

## Application of Molecular Simulation Techniques to Estimation of Gas Permeability in Zeolite Membranes

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### ABSTRACT

Molecular modeling of gas permeation through zeolite membranes with/without intercrystalline region was carried out. Molecular dynamics (MD) and Monte Carlo (MC) simulations were performed to estimate the diffusion coefficient and adsorption parameters respectively, and our proposed combined method of molecular simulation techniques with a permeation theory (CMP) was used to estimate gas permeability. The calculated permeability of gases (Ar, He, Ne, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>) at 301 K for the single crystal membrane model was about one order of magnitude larger than the experiential values, although the dependence on the molecular weight of the permeating species agreed with experiments. On the other hand, the estimated permeability using the diffusivity and adsorption parameters of the intercrystalline region model was in good agreement with the experiments. The consistency between experiments and the estimated values means the importance of considering the intercrystalline region and the validity of CMP method to predict the performance of zeolite membranes.

### INTRODUCTION

Zeolite membranes have received much attention recently because of the possible uses deriving from their molecular sieving and preferential adsorption properties for separation processes. Of particular interest are MFI-type zeolite membranes, including ZSM-5 and its pure silica type silicalite-1. Zeolite membranes are usually prepared as thin layers of an assembly of small zeolite crystals, probably including many intercrystalline regions that influence their performance. The condition of the intercrystalline regions will depend greatly on their synthesis conditions. Characterization of the intercrystalline region by direct experimental methods is difficult because their size is in the range of a few nanometers. The relationship between the structure of the intercrystalline region and the membrane's performance are, therefore, still not fully understood. Because of this background, methodology based on theoretical models is thought to be indispensable to explain and improve the performance of conventional zeolite membranes.

Attempts to explain the experimental permeation data based on a theoretical method have been reported [1-3]. These reports, however, have discussed membrane performance by assuming that zeolite membranes consist of a perfect single crystal, and they omitted discussion about the influence of the intercrystalline region on membrane performance. In this paper, we modeled zeolite membranes and estimated their ability in gas permeability. Two

models, namely the single crystal membrane model and the intercrystalline region membrane model, are used to investigate the effect of intercrystalline region structure on gas permeability. Molecular dynamics (MD) and Monte Carlo (MC) simulation techniques were applied to estimate the diffusivity and adsorption parameter, and using these parameters a CMP method is applied to predict the permeability of various gases through a membrane. The comparison of the estimated permeability with the previously reported experimental values was made to check the validity of CMP method.

## METHOD

An *NVE* ensemble MD simulation and a grand canonical ensemble MC (GCMC) simulation were performed to estimate a diffusion coefficient and an adsorption isotherm, respectively. Non-bonding interactions between methane and atoms in the zeolite framework were represented by a function of the 12-6 Lennard Jones type. Electrostatic interaction between them was not significant and was neglected. The zeolite framework was considered to be rigid during the MD simulations to reduce the computational cost. Potential parameters of the 12-6 Lennard Jones function used in this study were optimized to reproduce the experimental data well for the isosteric heat of adsorption [4]. Adsorption isotherms were estimated from 500 000 MC steps run with 200 000 steps for sampling. The cut-off length was 1.37 nm. Simulations were carried out under the three-dimensional periodic boundary condition. In the MD calculation 200 molecules were set at one MD unit cell, although intermolecular interactions between adsorbates were completely ignored. Anisotropic and isotropic diffusivities were evaluated from MD results using Einstein's equation. The MD run of 2 ns (single crystal model), 8 ns (intercrystalline region model) were carried out at least.

An MFI-type silicalite membrane was modeled as a zeolite membranes. The silicalite crystal structure is represented by the *Pnma* space group (orthorhombic), with lattice parameters  $x = 2.0022$  nm,  $y = 1.9899$  nm,  $z = 1.3383$  nm. The single crystal model consisted of 12 ( $2 \times 2 \times 3$ ) silicalite unit cells containing 1152 silicon and 2304 oxygen atoms. The intercrystalline region model (a) was constructed from 12 ( $3 \times 2 \times 2$ ) silicalite unit cells containing 1152 silicon, 2336 oxygen and 64 hydrogen atoms. The intercrystalline region model (b) was constructed from 18 ( $2 \times 3 \times 3$ ) silicalite unit cells containing 1728

