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Gas Permeation Through Zeolite Single Crystal Membranes

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Abstract. Diffusion of methane and argon mixtures through single crystal membranes is studied using the Dual-Control Volume-Grand Canonical Molecular Dynamics method. This study focuses on understanding the impact of crystal structure on surface resistance and membrane performance by comparing diffusion through silicalite, mordenite, $AlPO_4$-5 and ZSM-12. Results showed that the contribution of surface resistance on membrane selectivity varies with the structure of the zeolite framework. Surface resistance is larger and longer range in silicalite, with an overall trend of silicalite $>$ ZSM-12 $>$ mordenite $>$ $AlPO_4$-5. This difference is attributed primarily to the smaller diameter of the silicalite pores, but the one-dimensional pore systems also seem to focus the translational momentum such that the surface resistance is smaller and shorter range.

Keywords: gas diffusion, selectivity, molecular simulation, mass-transfer resistance, surface barrier

1. Introduction

In the diffusion of gas permeants through zeolite membranes, surface resistances exist at the pore entrances and exits due to the discontinuity in the crystal potential field (Kocirik et al., 1988; Ford and Glandt, 1995). As progress is made toward thinner and higher flux membranes, the surface effects should become more significant. We would like to understand how these surface resistances impact selectivity. While experimental analysis has not identified a clear role of surface resistance, a number of molecular simulations and continuum theories have suggested that there should be such an effect (Barrer, 1987; Kocirik et al., 1988; Karger and Ruthven, 1992).

The single crystal membrane (SCM) technique (Sun et al., 1996; Talu et al., 1998), is based on the direct measurement of diffusive flux through the zeolite at transient and steady state conditions and allows bridging between the microscopic and macroscopic of techniques because it is absent of inter-crystalline resistances. Entrance and exit barriers are the only existing surface-resistance types in the case of SCM, since a single zeolite crystal forms the membrane. Therefore, there are only three contributions comprising the diffusion process of a gas molecule through the SCM: entrance to the pores (adsorption), intra-crystalline diffusion, and exit from the pores (desorption). The challenge for the experimental method is that the thickness of the crystal in the flux direction is roughly 100 μm thick, so thick that surface resistances are overwhelmed by the intra-crystalline resistance. Nevertheless, polycrystalline membranes are being synthesized with thickness near 10 μm and individual grains of order 1 μm. Thus the 1 μm thickness is of interest, despite the difficulty of adapting the SCM technique

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experimentally. This leads us to simulate idealized SCM's of thickness ~0.1 μm that are hypothetical in the context of current experimental capability but permit detailed study of surface resistances.

The variation of mass transfer resistances with the membrane thickness was first observed by Martin and co-workers (Martin et al., 2001), who studied the diffusion of methane through silicalite membranes ranging in thickness from 2 to 16 nm. Their work showed that the surface resistance increased as the membrane became thicker, contradicting initial assumptions that the resistances at the surface were constant beyond the first few angstroms inside the surface. But our previous simulations (Ahunbay et al., 2002) showed that the effect was apparent even at different crystal orientations and for thicker crystals. Although the surface resistance eventually must approach a limiting value, the membrane thickness before this approach is unexpected. The range of the thickness when this limit is approached is what we refer to as the "range" effect.

In this work is we applied the Dual Control Volume-Grand Canonical Molecular Dynamics (DCV-GCMD) method to understand the impact of zeolite structure on the surface resistances existing at the entrance and exit of zeolite single crystal membranes. For our purpose, we studied diffusion of CH_4 + Ar mixtures through the four different zeolites with different crystal structures: silicalite, mordenite, $AlPO_4$-5 and ZSM-12, which allowed us to understand how the mass-transfer resistance at the interface alters selectivity and permeance of the crystal.

2. DCV-GCMD Simulations

Four different zeolites types were considered in this work: silicalite, mordenite, $AlPO_4$-5, and ZSM-12. This selection allows the study of frameworks with different channels systems and pore diameters. The characteristics of the zeolites used in this simulation study are summarized in Table 1.

