Selective Membranes

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Covalent Post-Functionalization of Zeolitic Imidazolate Framework ZIF-90 Membrane for Enhanced Hydrogen Selectivity**

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Metal–organic frameworks (MOFs) are being evaluated for several applications, such as gas adsorption, molecular separation, drug delivery, and catalysis owing to their well-defined, adjustable, and open pore framework structures.[1–5] Apart from the use of MOFs as powders, supported MOF layers are of interest for various potential applications as separating membranes, sensors, and other functional layers.[6–12] Among the reported MOFs, the subfamily of zeolitic imidazolate frameworks (ZIFs), which are based on transition metals (Zn, Co) and imidazolate linkers,[13–15] have emerged as candidates for the fabrication of molecular sieve membranes owing to their zeolite-like permanent porosity, uniform pore size, and exceptional thermal and chemical stability. Recently, a few ZIF membranes have shown promising molecular sieve performances that are better than the Knudsen mechanism.[***][16–21] However, there is still a long way ahead before robust synthetic strategies can be developed.[22] Normally, the organic linkers of MOFs cannot form covalent bonds with surface OH groups of the supports, which causes problems in the heterogeneous nucleation of MOFs on support surface.[23] Furthermore, similar to zeolite membranes, most of the MOF layers are polycrystalline with intercrystalline grain boundaries, which are detrimental to the membrane selectivity.[24] Therefore, post-modification, such as chemical vapor deposition (CVD) or covalent functionalization, is helpful to minimize the non-selective transport through the intercrystalline gaps.[25–27] The post-synthetic modification of MOFs has turned out to be an effective and versatile strategy to improve and fine-tune their physical and chemical properties.[28–33] Herein, we present the covalent post-functionalization of MOF molecular sieve membranes to increase the selectivity of a ZIF-90 membrane.

Recently, we have prepared the molecular sieve ZIF-90 membranes by using 3-aminopropyltriethoxysilane (APTES) as covalent linker between the ZIF-90 layer and the Al_2O_3 support by an imine condensation reaction.[34] The ZIF-90 membrane is thermally and hydrothermally stable and shows molecular sieve performance, with a H_2/CH_4 selectivity of more than 15. On the other hand, the H_2/CO_2 selectivity was found to be only 7.2, as the pore size of ZIF-90 (0.35 nm) is larger than the kinetic diameter[*] of CO_2 (0.33 nm). The separation of H_2 and CO_2 is important for example, for the hydrogen production by steam reforming of methane including the water gas-shift strategy.[35]

As reported by Yaghi and co-workers, the free aldehyde groups in the ZIF-90 framework allow the covalent functionalization with amine groups by an imine condensation reaction.[36] Based on this reaction (Supporting Information, Figure S1),[37–39] in the present work we report the covalent post-functionalization of a ZIF-90 membrane by ethanolamine to enhance its H_2/CO_2 selectivity (Figure 1). Two effects can be expected: the imine functionalization can constrict the pore aperture of ZIF-90 and prevents larger molecules from accessing the pores,[36] and the covalent post-functionalization can reduce non-selective transport through invisible intercrystalline defects, thus enhancing the separation selectivity. Therefore, covalently post-functionalized

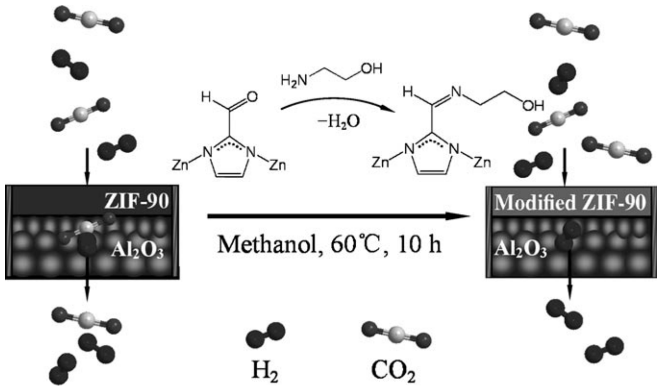

Figure 1. Covalent post-functionalization of a ZIF-90 molecular sieve membrane by imine condensation with ethanolamine to enhance H_2/CO_2 selectivity.

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[***] At defects, such as grain boundaries, pinholes, and hairline fractures, transport does not occur by the molecular sieve principle, but unselectively according to the Knudsen mechanism. The separation factor is the square root from the ratio of the molecular masses.

