Gas Permeation through Zeolite-Alumina Composite Membranes

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Mordenite (MOR) and ferrierite (FER) membranes without any pinhole and crack were synthesized by a vapor-phase transport method. The permeance of H_2, He, CH_4, N_2, O_2 and CO_2 was determined at 290 – 400 K, which showed minimum with increasing temperatures for most cases. In the parallel diffusion model was proposed, molecules adsorbed in a micropore are assumed to diffuse in parallel through the central region of the pore and along the wall region of the pore. This parallel diffusion model accounts for the effect of pore size of MOR and FER on the permeation and expresses the experimental data well. The interaction between gas molecules and pore walls are evaluated for each gas.

Introduction

Much attention has been paid to inorganic membranes having molecular sieving properties for gas separation and membrane reactors due to their high thermal resistance, chemical inertness, and high mechanical strength. Zeolites are very promising materials for such molecular sieving membranes because of their unique pore sizes.

In most researches on zeolitic membranes, ZSM-5 (MFI) membranes have been synthesized by conventional hydrothermal synthesis. Tsikoyiannis and Hagg (1992) synthesized a self-supporting MFI membrane on a Teflon slab. However, for the lack of its mechanical strength, porous materials have been used to support a thin layer of zeolite (Geus et al., 1992, 1993; Yan et al., 1995; Sano et al., 1994).

Permeation measurements of single-component gas including inorganic gases and light hydrocarbons such as n-butane and i-butane through MFI membranes have previously been studied. Jia et al. (1993) reported that the permeance ratio as high as 6.2 for n-butane over i-butane through an MFI membrane was obtained. The results from several other groups also show higher permeances of n-butane than that of i-butane. Yan et al. (1995) synthesized defect-free MFI membranes on a porous α-alumina support and observed good permeation selectivities for butane isomers: the permeability ratio of n-butane to i-butane was 18 to 303 K. Transient gas permeation measurements were performed by Geus et al. (1993) for CH_4, n-butane, neon, i-butane at room temperature. Those values were in the following order: $CH_4 > n$-butane > neon > i-butane. In particular, they found that the permeance ratio of n-butane to i-butane was as high as 64 at 298 K.

The permeation tests for a mixed gas through zeolitic membranes have been performed using a Wicke-Kallenbach cell. Tsikoyiannis and Hagg (1992) studied the permeances for three binary mixtures (O_2/N_2, H_2/CO_2, and n-hexane/2,2-dimethylbutane) through self-supporting MFI membranes at 296 and 322 K. The observed selectivity for an n-hexane/2,2-dimethylbutane mixture was 17.2, much higher than that in the Knudsen region, 1. Bai et al. (1995) reported that the separation selectivities for H_2/SF_6 and H_2/i-butane were 12.8 and 11.9, respectively, at 583 K, and were significantly greater than those predicted from the Knudsen diffusion mechanism. Geus et al. (1993) studied the permeation behavior of the 50/50 methane/n-butane mixture with elevating temperature. n-Butane, which was preferentially adsorbed at lower temperatures, was desorbed with increasing temperature, and methane started to permeate at a higher temperature. Similar trends have been found for H_2/n-butane mixture (Kapteijn et al., 1995). The H_2 permeation flux at a steady state was reduced by a factor of more than 100 compared with that for a single-component measurement, while the n-butane flux remained unaltered, indicating that the permeation behavior of n-butane was hardly affected by the permeation of H_2.

Shah et al. (1993) and Sun et al. (1996) fabricated MFI (Al-free) membranes by embedding a large (300 × 100 × 100

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μm) single MFI crystal in an epoxy resin to measure the transport rates of C_1–C_4 and aromatic hydrocarbons in an MFI crystal. The diffusivities of both *n*-butane and *i*-butane in MFI crystals were determined as about 10^{-12} $m^2 \cdot s^{-1}$. Lewis et al. (1997) synthesized large single crystals of pure-silica ferrierite (FER) ($600 \times 500 \times 20$ μm). They mounted the FER crystal so that only the ten-membered or eight-membered ring channels are accessible for gas permeation. Methane, *n*-butane, and *i*-butane were used for the gas permeation tests. They showed that the ten-membered ring channel was permeable to these three kinds of the gases, but the eight-membered ring channel was permeable to only methane.

