Gas Permeation Through DDR-Type Zeolite Membranes at High Temperatures

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DDR-type zeolite membranes were prepared by the secondary growth method on porous α-alumina disk, followed by on-stream counter diffusion chemical vapor deposition modification to eliminate the intercrystalline micropores. Single gas permeation of He, H_2, CO_2, and CO through this zeolite membrane before and after CVD modification was measured in 25–500°C. Intracrystalline diffusivities for these four gases in DDR-type zeolite were obtained from the permeation data above 300°C to examine the effects of the size and molecular weight of permeating gases on diffusion and permeation rate for this zeolite membrane. For the unmodified DDR-type zeolite membrane with presence of a small amount intercrystalline micropores the diffusivity (or permeance) with a low activation energy depends on both the size and molecular weight of permeating gases. For the CVD-modified DDR-type zeolite membrane with intercrystalline micropores eliminated, the activation energy for diffusion and diffusivity increases with increasing molecular size of the permeating gases. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 1478–1486, 2008

Keywords: DDR-type zeolite membrane, gas permeation, diffusivity, high temperatures, diffusion theory

Introduction

Zeolites are crystalline aluminosilicates materials having micropores (zeolitic pore) in their structures. They are built up by various connections of TO4 (T = Si or Al) tetrahedral which result in the various zeolitic pore sizes and structures. Small gas permeation and separation data evaluated for a wide temperature range in small and intermediate zeolites, i.e., A-type, DDR-type, and MFI-type will provide improved understanding of gas diffusion and permeation properties of these materials. Such data are important to applying these materials to future industrial processes such as hydrogen production, CO_2/N_2 separation, and hydrocarbon separation.

A-type zeolite membranes have been extensively studied. Their use has been mainly for separations of liquid mixtures by pervaporation.[1,2] NaA zeolite membranes have exhibited high water to ethanol separation factor over 10,000 by pervaporation at 75°C.[3] High separation performances are attributed to the preferential adsorption of water molecules by zeolitic pores. This preferential adsorption is due mainly to the fact that the surface nature of A-type zeolite is hydrophilic; a result of the low Si/Al ratio in the framework. A few research groups have reported the small gas permeation characteristics for A-type zeolite membrane.[4,5] Aoki et al.[4] suggested that the behavior for NaA zeolite (d_p = 0.41 nm) membrane was dominated by the molecular sieving mechanism, despite the presence of defects larger than the structural pores. Another consequence of the low Si/Al ratio found in A-type zeolite is a lack of thermal stability, which is why no work on its gas permeation characteristics at high temperatures (>300°C) has been reported.

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MFI-type zeolite structure contains two channels: a straight channel along the *b*-axis with circular openings of $0.54 \times 0.56\ \mathrm{nm}^2$ and a sinusoidal channel along the *a*-axis with elliptical openings of $0.51 \times 0.55\ \mathrm{nm}^2$.[6] This particular zeolite is attractive for gas separation membrane due to its resilience in harsh conditions stemming from its high thermal and chemical structure stability.[7] MFI-type zeolite membranes offer potential applications for separation of hydrocarbon isomers.[8–11] This is due to a dual effect of molecular sieving of permeating gas molecules by the zeolitic pores from size and shape selectivity as well as the preferential adsorption by zeolitic pores governed by the surface chemistry.

Gas permeation through MFI and other type zeolite membranes has been extensively studied.[1] Most work was focused on the temperature and pressure dependency of gas permeance through zeolite membranes, which could be well explained by Stefan-Maxwell flux equation incorporating the diffusivity equation developed by Xiao and Wei[12] and a proper equilibrium adsorption isotherm equation. However, experimental work showing the effects of the size or molecular weight of permeating gases, particularly those of light gases, on permeation (or diffusion) properties of a zeolite membranes are scarce,[13,14] and the limited results are inconsistent or confusing. For example, Lovallo and Tsapatsis [13] reported H_2/N_2 permselectivity of 60 at 150°C for a silicalite membrane. The permeances of H_2, N_2, and O_2 increase with increasing temperature. Lai et al.[14] reported high H_2/CH_4 permselectivity of 1000 at 25°C with larger activation energy of H_2 permeation (24–31 kJ mol^{-1}) on ZSM-5 membranes. On the other hand, Min et al.[15] reported activated permeation behavior of H_2 and He with below Knudsen selectivity of H_2/N_2 at temperatures around 400°C. On contract, the permeance of hydrogen, though with a larger kinetic diameter, is always larger than that of helium through the medium pore MFI-type[15,16] and small pore DDR-type[17] membranes.

For diffusion in zeolites, Xiao and Wei[12] developed a theory that can predict the diffusivity of a single species in zeolite micropores from temperature, relative size of the gas molecule to the zeolite pore, and gas molecular loading in the microporous material. For diffusion of small gases with weak adsorption affinity with zeolites or at high temperatures, molecules in the zeolite pores retain their gas characteristics, though their movement is restricted and has to overcome the energy barrier imposed by the zeolite pore structure. Under these conditions, they predicted that for a given zeolite the activation energy depends strongly on the ratio of kinetic diameter of the diffusion gas molecule to the zeolite pore diameter, $\lambda\ (=d_\mathrm{m}/d_\mathrm{p})$ when $\lambda > 0.5$, and weakly on the ratio of kinetic diameter to the Lennard–Jones length constant for molecule $(d_\mathrm{m}/\sigma_\mathrm{m})$.[12] This theory provides the basis to examine the efforts of the size or molecular weight on gas permeation through zeolite membranes. However, experimental efforts on studying the effects of the molecular size or weight on gas permeation (or diffusion) in zeolite membranes is complicated by the difficulty in obtaining high quality zeolite membranes without intercrystalline pores and measuring equilibrium adsorption of gases on the zeolite film which is coated on a much thick inorganic support. Furthermore it is difficult to measure the diffusivity for small gases with weak adsorption affinity with zeolite or at high temperatures as most diffusion measurement techniques rely on the adsorption of gases in zeolite pores and many zeolites are not stable at high temperatures.

