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A method for increasing permeability in O₂/N₂ separation with mixed-matrix membranes made of water-stable MIL-101 and polysulfone†**Harold B. Tanh Jeazet,^a Claudia Staudt^{*b} and Christoph Janiak^{*a}***Received 25th October 2011, Accepted 23rd December 2011*

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Water-stable MIL-101 microcrystals adhere well to polysulfone (PSF) and yield a very robust mixed-matrix MIL-101-PSF membrane for the O₂/N₂ separation with a selectivity of 5–6 and an unsurpassed O₂ permeability increase by a factor of four to above 6 barrer for MIL-101 loadings of 24%.

For the separation of mixtures which occur in nearly all production processes in the chemical industry, membrane processes can be used as an economically friendly and energy saving method. Compared to conventional separation facilities where distillation, extraction or adsorption processes are applied, membrane based devices are much smaller and can be processed at lower temperatures. As a result, energy savings of up to 50% of the production costs can be reached by application of this technology.¹ Currently the worldwide membrane market has a steady growth of approximately 10–15% each year.² Separation processes applied in an industrial scale are natural gas treatment (removal of CO₂), hydrogen isolation and recovery, oxygen enrichment from air (medical devices) and nitrogen enrichment from air (used as protecting atmosphere for oxygen sensitive compounds).³ Other membrane based processes with fast growing market relevance are vapor recovery systems,⁴ monomer recovery units, *e.g.* ethylene/N₂ or propylene/N₂,^{5,6} the dehydration of organic solvents and the removal of polar low molecular weight components in equilibrium reactions.⁷ Of high interest would be pre- or oxyfuel combustion O₂/N₂ separation processes so that coal-fired power plants can be fed with (almost) pure oxygen to yield only CO₂/water which is easier to separate than CO₂/N₂ in a post-combustion CO₂ capture.⁸ Currently a major part of the commercially applied membrane materials are polymers. Compared to inorganic materials they are cheap to produce and easy to process as flat sheet or hollow fiber membranes.

However inorganic materials such as zeolites offer certain advantages over polymers with regard to their high permeability

and selectivity due to their specific pores and high porosity. A combination of both materials leads to new membranes which are called mixed-matrix membranes (MMMs). The first MMMs were prepared in the 1980s and have been increasingly investigated in recent years.⁹ Separation properties obtainable with MMMs can be far above the Robeson “permeability *versus* selectivity” upper bond provided for most of the industrial relevant mixtures.¹⁰ As filler materials different types of inorganic additives, impermeable and permeable ones, can be used. However the permeability is reduced in most cases, which is an undesirable effect. The economics of membrane processes is mainly determined by selectivity and permeability. With low selectivity the separation processes have to be multi-step, which translates into higher operative complexity and costs. The permeability decides which membrane area or how many membrane modules are needed to realize the separation process. Membranes with a high permeability are needed for large-volume gas feed streams as in natural gas treatments or for pre-combustion O₂/N₂ separation.

If porous inorganic additives, *e.g.*, zeolites or metal organic frameworks (MOFs) could be applied with a pore diameter larger than the kinetic diameter of one gas component but smaller than the other one, a strong improvement of permeability would be expected, which is economically very attractive for large scale applications if the selectivity does not change. Thereby MOFs are highly promising additives since they offer various advantages over zeolites.^{11–15} For example, ligands with a broad variety of functionalities are possible which enable MOFs to interact very strongly with the polymer bulk material so that the formation of micro gaps between inorganic and organic phase, which often cause losses in selectivity, can be avoided. For the preparation of MMMs a perfect interaction between the two components is extremely important in order to obtain materials with optimized separation properties. Furthermore MOFs are not only tuneable concerning their chemical groups, but also for their pore volume and surface area.¹⁶

Different from the studies of continuous (pure) MOF membranes^{12,14,17} or studies of MOFs for selective gas adsorption (capture)¹⁸ we present here results on the O₂/N₂-separation with a MMM of 3D- $\{[\text{Cr}_3(\text{O})(\text{BDC})_3(\text{F},\text{OH})(\text{H}_2\text{O})_2] \cdot \sim 25\text{H}_2\text{O}\}$, BDC = benzene-1,4-dicarboxylate (terephthalate), MIL-101¹⁹ with polysulfone (PSF) (Fig. 1). Although it has been shown in the last few years that several MOFs are extremely interesting for the

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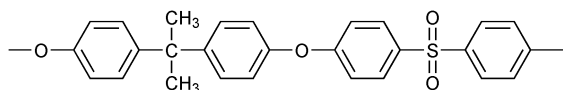


Fig. 1 Polysulfone repeating unit.

