Permeation Properties of Hydrogen and Water Vapor Through Porous Silica Membranes at High Temperatures

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Silica and cobalt-doped silica membranes that showed a high permeance of 1.8×10^{-7} *mol* m^{-2} s^{-1} Pa^{-1} *and a* H_2/N_2 *permeance ratio of* ~730, *with excellent hydrothermal stability under steam pressure of 300 kPa, were successfully prepared. The permeation mechanism of gas molecules, focusing particularly on hydrogen and water vapor, was investigated in the 300–500°C range and is discussed based on the activation energy of permeation and the selectivity of gaseous molecules. The activation energy of* H_2 *permeation correlated well with the permeance ratio of* He/H_2 *for porous silica membranes prepared by sol–gel processing, chemical vapor deposition (CVD), and vitreous glasses, indicating that similar amorphous silica network structures were formed. The permeance ratios of* H_2/H_2O *were found to range from 5 to 40, that is, hydrogen (kinetic diameter: 0.289 nm) was always more permeable than water (0.265 nm).* © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 618–629, 2011

Keywords: silica membrane, hydrogen, activation energy of permeation, water, kinetic diameter

Introduction

Amorphous silica consists of a silica network structure that is stable up to 1000°C, and it is known that the amorphous silica network allows permeation of the smallest molecules such as helium (kinetic diameter: 0.26 nm) and hydrogen (0.289 nm), but not larger molecules such as nitrogen (0.36 nm).[1–3] Therefore, silica membranes for hydrogen separation, which have drawn a great deal of attention for future application to processes for the production and purification of hydrogen,[4–8] have been prepared using amorphous silica by various techniques such as CVD and sol–gel processing. The permeation of helium and hydrogen through silica glass, including vitreous glass, was reported in the 1960s.[9] Silica membranes for hydrogen separation were first reported in 1989[10] when amorphous SiO_2 membranes were prepared by CVD; later, in 1990,[11] they were prepared by sol–gel processing. Both techniques allow formation of amorphous silica networks consisting of $Si{-}O{-}$ bonding and $-SiOH$ groups, and the corresponding porous structures range from 0.2 to 0.5 nm in size.[12] Sol–gel processing has the great advantage of pore size control based on the size of silica sols and the starting precursors, with low-temperature synthesis of mixed oxides by mixing metal ions into silica.[13–17] Recently, a

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silica network design, including the network size most effective for gas permeation and for surface properties, was proposed using structured alkoxides.[18] Using organic–inorganic hybrid alkoxides, which contain organic groups between two silicon atoms, such as with bis(tri-ethoxysilyl) ethane, very highly permeable hydrogen separation membranes were successfully prepared by tuning the size of the silica network. It should be noted that zeolite membranes, which have been developed in the last decade and commercialized for dehydration of aqueous organic mixtures such as aqueous ethanol, could not separate hydrogen from nitrogen because they have pore sizes that are larger than silica networks.

Although silica shows high stability at high temperatures under dry gas conditions, it has been reported that it is not stable enough in humidified air, even at room temperature; H_2 permeance decreases with time under hydrothermal conditions.[19–24] This is thought to be caused by densification of the silica network; siloxane bonding is broken to form silanol functional groups, which reduces the effective pore size and is subject to rearrangement of silanol groups, which results in a denser structure. Extensive research, including CVD[24–26] and hydrophobic membranes,[27–29] has been carried out to develop hydrogen separation membranes that can be used at high temperatures in a steam atmosphere for possible use in the production of hydrogen for fuel cell systems. We previously proposed composite oxides with silica and various types of metal ions such as Zr, Al, Mg, and Ni, for improved stability in hydrothermal conditions, prepared by sol–gel processing.[17,22,30,31] Among the metals, Ni was the first reported to be effective in improving hydrothermal stability. We also reported improved hydrothermal stability by doping Co into silica with different Si/Co compositions by sol–gel processing, and applied this method to hydrogen separation.[31] The Co-doped silica with improved hydrothermal stability was also investigated by other research groups based on permeation experiments.[32,33] However, the permeation properties through microporous silica membranes that consist of silica networks, including hydrogen and helium at high temperatures, are not well understood. Moreover, the permeation of water vapor has been reported in a limited number of papers, probably due to the difficulty of measuring the permeation rate of water vapor and the low stability of microporous silica membranes in a steam atmosphere.[6,7] For this paper, the permeation characteristics of various types of gaseous molecules were investigated in the range of 300–500°C, and they are discussed here based on the activation energy of permeation and selectivity of gaseous molecules, which are intrinsic properties that reflect the pore size and pore chemistry of microporous silica.