Recently, a novel synthetic method, vapor-phase transport (VPT), has developed for crystallization of zeolite powders and zeolitic membranes. In the VPT method, zeolites are crystallized from dry aluminosilicate gels under vapors of organic templates and/or water. Xu et al. (1990) have first synthesized MFI powders by the VPT method. Kim et al. (1993) and Matsukata et al. (1993) showed that various kinds of zeolites can by synthesized by the VPT method.

We have applied the VPT method to synthesize zeolitic membranes composed of FER (Matsukata et al., 1994a), mordenite (MOR) (Nishiyama et al., 1995, 1996), and a mixture of FER and MFI (Matsukata et al., 1994b) on a porous alumina support. Yan et al. (1995) postulated that a defect-free zeolitic membrane is possible to be synthesized hydrothermally by the intergrowth of crystals formed on the surface of support. On the other hand, we have proposed that a defect-free zeolitic membrane can be obtained when a compact composite layer consisting of zeolite crystals and a porous support is formed (Nishiyama et al., 1996).

In this study, we synthesized defect-free MOR and FER membranes on a porous alumina support by the VPT method. The dimension of the main channel of MOR (0.65×0.70 nm) is larger than that of FER (0.42×0.54 nm). Permeation tests of gases were carried out using these zeolitic membranes. We shall propose a parallel diffusion model and analyze the temperature dependence of permeances for gases. The effect of the pore size on permeation properties was discussed using the diffusion model.

Experimental Studies

Preparation of MOR and FER membranes

Preparation of Dry Gel on Porous Alumina Support. MOR and FER membranes with an effective membrane area of 2 cm^2 were synthesized from different types of parent gels. Both types of parent gel were prepared at room temperature. For the synthesis of the MOR membrane, colloidal silica containing 30.3 wt. % of SiO_2 and 0.42 wt. % of Na_2O (ST-S; Nissan Chem. Ind.) was used as silica source. Aluminum sulfate anhydride, $Al_2(SO_4)_3$, (Wako Pure Chem. Ind. Co.) was used as the alumina source. A NaOH solution was added to colloidal silica to adjust the pH of gel. The resultant gel was mixed with an $Al_2(SO_4)_3$ aqueous solution. The composition of the parent gel was $10Na_2O$: Al_2O_3: 25 SiO_2: 700 H_2O. A porous alumina plate with an average pore diameter of 0.1 μm (Nihon Gaishi Co.) was used as support. The support was dipped in the parent gel for 1 day and dried for 2 h at 363 K.

For the synthesis of the FER membrane, the parent gel was prepared in the same procedure as that described above, except for using different source materials. Sodium silicate solution containing 35–38 wt. % of SiO_2 and 17–19 wt. % of Na_2O (Kanto Chem. Co.) and concentrated H_2SO_4 were used as the silica source and pH adjustment agent, respectively. The composition of the gel was $12Na_2O$: Al_2O_3: 25 SiO_2: 700 H_2O. The surface of the support was treated with colloidal silica at the pH of about 10 to depress the dissolution of alumina from the support (Nishiyama et al., 1996). The treated support was dipped in the parent gel. By evacuating the support from one side, the gel was forced to penetrate into the pores of the alumina support.

Crystallization. A mixture of triethylamine(Et_3N), ethylenediamine(EDA) and water was poured into the bottom of an autoclave as the vapor source. The composition was 1.5 Et_3N: EDA: 3.0 H_2O. The porous alumina support coated with aluminosilicate dry gel was set in the autoclave. The gel was crystallized in the mixed vapors of Et_3N, EDA and water under autogeneous pressure at 453 K for 4 days. The membranes were rinsed with deionized water and dried at 363 K overnight. An as-synthesized membrane was calcined at 773 K for 4 h. We adopted 0.1 $K \cdot min^{-1}$ of the heating rate at the temperature range 473–773 K. Products were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM).

