Supporting information to:

Modelling Permeation of CO$_2$/CH$_4$, N$_2$/CH$_4$ and CO$_2$/Air Mixtures Across a DD3R Zeolite Membrane.

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1 Introduction
In this supporting information more detailed results are presented to support the main paper. Particular emphasis is on a detailed study on the influence and modelling of the support effects, defect characterization and the influence of concentration polarization effects. Moreover, several aspects related to single component and mixture adsorption modelling are evaluated.

2 Experimental: Support permeation experiments
In this study an asymmetric disc-shaped zeolite membrane has been used that consists of a thin zeolite layer on top of a macro-porous $\alpha$-alumina support. To determine the influence of the support on the composite membrane permeation properties, permeation measurements with a bare support have been carried out. The support is supplied by NGK insulators and has a reported pore size of 600 nm, a thickness of 1.5 mm and a diameter of 18.5 mm. The support was sealed by a custom made silicon o-ring leaving a 12.5 mm free diameter and a membrane area of $1.23 \times 10^{-4} \text{m}^2$ available for permeation. The permeance of $\text{H}_2$, $\text{CO}_2$, $\text{N}_2$, $\text{He}$ and $\text{CH}_4$ were determined in pressure drop operation (no sweep gas). The temperature was varied between 303 and 373 K. The feed pressure was varied between 110 and 150 kPa, the permeate pressure was always at atmospheric pressure. The feed flow rate was set to 100 ml min$^{-1}$ (STP), the permeate flow was measured by a bubble flow meter.

3 Results
3.1 Support effects
To isolate the influence of the membrane support on the flux through the composite membrane permeation experiments through a bare support have been performed. The main objective of these measurements is to obtain an accurate description of the mass transport through the support. For the description of mass transport in the macro-porous support the so-called Binary Friction Model (BFM) is applied [1]. A single component flux ($N_i$) through the macro-porous support can be represented as:

$$N = -\frac{1}{RT} \frac{\varepsilon}{\tau} \left( D_{Kn} + \frac{B_0 \bar{p}}{\eta} \right) \frac{\Delta p}{\delta_{supp}},$$

where $\eta$ is the viscosity, $\delta_{supp}$ the support thickness, $D_{Kn}^{eff}$ the effective Knudsen diffusivity, $B_0^{eff}$ the effective permeability, $R$ the gas constant, $T$ the temperature and $p$ the pressure. The effective Knudsen diffusivity and effective permeability (for cylindrical pores) are defined as:
\[
D_{Kn,j}^{\text{eff}} = \frac{d_0}{3} \sqrt[3]{\frac{8RT}{\pi M_i}}, \quad B_0^{\text{eff}} = \frac{d_0^2}{32}.
\]  

Equations (1) and (2) can be cast into the form \( y = ax + b \) to estimate the ratio of the support porosity and tortuosity:

\[
\frac{N_{RT}}{\Delta p} \frac{\bar{p}}{v_m} = \frac{\varepsilon}{\tau} \frac{d_0}{3\delta_{supp}} + \frac{\varepsilon}{32\delta_{supp}} \frac{d_0^2}{\eta v_m}, \quad v_m = \sqrt[3]{\frac{8RT}{\pi M}}.
\]  

A plot of \(-NRT\Delta p^{-1}v_m^{-1}\) versus \(p_{avg}^{-1}\eta v_m^{-1}\) is presented in Figure 1. This plot is based on permeation experiments of He, H\(_2\), CO\(_2\), N\(_2\) and CH\(_4\) through the bare support in a temperature range of 303 to 373 K. A good correlation between the model and experiments is obtained. Given the pore size (600 nm) and thickness (1.5 mm) of the support the \(\varepsilon\tau^{-1}\)-factor can be estimated independently from the tangent and the intercept with the \(y\)-axis of the curve. Both lead to a \(\varepsilon\tau^{-1}\) value of 0.11.

![Figure 1](image_url)

**Figure 1.** Correlation of permeation measurements of He, H\(_2\), CH\(_4\), CO\(_2\) and N\(_2\) through an \(\alpha\)-alumina support to the support pore size \((d_0)\), tortuosity \(\tau\) and porosity \(\varepsilon\). The properties listed on the x- and y-axis are based on a rearrangement of a mathematical description of a mass transport mechanism that involves Knudsen diffusion and viscous flow as presented in the text (Eq. (1)).