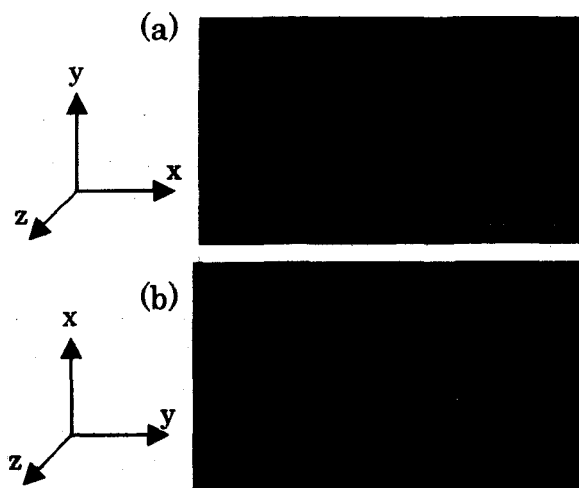


Figure 1 Computer graphics of the intercrystalline region models used in the GCMC and MD simulations. (a) The intercrystalline region model along the  $y$ -direction having (100)s urface. (b) The intercrystalline region along the  $x$ -direction having (010) surface.

silicon, 3504 oxygen and 96 hydrogen atoms. These structures are illustrated in Figure 1. As shown in the figure, the intercrystalline region models have two surfaces: (100) and (010) respectively. These surfaces were constructed by breaking the zeolite framework at a certain position. For model (a), the oxygen – silicon bonds at certain  $y$ - $z$  plane were broken, while for model (b) the oxygen – silicon bonds located at certain  $x$ - $z$  plane were broken. The position of the breaking plane was chosen so that the number of the broken bonds was a minimum. Unsaturated bonds on the surfaces were terminated by hydrogen or hydroxyl groups, forming a silanol group. The distance between the faced two surfaces is defined as the width of the intercrystalline region.

We briefly describe here the CMP method. In the CMP method, the estimate of permeability is derived from a combination of an adsorption isotherm and a corrected diffusivity, which are obtained by MD and GCMC simulations, based on the adsorption–diffusion model. The relationship between the self-diffusion coefficient and the corrected diffusion coefficient,  $D_0$ , is derived on the assumption that self-diffusivity is proportional to the concentration of vacant adsorption sites. The flux is calculated by Fick's law, and the required mutual diffusivity is calculated using Darken's equation. Finally, if the pressure on the permeate side is assumed to be zero [2], the permeability,  $P$ , through a membrane, is expressed as follows:

$$P = \frac{\rho D_0 q_m}{P_0} \ln(1 + K_A p_0) \quad (1)$$

where  $\rho$  is the density of the membrane,  $K_A$  and  $q_m$  are the Langmuir parameters, and  $p_0$  is the feed pressure. However, the Langmuir adsorption model is sometimes insufficient to describe the adsorption isotherm. In such a case, the dual-site Langmuir model [5] was introduced instead of the simple Langmuir model. In this model, sites  $A$  and  $B$  are identified with the respective saturated adsorbed amount  $q_{mA}$  and  $q_{mB}$ . The dual-site Langmuir constants for adsorption at the two sites  $A$  and  $B$  are  $k_A$  and  $k_B$ . Permeability when the dual-site Langmuir model is assumed is expressed as:

$$P = \frac{\rho D_{S(\theta=0)}}{P_0} \{q_{mA} \ln(1 + k_A p_0) + q_{mB} \ln(1 + k_B p_0)\} \quad (2)$$

The Langmuire parameters used in this study are listed in our previous report [4].