The highly siliceous DDR (Deca-Dodecasil 3R)-type zeolite contains pores formed by a polyhedron with an oxygen eight-membered-ring. This zeolite has a high thermal stability allowing a study of gas permeation (or diffusion) at high temperatures at which adsorption is negligible. This avoids the necessity to measure equilibrium of gas adsorption in the supported, thin zeolite film. Furthermore, this zeolite has small pore openings ($0.36 \times 0.44\ \mathrm{nm}^2$)[18] making it an ideal candidate to study the effects of size or molecular weight of gases on permeation or diffusion properties for zeolites and zeolite membranes. However, obtaining reliable data to examine these effects is challenging, as it requires preparation of high quality DDR-type zeolite membranes and measurements of gas permeation through the zeolite membranes at high temperatures. The article reports on synthesis of high quality DDR-type zeolite membranes and properties of gas permeation and diffusion of small gas molecules (He, H_2, CO_2, CO) in DDR-type zeolite membranes in a wide temperature range up to 500°C, with an objective to clarify the effects of molecular weight and size of small gases and the size of zeolite pores on gas permeation and diffusion in zeolites and zeolite membranes.

Experimental

Preparation and characterization of DDR-type zeolite membrane

The method of synthesizing pure DDR crystals was first reported by den Exter et al.[19] In later work, Tomita and coworkers[17,20] used the method to produce seed crystals for a DDR-type membrane synthesized by a secondary growth method. The surface of ceramic supports were coated with a seed solution that consisted of DDR crystals dispersed in deionized water. Synthesis of the DDR crystals required growth of a precursor solution containing the molar ratio of 47 1-adamantanamine: 100 silica: 404 ethylenediamine: 11,240 water in a pressure vessel at 160°C for 25 days. The precursor solution was prepared by adding 1-adamantamine rapidly to a mixture of ethylenediamine and water. The solution was then shaken for an hour and heated to 95°C for an additional hour under stirring conditions. After cooling in ice, tetramethoxysilane was added drop-wise while the stirring was continued.

The growth of a continuous DDR membrane on the seeded supports was performed by a secondary growth with a precursor solution consisting of 1 silica: 0.063 1-adamantamine: 1 ethylenediamine: 33 water. This solution was prepared in the same manner as described above. The seeded support was immersed in the solution within a pressure vessel and growth was performed at 155°C for 48 h. To remove the template from the occluded pores calcination was required at 700°C for 5 h.

The phase structure, morphology, and thickness of the supported DDR-type zeolite membranes were characterized by using XRD (Bruker, Cu Kα radiation) and SEM (Philips, XL 30). The XRD measurements were performed by step-wise scanning (2θ step-size: 0.025°, $5° < 2\theta < 40°$).

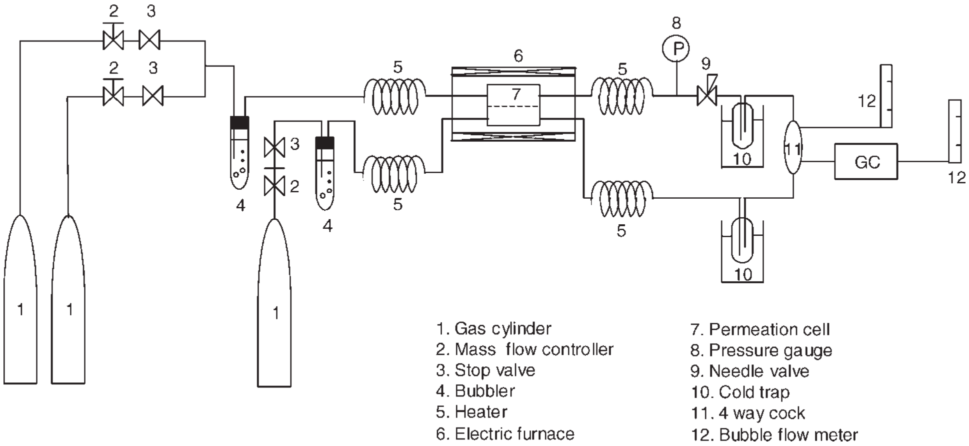

Figure 1. Experimental apparatus for gas permeation (without bubblers) and counter diffusion CVD modification (with bubblers included for precursors).