In all modelling results the support effects are accounted for. Mass transport through the macro-porous support is modelled by the Binary Friction Model (BFM) developed by Kerkhof [1]. The BFM is a Maxwell-Stefan type model which accounts for friction between...
the molecules and the wall by viscous forces and Knudsen type friction and impulse exchange between the different species.

The base equation to start from is:

\[
\frac{\tau}{\varepsilon} \nabla p_i = RT \cdot \sum_{j=1}^{n} \phi_j \left( x_i N_j - x_j N_i \right) \frac{D_{ij}}{D_j} - f_{im}RT \cdot N_i
\]  

(4)

where the wall friction factor \((f_{im})\) can be represented as:

\[
f_{im} = \left( D_{Kn} + \frac{B_0}{\kappa_i} \right)^{-1}.
\]  

(5)

Note that \((\varepsilon / \tau)^{-1}\) is added to the left hand side of Eq. (4) to account for the effectiveness of the diffusivities and permeability. The definitions of the Knudsen diffusivity \((D_{Kn})\) and permeability \((B_0)\) have been presented in Eq. (2). \(\kappa_i\) is based on the pure component viscosities \(\eta_i\), total pressure, molar fractions \((x_j)\) and the interaction parameter \(\xi_{ij}\):

\[
\kappa_i = \frac{1}{p_{tot}} \sum_{j=1}^{n} x_j \xi_{ij}.
\]

(6)

\(\xi_{ij}\) can be estimated as proposed by Wilke [2]:

\[
\xi_{ij} = \left[ 1 + \left( \frac{\eta_i}{\eta_j} \right)^{1/2} \left( \frac{M_i}{M_j} \right)^{1/4} \right]^{1/2} \left[ 8 \left[ 1 + \frac{M_i}{M_j} \right] \right]^{1/2}.
\]

(7)

The exchange diffusivity \((D_{ij})\) is estimated using the method of Fuller et al. [3]:

\[
D_{ij} = \frac{10^{-7} T^{1.75} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2}}{p_{tot} \left( \left[ \sum v_i \right]^{1/3} + \left[ \sum v_j \right]^{1/3} \right)^2}
\]

(8)

The summation of the atomic diffusion volumes \((v)\) leads to the molar diffusion volume. The correction factor for diffusion in the transition region \((\phi_j)\) is assumed to be a function of the ratio of some averaged mean free path \((\lambda_{ij})\) and the pore radius \((r_0)\):

\[
\lambda_{ij} = \frac{kT}{\sqrt{2 \pi \sigma_{ij}^2 p_{tot}}}
\]

(9)

where \(\sigma_{ij}\) is an averaged collision diameter of components \(i\) and \(j\). The collision diameters of \(\text{CO}_2\), \(\text{N}_2\) and \(\text{CH}_4\) are 0.394, 0.38 and 0.376 nm, respectively. At the highest \(T (373 \text{ K})\) and the
lowest $p$ (101.3 kPa) the mean free path is the longest. At these conditions the Knudsen numbers ($d_o/\lambda$) are 5.6, 6.7 and 7.5 for CO$_2$, N$_2$ and CH$_4$, respectively. Therefore it is assumed that $\phi_0 = 1$.

The support plays relatively a minor role in the permeation results. The relative transport resistance contribution of the support is illustrated by the percentage of the partial pressure drop over the support of the total pressure drop over the composite membrane. This percentage is the highest in case of CO$_2$ and ranges from 7% at low temperature up to 1% at 373 K due to the different transport mechanisms in the zeolite and support layer. The negative apparent activation energy for diffusion in the zeolite layer increases the transport resistance in the zeolite layer with temperature compared to the support layer where a combination of viscous flow, Knudsen diffusion and gaseous diffusion occurs. For N$_2$ and CH$_4$ the pressure drop over the support compared to the pressure drop over the total membrane is always below 0.4 and 0.01 %, respectively.