Evaluation of the compactness of zeolitic membranes

The compactness of the products was checked by the permeation of 1,3,5-triisopropylbenzene (TIPB) at room temperature. The zeolitic membrane, attached on an end of a stainless tube with a cross-sectional area of 2.2 cm^2, was placed in liquid TIPB. The permeation side was kept under vacuum. The permeant was collected for 10 h in a cold trap using liquid nitrogen. After that, we put 3–5 cm^3 of methanol and 6.1×10^{-6} mol of *n*-octane into the trap. Methanol was used as a solvent and *n*-octane as a standard material. We injected 4 μL of the mixture into a gas chromatograph. We assumed that peak areas less than five counts cannot be detected on an integrator. Then, the minimum detectable flux was determined as 1×10^{-9} $mol \cdot m^{-2} \cdot s^{-1}$ under our experimental conditions.

Gas permeation test

The permeances of H_2, He, CH_4, N_2, O_2 and CO_2 through the zeolitic membranes were determined. The pressure difference between the feed and permeate sides was kept at 0.2 MPa. The permeation side was set at an atmospheric pressure. The permeation rates of gases through the zeolitic membranes were measured at 290–400 K. The experimental apparatus for the gas permeation tests was shown by Matsukata et al. (1994a).

Results and Discussion

Figure 1 shows the XRD patterns from MOR and FER membranes. These patterns were similar to those from common powder MOR and FER, respectively, indicating that randomly-oriented polycrystalline MOR and FER were formed on the alumina support.

The pervaporation of TIPB, which has a kinetic diameter

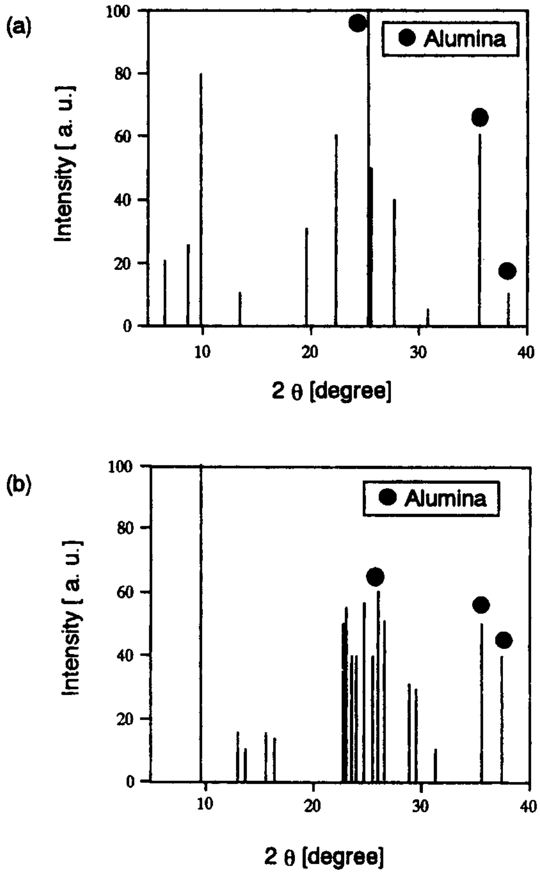

Figure 1. XRD patterns for (a) MOR and (b) FER membranes.

(0.85 nm) greater than the pore dimensions of MOR and FER, was carried out. No permeation of TIPB was detected through both zeolitic membranes. The minimum detectable flux was 1×10^{-9} $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ under our experimental conditions as described above. These zeolitic membranes were practically defect-free.

We performed the permeation tests of benzene before and after the permeation test of TIPB. The flux of benzene after the permeation test of TIPB was 7×10^{-5} $\text{mol}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$ and almost the same as that before the permeation test of TIPB. No TIPB was detected in the later permeation test of benzene. Thus, we concluded that no TIPB existed in the micropore of FER. In addition, the TIPB adsorbed around the entrance of micropore could easily be substituted by benzene. Therefore, there clearly existed no pinhole and no crack, which would allow the entrance of TIPB into the FER membrane.