The membrane diffusion simulations have been carried out using the DCV-GCMD method (Heffelfinger and van Swol, 1994; MacElroy, 1994; Thompson et al., 1998). The details of the simulation procedure are similar to that of our recent work (Ahunbay et al., 2005). Permeant-permeant and permeant-zeolite interactions were modeled using the Lennard-Jones (LJ) potential model. The same permeant-zeolite parameters were used for all zeolite types. The zeolite frameworks were assumed all-siliceous and rigid. The silicon atoms in the zeolite were neglected. All interactions between existing molecules were described by the 12-6 LJ potential.

Table 1. Characteristics of the zeolite frameworks considered in this study.

	Channel system		Pore diameter (Å)
Silicalite	3-dimensional:	Straight channels	5.7 × 5.2
		Zigzag channels	5.4
Mordenite	1-dimensional:	Straight channels	6.5 × 7.0
		Side pockets	2.6 × 5.7
$AlPO_4$-5	1-dimensional:	Straight channels	7.3
ZSM-12	1-dimensional:	Straight channels	5.6

The pure LJ parameters for the permeants, and those for the permeant-zeolite interactions used in this work are listed in Table 2. The potential and the force vector for permeant-zeolite interactions were evaluated using the pretabulation method that takes in the account the symmetries of the zeolite unit cells. The cross-interaction parameters between permeants in a mixture were calculated using the Lorentz-Berthelot mixing rules. The potential parameters for CH_4 and Ar are the same as those we had used in our previous works (Ahunbay et al., 2002, 2004), With this selection of parameters, note that lower diffusivities for CH_4 were obtained compared to previous works in the literature. However, this allows us to study the effect of difference in size between two penetrants, since both molecules have very similar gas-crystal interaction energies, while their gas-crystal interaction size and molecular weight differ significantly. With this parameter selection, the intra-crystalline diffusivity of Ar (2.52×10^{-5} s/cm^2) is slightly higher than that of CH_4 (2.28×10^{-5} s/cm^2). The table also includes a second set of interaction parameters for methane denoted by CH_4^* that yield similar equilibrium concentration and heat of adsorption as the first set of parameters, but gives a diffusivity of 3.31×10^{-5} s/cm^2. The heats of adsorption were calculated as −15 kJ/mol for Ar, and −18 kJ/mol for CH_4 and CH_4^*.

3. Results

The flux due to a pressure gradient through a intra-crystalline region of thickness L is,

$$J = -\frac{D_t}{RT}\frac{\Delta P}{L} = -\left(\frac{\partial f}{\partial c}\right)_T \frac{D_0}{RT}\frac{\Delta P}{L}, \qquad (1)$$

Table 2. Lennard-Jones potential parameters for CH_4 and Ar in zeolites.

	σ_{GG} (Å)	ε_{GG} (K)	σ_{GZ} (Å)	ε_{GZ} (K)	Ref.
CH_4	3.73	148	3.64	96.5	(Smit and Siepmann, 1994)
Ar	3.42	124	3.17	95.61	(Clark et al., 1998)
CH_4^*	3.73	148	3.214	133.5	(Goodbody et al., 1991)

where D_t is uncorrected intra-crystalline transport diffusivity, and P is the pressure in equilibrium with a given concentration inside the crystal. Since the transport diffusivities vary with concentration (Karger and Ruthven, 1989), the corrected diffusivities D_0 were calculated using Darken's approximation, where f is the fugacity of the gas phase in equilibrium with the permeant concentration c inside the zeolite. Darken's approximation describes the corrected diffusivity of a molecule assuming it is independent of concentration and equals to its self-diffusivity at zero loading. Note that this approximation is valid for CH_4 and Ar, but it does not hold for large molecules such as CF_4 in silicalite (Skoulidas and Sholl, 2002). Then, Eq. (1) can be rewritten as,

$$J = -\left(\frac{\partial f}{\partial c}\right)_T \frac{1}{RT}\frac{\Delta P}{R_{\text{intra}}}, \tag{2}$$

where $R_{\text{intra}} = L/D_0$ is the intra-crystalline mass-transfer resistance.

The total mass-transfer resistance can be expressed as the sum of individual resistances to adsorption, intra-crystalline transport and desorption (Ahunbay et al., 2002). This allows individual evaluation of the surface resistances at the entrance and exit by separate simulation involving only one of the surface resistances. Then the overall diffusion coefficient becomes

$$D_t(c) = \left(\frac{\partial f}{\partial c}\right)_T \left[R_{\text{ads}} + \frac{L}{D_0} + R_{\text{des}}\right]^{-1}. \tag{3}$$

In our previous work (Ahunbay et al., 2004) the mass-transfer resistances were calculated for CH_4 and Ar diffusing through silicalite membranes oriented along the [0 0 1]-axis of the unit cell. This orientation was selected since it is the actual orientation used in the silicalite SCM experiments. The variations of surface resistances with the membrane thickness were evaluated through the silicalite membrane from individual simulations of adsorption, intra-crystalline transport and desorption steps of the diffusion process.

