.

APTES modification of the support surface: Porous $TiO_2$ and $\alpha$-$Al_2O_3$ disks were treated with APTES (0.2 mM in 10 mL of toluene) at 110 °C for 1 h under argon[22] to deposit an APTES monolayer on the support surface.

Synthesis of ZIF-22 membrane: The ZIF-22 membrane was prepared by a simple solvothermal reaction of zinc nitrate hexahydrate (0.136 g) and 5-azabenzimidazole (0.5 g) in DMF (8 mL). The APTES-treated or APTES-free $TiO_2$ supports were placed horizontally in a Teflon-lined stainless steel autoclave, which was filled with synthesis solution and heated at 150 °C in an air oven for 3 d. After solvothermal reaction, the ZIF-22 membrane was washed with DMF several times, and then dried in air at 100 °C overnight.

Synthesis of ZIF-8 membrane: The ZIF-8 membrane was prepared according to the procedure reported elsewhere.[19] A solid mixture of 1.078 g of zinc chloride, 0.972 g of 2-methylimidazole, and 0.540 g sodium formate was dissolved in 80 mL of methanol by ultrasonic treatment. APTES-treated or APTES-free $\alpha$-$Al_2O_3$ supports were immersed in the solution and left to stand for 20 min. To prevent precipitation on the surface of the planar support, it was oriented at 90° by a Teflon holder. Afterwards the solution with the support was placed in a 200 mL Teflon autoclave and heated in a microwave oven (Ethos 1, MLS) at a rate of $8\,°C\,min^{-1}$ to 100 °C for 4 h. After cooling, the membrane was washed with methanol and dried for 1 d over silica gel at room temperature and slightly reduced pressure.

Synthesis of ZIF-7 membrane: The solution for synthesis of ZIF-7 membrane was prepared according to a previous procedure.[20] 0.28 g of zinc nitrate hexahydrate and 0.16 g benzimidazole were dissolved in 15 mL of DMF with stirring. The APTES-treated or APTES-free $\alpha$-$Al_2O_3$ supports were placed horizontally in a Teflon-lined stainless steel autoclave, which was filled with synthesis solution and heated at 130 °C in an air oven for 2 d. After cooling, the membrane was washed with DMF and dried at 100 °C over night.

Characterization of ZIF membranes: SEM images were taken on a Jeol JSM-6700F with a cold-field emission gun operating at 2 kV and 10 μA. The composition of the ZIF-22 membrane was confirmed by energy-dispersive X-ray spectroscopy (EDXS) by using the same SE microscope at 20 kV and 20 μA. The XRD patterns were recorded at room temperature under ambient conditions with a PANalytical diffractometer (X′Pert-MPD, $Cu_{K\alpha1,2}$ with $\lambda_1 = 154.05$, $\lambda_2 = 154.43$ pm) at 40 kV and 50 mA.

Permeation of single gases and separation of mixed gases: For single-gas and mixed-gas permeation, the supported ZIF-22 membrane was sealed in a permeation module with silicone O-rings. The feed gases were fed to the top side of the membrane, and sweep gas was fed on the permeate side to keep the concentration of permeating gas low and provide a driving force for permeation. The total pressure on each side of the membrane was atmospheric. For both single- and mixed-gas permeation, the fluxes of feed and sweep gases were determined with mass flow controllers, and a calibrated gas chromatograph (HP6890) was used to measure the gas concentrations, as shown in Figure S3 of the Supporting Information. The separation factor $\alpha_{i,j}$ of a binary mixture permeation is defined as the quotient of the molar ratios of the components *i* and *j* in the permeate divided by the quotient of molar ratio of components *i* and *j* in the retentate.[33]

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