From the viewpoint of the transport mechanism through porous membranes, according to the size of the membrane pores and the mean free path, gaseous molecules permeate porous membranes via four types of permeation mechanisms: viscous flow, Knudsen flow, surface diffusion, and activated diffusion.[34–37] In viscous flow, where molecular collisions and exchanges in the momentum occur inside pores, no separation is expected in mixed gaseous systems. The Knudsen diffusion mechanism is dominant in the case of porous membranes having pore sizes smaller than the mean free path. Molecules collide with pore walls more frequently than the permeating molecules. In the surface diffusion mechanism, which is dominant for systems with strong interaction between porous membranes and permeating gases such as CO_2 and water vapor, at low temperatures, adsorbed molecules diffuse along the adsorption gradient from a high- to a low-pressure stream. Activated diffusion, where high separation can be expected, is the permeation mechanism in which permeance, defined as the permeation rate per unit membrane area, unit time, and unit pressure difference, increases with temperature. Activated diffusion can be caused by two mechanisms: vibration of the membrane matrix, mostly in the case of dense polymeric membranes, and a molecular sieving mechanism, in the case of porous inorganic membranes. Obviously, the molecular size of permeating molecules is very important in determining the transport mechanism through porous membranes.[34–37] Several ways of defining molecular size are available, including kinetic diameter and Lennard-Jones collision diameter.[38–42] Kinetic diameter has been used most commonly to discuss adsorption in adsorbents and permeation through microporous materials. This diameter is determined as the molecular distance at the minimum potential using the Lennard-Jones potential for nonpolar spherical molecules. The kinetic diameters of polar gases are determined based on the Stockmayer potential, which considers both the Lennard-Jones potential and the electrostatic interaction. However, very few papers have discussed which molecular sizes are appropriate for permeation and diffusion through amorphous silica networks where only the smallest molecules are allowed to permeate.

In this study, hydrothermally stable Co-doped silica membranes were fabricated and applied to evaluate the transport mechanisms of the smallest gases, such as He, H_2, and water vapor. The transport mechanisms of He and H_2 through the amorphous silica network are discussed extensively and compared with those through CVD silica membranes. He and H_2 were used as probe molecules, because the permeation properties of the smallest molecules will offer structural information about amorphous silica networks, and we propose a novel correlation between the activation energy of permeation and selectivity of gaseous molecules, both of which are intrinsic properties of microporous silica membranes. Moreover, the transport mechanism of water vapor (a polar molecule) is also discussed.

Experimental

Membrane preparation

Metal-doped silica sol solutions were prepared using tetraethoxysilane (TEOS) and a metal nitrate, such as $Co(NO_3)_2{\cdot}6H_2O$ or $Ni(NO_3)_2{\cdot}6H_2O$, as the starting chemicals. TEOS was hydrolyzed and condensed in an ethanol solution mixed with a specified amount of metal nitrate and water. The molar ratios of Si/Co and Si/Ni were adjusted from 9/1 to 2/1, whereas TEOS concentrations were kept at 2.0, 1.0, and 0.5 wt %. The following is the typical preparation procedure using 1.0 wt % Co-doped silica sol (based on the weight of TEOS) with a Si/Co of 2/1. In this study, 5.0 g of TEOS was added to a mixture of 50 g of ethanol and 6.98 g of $Co(NO_3)_2{\bullet}6H_2O$, followed by hydrolysis and condensation for 12 h. Additional water was added to achieve a total weigh of 500 g, and the pH of the sol solution was