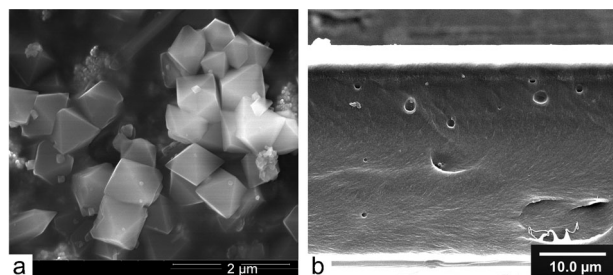


Fig. 2 SEM images (a) of MIL-101 microcrystals and (b) of the cross-section of the pure polysulfone (PSF) membrane.

fabrication of MMMs with very attractive separation characteristics (see ESI† for some specific examples), so far no discussion has been started on the long term stability of these additives. The hydrothermal stability of MOFs is a key and often overlooked issue for their potential applications in gas storage and separation. MOF-5 and the IRMOF-series have a low moisture stability, and HKUST-1 ($\text{Cu}_3(\text{BTC})_2$) is intermediate but eventually decomposes.²⁰ The MIL compounds, including MIL-101²¹ and ZIF-8, are of high water stability.^{22,23} In industrial gas separation processes moisture is a major concern and it is economically not feasible to use completely dry feed gas streams in order to prevent the membrane from degradation. Therefore in this work hydrolytically stable MOF materials were investigated as additives for the preparation of mixed-matrix membrane materials.

MIL-101 was synthesized according to the previously reported procedure and washing cycles (see ESI†).¹⁹ The synthesized MIL-101 particles (Fig. 2a) were used to fabricate membranes with the commercial polymer polysulfone (PSF) (see ESI†). Scanning electron microscopy (SEM) images of cross-sections of the pure polymer membrane and of the fabricated MMMs are depicted in Fig. 2b and 3, respectively. The MIL-101 crystals showed excellent adhesion with the polymer matrix as the membrane cross-section morphology reveals the formation of circular cavities and polymer veins (elongated matrix segments) with increased plastic deformation of the polymer (Fig. 3). Interfacial voids were absent, and the MOF particles were homogeneously distributed in the polysulfone matrix. Good dispersion and contact can be easily achieved as shown in Fig. 3a and b. Particle aggregation becomes obvious at the 24% loading (Fig. 3c). The MMMs remain flexible even at 24% loading.

Results of O_2 and N_2 gas permeation and separation experiments with MIL-101-polysulfone membranes are shown in Fig. 4 and 5 (Table S1 and S2 in ESI†). The experiments were made on mixed-matrix membranes containing 8, 16 and 24 wt% of MIL-101 particles. Each type of membrane was fabricated and measured three times to provide reliable error estimates. The permeation measurements were conducted over 48 h at each point without showing any change in performance or membrane degradation.

Gas-transport properties were also evaluated on mixed-matrix membranes containing 8 wt% loads of four selected known MOFs (Table S1 and Fig. S1 in ESI†) and we observed much

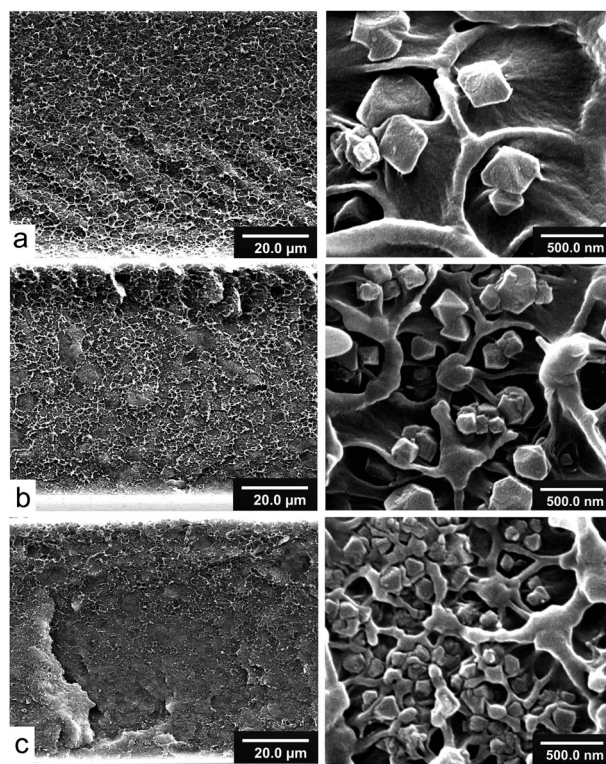


Fig. 3 SEM cross-sections of MIL-101-PSF membranes based on 400 mg of PSF with different loadings of MIL-101: (a) 8 wt% ($d = 55 \mu\text{m}$), (b) 16 wt% ($d = 59 \mu\text{m}$) and (c) 24 wt% ($d = 60 \mu\text{m}$); d is the average membrane thickness.