## RESULTS AND DISCUSSION

### *Singly crystal membrane model*

The permeability of various gases (Ar, He, Ne, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>) in the single crystal model was estimated from the calculated adsorption parameters and diffusion coefficient. To estimate the permeability, Eq. (2) was used for nitrogen and oxygen, while for other gases Eq. (1) was used. The feed and permeate pressure were assumed to be 101.3 kPa and 0 kPa, respectively. The temperature is 301 K. Table 1 shows the calculated anisotropic and isotropic

Table 1 Calculated anisotropic and isotropic permeabilities of inorganic gases

Gas	Isotropic ( $10^{-12}$ molm/m <sup>2</sup> sPa)	Anisotropic (x / y / z direction) ( $10^{-12}$ molm/m <sup>2</sup> sPa)
He	9.2	10 / 19 / 1.7
Ne	13	16 / 24 / 2.1
Ar	64	79 / 125 / 16
N <sub>2</sub>	120	128 / 221 / 24
O <sub>2</sub>	72	56 / 144 / 15
CH <sub>4</sub>	170	200 / 270 / 26

Table 2 Amount of adsorption of gases in silicalite at 101.3 kPa

Adsorbate	q (mmol/g)
He	0.00675
Ne	0.0193
Ar	0.285
N <sub>2</sub>	0.498
O <sub>2</sub>	0.482
CH <sub>4</sub>	0.504

permeabilities. For the noble gases, the permeability of helium and neon are much smaller than that of argon, and the permeability increases with an increase in molecular weight, although the self-diffusivities of helium and neon were larger than that of argon. Table 2 shows the equilibrium amount of adsorption in silicalite at 101.3 kPa and 301 K, which corresponds to the feed pressure used in the calculation of permeability. The order of adsorbate according to the amount of adsorption corresponds with the order of the permeability. This means that the influence of adsorption properties on gas permeability is dominant in the permeation of investigated inorganic gases.

Figure 2 shows the comparison of the calculated isotropic permeabilities with the experimental data [6,7]. It is found that the dependence of gas permeability on the molecular weight is similar to that from experiments, although the calculated values differ from the experimental data by about one order of magnitude. This qualitative agreement means that the permeation mechanism of investigated gases is fundamentally explained by a CMP model.

Above discussion assumed that zeolite membranes consist of a perfect single crystal, and the influence of the intercrystalline region on membrane performance was omitted. This assumption may be the reason why theoretical estimates using molecular simulation techniques tend to overestimate the gas permeability compared to experimental results.

#### *Intercrystalline region membrane model*

GCMC simulations were performed to obtain the adsorption isotherms (Ar, He, Ne, CH<sub>4</sub>) using the intercrystalline region model. Intercrystalline region models having different intercrystalline region widths – 0.5 nm, 1 nm, 1.5 nm, and 2 nm – were examined. Calculated

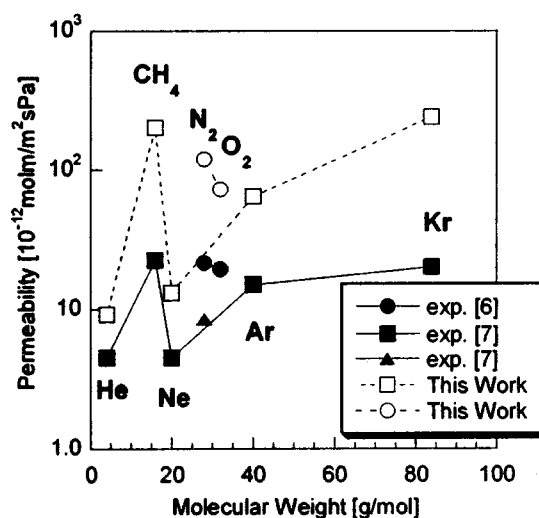


Figure 2 Estimated permeability of various gases in silicalite at 301 K.

isotherms of methane using the intercrystalline region models were the same as those that were calculated using the single crystal model under a pressure of 2000 kPa. This is because gas molecule is preferentially adsorbed in the zeolite pores rather than the intercrystalline region (see Fig. 3). In the higher-pressure range (over 2000 kPa) the amount of adsorption in the intercrystalline region model exceeds that in the single crystal model. This is because the molecules begin the adsorption in the intercrystalline region. As the length of intercrystalline region increases, the saturated amount of adsorption became large. From these results, we can conclude that the influence of the intercrystalline region on the adsorption isotherm of methane can be ignored if the operating pressure is lower than 2000 kPa. Since experiments have usually been done below 2000 kPa, the contribution of adsorption in the intercrystalline region to the total amount of adsorption is not significant. Similar trend was observed in the isotherms of other gases (Ar, He, Ne).