Gas permeation measurements and counter diffusion CVD modification for DDR-type zeolite membrane

Figure 1 shows schematic diagram of experimental apparatus for gas permeation and counter diffusion CVD modification. The membrane was fixed in a stainless steel cell with the zeolite layer facing the upstream, and was sealed by graphite rings. The leakage flow, which comes from graphite rings, is about 8×10^{-11} to 2×10^{-10} mol m^{-2} s^{-1} Pa^{-1}, and at high temperatures (450–500°C), the leakage flow slightly increases about 10–20%.[21] It should be noted that good sealing of the zeolite membrane at high temperatures requires adequate design of the cell and graphite ring seals, proper installation of the zeolite membrane in the cell, and controlled temperature ramping rate. The liquid bubblers shown in the schematic were absent during the permeation experiments, but were used for liquid precursors during CVD modification.

In gas permeation equipments, single gas of He, H_2, CO_2, or CO of industrial grade was fed at flow rate of 100 cm^3 min^{-1} in the cross-flow mode over the zeolite film surface of the membrane disk at 300 kPa. The downstream surface of the zeolite membrane disk was swept by nitrogen at the flow rate of 12 cm^3 min^{-1} in the atmospheric pressure. The flow rates and compositions of the retentate and permeate were respectively measured or analyzed by bubble flow meters and gas chromatography with a TCD detector (5973 Agilent GC/MS system with stainless-steel column; HAYESEP DB 100/120 (ALLTECH)). Permeation experiments were conducted in 25–500°C (heating/cooling rate: 30°C h^{-1}).

Some of the DDR-type zeolite membranes were modified by counter diffusion CVD on the setup shown in Figure 1, with addition of bubblers respectively filled with tetraethylorthosilicate (TEOS, 98% Sigma-Aldrich) and water. N_2 was used as the carrier gas and the flow rate was kept at 100 cm^3 min^{-1} by a mass flow meter. The carrier gas with TEOS vapor was fed to the zeolite film surface while that with water vapor to the alumina support side of DDR membrane. The concentration of tetraethylorthosilicate (TEOS, 98% Sigma-Aldrich) and/or water vapor was controlled by changing the bubbling temperature. In this work, both bubbler temperatures were kept at room temperature. The reaction (substrate) temperature was kept at 500°C. The gas permeation experiments on the CVD-modified zeolite membranes were performed on-line during the modification. The single gas permeation experiments were performed by replacing the feeds of TEOS and water containing carrier gases with the single permeating as described above in the specified intervals of CVD modification.

Results and Discussion

DDR-type zeolite membranes and gas permeation properties

The SEM images of the cross section and surface of the DDR-type zeolite membranes after secondary growth are given in Figure 2. As shown in these micrographs, crack-free continuous DDR-type zeolite film could be formed on porous alumina support. The thickness of secondary growth zeolite layer is around 10 μm. The grains after secondary growth are around at 5 μm and well intergrown.

Figure 3 shows XRD pattern of the DDR-type zeolite membrane. The appearance of the deflection peaks from alumina comes from the support confirming the small thickness of the DDR-type zeolite layer. The rest peaks are characteristic of the DDR-type zeolite structure.

Figure 4 shows single gas permeation characteristics of DDR-type zeolite membrane at 25–500°C. The broken line (no symbols) at the bottom of this figure shows a reference curve to compare the slope of the temperature dependency of the permeance with the Knudsen behavior. The permeances of He and H_2 decrease with decreasing temperature in a manner similar to activated permeation above 100°C, while below 100°C these permeances increase with decreasing temperature somewhat like Knudsen permeation. Even in an activated permeation mechanism at high temperatures, the permeance of H_2 for DDR-type zeolite membrane is slightly larger than that of He.

The permeance of CO also decreases with decreasing temperature above 100°C, while below 100°C the permeance slightly increases with decreasing temperature. On the other hand, the permeance of CO_2 increases drastically with decreasing temperature in a manner similar to surface-diffusion

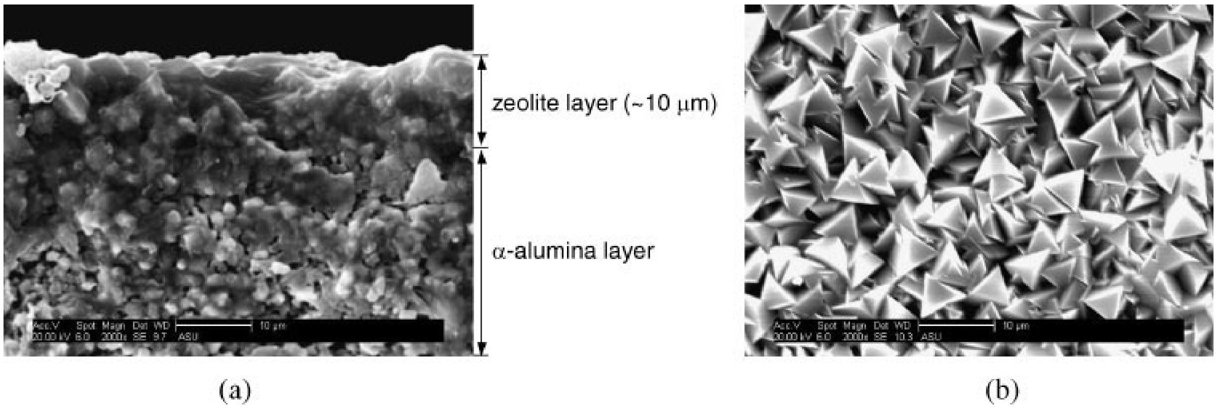

Figure 2. SEM image of the cross section of the DDR-type zeolite membrane after secondary growth (a) and surface of membrane (b).

mechanism. Even though the kinetic diameter of CO_2 (d_m = 0.33 nm) is larger than that of He (d_m = 0.26 nm) and H_2 (d_m = 0.289 nm), the permeance of CO_2 is larger than those of He and H_2 below 100°C.