Figure 2 shows the SEM images of the cross-sectional views for the MOR and FER membranes. A composite layer consisting of porous alumina and zeolite was clearly formed. Voids among the MOR or FER crystals on the porous alumina support were observed in the SEM images for both membrane surfaces. We thus believe that the zeolite-alumina composite layer is compact. The thickness of the composite layer was about 20 μm for the MOR membrane and 40 μm for the FER membrane. A detailed discussion on the structure of these zeolite-alumina composite layer will be reported in the near future.

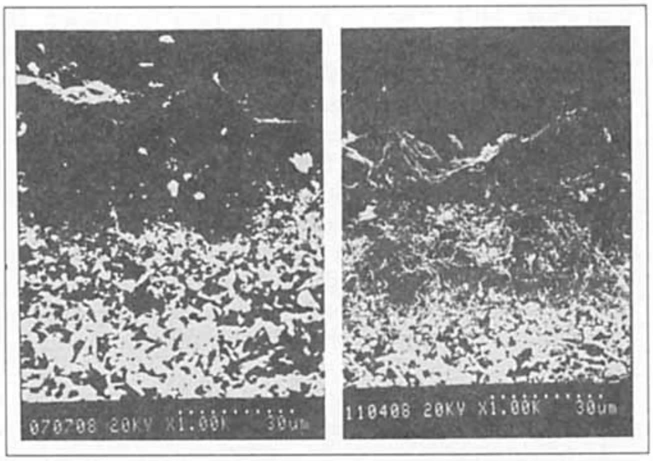

Figure 2. SEM images of the cross-sectional views of (a) MOR and (b) FER membranes.

Figure 3 shows the permeances of H_2, He, CH_4, N_2, O_2 and CO_2 through the MOR and FER membranes in the temperature range from 290 to 400 K. Judging from the results of the permeation tests of TIPB, we concluded that these gases permeated through the micropores of zeolite. The permeance of each gas through the MOR membrane was about 100 times greater than those through that of FER. This is due presumably to the pore diameter of MOR larger than that of FER, since the thickness of the compact layer in the MOR membrane was almost comparable to that of FER as described above.

The permeances of H_2, He and CH_4 through the MOR membrane monotonously increased with increasing temperature, indicating that the controlling mechanism of permeation did not change in this temperature range. This temperature dependence of the permeances is evidently caused by the activated diffusion. The permeances of gases through the MOR and FER membranes, except for H_2, He, and CH_4 through the MOR membrane, showed minimums with increasing temperature, suggesting that a different controlling mechanism should be taken into consideration.

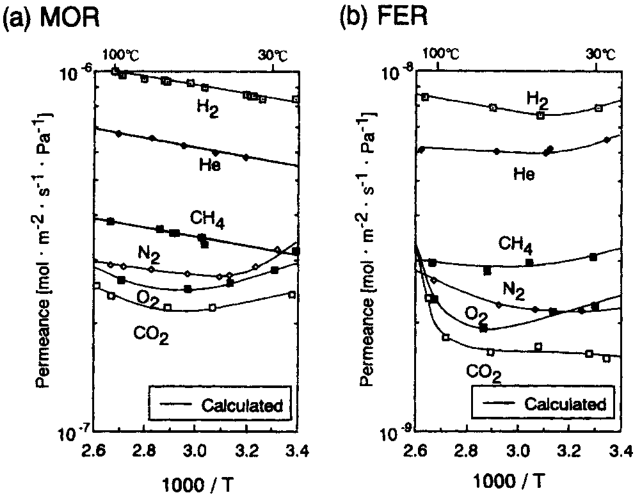

Figure 3. Permeances of single gases through (a) MOR and (b) FER membranes.