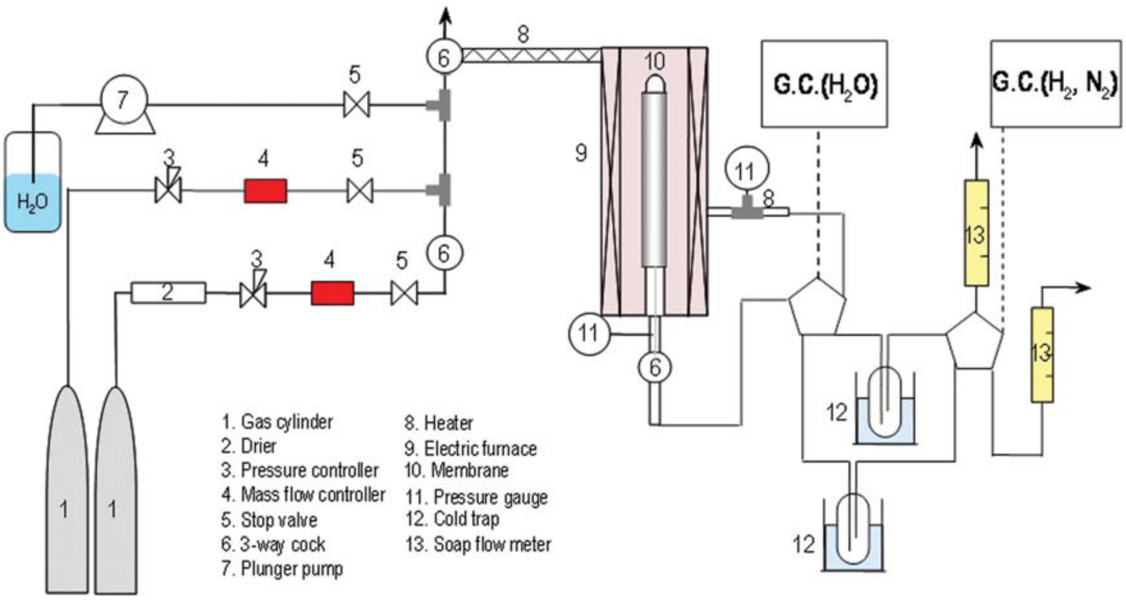

Figure 1. Schematic diagram of experimental apparatus.

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controlled at pH 1.2 by adding 2.0 g of HNO_3, followed by another condensation for 12 h.[30,31]

Porous α-alumina cylindrical microfiltration membranes (length: 90–300 mm; outer diameter: 10 mm; inner diameter: 8 mm; nominal pore size: 1 μm; porosity: 50%) were used as substrates of hydrogen separation membranes. First, α-alumina particles of 0.2 μm in diameter were deposited on the microfiltration membrane, and fired at 550°C to reduce the pore size enough for further sol coating. Next, colloidal sol solutions of SiO_2-ZrO_2 (Si/Zr = 1/1) were coated on the substrates, which were heated at 200°C using a cloth wet with the sol solution to fabricate intermediate layers having approximate pore sizes of 1 nm. Finally, silica or Co-doped silica sols were further coated and fired for 30–60 min at 600°C under a steam partial pressure of 90 kPa. The detailed procedure may be found in a previous article.[31]

Measurement of gas permeance

Permeation rates of Co-doped silica membranes were measured using an apparatus schematically shown in Figure 1. A mixture of steam and nitrogen was fed for a specific time, followed by pure nitrogen to dry the membrane completely, and then the permeation rates of pure He, H_2, and N_2 were measured. By repeating this procedure, the time course of permeation rates was recorded. Steam partial pressure was controlled by the total pressure in the range of 90–300 kPa. After a steady state was reached, the temperature dependencies of permeation rates were measured from 300 to 500°C to determine the activation energy of permeating gases.