At the steady state, single gas permeance through a zeolite membrane can be obtained by[1]:

$$F = \frac{\phi}{L(P_f - P_p)} \int_{q_f}^{q_p} D_c \left(\frac{d \ln P}{d \ln q} \right) dq \tag{1}$$

where q_p and q_f are the concentrations of the permeating gas in the zeolite membrane at the feed and permeate side, respectively, ϕ is a constant accounting for the membrane porosity and totuosity factor, and D_c is the gas diffusivity in zeolite. The above equation correlates the permeance to the diffusivity, sorption equilibrium properties, membrane thickness, and the upstream and downstream pressures. For gas-zeolite systems with a linear adsorption isotherm ($q = KP$) where K is adsorption equilibrium constant, Eq. 1 is deduced to:

$$F = \frac{\phi}{L}(D_c K) \tag{2}$$

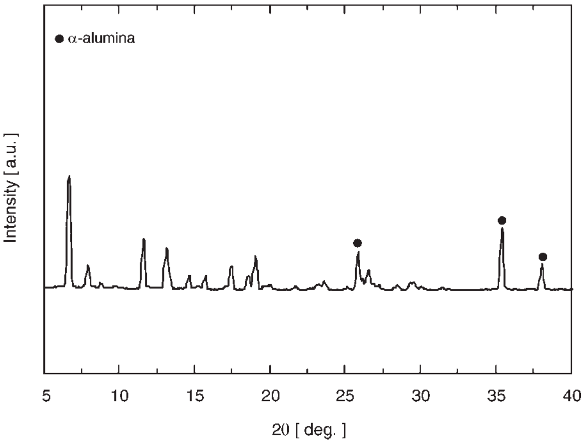

Figure 3. XRD pattern of DDR-type zeolite membrane.

For diffusion of small gases with weak adsorption affinity with zeolites, Xaio and Wei[12] proposed the following gas translational diffusion model to predict diffusivity in zeolite pores:

$$D_c = \frac{\alpha}{z} \left(\frac{8RT}{\pi M} \right)^{1/2} \exp\left(\frac{-E_d}{RT} \right) \tag{3}$$

where E_d is the energy barrier for diffusion of the gas in the micropores, which is determined by the relative size of diffusing gas molecule to the zeolite pore size; M is the molecular weight of the diffusing gas; α is the diffusion length (or distance between two adjacent sites, $\alpha = d_p$ for Knudsen diffusion and is about 1 nm for diffusion in MFI-type zeolite), z is the diffusion coordination number (four for MFI type zeolite). As shown in Eq. 3, the diffusivity in zeolites is deter-

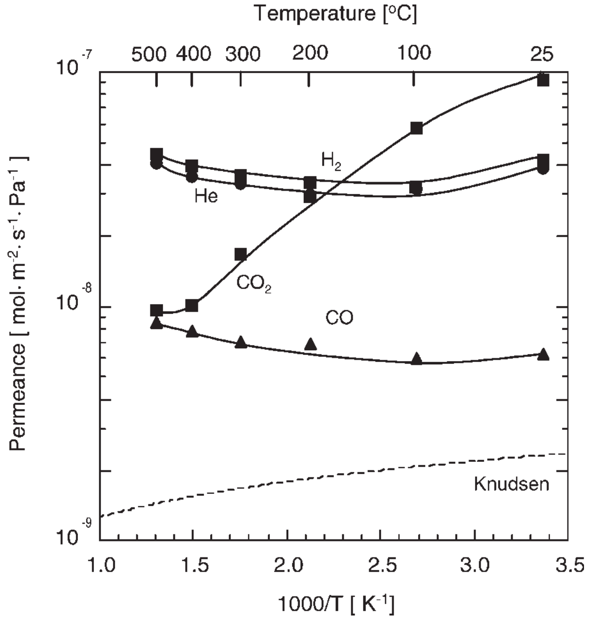

Figure 4. Single gas permeation characteristics of DDR-type zeolite membrane at 25–500°C.

Table 1. Activation Energy of He, H_2, CO_2, and CO Diffusion for DDR-Type Zeolite Membrane Before and After Counter Diffusion CVD Modification

		Activation Energy E_d (kJ moI^{-1})		
	λ (d_m/d_p) (−)	Before CVD Modification	After CVD Modification	Ratio (E_d(After)/ E_d(Before)) (−)
He	0.65	6.18	6.66	1.08
H_2	0.73	6.45	9.62	1.49
CO_2	0.83	–	12.8	–
CO	0.94	7.04	15.5	2.21

mined and can be predicted by molecular weight, M, and the activation energy for diffusion, E_d.

For diffusion of small molecules with a weak adsorption affinity with zeolite pores, or at high temperatures, $K = 1/RT$, inserting Eq. 3 into Eq. 2 gives:

$$F = \frac{\phi}{L}\frac{\alpha}{z}\left(\frac{8}{\pi MRT}\right)^{1/2}\exp\left(\frac{-E_d}{RT}\right) \tag{4}$$

If E_d is close to zero, both molecular weight and the size of permeating molecules determine the gas diffusivity or permeance.