At higher temperatures, the temperature dependency of the permeances of all gases through both membranes indicated that the activated diffusion mechanism governed permeation: the interaction between molecules and pore wall played dominant role of permeation. It can be said that at lower temperatures the molecule-pore wall interaction significantly contributed to permeation mechanism. Therefore, we excluded the contribution of Knudsen diffusion mechanism.

Analysis of the permeance through the membranes

Barrer (1990, 1991) first discussed the permeation through a zeolitic membrane. His theory was based on the assumption that the entry of molecules into the membrane and their escape from there proceed via an externally adsorbed layer, which is called the interface process. He concluded that the contribution of the interface processes to the steady flow through zeolitic membrane would become less significant with increasing temperature and membrane thickness. On the basis of his theory, the role of the interface processes would be negligibly small at room temperature if the membrane thickness is greater than 1 μm, indicating that the rate-limiting process of the permeation through zeolitic membranes is the intracrystalline diffusion in the micropores of zeolite under our experimental conditions.

Shelekhin et al. (1995) modeled the single gas permeation through the molecular-sieve glass membranes. In their model, the total concentration of gas molecules inside the membrane is the sum of the gas-phase and adsorbed-phase concentrations. They concluded that the effect of the adsorbed diffusant on the total flow is significant for highly adsorbable gas.

Shelekhin's approach and the simple Fick formulation considering the concentration dependence of diffusivity cannot account for the appearance of the minimum permeances through the MOR and FER membranes. To explain the temperature dependence, the micropores of zeolite should be considered as the energetically heterogeneous surface. Seidel and Carl (1989) and Kapoor and Yang (1989) assumed that the surface consists of parallel paths such that each path has uniform, but different, energy, and surface diffusion occurs along these parallel paths. Their parallel-paths assumption contains a continuous energy distribution. Their parallel paths conception is, however, rather complicated. Actually, molecules in the micropore collide with each other and with the wall of the micropore as depicted in Figure 4a. We consider two parallel paths in the micropores in our simplified parallel diffusion model as depicted in Figure 4b. The molecules adsorbed in the micropore diffuse in parallel through the central region of a pore and along the wall region of a pore. In other words, there are two types of molecules with different adsorption energies and activation energies of diffusion in the micropores.

We assumed that the adsorption equilibrium between the center and wall region of the pores is always accomplished and that the movement of molecules between the center and wall regions of the pores is very rapid and that in the direction parallel to zeolite pores is relatively slow. The ratio of the numbers of molecules diffusing through each path expresses the probability of the existence of molecules in each path.

Furukawa and Nitta (1997) have recently studied gas permeation through nanoporous carbon membranes by nonequilibrium molecular dynamics. They showed the snapshots in simulation cell for ethane in the pore of four different pore widths. According to their snapshots, most of molecules in the broad pore diffused near the wall. However, in narrower pore of carbon, the number of the molecules diffusing around the center of pore became increased, suggesting that a parallel diffusion possibly occurs in the micropores of zeolites for small molecules. Their results strongly support that the parallel diffusion model is a reasonable concept.

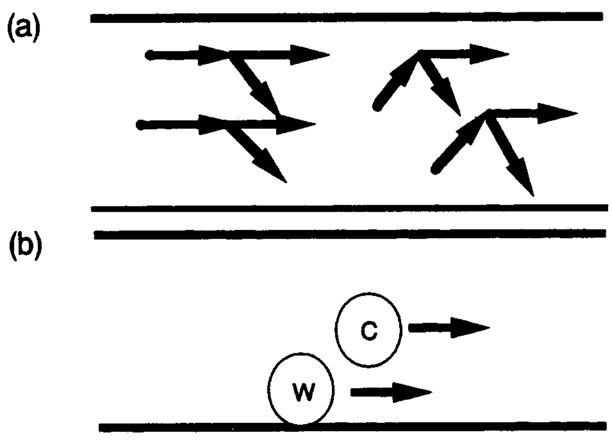

Figure 4. Parallel diffusion model.

