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A High-Performance Gas-Separation Membrane Containing Submicrometer-Sized Metal–Organic Framework Crystals**

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Metal–organic frameworks (MOFs) are an emerging class of nanoporous materials comprising metal centers connected by various organic linkers to create one-, two-, and three-dimensional porous structures with tunable pore volumes, surface areas, and chemical properties. Several thousand MOF materials have been synthesized and their numbers continue to grow rapidly.[1] MOFs are predicted to be highly attractive for application in gas-separation membranes[2] and also have a range of other potential applications, for example in selective gas adsorption,[3] hydrogen storage,[4] catalysis,[5] and sensing.[6] Recently, thin continuous MOF membranes for gas separation have been reported by several authors using MOFs such as MOF-5,[7] HKUST-1 ($Cu_3(BTC)_2$),[8] Cu-(hfipbb)$(H_2hfipbb)_{0.5}$,[9] and ZIF-8.[10] However, the gas-permeation properties (permeability and selectivity) have so far not been found to be technologically attractive. This may have several reasons, such as membrane defects and related processing issues, use of MOFs with low selectivity, and unfavorable orientation of crystals in the membrane.

An alternative route to high-performance MOF membranes is to incorporate them into polymers to obtain nanocomposite (mixed-matrix) membranes. The incorporation of nanoporous molecular sieves such as zeolites into polymeric membranes has attracted much attention, since one can in principle combine the size/shape selectivity of nanoporous materials with the processibility and mechanical stability of polymers.[11] However, zeolite/polymer composite membranes often have defective morphologies characterized by void spaces between the zeolite particles and the polymeric matrix, leading to poor gas-separation performance since the gas molecules bypass the zeolite particles.[11,12] Recent approaches to address the issue of interface compatibilization are emerging.[13] On the other hand, the use of MOFs in mixed-matrix membranes provides several potential advantages over zeolites. The control of MOF/polymer interface morphology is easier than that of the zeolite/polymer interface, since the organic linkers in MOFs have better affinity with polymer chains than the inorganic zeolites do, and the surface properties of MOFs can be easily tuned by functionalization with various organic molecules if necessary.[14] In general, MOFs also have higher pore volumes and lower density than zeolites, and hence their effect on the membrane properties can be greater for a given mass loading. Recently, several MOF mixed-matrix membranes such as Cu-BPY-HFS (Cu-4,40-bipyridine hexafluorosilicate) in Matrimid,[15] HKUST-1 in poly(sulfone),[16] MOF-5 in Matrimid,[17] and Cu-TPA (terephthalic acid) in poly(vinyl acetate)[18] have been reported. Although a high degree of MOF/polymer adhesion (as characterized by scanning electron microscopy) was found, the gas-separation performance of these membranes was not high. In addition to the control of interface morphology, the selection of appropriate MOF/polymer pairs is indispensable for high-performance mixed-matrix membranes, a fact emphasized in theoretical predictions.[19]

ZIF-90 (zeolitic imidazolate framework-90) is an attractive MOF for application in CO_2-selective mixed-matrix membranes. ZIF-90 has a sodalite cagelike structure with 0.35 nm pore windows, through which size exclusion of CH_4 from CO_2/CH_4 mixtures is possible.[20] Furthermore, the imidazole linker in ZIF-90 contains a carbonyl group, which has a favorable chemical noncovalent interaction with CO_2.[21] Submicrometer-sized crystals of a related MOF material, ZIF-8, have recently been reported.[22] So far, ZIF-90 crystals have been synthesized by the conventional solvothermal method. However, their size (ca. 100 μm) is too large for use in thin mixed-matrix membranes (which require submicrometer-sized crystals).[20] Herein, we describe the synthesis of submicrometer-sized ZIF-90 crystals by a novel method, namely nonsolvent-induced crystallization. The ZIF-90 crystals were thoroughly characterized, and we compare them with solvothermally synthesized ZIF-90. Mixed-matrix membranes were then fabricated using three poly(imide)s as polymer matrices, and their CO_2/CH_4 separation properties were investigated. In particular, we demonstrate the first MOF-containing gas-separation membranes with technologically attractive properties.