### 3.2 Defect flow

To assess the quality of the membrane, isobutane permeation experiments have been performed. Isobutane is too large to fit into the DDR pores and can only pass through the membrane defects. Figure 2 shows the isobutane permeance at 303 and 373 K as a function of the feed pressure. A very low permeance ($\sim 5 \cdot 10^{-12}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$) is found which demonstrates the excellent quality of the membrane. The permeance is not significantly dependent on the feed pressure. This excludes a significant contribution of viscous flow. Assuming that the permeation mechanism is purely Knudsen flow leads to an acceptable description of the permeance represented by the lines in Figure 2.

The molar mass dependency of the Knudsen diffusion (cf. Eq. (2)) leads to an expected defect flow of about 0.7, 1.1 and $1.9 \cdot 10^{-11}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ at 303 K for CO$_2$, N$_2$ and CH$_4$, respectively. In case of CH$_4$ the defect flux is accounted for in the single component and mixture modelling.
Figure 2. Isobutane permeance through the DD3R membrane at 303 and 373 K as a function of the feed pressure. He is used as sweep gas; permeance pressure 101 kPa. Lines represent modeling results assuming purely Knudsen flow through defects.

3.3 Concentration polarization

Concentration polarization effects can have a large influence on the permeation results, particularly when the flux through the membrane and the selectivity are high. These conditions are most likely met in case of the CO$_2$/CH$_4$ mixture permeation data through the DD3R membrane. Since the CO$_2$/CH$_4$ selectivity is very high ($\geq$ 100) the CO$_2$ partial pressure at the surface of the membrane could be much lower than its concentration in the bulk if concentration polarization effects play a role. For CH$_4$ the opposite would be true. Increasing the total feed flow rate can reduce the boundary layer thickness and consequently the mass transport resistance in this layer which can lead to an increased CO$_2$ and a decreased CH$_4$ flux at increased feed flow rate.

To investigate these effects the total feed flow rate of an equimolar CO$_2$/CH$_4$ mixture is increased from 100 to 500 ml min$^{-1}$ (STP). This has been done for two situations: 1) 10 bar total feed pressure and 303 K and 2) 2 bar total feed pressure and 233 K. The first case represents a situation with a high CO$_2$ flux and high selectivity, the second case represents a situation with a very high selectivity and a somewhat lower CO$_2$ flux. It is good to realize at this point that in the membrane module both the feed and the sweep gases are fed perpendicular onto the centre of the disc-shaped membrane. In both cases the effect of the increase of the feed flow rate are very low. The CO$_2$ permeance increases with only 3 % in case 1 and remained constant in case 2. CH$_4$ is a poor indicator due to its very low
concentrations at the permeate side. But no changes larger than 10 % have been observed. It can be concluded that concentration polarization effects play no significant role in the current study.

3.4 He sweep gas effects

All membrane permeation experiments have been carried out with He as sweep gas. The back-permeance of He could have an influence on the feed gas membrane permeance [4]. The feed gas permeance could be reduced due to correlation ('friction') effects of the He molecules with the feed gas molecules in the zeolite crystal layer or in the macro-porous support. Earlier permeation study through the same DD3R membrane pointed out that intra-crystalline correlation effects appear to be almost absent in most cases [5]. This appears to be a typical property of small-pore cage-like zeolites [6], which can be understood by realizing that transport seems to be controlled by relatively weak adsorbing window sites [7]. Correlations between different species only become apparent at a significant occupancy. Therefore, intra-crystalline correlation effects of the very weakly adsorbing He are neglected in the modelling work.