Based on Barrer (1990)'s discussion, we assumed that the rate-limiting process of permeation through a zeolitic membrane is intracrystalline diffusion. The diffusive flux is generally written as

$$J = -D_F \frac{dC}{dx} = -D \frac{d \ln p}{d \ln C} \frac{dC}{dx} = -D \frac{d \ln p}{d \ln C} \frac{dC}{dp} \frac{dp}{dx}. \quad (1)$$

In this case, the adsorption equilibrium at the interface between the gas phase and membrane is accomplished. If gas adsorption on a zeolitic membrane at temperatures higher than room temperature is assumed to follow Henry's law, the derivatives are

$$\frac{d \ln p}{d \ln C} = 1, \quad \frac{dC}{dp} = \frac{K_H}{RT} = \frac{K_{H0}}{RT} \exp\left(\frac{q_{st}}{RT}\right) \quad (2)$$

where K_H and q_{st} represent Henry's constant and isosteric heat of adsorption, respectively. This model does not consider molecule-molecule interaction but wall-molecule interaction, because the low concentration (Henry law) region is assumed here. Diffusivity in activated process can be written as

$$D = D_0 \exp\left(\frac{-E}{RT}\right) \quad (3)$$

where D and E represent diffusivity and activation energy of diffusion, respectively. By introducing Eqs. 2 and 3 into Eq. 1, we obtain

$$J = -\frac{D_0 K_{H0}}{RT} \exp\left(\frac{q_{st} - E}{RT}\right) \frac{dp}{dx}. \quad (4)$$

At the steady state,

$$\frac{dJ}{dx} = 0, \quad \text{then} \quad \frac{dp}{dx} = \frac{\Delta p}{d} \tag{5}$$

where Δp represents the pressure difference. The permeance through a zeolitic membrane is, then, expressed as

$$P = -\frac{\theta}{\tau d} \frac{D_0 K_{H0}}{RT} \exp\left(\frac{q_{st} - E}{RT}\right). \tag{6}$$

Here, a parallel diffusion mechanism is applied to Eq. 6. The molecules adsorbed in the micropore diffuse in parallel through the central region of a pore and along the wall region of a pore. The permeance is expressed as the sum of both contributions:

$$P = -\frac{\theta}{\tau d} \sum_{i = c,w} \frac{D_{0,i} K_{H0,i}}{RT} \exp\left(\frac{q_{st,i} - E_i}{RT}\right). \tag{7}$$

Suffixes, c and w, correspond to the diffusion through the central region of a pore and along the wall region of the pore, respectively.

We considered that both types of diffusion contributed to the permeation of gases under these experimental conditions, except for the permeation of H_2, He and CH_4 through the MOR membrane. The parameter fitting was carried out using Eq. 7 on the assumption that molecules dominantly diffuse through the central region at higher temperatures and along the wall region at lower temperatures. The parameter fitting contains a set of two adjustable parameters, $\epsilon D_0 K_{H0}/\tau d$ and $q - E$, for each path. Solid lines in Figure 3 represent the values calculated from Eq. 7. The proposed parallel diffusion model expresses the experimental data well.

Based on the calculated results, we separated the permeance, P, into two types of mass transportation through the central region of a pore, P_C, and along the wall region of a pore, P_W, where $P = P_C + P_W$. Figure 5 shows the temperature dependence of P_C, P_W and P calculated for He and CO_2 through the FER membrane, suggesting that the diffusion along the wall region of the FER pore cannot be ignored even for the permeation of He. The adsorbable gas, CO_2, diffuses dominantly along the pore wall at room temperature for the FER membrane.

Figure 6 shows the ratios of P_W to P for each gas. The diffusants along the wall region were more dominant through the FER membrane compared with those through the MOR membrane. This seems reasonable because the interaction between molecules and a pore wall should become more significant in a narrower pore. In the MOR membrane, H_2, He and CH_4 exclusively diffused through the central region of the pore. In other words, the interaction between molecules and the pore wall of MOR was not strong enough to make the diffusion along the pore wall remarkable. For both membranes, the values of P_W/P for CO_2 were greater than any other gas and those for He were the smallest. These results imply that the parallel diffusion model can account for the effect of the interaction between molecules and a pore wall.