The morphology of our ZIF-90 crystals is shown in Figure 1. In general, the synthesis of smaller crystals requires reaction conditions that favor nucleation over crystal growth. Particle-size control proved difficult in conventional solvothermal synthesis. We crystallized small ZIF-90 particles at room temperature by the rapid addition of a nonsolvent to the reagent solution (see the Supporting Information), leading to supersaturation of the solution. The nucleation rate can be

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Supporting information for this article (including details on the synthesis of submicrometer-sized ZIF-90 particles, ZIF-90 characterization data, the fabrication of mixed-matrix membranes, and permeation measurements) are available on the WWW under http://dx.doi.org/10.1002/anie.201006141.

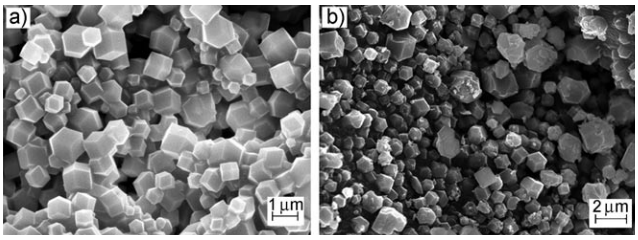

Figure 1. SEM images of submicrometer-sized ZIF-90 particles; a) ZIF-90A synthesized using methanol as a nonsolvent; b) ZIF-90B synthesized using deionized water as a nonsolvent.

thereby increased, leading to the formation of a large number of small crystals within a short reaction time (30 min). Two nonsolvents, methanol and deionized water, were used for room-temperature crystallization of ZIF-90 in DMF solvent. In both cases, well-defined crystals were prepared. The size of the ZIF-90 particles formed in the DMF/methanol mixture (ZIF-90A, Figure 1a) is (0.81 ± 0.05) µm as measured by dynamic light scattering (also see the Supporting Information). Particles with a broader size distribution [(2.00 ± 0.66) µm] were also made in a DMF/water mixture (ZIF-90B, Figure 1b). These crystals are much smaller than those made conventionally (ca. 100 µm).[20]

The high crystallinity and framework type of the synthesized particles were verified by powder X-ray diffraction (XRD) analysis (see the Supporting Information). Thermal gravimetric analysis (TGA) and temperature-programmed in situ XRD measurements showed that ZIF-90 A is stable up to 290 °C while ZIF-90B is stable up to 400 °C (see the Supporting Information). Solvothermally synthesized ZIF-90 crystals are reported to be stable up to 250 °C.[20] This may imply that our ZIF-90 crystals (especially ZIF-90B) have better framework integrity and fewer defects than the conventionally synthesized material. Other ZIF materials are known to be stable up to 400 °C as a result of the strong chemical bonds between imidazole linkers and zinc metal centers.[23] Nitrogen physisorption isotherms of our ZIF-90 particles, as well as pore volumes and BET surface areas calculated from the isotherms, are shown in the Supporting Information. The properties of solvothermally synthesized ZIF-90 are also shown. As-made ZIF-90A and ZIF-90B have high pore volumes and surface areas close to those of the purified solvothermally made material, implying that the precipitation of amorphous materials is strongly inhibited under our reaction conditions. We conclude that our method produces high-quality submicrometer-sized ZIF-90 crystals suitable for membrane fabrication.

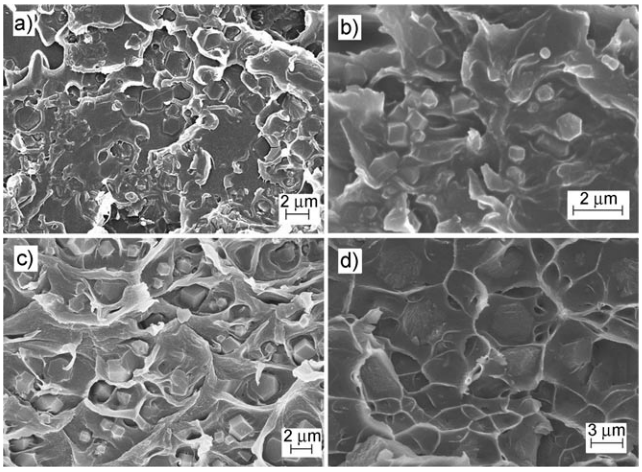

Figure 2. SEM images of cross-sections of mixed-matrix membranes containing ZIF-90 crystals; a) ZIF-90A/Ultem, b) ZIF-90A/Matrimid, c) ZIF-90A/6FDA-DAM, and d) ZIF-90B/6FDA-DAM.