The water permeation rate was measured in the mixture of H_2/H_2O and N_2/H_2O under a total pressure of 200–500 kPa. The permeate stream was kept at atmospheric pressure. The permeate flux of water was determined in two ways: a weighing method and a gas chromatography (GC) method. In the weighing method, water vapor was collected in a cold trap after the permeate stream line, which was heated higher than 100°C. In the GC method, the retentate and permeate streams were analyzed using two gas chromatographs (GC-8A, Shimadzu Co.) with TCD detectors. One GC was equipped with a Porapak T column for analysis of CO_2 and H_2O and the other with a Molecular Sieve 5 Å for analysis of N_2 and H_2. The permeance of H_2O was measured using a feed of N_2/H_2O or H_2/H_2O mixture (mole ratio of 1/1). Permeate and retentate flow rates of noncondensable gases such as H_2 and N_2 were measured using soap-film meters.

Results and Discussion

Time course of gas permeance through microporous silica membranes

Figure 2a shows the TEM cross sectional image of the top layer with 10 μm depth of a Co-doped silica membrane, which was observed using a TOPCON (Model EM002b, Tokyo, Japan). The sample was prepared using a focused ion beam (FIB) and tungsten was deposited on the surface of the top layer. The Co-doped silica membrane showed a composite membrane structure, consisting of an α-alumina substrate that was prepared using α-alumina particles several microns in size (pore size: 1 μm), an intermediate layer prepared using α-alumina fine particles (200 nm in diameter), a SiO_2-ZrO_2 layer, and a Co-doped silica top layer for hydrogen separation according to the preparation procedure. Figure 2b shows a high-resolution TEM image of the Co-doped SiO_2 coated on the SiO_2-ZrO_2 intermediate layer. A thin Co-doped SiO_2 layer was observed as a layer consisting of a finer structure than the SiO_2-ZrO_2 layer. The estimated thickness of the Co-doped SiO_2 layer was ~50 nms and that of the SiO_2-ZrO_2 layer was several hundred nms. Figure 3 shows a TEM image with the composition of the top layer, analyzed by energy-dispersive X-ray spectroscopy (EDS). EDS shows that the top layer, with an approximate depth of

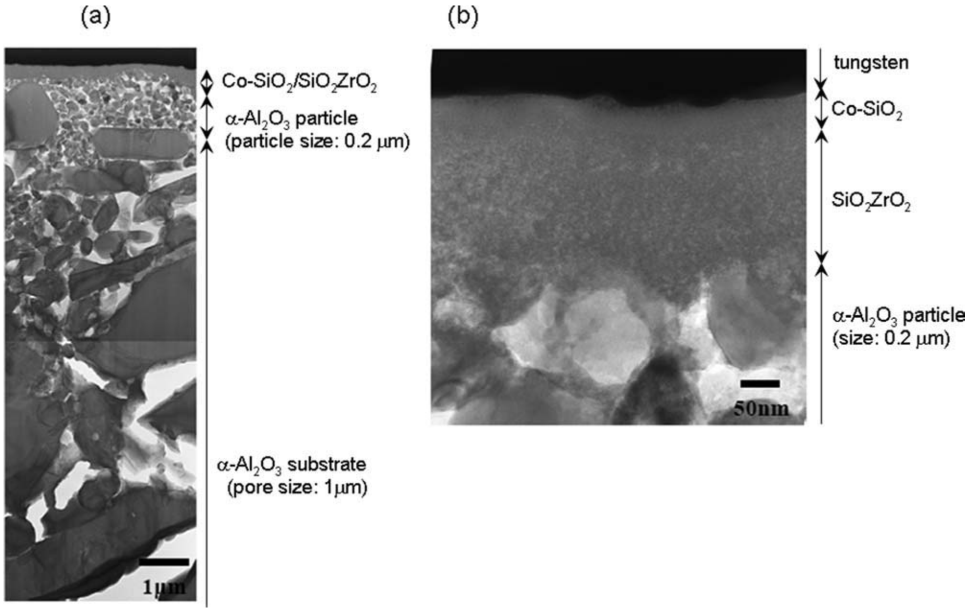

Figure 2. Transmission electron microscopy (TEM) image of Co-doped silica membranes (a) cross section with 10 μm depth and (b) top layer cross section with high magnification.