The activation energy of gas diffusion was obtained by regressing Eq. 4 with the experimental permeation data at different temperatures above 300°C (to ensure validity of Eq. 2 and $K = 1/RT$). The activation energy for diffusion for He, H_2, and CO gases in the DDR-type zeolite are given in Table 1. Similar data for CO_2 were not calculated because the permeation data shows that adsorption still pays a significant role in gas permeation for CO_2 through the unmodified DDR-type zeolite membranes at temperatures above 300°C, as shown in Figure 4. The activation energy for the three gases, despite of different molecular sizes, is comparable; He: 6.18 kJ mol^{-1}, H_2: 6.45 kJ mol^{-1}, CO: 7.04 kJ mol^{-1}. If the average pore size of DDR-type zeolitic is assumed to be about 0.4 nm, the activation energy of CO permeation should be much higher than that of He and H_2 due to the fact that the ratio of λ ($=d_m/d_p$) for CO molecule ($\lambda = 0.94$) is larger than that of He ($\lambda = 0.65$) and H_2 ($\lambda = 0.73$) molecules.[12]

The discrepancy mentioned above is most likely due to the existence of intercrystalline gaps in the DDR-type zeolite membrane, giving a larger average pore size for the zeolite membrane than zeolitic pores. Since the as-synthesized DDR type zeolite membranes have very small SF_6 permeance[17] (below 10^{-11} mol m^{-2} s^{-1} Pa^{-1}), these intercrystalline gaps (or defects) must be very small in size and quantity. However, their presence has a strong influence on the gas permeation and selectivity of these small gas molecules. Thus, to show true gas permeation (diffusion) characteristics for the DDR-type zeolites, DDR-type zeolite membranes should be modified to eliminate possible intercrystalline pores.

CVD modification and gas permeation properties of modified membranes

It is well known that many polycrystalline zeolite membranes include not only zeolitic pores but also intercrystalline gaps. Because the total permeation flow cannot be separated to the flow through the defects and flow through the zeolitic pores, it makes it difficult to determine the gas permeation behavior through just the zeolitic pores. A counter diffusion CVD modification technique is effective tool to modify defects and intercrystalline gaps in a membrane while avoiding blocking the zeolite pores.[22] Nomura et al.[22] conducted counter diffusion CVD technique to plug the intercrystalline gaps and defects in a silicalite membrane. Tetramethylorthosilcate (TMOS) and tetraethylorthosilicate (TEOS) were used as the reactants. Since the molecules of these silica sources are larger than the zeolitic pores, they are not expected to enter into the zeolitic pores of MFI-type or DDR-type zeolites.

To determine the small gas permeation behavior through only the structural pores of DDR-type zeolite membrane, the DDR-type zeolite membrane sample shown in Figure 4 was modified by counter diffusion CVD techniques on the permeation setup shown in Figure 1. Figure 5 shows observed gas permeance changes at 500°C for DDR-type zeolite membrane (same membrane in Figure 4) as a function of counter diffusion CVD modification time. The CVD modification results in decrease in the permeance for all the four gases. The extent of reduction in gas permeance by CVD modification increases with the size of permeating gases (i.e., the gas permeance of the 58-h CVD-modified membrane is about 75, 55, 40, and 25% of that of unmodified membrane for CO, CO_2, H_2, He). The unmodified DDR-type zeolite membrane has a higher permeance for larger H_2 than that for smaller He. The H_2/He selectivity is reversed for the CVD-modified DDR-type zeolite membrane, indicating that the small

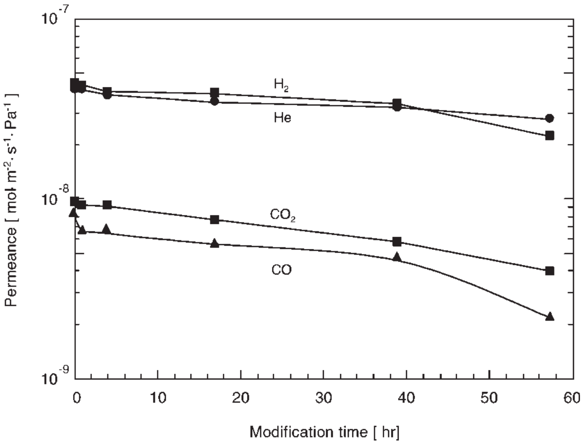

Figure 5. Observed gas permeance changes at 500°C for DDR-type zeolite membrane (same membrane in Figure 4) as a function of counter diffusion CVD modification time.