One can note that the permeation behavior depends clearly on not only the pore size of zeolites but also the SiO_2/Al_2O_3 ratio of zeolites. Sun et al. (1996) used a membrane made of a large single crystal of pure-silica MFI with a size of 100 × 100 × 300 μm for the single-gas permeation tests of methane, ethane, propane and butane. The permeances of these gases through a single-crystal of MFI increased with increasing temperature in the temperature range 303–343 K. Lewis et

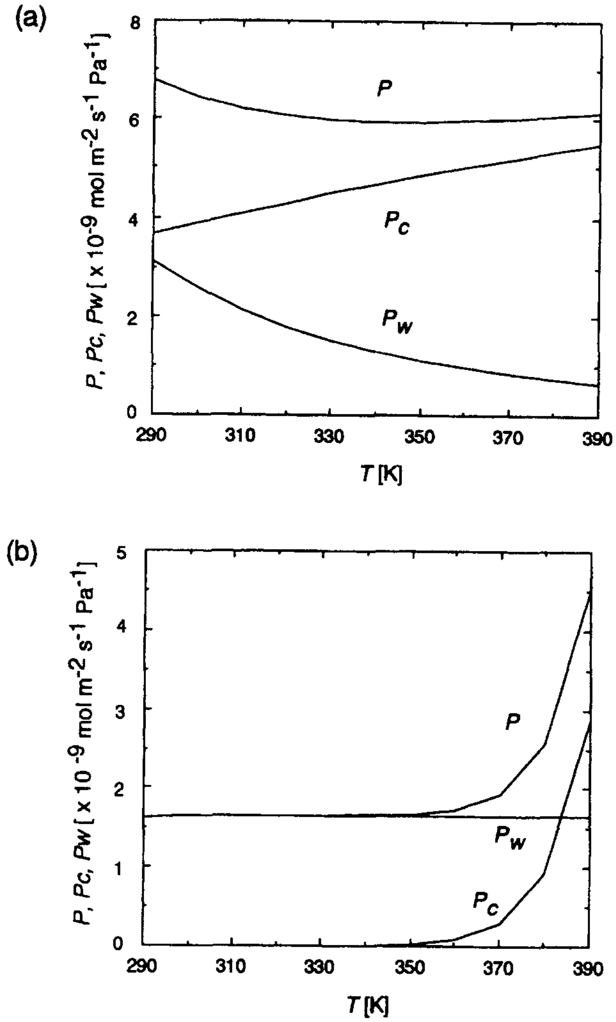

Figure 5. P, P_c, and P_w for (a) He and (b) CO_2 through FER membrane.

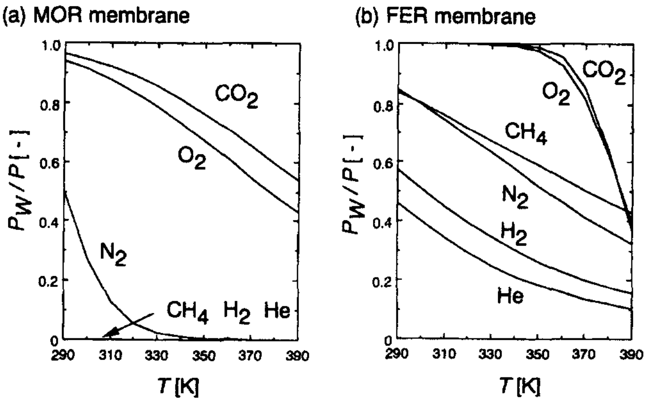

Figure 6. Temperature dependence of P_w/P.