The effect of the He back-permeance on the feed gas fluxes through the support is investigated by a modelling study. Mass transport is modelled by the BFM [1] described above. The permeate compositions have been determined experimentally and the BFM is used to calculate the partial pressures at the interface of the support and the zeolite top layer. The porosity and tortuosity of the support have been determined in section 3.1. Figure 3 shows the estimated partial pressure at the support-membrane interface as a function of the He back-permeance. Data are presented for the single component permeation of CO$_2$ and CH$_4$ at 303 K and 1000 kPa feed pressure. The curves in Figure 3 are representative for all studied conditions in this work. The influence of the He flux becomes significant when its flux is higher than $10^{-2}$ mol m$^{-2}$ s$^{-1}$. The effect on the normalized partial pressure is the same for a component with a high flux (CO$_2$, $N = 4.0 \times 10^{-2}$ mol m$^{-2}$ s$^{-1}$) as for a component with a very low flux (CH$_4$, $N = 1.2 \times 10^{-4}$ mol m$^{-2}$ s$^{-1}$). The effect of the He at high back-permeances on the feed gas partial pressure at the zeolite layer-support interface is not via the exchange diffusivity $D_{ij}$. To facilitate the high He back-permeance a sub-atmospheric total pressure is found at the interface. The total pressure gradient over the support that is now created needs to be compensated by an increased opposing partial pressure gradient of the feed gases. Hence, the feed gas partial pressure at the interface increases.
The He back-permeance was not determined in all experiments. However, the highest back-permeance measured is about $10^{-3}$ mol m$^{-2}$ s$^{-1}$. This value was measured using 101 kPa Ne as feed gas and 101 kPa He as sweep gas at 303 K [5]. Therefore, a stagnant He layer is assumed in all simulations.

![Figure 3](image-url)

*Figure 3. Influence of the He back-permeance on the estimated partial pressure at the support-membrane interface. The partial pressure is normalized to the situation with no back-permeance of He. Data are based on the extreme case (high fluxes) for the single component membrane permeation data of CO$_2$ and CH$_4$ at 303 K and 1000 kPa feed pressure. Helium is used as sweep gas at 101 kPa.*

### 3.3 Binary mixture adsorption

To model mixture permeance the individual and total loading in the mixture needs to be estimated. In case of the Reed Ehrlich approach both the total and individual loadings need to be calculated. A well-known method to calculate mixture loadings is the Ideal Adsorbed Solution Theory (IAST) [8]. In this approach mixture loadings are estimated based on single component adsorption isotherms. However, when adsorption becomes segregated the IAST may fail [9]. Since a better approach is lacking, the IAST will be used in our study. Recently, single component adsorption isotherms have been computed by Grand Canonical Monte Carlo (GCMC) methods of CO$_2$, CH$_4$ and N$_2$ up to saturation loading together with equal partial fugacity mixture isotherms of CO$_2$/CH$_4$, CH$_4$/N$_2$ and CO$_2$/N$_2$ in DDR at 303 K [10,11]. From these studies it followed that the weaker adsorbing component is underpredicted by the IAST. At 1000 kPa total pressure the predicted loading of CH$_4$ mixed with CO$_2$, N$_2$ mixed with CH$_4$ and N$_2$ mixed with CO$_2$ are about 60, 80 and 85 % of the GCMC value, respectively. The
stronger adsorbing component is only slightly overpredicted and the total loading is accurately predicted in these cases.

Besides this fundamental shortcoming of the IAST for heterogeneous adsorption systems errors can also be introduced when the single component isotherms are evaluated outside of the experimental range for which they have been measured. Figure 4 shows the pressure at which the single component isotherms are evaluated in case of CO₂/CH₄ and CO₂/N₂ mixtures at a total feed pressure of 1000 kPa. CO₂ is much stronger adsorbing than CH₄ and N₂. The CO₂ isotherm is evaluated close to its corresponding pressure in the mixture: 500 kPa. CH₄ and N₂ are evaluated at much higher pressures, especially at low temperatures. At 300 K the CH₄ isotherm is evaluated at 7000 kPa and N₂ at ~20,000 kPa. This means that in case of N₂ already at this point the experimental pressure range is exceeded and for CH₄ the same occurs below 300 K. Note that at a total feed pressure of 100 kPa the same picture as shown in Figure 4 is obtained, but then all pressures are roughly one order of magnitude lower.

Figure 4. Pressures at which the single component isotherms are evaluated when predicting binary mixture loadings for CO₂/CH₄ and CO₂/N₂ mixtures using the IAST. Data are calculated at a total feed pressure of 1000 kPa, mixtures are equimolar in the gas phase. Used dual site Langmuir parameters are listed in Error! Reference source not found.