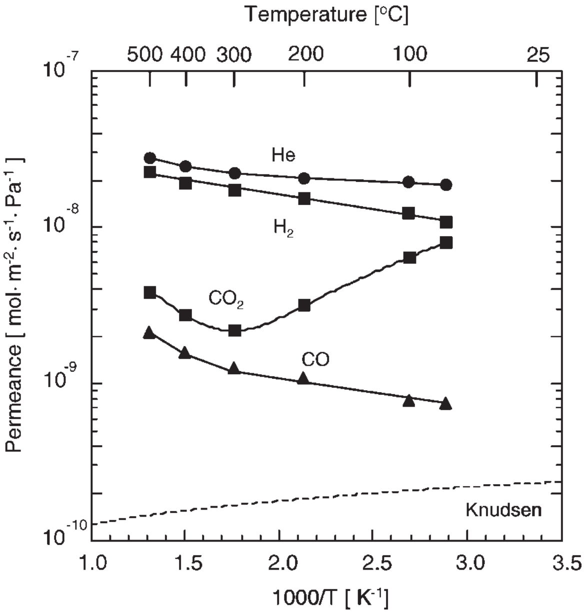

Figure 6. Single gas permeation characteristics of CVD modified DDR-type zeolite membrane (same membrane in Figure 4).

amount of the intercrystalline microporous defects have been eliminated. Since the permeance of CO decreases larger than that of H_2, H_2/CO permselectivity increases from 5.6 to 11 at 500°C.

After counter diffusion CVD modification, gas permeances for the four gases through DDR-type zeolite membrane at different temperatures were measured and the results are shown in Figure 6. The permeances of He, H_2, and CO increase with increasing temperature in 75–500°C. For CO_2 permeation, the temperature dependency of CO_2 permeance has a minimum at 300°C. The slope between 75 and 300°C is much larger than that of Knudsen diffusion, while, above 300°C, the permeance of CO_2 increases with increasing temperature in a manner similar to the activated permeation. This phenomenon is governed by adsorption–diffusion model, since CO_2 is thought to adsorb the DDR channels.[17,23] As temperature increases, the mass-transport mechanism shifts from the surface diffusion regime to the activated gaseous diffusion regime.

For nanoporous membranes with gas concentration in the membrane pores being same as that in the gas phase (under the conditions of higher temperatures) ($K = 1/RT$), Eq. 2 shows that D_c can be obtained from the permeance data at high temperatures by:

$$D_{\mathrm{c}} = \left(\frac{L}{\phi}\right) FRT \tag{5}$$

Here ϕ is the ratio of membrane porosity to tortuosity factor. To calculate diffusivity, DDR-type zeolite porosity of 0.26[24] was used as the membrane porosity. The membrane thickness estimated by SEM (about 10 μm) and the tortuosity factor of 1 were used in the calculation. It should be noticed that the absolute values of the diffusivities calculated from the permeance depends on the accuracy of these structural parameters which are difficult to measure. However, since for a given membrane same values are used for these membrane structural parameters in calculations of diffusivities for different gases at different temperatures, the diffusivity obtained by Eq. 5 is accurate to show the effects of temperature and size or molecular weight of permeating gas on diffusion at high temperatures.

Diffusivity data for He, H_2, CO_2, and CO at temperatures above 300°C were calculated from the permeance data by Eq. 5. The resulting diffusivity data for the four compounds are plotted, according to Eq. 3, as $D_c\ T^{-0.5}$ vs. T^{-1}, in Figure 7. The data can be correlated by straight lines with intercept and slope, respectively used to calculate the constant (α/z) and activation energy E_d for these four compounds. Values of (α/z) and E_d for the four compounds are plotted in Figure 8 vs. relative size of the gas molecule to the zeolite pore size, λ ($=d_m/d_p$). As shown, (α/z) is essentially independent of λ, while E_d increases with increasing λ. The results agree with the theoretical model of Xiao and Wei[12] with respect to the dependency of these two parameters on λ.

The values of (α/z) measured in this work for the DDR-type zeolites is about 10^{-11} m, smaller than that for larger pore MFI-type and A-type zeolites (2.5×10^{-10} and 2×10^{-10} m, respectively).[12] The value of (α/z) is directly proportional to the absolute value of diffusivity, which was calculated from the permeance with selected values for the three structural parameters for membrane (porosity, tortuosity, and membrane thickness). Thus, there is a certain degree of uncertainty in the absolute value of (α/z) for the DDR-type zeolite. For example, the value of (α/z) can be doubled if the tortorsity factor of 2 instead of 1 is used in calculation. Nevertheless, it is important to show that value of (α/z) is constant and does not vary with the relative size of gas molecules to the zeolite pore size.

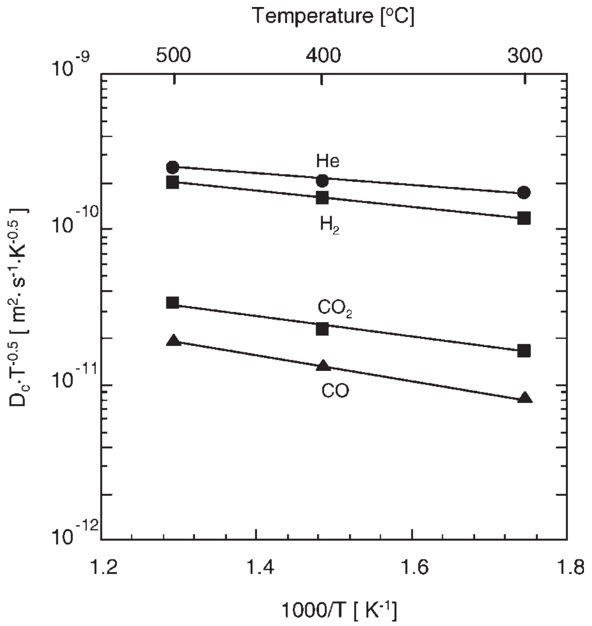

Figure 7. Temperature dependency of measured *Dc* $T^{-0.5}$ for CVD modified DDR-type zeolite membrane.