After evaluating the variation of surface resistance with crystal thickness for CH_4 and Ar diffusing through silicalite, the impact of these variations on the separation performance of binary mixtures was considered. For a binary mixture of permeants i and j, the separation performance of the membrane can be expressed by its selectivity:

$$\alpha_{i/j} = J_i/J_j. \tag{4}$$

The effect of membrane thickness on the selectivity was studied first for CH_4+Ar mixtures diffusing trough silicalite membranes by increasing the crystal thickness from 12 to 64 nm (Ahunbay et al., 2005). The simulations were performed at 298 K with the total feed pressure set to 4.55 bar, where the mole fraction of the CH_4 was 0.12. This feed concentration was selected such that it yielded an equimolar partition during the intra-crystalline simulations. The resulting selectivity showed that for a membrane of 12 nm the selectivity at the entrance is higher than the intra-crystalline selectivity. It approaches the intra-crystalline selectivity, as the membrane gets thicker after an initial sharp decrease. Similarly, the selectivity at the exits decreases until its value reaches that of intra-crystalline selectivity. These results agree well with the variation of surface resistances for pure CH_4 and Ar studied previously (Ahunbay et al., 2004). Since the surface resistance for CH_4 is stronger and the initial increase is sharper than that for Ar, the variation of the selectivity is more significant for the thinner membranes.

In the present work, the effect of zeolite frameworks was studied by comparing the surface resistances and the variation of selectivities for silicalite, $AlPO_4$-5, mordenite and ZSM-12. Since $AlPO_4$-5, mordenite and ZSM-12 have one-dimensional pore structures with straight channels, the silicalite simulations were repeated by reorienting the crystal along its straight channels ([0 1 0]-axis). Furthermore, the second set of LJ-interactions parameters in Table 1 (CH_4^*) was used as they yield better agreement with the experimental data (Ahunbay et al., 2004). Table 3 summarizes the

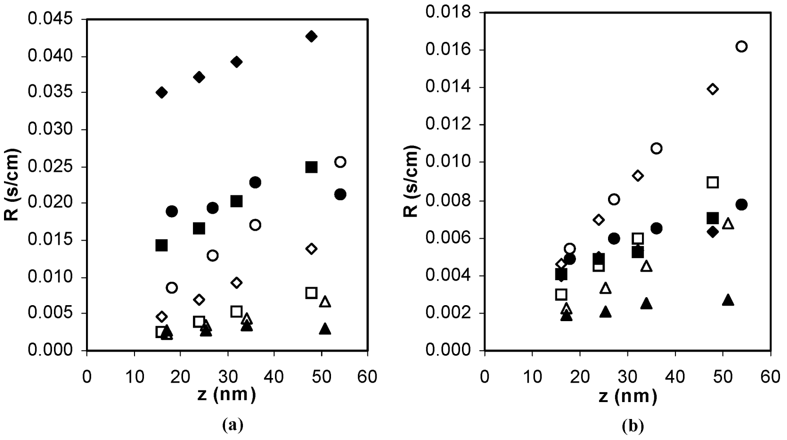
Table 3. Feed pressures to obtain a dimensionless equimolar intra-crystalline concentration of 0.025 in the CV I at 333 K, and the intra-crystalline diffusivities obtained at these conditions.

	p^{CVI}(bar)				D_0 ($\times 10^{-4}$ cm^2/s)			
	$AlPO_4$-5	MOR	Silicalite	ZSM-12	$AlPO_4$-5	MOR	Silicalite	ZSM-12
CH_4	1.60	0.40	0.47	0.50	7.59	2.10	3.44	6.12
Ar	5.25	2.75	2.50	2.25	7.53	3.34	3.14	5.36

feed pressures for all four zeolite types that yield an equimolar partition inside the crystal CV I, corresponding to a dimensionless concentration of 0.025 at 333 K. The value of the simulation temperature was selected high enough to allow CH_4 molecules entering and exiting the mordenite side pockets without being stuck inside: CH_4 molecules, having strong interactions with the mordenite framework, tend to be trapped by the side pockets, which creates also additional energy barriers for the diffusion (El Amrani, 1990). The resulting corrected intra-crystalline diffusivities for pure CH_4 and Ar calculated at these conditions are presented in the same table. The diffusivity in silicalite was measured in the direction of the straight channels. These results agree with the previous intra-crystalline studies in the literature (Goodbody et al., 1991; Tepper et al., 1999; Skoulidas and Sholl, 2003).