[*] The kinetic diameter is calculated taking into account then molecular geometry from Van der Waals radii and is the smallest diameter of a ring that can passed over a molecule.

ZIF-90 membranes should display an improved molecular sieving in the separation of H_2 from CO_2 and other gases.

The ZIF-90 membrane was prepared by the solvothermal reaction of Zn^{2+} ions and imidazolate-2-carboxyaldehyde (ICA) in *N,N*-dimethylformamide (DMF).[34] The as-prepared ZIF-90 membrane has a thickness of about 20 μm and consists of 5–10 μm well-intergrown ZIF-90 crystals. For covalent post-functionalization, the as-prepared ZIF-90 membrane was immersed in a solution of methanol and ethanolamine and refluxed for 10 h at 60 °C (Supporting Information, Figure S2).[36] X-ray diffraction (XRD, Supporting Information, Figure S3) confirms that the high crystallinity of the ZIF-90 membrane is unchanged by the imine functionalization. All XRD peaks of the modified ZIF-90 membrane match well with those of the as-prepared ZIF-90 membrane.[34] This result strongly indicates that the unusual thermal and chemical stability of ZIF-90 allow covalent framework functionalization under relative harsh reaction conditions. This stability of ZIF-90 has also been demonstrated by the reduction of the aldehyde groups of ZIF-90 to the alcohol groups through reaction with $NaBH_4$ in methanol.[36]

Before gas permeation, the imine-functionalized ZIF-90 membrane was activated on-stream at 225 °C by using an equimolar H_2/CO_2 mixture in the Wicke–Kallenbach permeation apparatus (Supporting Information, Figure S4). Figure 2 shows the variation of the H_2 and CO_2 permeance

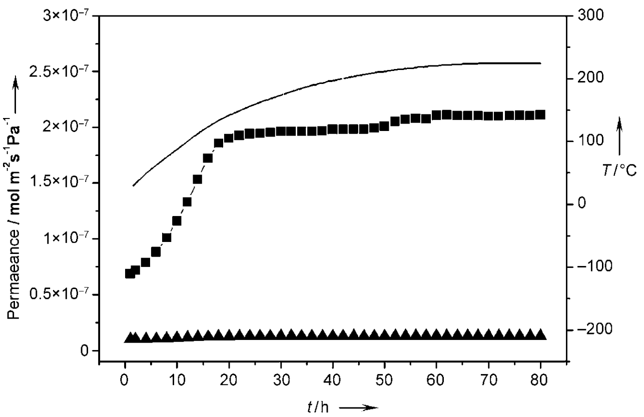

Figure 2. H_2 and CO_2 permeances from an equimolar H_2/CO_2 mixture through the imine-functionalized ZIF-90 membrane during on-stream activation. ■ H_2 permeance, ▲ CO_2 permeance, —— temperature.

from their binary mixture during the on-stream activation. Whereas the H_2 permeance increases remarkably with increasing temperature from 25 to 225 °C, the CO_2 permeance only slightly increases. It should be noted that the imine-functionalized ZIF-90 membrane is easier to activate than the as-prepared membrane, as the DMF solvent, which is difficult to remove, is exchanged by more volatile methanol during the covalent post-functionalization.[34] The membrane activation is completed at 225 °C for 20 h with a constant H_2 permeance of about 2.2×10^{-7} mol m^{-2} s^{-1} Pa^{-1} and a H_2/CO_2 separation factor of 16.4.

The volumetric flow rates of the single gases H_2, CO_2, N_2, and CH_4 and eqimolar binary mixtures of H_2 with CO_2, N_2, and CH_4 were measured by using the Wicke–Kallenbach technique. The permeances and separation factors are summarized in the Supporting Information, Table S1. Figure 3 shows the permeance of the single gases through

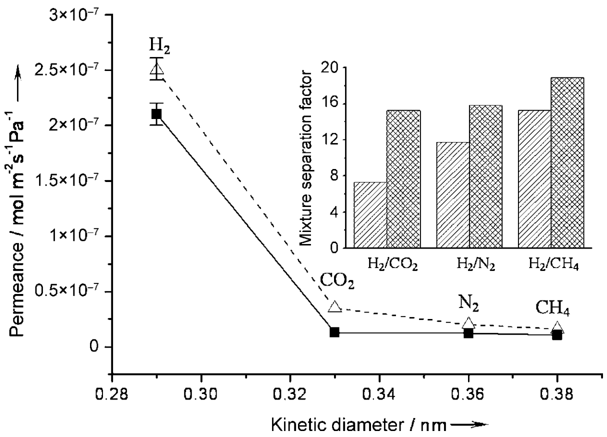

Figure 3. Single-gas permeances on the as-prepared (△) and imine-functionalized (■) ZIF-90 membrane at 200 °C and 1 bar as a function of the kinetic diameter (measured with a bubble counter). The inset shows the mixture separation factors for H_2 over other gases from equimolar mixture as determined by gas chromatography using the Wicke–Kallenbach technique before (hatched columns) and after (crossed columns) imine functionalization.