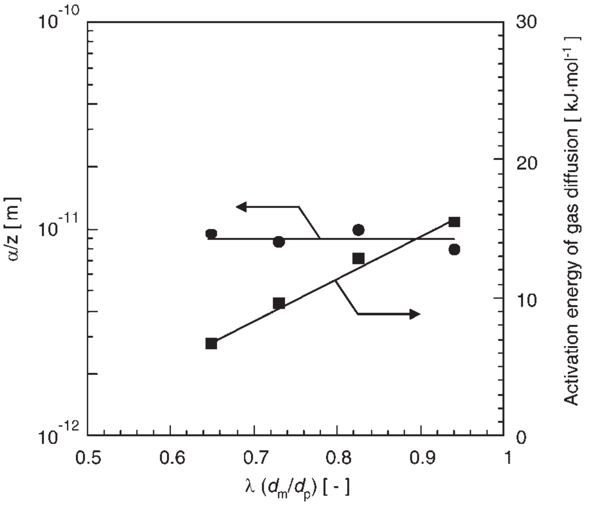

Figure 8. Calculated α/z and activation energy of gas diffusion for CVD modified DDR-type zeolite membrane as a function of the ratio of kinetic diameter of the diffusion gas molecule to the zeolite pore diameter λ (=dm/dp).

The activation energy for diffusion for the CVD-modified DDR-type zeolite membrane is compared in Table 1 with those for the unmodified DDR-type zeolite membrane. The CVD modified membrane exhibits much higher activation energy for diffusion with a stronger dependency on the relative size of the gas to zeolite pore size than the unmodified membranes. Obviously, the CVD modification has reduced the pore size of the DDR-type zeolite membrane possibly by eliminating the intercrystalline pores (note that the precursors for silica are too larger to enter zeolitic pores). Another possibility is formation of an amorphous microporous silica layer on the surface of DDR-type zeolite membrane after CVD modification. This can be excluded by hydrothermal stability tests, as it is well known the amorphous microporous silica membrane is structurally unstable at high temperatures in humid environments.[25–28]

To test the stability of the CVD-modified DDR-type zeolite membrane, gas permeance through the CVD-modified membrane after exposure to steam at 500°C for 6 h was measured. Table 2 compares the permeance and activation energy for four gases for the CVD-modified DDR-type zeolite membrane before and after exposure to steam at 500°C. The hydrothermal treatment cause negligible change in gas permeance and activation energy for the CVD-modified DDR-type zeolite membranes. The results show that the CVD-modified DDR-type zeolite membrane is hydrothermally stable. The unchanged permeation data for the CVD-modified DDR-type zeolite membrane after exposure to steam indicates that the silica is deposited into the intercrystalline gaps, rather as a thin amorphous layer on top of the zeolite membrane surface.

Figure 9 compares diffusivities for the four gases at 500°C for the unmodified and CVD-modified DDR-type zeolite membranes prepared in this work. For both membranes it is safe to assume that there is no adsorption of all four gases at 500°C. The data show that for the unmodified membrane the diffusivity depends on both size and molecular weight of permeating gas. Because of the presence of intercrystalline pores, the unmodified membranes have an average pore diameter (d_p) larger than the DDR-type zeolite pores. This gives smaller values for λ ($=d_m/d_p$) for all the molecules. It is known that the activation energy E_d decreases with decreasing λ. Thus the four gases have a smaller activation energy (about 6 kJ mol^{-1} for H_2, He, CO as shown in Table 1) for the unmodified DDR-type zeolite membrane. Because of the small activation energy with weak dependence on the kinetic size of the permeating gas, the preexponantial term in Eq. 3 which includes the molecular weight becomes important. In this case, the molecule with small molecular weight but larger kinetic diameter (like H_2) can have a large diffusivity or permeance than the molecular with larger molecular weight but smaller kinetic diameter (like He).

For CVD-modified DDR-type membranes, the intercrystalline pores are completely eliminated. Thus the membrane pore size is the same as the DDR-type zeolite pores. This gives larger values for λ ($=d_m/d_p$) for the four molecules, with a larger activation energy E_d which increases with the kinetic diameter of the permeating gases. Because of this, the exponential term on Eq. 3 which is a strong function of the size of permeating gas overweighs the preexponential term which is determined by the molecular weight of the permeating gas. Therefore for the high quality DDR-type membranes the diffusivity (or permeance) decreases with increasing size of the permeating gases.

As mentioned in introduction, no diffusion data in DDR-type zeolites at high temperatures are available in the literature. Two research groups reported room temperature diffusivities for gases such as CH_4 and CO_2 for the DDR-type zeolite structure estimated by the molecular dynamic simulations[29,30] and measured by pulsed field gradient (PFG) nuclear magnetic resonance (NMR) method.[31] These room temperature diffusivity data are in the same order of magnitude as the high temperature diffusivity data shown in Figure 9. It is difficult to compare the absolute values of the diffusivity data measured by the macroscopic membrane permeation

Table 2. Permeance and Activation Energy of He, H_2, CO_2, and CO Diffusion for CVD-Modified DDR-Type Zeolite Membrane Before and After Exposure to Steam at 500°C (Partial Pressure of Steam: 50 kPa)