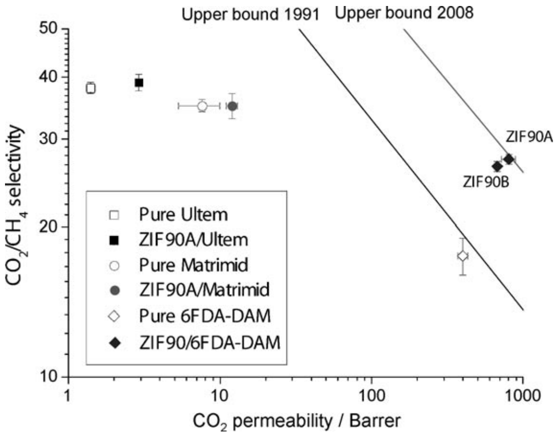

Figure 3. Gas-permeation properties of mixed-matrix membranes containing 15 wt% of ZIF-90 crystals measured with pure gases. Measurements were performed at 35 °C and 4.5 atm upstream pressure for Ultem and Matrimid membranes, and at 25 °C and 2 atm upstream pressure for 6FDA-DAM membranes. The data for pure Ultem and Matrimid are averaged values from the literature.[13b,24] The upper bounds for polymer membrane performance as defined in 1991 and 2008 are shown.

The synthesized ZIF-90 particles were used to fabricate nanocomposite membranes with three different poly(imide)s (Ultem, Matrmid, and 6FDA-DAM; see the Supporting Information). Scanning electron microscopy (SEM) images of the cross-sections of these membranes are shown in Figure 2. The ZIF-90 crystals showed excellent adhesion with the poly(imide)s without any surface-compatibilization procedures. Interfacial voids were absent, and the MOF crystals were well dispersed. Figure 3 shows the pure-component CO_2 and CH_4 gas-transport properties of mixed-matrix membranes containing 15 wt % of ZIF-90 crystals. Each type of membrane was fabricated and measured multiple times to provide reliable error estimates. Ultem and Matrimid mixed-matrix membranes showed significantly enhanced CO_2 permeability without any loss of CO_2/CH_4 selectivity (Figure 3). The lack of significant change in selectivity can be explained by the mismatch between the permeabilities of ZIF-90 (whose CO_2 permeability is estimated to be several thousand Barrer) and those of Ultem and Matrimid (1–10 Barrer, Figure 3). The Maxwell model predicts that when the gas permeability of the dispersed molecular sieve is much larger than that of the polymer matrix, there will be no enhancement in selectivity even if the dispersed molecular sieve is highly selective. The main significance of our data with these two types of mixed-matrix membranes is that the CO_2 throughput (permeability) of each membrane increased significantly (e.g., from 1.4 to 2.9 Barrer for Ultem) without any loss in CO_2/CH_4 selectivity. This clearly shows that the membranes are free of interfacial defects, which would have a pronounced adverse effect on the selectivity.

On the other hand, mixed-matrix membranes made with 6FDA-DAM (a highly permeable polymer) showed substantial enhancements in both CO_2 permeability and CO_2/CH_4 selectivity, indicating that the membrane is defect-free and that the permeabilities of the MOF and the polymer are well matched (Figure 3). Both ZIF-90A and ZIF-90B enhanced the separation significantly, but slightly better results were obtained from membranes containing smaller particles (ZIF-90A). The performance of ZIF-90/6FDA-DAM mixed-matrix membranes clearly transcends the polymer upper bound for polymeric membrane performance drawn in 1991, and reaches the technologically attractive region.

To evaluate the membrane performance under mixed-gas conditions, the CO_2/CH_4 binary mixture gas-permeation properties of both pure 6FDA-DAM and 15 wt% ZIF-90A/6FDA-DAM membranes were measured (Table 1). The enhanced gas-separation performance of the ZIF-90A/6FDA-DAM membrane is clearly seen. Interestingly, the CO_2/CH_4 mixed-gas selectivity of the ZIF-90 mixed-matrix membrane was even higher than the ideal selectivity measured by pure-component gas permeation, presumably because of the selective sorption and diffusion of CO_2 in the ZIF-90 crystals.

Table 1: Mixed-gas permeation properties of membranes at 25 °C and 2 atm total feed pressure with a 1:1 CO_2/CH_4 mixture.