Following the calculation of intra-crystalline diffusivities, the surface resistances were calculated for all four zeolites at different thickness. The simulations were carried out for full membranes, where both the adsorption and desorption resistances were present. The simulation conditions were the same as those presented in Table 3. The variations of these resistances are shown in Fig. 1. It can be seen that the magnitude of surface resistances is roughly proportional to the size of the permeants relative to the pore diameter. Ar in silicalite is exceptional in that its surface resistance is roughly equal to the resistance for mordenite and ZSM-12, while the surface resistance for CH_4 in silicalite is much larger than other resistances. It is also interesting to note that the intra-crystalline resistance is larger than the surface resistance for all Ar cases, but the surface resistance is larger for three of four CH_4 cases.

Finally, simulations of CH_4+Ar mixtures were carried out through all four zeolite membranes by setting the partial pressures to the values given in Table 3. The resulting selectivities and their variation with membrane thickness are shown in Fig. 2. This comparison of four different frameworks shows the surface resistances for zeolites with 1-dimensional framework have a very short range for surface resistances; the surface resistances reach their intra-crystalline values within few nanometers as the membrane thickness



(a)
(b)

Figure 1. Total surface resistances for (a) CH_4 and (b) Ar in four different zeolite types: (●) mordenite, (♦) silicalite, (■) ZSM-12, (▲)$AlPO_4$-5. Corresponding hollow symbols represent intra-crystalline resistances.

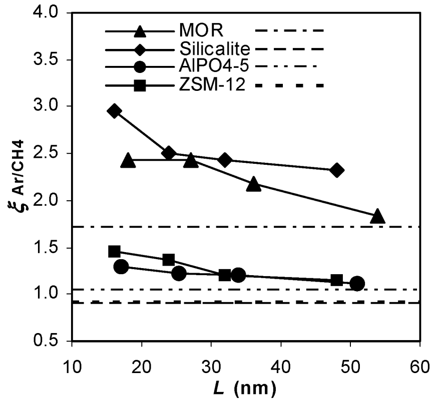


Figure 2. Comparison of selectivity towards Ar in four different zeolite types: mordenite, silicalite, $AlPO_4$-5 and ZSM-12. Symbols represent the membrane selectivity; broken lines represent the intra-crystalline selectivity.

increases. On the other hand, the dependence of surface resistance on membrane thickness is quite significant in silicalite and its range is much larger. Considering both silicalite and ZSM-12 have similar pore diameters, the main reason for this difference may be attributed to the three-dimensional framework of silicalite. Owing to the interconnected straight and zigzag channels, molecules penetrating into the membrane do not transmit the axial momentum since they escape to zigzag channels.

4. Conclusion

In this study, we showed by molecular simulations how surface resistance contributes to membrane performance by altering its selectivity. Depending on the structures of zeolite frameworks, surface resistances can significantly contribute to the over-all mass-transfer resistance to gas permeation. This contribution remains important over a distance beyond the surface, what we call the range of the surface resistance. Comparison of different zeolite types with different channel systems and pore diameters showed that the contribution of the surface resistance is more significant for silicalite, which has a three-dimensional channel system, in contrast to zeolites with one-dimensional channel system. The comparison between silicalite and ZSM-12, which have both similar pore diameters, especially illustrates this impact of the framework topology.

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References

Ahunbay, M.G., J.R. Elliott, and O. Talu, "The Diffusion Process of Methane Through a Silicalite Single Crystal Membrane," *J. Phys. Chem. B*, **106**, 5163–5168 (2002).

Ahunbay, M.G., J.R. Elliott, and O. Talu, "Surface Resistance to Permeation Through the Silicalite Single Crystal Membrane: Variation with Permeant," *J. Phys. Chem. B*, **108**, 7801–7808 (2004).

