Novel MOF-Membrane for Molecular Sieving Predicted by IR-Diffusion Studies and Molecular Modeling

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Metal-organic frameworks (MOFs) are new microporous materials, which might revolutionize gas separation as molecular sieve membranes.[1–3] The framework structure of these organic-inorganic coordination compounds is constructed of metal cations or clusters bridged by anionic organic linker molecules. Pore size and adsorption affinities can be altered by functionalizing the linker molecule, which is why MOFs are recommended as material for molecular sieving. From 1978 to 2010, the number of MOFs has grown exponentially,[4] so that there is an extensive reservoir of new promising microporous membrane materials. However, MOF membrane preparation is usually associated with a high preparation effort and (possibly) high cost for rare linker molecules, while the separation performance is highly uncertain. One of the most important criteria for a molecular sieve membrane with reasonable performance is selectivity above the Knudsen separation. The Knudsen constant of a gas mixture is defined as the ratio of the reciprocal square root of the molar masses. Often pinholes and cracks of membranes as well as poorly performing microporous materials show this type of selectivity. Even though there have been increasing attempts to develop MOF-based molecular sieve membranes,[5–10] only in recent publications membranes are reported, which perform better than the Knudsen separation.[11–15] In view of the cost of development and the uncertainty of the performance of new MOFs, a computer-based screening and pre-selection method is desired.

Currently, there are several groups researching methods to predict selectivity of MOF membranes by theoretical approaches.[16] Recently, in a pioneering work, Sholl et al. published a calculational screening method to estimate the H_2 / CH_4 separation performance of several hundred MOF membranes.[17] Their predictions agree remarkably well with permeation measurements of a MOF-5 membrane[9,10] with pore apertures of 8 Å[1] which is larger than the kinetic diameter of CH_4 (3.8 Å). In contrast, recent measurements on narrow-pore ZIF-7 and ZIF-8 membranes[18–20] show huge discrepancies with the predictions assuming rigid pore apertures.

As recently demonstrated, the permeation selectivity of a membrane can be estimated from the product of adsorption selectivity and diffusion selectivity.[21] However, the experimental determination of gas mixture diffusivity and adsorption is still a great challenge. In consequence of the loading dependency of the diffusivity from guest–guest and guest–framework interactions, predictions by models based on pure species gas data can deviate from the gas mixture experiment. Hence, in this work we combine experimental measurements by IR microscopy (IRM) with theoretical studies by grand canonical Monte Carlo simulations (GCMC)[22–24] to determine adsorption and diffusion data on ZIF-8. From these studies, we estimate the permeation selectivity of a ZIF-8 membrane as product of adsorption and diffusion selectivities and correlate the results with permeation data. As a member of the thermally and chemically stable family of zeolitic imidazolate frameworks (ZIFs),[25] ZIF-8[26–28] fulfills the basic stability requirement as membrane material. ZIF-8 crystallizes in a cubic sodalite type topology, where the large β-cages are connected by 6-membered ring windows. The sizes of the β-cages and the connecting 6-membered ring windows were estimated from XRD analysis to be 11.6 Å and 3.4 Å respectively.[26] ZIF-8 is not only a promising membrane candidate, but also represents an appropriate model system for our adsorption and diffusion studies due to the simple, isotropic pore network. Aiming towards refining of natural gas, in this work we focus on separation of CO_2 (kinetic diameter 3.3 Å) from CH_4 (kinetic diameter 3.8 Å) in a binary, equimolar gas mixture.

GCMC simulations were performed for simulating the CH_4 and CO_2 adsorption equilibrium of pure compound gases and the equimolar binary mixture in ZIF-8 for different temperatures and pressures (see Supporting Information, Section S1). From these data, pure compound, and gas mixture sorption isotherms were obtained.

By employing time and space resolved IRM,[29] we measured the sorption uptake/desorption of CO_2/CH_4 as a function of the partial pressures on large ZIF-8 single crystals, which were grown by a similar synthesis conditions as for the membrane preparation (Figure S2–1 in the Supporting Information). The GCMC studies were used to convert the IR adsorption data from arbitrary to absolute units. From the instationary sorption uptake/desorption profiles obtained by IRM, diffusion coefficients were determined by solving Fick's second law for the boundary conditions. For details of the method, see Supporting Information, Section S2.