15 nm from the surface, was composed of silicon (Si), zirconium (Zr), and cobalt (Co), although Co-doped silica sols were coated sequentially on the SiO$_2$-ZrO$_2$ intermediate layer. The composition at 15 nm in depth seems to be approximately the same as that at 200 nm, suggesting Co ion and/or Co-doped SiO$_2$ sols penetrated into the silica-zirconia layer.

Silica membranes have the great advantage of controllability of pore size in the sub-nanometer range; however, a serious problem yet to be resolved is that of hydrothermal

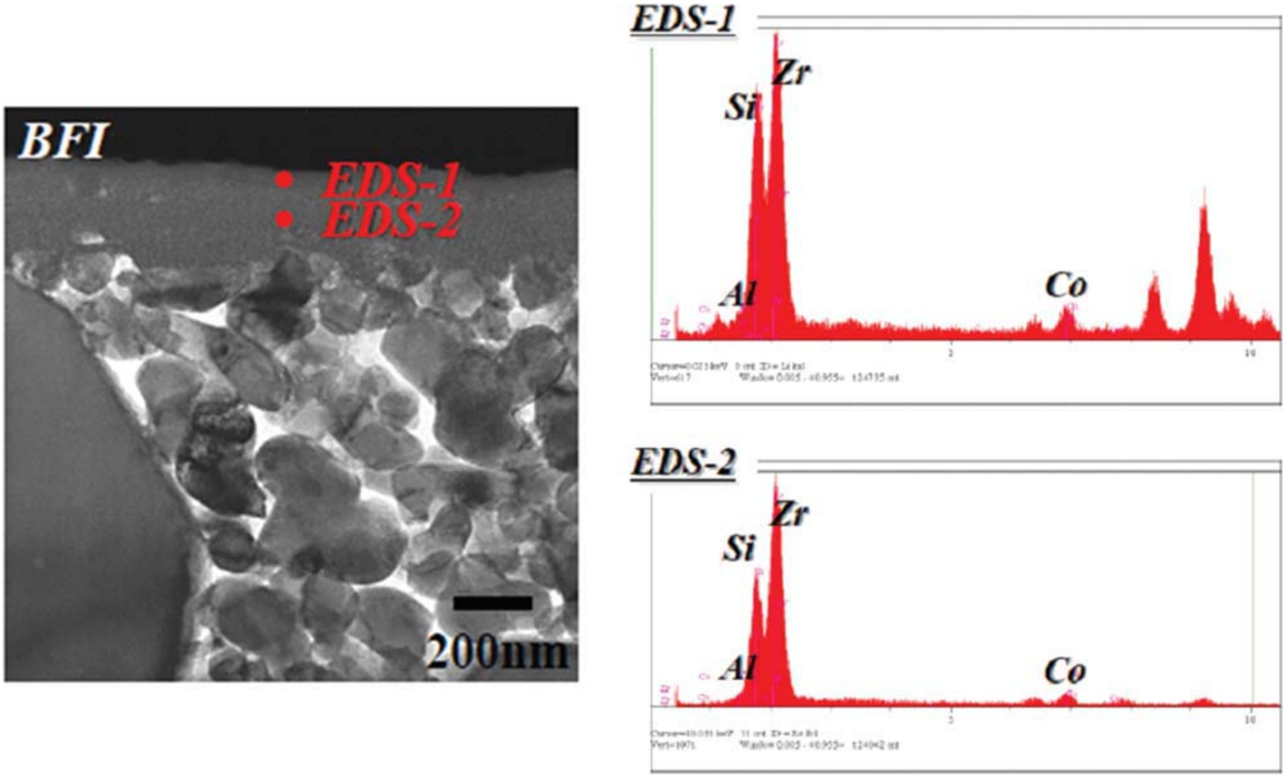

Figure 3. Energy-dispersive X-ray spectroscopy (EDS) with a TEM image of the cross section of a Co-doped silica membrane.