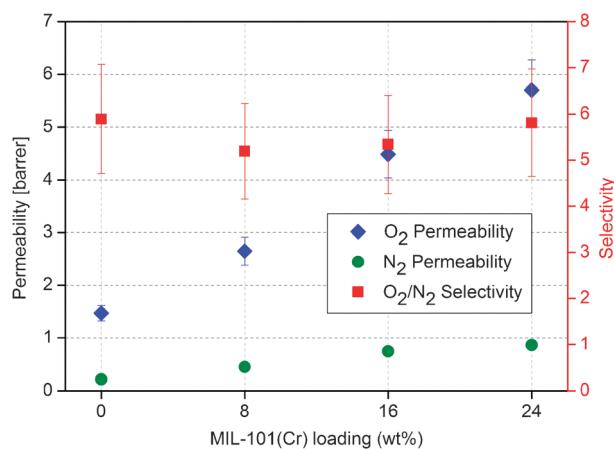


Fig. 4 O_2/N_2 permeability and separation performance of pure PSF and MIL-101-PSF membranes with different MIL wt% loadings (averaged values for different membrane thicknesses, cf. Table S2 (ESI†)).

higher O_2 permeability (> 2.5 barrer) with the MIL-101 membrane already at 8 wt% loads than with the other MOF-based membranes. This difference in permeability is due in part to different particle sizes of the MOF materials. Membrane defects and interfacial voids can be observed in the case of low performance MMMs (Fig. S2 in ESI†).

The experiments showed that the permeability of both gases increased with MIL-101 loading. At 24 wt% loading, the permeability of the membrane increased almost four times with respect to the pure polymer tested under the same conditions.

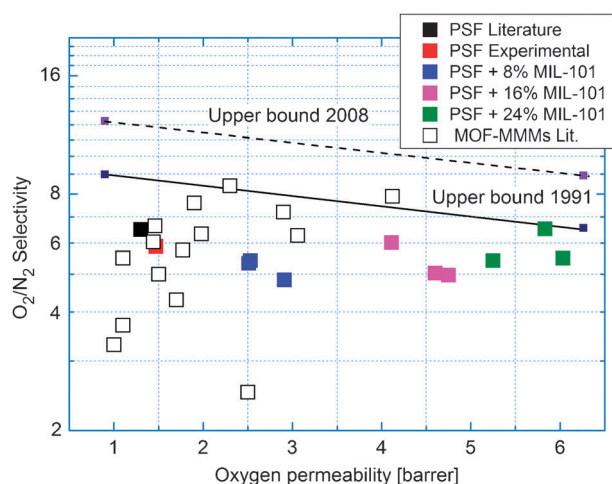


Fig. 5 Comparison of O_2/N_2 separation performance of MIL-101-PSF with other MOF-containing mixed-matrix membranes from literature data (for further details on MOF-MMM data points see Fig. S3 in ESI†).²⁸ The Robeson upper bounds for polymer separation performance as defined in 1991²⁴ and 2008¹⁰ are shown.

The O_2/N_2 selectivities do not show significant change but approximate the upper bound established by Robeson in 1991 (Fig. 5).²⁴

The essentially unchanged O_2/N_2 selectivity is consistent with literature results where permeability enhancements for MOF-MMMs could be found, but selectivity enhancements were less pronounced.²⁵ According to the Maxwell model,²⁶ even a strong increase in selectivity of the filler component would not result in appreciable gains in selectivity of the composite material.¹⁵ The inorganic filler can introduce an extra pore network but can also increase the intersegmental (d-)spacing between two polymer chains of the membranes. Increased polymer chain mobility facilitates diffusion of the gases (without affecting the selectivity).²⁷

The significant increase of O_2 and N_2 permeability of the MIL-101-PSF membranes without any loss in O_2/N_2 selectivity shows that the membranes are free of interfacial defects, which would have a pronounced opposite effect on the selectivity. Also, the presence of some agglomeration of the MIL-101 particles in the polymer at 24 wt% loading does not alter these properties.

In Fig. 5, we compare our results with results from other MOF-containing mixed-matrix membranes. The PSF-MIL-101 membranes clearly show much higher O_2 permeabilities (>4 barrer) than any other MOF-MMMs (see Table S3 and Fig. S3 in ESI† for details and references of other MOF-MMMs).

In summary, we have shown that MMMs containing the water-stable MIL-101 exhibited remarkable four-fold increase in the permeability of O_2 to technically needed values above 6 barrer, thereby keeping the high PSF selectivity for O_2 over N_2 of 5–6. High loads could be achieved with the MIL-101 particles showing very good adhesion with polysulfone in the mixed-matrix membranes and excellent long term stability. Yet, more work is needed for MOF-MMMs on the elucidation of transport mechanisms and selectivity properties and the roles of loading, geometry, pore size and nature of the molecular interactions on preferential adsorption.¹²

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