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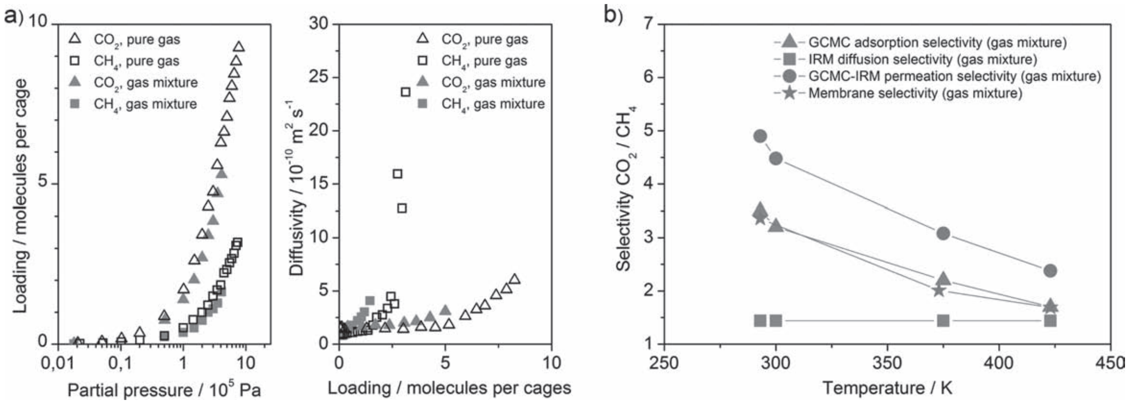

Figure 1. a) GCMC-IRM adsorption and diffusion results on ZIF-8 at room temperature. b) From GCMC-IRM studies estimated CO_2/CH_4 adsorption and diffusion selectivities as well as the mixture permeation selectivities of the ZIF-8 membrane shown in Figure 2a.

Figure 1a shows GCMC-IRM sorption isotherms and diffusivities for room temperature. The measured and simulated gas mixture sorption isotherms are in good agreement with the ideal adsorbed solution theory (IAST, Figure S2–4 in the Supporting Information). The IRM sorption studies also indicate a flexible nature of ZIF pore apertures, since CH_4 is adsorbed despite a kinetic diameter larger than the estimated crystallographic pore aperture size. Rather unexpected is the behavior of the diffusivity, since both the pure component and gas mixture diffusivities of CH_4 increase sharply with increasing loading, in contrast to CO_2. Even with respect to the flexible pore apertures, a moderate energy barrier for a large molecule passing the pore window and, hence, a diffusion hindrance would be expected. The diffusion behavior of CH_4 might be correlated to its preferred localized adsorption near the pore apertures, as shown by GCMC in the Supporting Information, Section 1.4.

From the adsorption and diffusion data, the adsorption and diffusion selectivities have been calculated. Since for increasing partial pressures/loadings (i) the adsorption of CO_2 is favored over that of CH_4, and (ii) the diffusion for CH_4 exceeds that of CO_2, both selectivities behave contrarily (Figure S2–3 in the Supporting Information). The CO_2/CH_4 permeation selectivity of a ZIF-8 membrane, as product of adsorption and diffusion selectivity, is predicted to be 4.9 from an equimolar gas mixture at 1×10^5 Pa partial pressure difference at room temperature (Figure 1b). In contrary, a Knudsen mechanism would predict an opposed permeation selectivity of CH_4 above CO_2 of about 1.7.

For validating the predictions from GCMC-IRM, we measured the temperature dependent permeation of pure CO_2 and CH_4 gases and as mixture through a ZIF-8 membrane (for detailed preparation method, see Supporting Information, Section 3). An SEM image of the cross section of the continuous ZIF-8 layer on top of the titania support is shown in **Figure 2a**. The measurements were carried out by the Wicke–Kallenbach technique (Figure S3–2 in the Supporting Information) for 1×10^5 Pa partial pressure difference. From the permeances (Figure 2b, left axis), pure and mixture gas selectivities (Figure 2b right axis) were calculated for different temperatures (see Supporting Information S3).