The permeability of various gases (Ar, He, Ne, CH<sub>4</sub>) in the intercrystalline region model is estimated using the parameters of the calculated adsorption isotherm and calculated  $D_0$ .  $D_0$  are a function of the width of the intercrystal region. Figure 4 presents the calculated permeability of various gases when the length of the intercrystalline region is 0.5 nm.

Calculated permeability were smaller than that for the single crystal model shown in Figure 2. This means that the permeability of an actual silicalite membrane, which has many intercrystalline regions, may show a lower permeability than that of the single crystal model. It is found in the comparison with the experimental results that the estimated permeability is

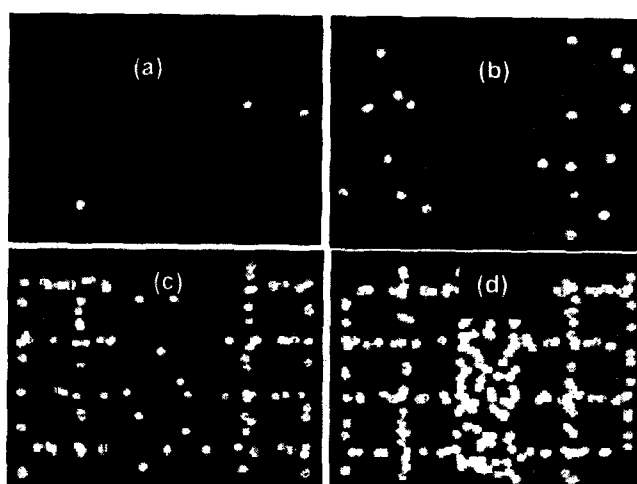


Figure 3 Snap shots of adsorbed methane molecules (indicated as sphere model) obtained from MC simulations. (a) 10 kPa, (b) 100 kPa, (c) 1000 kPa, (d) 10000 kPa.

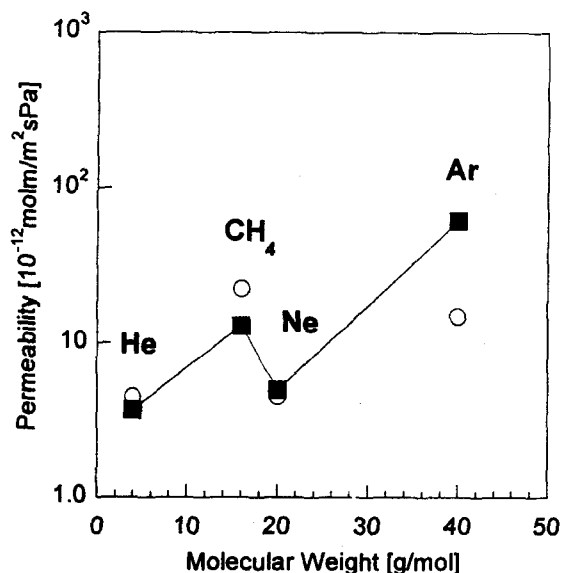


Figure 4 presents the calculated permeability of various gases when the length of the intercrystalline region is 0.5 nm. Keys: open circle = experiment [7], filled square = the intercrystalline region model.

in excellent agreement with the reported values if the length of intercrystalline region is approximately 0.5 nm. Some experiments [9, 10] reported the possible existence of a defect pore, with a pore size less than 1 nm, based on the kinetic diameter of permeable gases. This range of intercrystalline region is consistent with our estimation.

## CONCLUSION

Gas permeation through zeolite membranes were investigate by molecular simulation techniques. We applied the CMP method to estimate the permeabilities of various gases at about 301 K. Two zeolite membrane models, namely the single crystal model and the intercrystalline region model, were used in the permeability calculation in order to investigate the structural influence on gas permeability. For the single crystal membrane model, the calculated permeabilities were about one order of magnitude larger than the experiential values, although the dependence on the molecular weight of the permeating species agreed with the experiments. On the other hand, the permeability of methane calculated using the intercrystalline region model were in quantitatively agreement with the experiments, although the permeability values was a function of the width of the intercrystal region. The consistency between the experiments and the estimated values means the importance of considering the intercrystalline region in the evaluation of gas permeability in zeolite membranes and the validity of CMP method as a prediction method of permeability in zeolite membranes.

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