To estimate how well the currently estimated dual site Langmuir parameters predict the loading outside the experimental range a comparison is made with isotherms calculated from GCMC simulations up to saturation [7,12]. The results of N₂, CO₂ and CH₄ adsorption at 300 K (GCMC) and 303 K (experimental) are shown in Figure 5. A very good agreement between the experimental and GCMC results is found. In case of CO₂ the experimentally determined adsorption parameters provide a good prediction up to saturation loading. Analysis of the CO₂ profile shows two steps in the isotherm.
experimental data reach up to the beginning of the second step, thereby providing enough information to model up to saturation. In case of CH₄, three steps can be distinguished. The experimental data reach up to the beginning of the second step and consequently the first two steps are described accurately. Note that in a previous work CH₄ adsorption data were presented up to 120 kPa [5]. In this case only information on the first step of the isotherm was available and also a much lower saturation loading was obtained from fitting this data. It was the most difficult to extract reliable adsorption constants from the N₂ data. Clearly the assumed total saturation loading in the fitting procedure leads to an overprediction of the N₂ loading outside of the experimental range.

Li et al. [13] used the Statistical Model Isotherm (SMI) proposed by Ruthven [14] to obtain an isotherm up to the theoretical saturation loading based on relative low pressure data. The advantage of this approach would be an improved extrapolation of the isotherm at high pressure. Li et al. claimed that this isotherms is particularly suited for small-pore cage-like zeolites like CHA and DDR [13]. The loading in this case can be described as follows:

\[
q_i = \frac{q_i^{sat}}{\Omega} \left\{ \frac{1 - \frac{m}{\Omega_i + 1}}{1 - \frac{1}{\Omega_i + 1}} \right\}^m, \\
\]

\[
1 + K_i p_i + \sum_{m=2}^{\Omega} \frac{(K_i p_i)^m}{(m-1)!} \left[ \frac{1 - \frac{m}{\Omega_i + 1}}{1 - \frac{1}{\Omega_i + 1}} \right]^m,
\]

where \( \Omega \) represents the maximum number of molecules per cavity. The use of this isotherm is now evaluated by fitting the SMI to the GCMC data of CO₂, N₂ and CH₄ up to 1000 kPa; the higher pressure data are predicted based on this model fit. The maximum number of molecules per cage are assumed to be 5, 5 and 6 for CO₂, CH₄ and N₂, respectively. The SMI prediction is good in case of CO₂, but very poor for CH₄ and N₂ (Figure 4). Clearly one should be very cautious to rely on model extrapolations of this type of isotherm.
Figure 5. Comparison of experimental adsorption data (open symbols) of CO$_2$, N$_2$ and CH$_4$ in DD3R crystals at 303 K with isotherms obtained from GCMC simulations at 300 K (closed symbols) [7,12]. Solid lines represent model fit results of the experimental data. Dashed lines are modeling results of the statistical model isotherm [14]; the model fit is based on data up to 1000 kPa, above 1000 kPa the lines represent model predictions.

Single component isotherms of CO$_2$, N$_2$, CH$_4$ have been calculated from GCMC simulations between 195 to 573 K. These data have been fitted by a three-site Langmuir isotherm of which the constants are listed in refs [7,12]. Given the good agreement of the experimental and GCMC isotherms it is assessed if using the GCMC isotherms as input for the IAST calculations has advantages over using the experimental isotherms. Figure 6 shows the loading prediction of a mixture of CO$_2$/CH$_4$ and CO$_2$/N$_2$ at equal partial pressure of 500 kPa.
The CO\(_2\) loading is only presented in a mixture with N\(_2\) because it is nearly identical to its loading in a mixture with CH\(_4\). Only the N\(_2\) loading is quite sensitive to the input isotherm parameters: it is higher when the experimental isotherms are used. This is due to the overprediction of the N\(_2\) loading by these model fit parameters at pressures outside of the experimental range, as shown in Figure 4. Note that Figure 6 also reveals strong competitive adsorption effects of CO\(_2\) over N\(_2\) and CH\(_4\) pushing their loadings downward, specifically at low temperatures.

Figure 6. Mixture loadings predicted by the IAST of CO\(_2/\)CH\(_4\) and N\(_2/\)CO\(_2\) mixtures with equal partial pressure at a total pressure of 1000 kPa. Solid lines are predictions using the experimental adsorption data and dashed lines GCMC data fits, respectively.
References