Both the CO_2/CH_4 pure and mixture gas selectivities at room temperature are about 3.5 and hence anti-Knudsen as predicted from GCMC-IRM studies. Although the predictions are based on a simple model, and the IRM data were obtained under ideal conditions on single crystals, the selectivity derived from the model is remarkably close to the selectivity of the ZIF-8 membrane (Figure 1b). For elevated temperatures, GCMC adsorption selectivity and membrane selectivity show almost coinciding trends. It is concluded that, therefore, permeation on the ZIF-8 membrane is adsorption controlled rather than diffusion controlled. In a good approximation the diffusion selectivity can be assumed constant over the narrow temperature range under study.

The slight overestimation of the GCMC-IRM permeation selectivity in respect to the membrane measurements can be explained by the non-ideal structure of the ZIF-8 membrane. In contrast to single crystals, the membrane layer is polycrystalline, where grain boundaries might contribute to an unknown mass transport.

In conclusion, we applied a combination of a theoretical (GCMC) and an experimental (IRM) method to estimate the CO_2/CH_4 permeation selectivity of a ZIF-8 molecular sieve membrane. The results fit the experimentally measured permeation selectivities of a recently developed ZIF-8 membrane remarkably well. As shown both in earlier works[16,17] and this works, it is generally possible to predict the membrane selectivity,

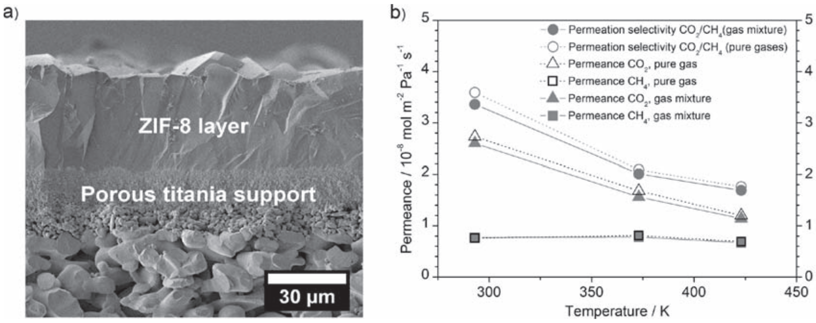

Figure 2. a) SEM image of the cross-section of the ZIF-8 membrane. b) Measured permeances of CO_2 and CH_4 as pure components and from their binary mixture as well as ideal and mixture permeation selectivities as a function of temperature.

either by experimental or theoretical approaches and, hence, screen porous materials for membrane applications, thus saving time and effort in R&D. Although there are similarities with other porous materials like zeolites, MOFs show unique features and behaviors. Although the pore aperture of ZIF-8 is estimated to be smaller than the diameter of CH_4, the larger molecule can pass through. A sharp molecular sieve separation is neither predicted from GCMC-IRM diffusivity data nor observed in the membrane permeation measurements. This findings might indicate the pore apertures are rather flexible than rigid. In consequence, models assuming rigid pores might show only limited accuracy in MOF membrane screening and, hence, should be evolved to take flexibility into consideration.

Experimental Section

Membrane synthesis and permeation measurements: A porous titania support was used in a microwave assisted solvothermal reaction of 2-methylimidazole (0.975 g), sodium formate (0.538 g) and zinc chloride (0.808 g) in methanol (80 ml). After 4 h at 100 °C, a dense layer of ZIF-8 formed on the surface. For detection in gas permeation experiments a HP Agilent 6890N gas chromatograph was used.

Infrared microscopy: The IR micro-imaging device used in this study consists of a spectrometer (Bruker Vertex 80 v) attached to an IR microscope (Bruker Hyperion 3000) equipped with a Focal Plane Array (FPA) detector. For measurements, several selected crystals were placed in an IR cell with IR transparent CaF_2 windows.

Grand Canonical Monte Carlo Simulations: The GCMC simulations were performed using the BIGMAC code developed by T.J.H. Vlugt (see Supporting Information, Section S2, Refs. [21–24]) as basis. The code was modified to handle rigid molecular structures and charges.

Scanning electron microscopy: The SEM image of the membrane cross section (Figure 2a) was taken on a JEOL JSM-6700F at 1 kV accelerating voltage, 5 µA current and a working distance of 15 mm.

Supporting Information

Detailed methods descriptions are available in Supporting Information. Supporting Information is available from the Wiley Online Library or from the author.

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