Membranes	CO_2 permeability [Barrer]	CO_2/CH_4 Selectivity
pure 6FDA-DAM	390	24
15 wt% ZIF-90A/6FDA-DAM	720	37
15 wt% ZIF-90B/6FDA-DAM	590	34

The intrinsic gas-transport properties of ZIF-90 are as yet unknown. Based on the above gas-permeation results and the Maxwell model, we can estimate the CO_2 and CH_4 permeabilities of the ZIF-90 crystals at 25 °C. The CO_2 permeability of ZIF-90 was found to be approximately 8000 Barrer and the CO_2/CH_4 selectivity was approximately 250 (pure component) or 400 (binary). Based on these results, it is clear that small-pore MOFs such as ZIF-90 can be used in highly selective gas-separation membrane materials, as predicted by computational studies.[2,19]

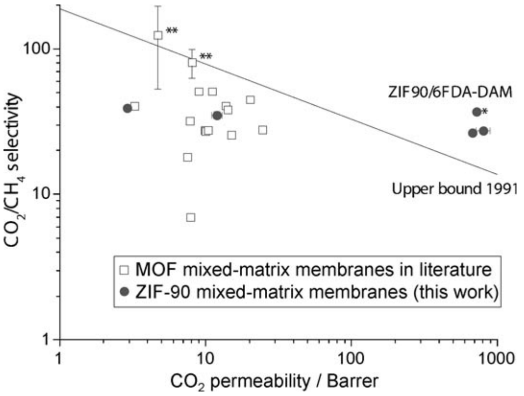

Figure 4. CO_2/CH_4 separation performance of the present ZIF-90 mixed-matrix membranes, compared with the compiled data on MOF-containing mixed-matrix membranes.[15–18,25] Data marked by * is based upon our mixed-gas permeation measurements. Data from previous work marked with ** carries a large error bar owing to inaccuracy in measuring low permeabilities.[25] The upper bound for polymer performance as defined in 1991 is shown.

In Figure 4, we compare our results with a compilation of results from other MOF-containing mixed-matrix membranes previously reported. As expected, the performances of ZIF-90 membranes with Ultem and Matrimid are located in the same region as other MOF mixed-matrix membranes. This region is considered technologically unattractive because of the low permeability. In contrast, our ZIF-90/6FDA-DAM membranes clearly transcend the trade-off between permeability and selectivity observed in previous work. Specifically, our ZIF-90/6FDA-DAM membranes showed much higher CO_2 permeability (> 700 Barrer) than any other MOF-based mixed-matrix membrane, combined with a good CO_2/CH_4 mixed-gas selectivity of 37. Recently, Merkel et al.[26] emphasized that ultrahigh membrane selectivity is not of primary concern for many large-scale gas separations, for example, CO_2 capture from flue gases or natural gas. This is because the downstream concentration of the more permeable component plateaus as the selectivity continues to increase. A membrane with very high permeability and good selectivity may be more industrially attractive. For example, the data in Table 1 for the ZIF-90 A/6FDA-DAM membrane, when extrapolated to a 1-micrometer-thick membrane on a hollow fiber platform, yields 720 gas-permeation units (GPUs) of CO_2 permeance at a selectivity of about 37, whereas commercial membranes achieve a CO_2 permeance of approximately 100 GPU and selectivity of about 15. Furthermore, a pure-component permeation measurement for N_2 on the ZIF-90 A/6FDA-DAM membrane (at 25 °C and 2 atm upstream pressure) showed an ideal CO_2/N_2 selectivity of 22 as compared to 14 for pure 6FDA-DAM. This result indicates that the present membranes are also promising for the separation of CO_2 from flue gases. The transport properties of rigid glassy polymers such as 6FDA-DAM are affected by annealing below the glass transition temperature. Nevertheless, since the same temperature of 230 °C was used to anneal both the pure and ZIF-containing membranes, the enhancements shown are unambiguous.

In summary, we have fabricated a high-performance gas-separation membrane containing a MOF material. We first synthesized ZIF-90 crystals with submicrometer and 2 μm sizes by a nonsolvent-induced crystallization technique. Characterization by XRD, TGA, and nitrogen physisorption revealed that the ZIF-90 crystals have high crystallinity, microporosity, and thermal stability. The ZIF-90 particles showed good adhesion with polymers in mixed-matrix membranes without any interface compatibilization procedures. We have demonstrated that membranes containing

ZIF-90, specifically ZIF-90/6FDA-DAM membranes, have unprecedented high performance for CO_2/CH_4 separation and promising CO_2/N_2 separation properties. To obtain such a performance enhancement and enable scale-down of the membrane thickness, a highly selective MOF must be used in the form of submicrometer-sized crystals, and moreover it must be matched with a highly permeable polymer.

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