the ZIF-90 membrane at 200 °C and 1 bar before and after imine functionalization as a function of the kinetic diameters of the permeating molecules. As shown in Figure 3 and the Supporting Information, Table S1, the H_2 permeance is much higher than those of the other gases, and there is a clear cut-off between H_2 and the other more bulky gases. Compared with the as-prepared ZIF-90 membrane,[34] all single gas permeances decrease slightly on the modified membrane, as the pore aperture of the imine-functionalized ZIF-90 was constricted by covalent functionalization.[36] The ideal separation factors as the ratio of the single gas permeances of H_2 from CO_2, N_2, and CH_4 are 15.7, 16.6, and 19.3, which by far exceed the corresponding Knudsen coefficients (4.7, 3.7 and 2.8), respectively, which suggests that the imine-functionalized ZIF-90 membrane has a high hydrogen selectivity.

The molecular sieve performance of the imine-functionalized ZIF-90 membrane was confirmed by the separation of the equimolar mixtures of H_2 with CO_2, N_2, and CH_4 at 200 °C and 1 bar (Figure 3, inset). The H_2 permeance in mixtures (1.9–2.1×10^{-7} mol m^{-2} s^{-1} Pa^{-1}) is only slightly lower than that of the single gas permeance of H_2, suggesting that larger molecules (CO_2, N_2, and CH_4) only slightly influence the permeation of the highly mobile H_2. A similar experimental finding was recently reported for the as-prepared ZIF-90[34] and ZIF-8[16] membranes. For the 1:1 binary mixtures, the real mixture separation factors for H_2/CO_2, H_2/N_2, and H_2/CH_4 after treatment at 60 °C for 10 h (Supporting Information, Table S2, M2) are 15.3, 15.8, and 18.9, which are higher than those from the as-prepared ZIF-90 membrane (7.3, 11.7, and

15.3). The covalent post-functionalization controls the membrane permeance and selectivity in the usual way. With longer modification times (24 h at 60 °C; Supporting Information, Table S2, M3), the permeance decreases (to $1.4\times10^{-8}\,mol\,m^{-2}\,s^{-1}\,Pa^{-1}$) parallel to an increase in selectivity to 62.5. As reported previously,[36] in the case of a complete covalent functionalization (24 h) of ZIF-90, the presence of the imine functionality in the framework severely constricts the pore aperture and thus prevents N_2 (0.36 nm) molecules from accessing the interior of the pores at all.

To investigate the thermal stability of the imine-functionalized ZIF-90 membrane, the operating temperature for separation of H_2/CO_2 was increased from 25 to 225 °C at 1 bar. The H_2 permeance increases from 1.0×10^{-7} to $2.1\times10^{-7}\,mol\,m^{-2}\,s^{-1}\,Pa^{-1}$, while the CO_2 permeance only slightly increases from 1.2×10^{-8} to $1.3\times10^{-8}\,mol\,m^{-2}\,s^{-1}\,Pa^{-1}$, and thus the H_2/CO_2 mixture separation factor rises from 8.3 to 16.2 (Supporting Information, Figure S5). This phenomenon can be explained by an adsorption–diffusion model. At low temperatures, ZIF-90 adsorbs CO_2 more strongly than H_2, thus blocking the diffusion paths of the rarely adsorbed but highly mobile H_2. When the temperature increases, less CO_2 becomes adsorbed, and more H_2 can diffuse owing to the resulting free volume,[40] leading to an enhancement of H_2 permeance. The imine-functionalized ZIF-90 membrane was tested at a higher temperature of 325 °C for 24 h, and the modified ZIF-90 membrane still keeps its high separation performances with a H_2 permeance of about $3.8\times10^{-7}\,mol\,m^{-2}\,s^{-1}\,Pa^{-1}$ and a H_2/CO_2 selectivity of 20.4, indicating that the modified ZIF-90 membrane has a high thermal stability. Furthermore, the imine-functionalized ZIF-90 membrane shows completely reversible separation behavior between 25 and 225 °C. The permeances measured during the cooling-down process are consistent with those during the heating-up. The ZIF-90 membrane can keep its high H_2/CO_2 selectivity when the H_2 partial pressure increases from 0.5 to 1.5 bar corresponding to feed pressures of 1 to 3 bar (Supporting Information, Figure S6).