Table 1. $(q_{st} - E)$ and $(\epsilon D_0 K_{HO}/\tau d)$ for MOR and FER Membranes

		$q_{st,c} - E_c$ [kJ·mol^{-1}]	$\epsilon D_{0,c} K_{H0,c}/\tau d$ [m·s^{-1}]	$q_{st,w} - E_w$ [kJ·mol^{-1}]	$\epsilon D_{0,w} K_{H0,w}/\tau d$ [m·s^{-1}]
MOR	H_2	−5.1	1.9×10^{-3}		
	He	−5.5	1.5×10^{-3}		
	CH_4	−5.0	7.1×10^{-4}		
	N_2	−6.6	5.7×10^{-4}	34	5.3×10^{-17}
	O_2	−23	8.8×10^{-2}	4.9	1.1×10^{-5}
	CO_2	−27	1.9×10^{-1}	2.1	2.9×10^{-5}
FER	H_2	−9.8	5.9×10^{-5}	8.9	3.4×10^{-8}
	He	−6.6	1.6×10^{-5}	12	6.3×10^{-9}
	CH_4	−14	5.0×10^{-5}	4.2	1.4×10^{-7}
	N_2	−19	2.6×10^{-4}	3.9	1.1×10^{-7}
	O_2	−110	3.8×10^{9}	0.7	5.2×10^{-7}
	CO_2	−140	1.6×10^{13}	−2.8	1.5×10^{-6}

al. (1997) also carried out single-gas permeation tests of methane using a membrane made of a single crystal of pure-silica FER (600×500×20 μm). The permeances of methane through the pure-silica FER membrane increased with increasing temperature in the temperature range 323–398 K.

Through pure-silica zeolite membranes, the diffusants in central region of the pore should be dominant compared with those through Al-containing zeolite membranes. Thus, minimum permeances should appear at lower temperatures for pure-silica zeolite membranes.

Table 1 summarizes the fitting parameters, $(q_{st,i} - E_i)$ and $\epsilon D_0/\tau d K_{H0}$. All the values of $(q_{st,w} - E_w)$ were much greater than those of $(q_{st,c} - E_c)$: the values of $(q_{st,w} - q_{st,c})$ were much greater than those of $(E_W - E_C)$. This result suggests that the activation energies of diffusion along the pore wall, E_W, are not much greater than those through the central region of pore, E_C, although there are large differences in the heats of adsorption between molecules on the pore wall, q_{stw}, and in the central region, q_{stc}. The value of $(q_{st,c} - E_C)$ for CO_2 was much less than that of any other gas for both MOR and FER membranes, possibly suggesting that the activation energy, E_C, of CO_2 was much greater than those for other gases.

Conclusions

The permeances of H_2, He, CH_4, N_2, O_2 and CO_2 through defect-free MOR and FER membranes were determined at 290–400 K. The temperature dependencies of the permeances were analyzed using a parallel diffusion model in which the permeance was separated into two contributions, molecules diffusing through the central region of the pore and along the wall region of the pore. The contribution of the diffusion at the wall region to the total permeation decreased with increasing temperature. The effect of diffusion along the pore wall on the total permeation was significant for adsorbable gas-like CO_2. In contrast, the diffusion through the central region of the pore was dominant for He. The molecules, which diffuse along the pore wall, were more dominant through the FER membrane compared with those through the MOR membrane, indicating that the effect of difference in the pore size between MOR and FER appeared. The proposed parallel diffusion model is useful for analyzing the interaction between gas molecules and a pore wall.

Acknowledgments

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Notation

C = concentration of molecule in membrane, mol·m^{-3}
D_F = Fickian diffusivity, m^2·s^{-1}
D = intrinsic diffusivity, m^2·s^{-1}
d = membrane thickness, m
E = activation energy, J·mol^{-1}
J = flux, mol·m^{-2}·s^{-1}
K_H = Henry's constant
p = pressure, Pa
Δp = pressure difference, Pa
P = permeance, mol·m^{-2}·s^{-1}·Pa^{-1}
q_{st} = isosteric heat of adsorption, J·mol^{-1}
R = gas constant, 8.314 J·mol^{-1}·K^{-1}
T = temperature, K
x = direction coordinate, m
θ = porosity of membrane
τ = tortuosity of membrane

Subscripts

c = center of pore
i = c or w
w = wall of pore
0 = constant

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