	Activation Energy E_d (kJ mol^{-1})		Permeance at 500°C (10^{-8} mol m^{-2} s^{-1} Pa^{-1})	
	Before Exposure to Steam	After Exposure to Steam	Before Exposure to Steam	After Exposure to Steam
He	6.66	6.73	2.79	2.74
H_2	9.62	9.71	2.24	2.18
CO_2	12.8	13.2	0.38	0.39
CO	15.5	15.9	0.20	0.18

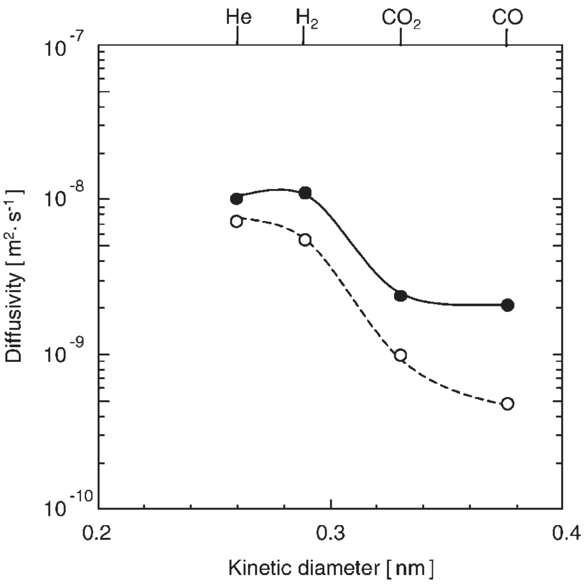

Figure 9. Kinetic diameter dependency of measured diffusivity for DDR-type zeolite membrane at 500°C before and after counter diffusion CVD modification (closed symbols on solid line: before CVD modification, open symbols on broken line: after CVD modification).

method with those measured or estimated by the microscopic NMR and molecular simulation methods because the gas-zeolite system was under different conditions. Nevertheless, the dependency of the diffusivity on the size of molecule for the DDR-type zeolites obtained by the NMR and molecular simulation is same as what is shown in Figure 9 for the CVD modified DDR-type zeolite membranes.

Conclusions

High quality DDR-type zeolite membranes were prepared by secondary growth method on porous α-alumina disk. The high thermal stability of the DDR-type zeolite membranes allows measurement of gas permeance and diffusion for the DDR-zeolite in a wide temperature range up to 500°C. Permeance data at temperatures above 300°C at which gas adsorption on zeolites can be negligible can be used to calculate intracrystalline diffusivity for DDR-type zeolite. For the as-synthesized DDR-type zeolite membranes, single gas permeance (or diffusivity) decreases as $H_2 > He > CO$, which is determined by both molecular size and weight of the permeating gases. This indicates the presence of intercrystalline pores in the as-synthesized DDR-type zeolite membranes. The permeance of CO_2 decreases with increasing temperature due to the strong effects of CO_2 adsorption on the zeolite film. On-stream CVD modification is effective in sealing intercrystalline pores of the DDR-type zeolite membranes. The CVD modification improves permselectivity for hydrogen over other gases.

Intracrystalline diffusivities of He, H_2, CO_2, and CO in DDR-type zeolites were obtained from the permeation data under the conditions of negligible adsorption (at temperatures above 300°C) to examine the effects of the size and molecular weight of permeating gases on diffusion and permeation rate in DDR-type zeolite membranes. For the unmodified DDR-type zeolite membranes with an average membrane pore size larger than the DDR-type zeolite pores due to the presence of the intercrytsalline pores, the diffusivity (or permeability) depends on both the size and molecular weight of permeating gases. For CVD-modified DDR-type zeolite membranes with intercrystalline pores eliminated, the activation energy for diffusion is larger and increases with increasing size of the permeating gases. Thus for the CVD-modified DDR-type zeolite membranes, the diffusivity (and gas permeance) is determined by the size of the permeating gases. The high temperature diffusion data for the small gases in the DDR-type zeolites measured by the macroscopic membrane permeation method are consistent with the theory of translation gas diffusion in zeolites proposed by Xiao and Wei.

Notation

D_c = gas diffusivity in zeolite, $m^2\ s^{-1}$
d_p = pore diameter of zeolite structure, m
d_m = kinetic diameter of molecules, m
E_d = activation energy for diffusion, J mol^{-1}
F = permeance, mol $m^{-2}\ s^{-1}\ Pa^{-1}$
K = adsorption equilibrium constant, Pa^{-1}
L = membrane thickness, m
M = molecular weight, g mol^{-1}
P_f = feed (upstream) side pressure, Pa
P_p = permeate (downstream) side pressure, Pa
q_f = concentration of the permeating molecule in the membrane at feed (upstream) side, mol m^{-3}
q_p = concentration of the permeating molecule in the membrane at permeate (downstream) side, mol m^{-3}
R = gas constant, J $mol^{-1}\ K^{-1}$
T = absolute temperature, K
z = diffusion coordination number, dimensionless

Greek letters

α = diffusion length (or distance between two adjacent sites), m
ϕ = constant accounting for membrane porosity and totuosity factor, dimensionless
λ = the ratio of kinetic diameter of the diffusion molecule to the zeolite pore diameter, dimensionless
π = circular constant, dimensionless
σ_m = Lennard-Jones length constant for molecule, m

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