Ahunbay, M.G., J.R. Elliott, and O. Talu, "The Effect of Surface Resistances on the Diffusion of Binary Mixtures in the Silicalite Single Crystal Membrane," *J. Phys. Chem. B*, **109**, 923–929 (2005).

Barrer, R.M., *Langmuir*, **3**, 309 (1987).

Clark, L.A., A. Gupta, and R.Q. Snurr, "Siting and Segregation Effects of Simple Molecules in Zeolites MFI, MOR, and BOG," *J. Phys. Chem. B*, **102**, 6720–6731 (1998).

El Amrani, S., "Etude de la diffusion des gaz rares dans les zeolithes par la dynamique moleculaire," PhD Thesis; University of Lyon, France (1990).

Ford, D.M. and E.D. Glandt, "Steric Hindrance at the Entrances to Small Pores," *J. Mem. Sci.*, **107**, 47–57 (1995).

Goodbody, S.J., K. Watanabe, D. MacGowan, J.P.R.B. Walton, and J. Quirke, "Molecular Simulation of Methane and Butane in Silicalite," *J. Chem. Soc., Faraday Trans*, **87**, 1951–1958 (1991).

Heffelfinger, G.S. and F. van Swol, "Diffusion in Lennard-Jones Fluids using Dual Control Volume Grand Canonical Dynamics Simulation(DCV-GCMD)," *J. Chem. Phys.*, **100**, 7548–7552 (1994).

Karger, J. and D.M. Ruthven, "On the Comparison Between Macroscopic and NMR Measurements of Intracarystalline Diffusion in Zeolites.," *Zeolites*, **9**, 267–281 (1989).

Karger, J. and D.M. Ruthven, *Diffusion in Zeolites and Other Microporous Solids*, Wiley, New York, 1992.

Kocirik, M., P. Struve, K. Fiedler, and M. Bulow, "A Model for the Mass-transfer Resistance at the surface of Zeolite Crystals," *J. Chem. Soc., Faraday Trans. 1*, **88**, 3001 (1988).

MacElroy, J.M.D., "Nonequilibrium Molecular Dynamics Simulation of Diffusion and Flow in Thin Microporous Membranes," *J. Chem. Phys.*, **101**, 5724 (1994).

Martin, M.G., A.P. Thompson, and T.M. Nenoff, "Effect of Pressure, membrane Thickness, and Placement of Control Volumes on the Flux of Methane through Thin Silicalite Membranes: A Dual Control Volume Grand Canonical Molecular Dynamic Study," *J. Chem. Phys.*, **114**, 7174–7181 (2001).

Skoulidas, A.I. and D.S. Sholl, "Transport Diffusivities of CH4, CF4, He, Ne, Ar, Xe, and SF6 in Silicalite from Atomistic Simulations," *J. Phys. Chem. B*, **106**, 5058–5067 (2002).

Skoulidas, A.I. and D.S. Sholl, "Molecular Dynamics Simulations of Self-Diffusivities, Corrected Diffusivities, and Transport Diffusivities of Light Gases in Four Silica Zeolites To Assess Influences of Pore Shape and Connectivity," *J. Phys. Chem. A*, **107**, 10132–10141 (2003).

Smit, B. and J.I. Siepmann, "Computer-Simulations of the Energetics and Siting of *n*-Alkanes in Zeolites," *J. Phys. Chem-Us.*, **98**, 8442–8452 (1994).

Sun, M.S., O. Talu, and D.B. Shah, "Diffusion Measurements through Embedded Zeolite Crystals," *AIChE Journal*, **42**, 3001–3007 (1996).

Talu, O., M.A. Sun, and D.B. Shah, "Diffusivities of *n*-Alkanes in Silicalite by Steady-State Single-Crystal Membrane Technique," *AIChE Journal*, **44**, 681–694 (1998).

Tepper, H.L., J.P. Hoogenboom, N.F.A. van der Vegt, and W.J. Briels, "Unidirectional diffusion of methane in $AlPO_4$-5," *Journal of Chemical Physics*, **110**, 11511–11516, (1999).

Thompson, A.P., D.M. Ford, and G.S. Heffelfinger, "Direct Molecular Simulation of Gradient-Driven Diffusion," *J. Chem. Phys.*, **109**, 6406 (1998).