The development of steam-stable molecular sieve membranes is highly desired as water is usually present in traces in every gas.[41] As reported previously,[34] the ZIF-90 membrane shows a high hydrothermal stability. Furthermore, the imine-functionalized ZIF-90 membranes consistently exhibit a high stability in the presence of steam; both H_2 permeance and H_2/CO_2 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 as the kinetic diameter of H_2O is only 0.26 nm, which is smaller than the pore size of ZIF-90 (0.35 nm).[42]

MOF layers are usually polycrystalline and contain intercrystalline defects, which spoil membrane selectivity. By the imine condensation reaction, a novel covalent post-functionalization strategy has been developed to modify the ZIF-90 molecular sieve membrane to enhance its hydrogen selectivity. The post-functionalization strategy was helpful in eliminating invisible intercrystalline defects of the ZIF-90 layer, thus enhancing the molecular sieving performances of

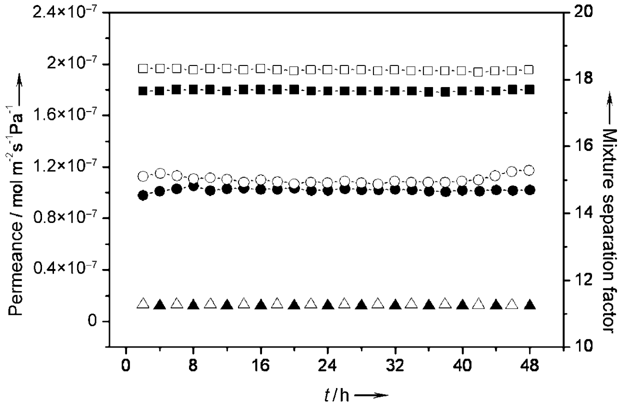

Figure 4. Hydrothermal stability measurement of the imine-functionalized ZIF-90 membrane for the separation of an equimolar H_2/CO_2 mixture upon addition of 3 mol% steam at 200 °C. Open symbols: without steam, filled symbols: with steam; □ H_2 permeance, △ CO_2 permeance, ○ separation factor; ■ H_2 permeance, ▲ CO_2 permeance, ● separation factor.

the ZIF-90 membrane. Furthermore, the presence of the imine functionality in ZIF-90 can constrict the pore aperture, thus improving molecular sieving for the separation of H_2 from CO_2 and other large gases. By covalent post-functionalization, the H_2/CO_2 selectivity could be increased from 7.3 initially to 62.5. The modified ZIF-90 membrane showed stability in 3 vol% steam at 200 °C for 48 h and thermal stability at 325 °C in the H_2/CO_2 separation for at least 24 h.

Experimental Section

Chemicals were used as received: zinc nitrate tetrahydrate (> 99%, Merck), imidazolate-2-carboxyaldehyde (ICA; > 99%, Alfa Aesar), 3-aminopropyltriethoxysilane (APTES; 98%, Abcr), ethanolamine (Aldrich), toluene (Acros), and *N,N*-dimethylformamide (DMF, Acros). Porous α-Al_2O_3 disks (Fraunhofer Institute IKTS, formerly HITK/Inocermic, Hermsdorf, Germany; 18 mm in diameter, 1.0 mm in thickness, 100 nm α-Al_2O_3 particles in the top layer) were used as supports.

The ZIF-90 membrane was prepared as reported previously.[34] The APTES-treated α-Al_2O_3 supports[43] 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.

Covalent functionalization of ZIF-90 membrane: The as-prepared ZIF-90 membrane was immersed in a solution of 1.76 mol L^{-1} ethanolamine in methanol and heated at reflux (60 °C) for 0–24 h.[36]

Characterization of ZIF-90 membrane: 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 VANDANCE X-ray diffractometer with CuKa radiation at 40 kV and 40 mA.

Permeation of single gases and separation of mixed gases: For the single-gas and mixture-gas permeation, the supported ZIF-90 membrane was sealed in a permeation module with silicone O-rings. The sweep gas N_2 (except for the N_2 permeation measurement, where CH_4 was used as sweep gas) 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 1 atm. 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. The separation factor $\alpha_{i,j}$ of a binary mixture 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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