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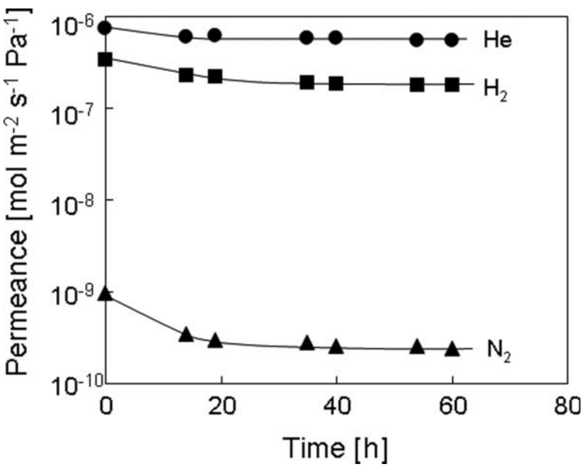

Figure 4. Time course of gaseous permeance through a Co-doped silica membrane (Mem-CoSi-1, steam partial pressure of 300 kPa, 500°C).

stability. Under hydrothermal conditions, gaseous permeance decreases by densification of the silica network where helium and hydrogen can permeate. The mechanism for densification of the silica network under hydrothermal conditions has been explained as the breakage of siloxane bonding and the generation of silanol groups, followed by the recombination and rearrangement of silanol groups into a siloxane network. The decreased flux under hydrothermal conditions is one of the most important problems to be solved for the practical application of silica microporous membranes, because one of the possible applications would include the separation of mixed gases that contain steam at high pressures, such as steam reforming of methane.[4–8] Metal doping such as Ni and Co was proposed to increase the hydrothermal stability by several groups.[31–33] Figure 4 shows the time course of permeance through a Co-doped silica (Si/Co = 2/1) membrane (which was prepared by firing under steam partial pressure of 90 kPa) at a steam partial pressure of 300 kPa. Permeance was measured periodically during the hydrothermal treatment. After a specified interval, the membrane was dried by feeding a sufficient amount of nitrogen to dry the membrane in the feed and the permeate stream, and the gaseous permeance was measured. Co-doped silica membrane showed slightly decreased He and H_2 permeance during the first several hours under hydrothermal conditions, and reached a steady permeance. Nitrogen showed very low permeance, and did not show an appreciable change during hydrothermal treatment. H_2 showed a permeance of 1.8×10^{-7} mol m^{-2} s^{-1} Pa^{-1} with H_2/N_2 separation factors of 730 after hydrothermal conditions (500°C and a steam pressure of 300 kPa), whereas helium showed 5.5×10^{-7} mol m^{-2} s^{-1} Pa^{-1} with He/N_2 separation factors of 2,230. Co-doped silica showed high H_2 permeance and a high H_2/N_2 permeance ratio with duration of as long as 60 h, showing improved hydrothermal stability of metal-doped silica. It can be concluded that the hydrothermal stability of amorphous silica was improved by incorporating metals such as Ni and Co into a silica matrix.

Based on XRD analysis of Co-doped SiO_2 powder, the doped Co was impregnated in the silica matrix, whereas only a certain amount of Co formed crystalline Co_3O_4, ~20 nm in size, and existed outside the silica network.[31] Co-doped SiO_2 showed excellent stability under hydrothermal conditions and in a reductive/oxidative atmosphere that was attributed to the doped Co, which could be impregnated in the silica matrix as metal ions,[41] covalently bound compounds[42] such as Si—O—Co—, or as tiny crystals that cannot be detected by XRD. The densification of the silica network under hydrothermal conditions can be explained by the disruption of the siloxane network, generation of silanol groups, and subsequent recombination and rearrangement of silanol groups into the siloxane network. One possible mechanism that could prevent the densification of a silica network[31] is that doped cobalt, which may exist as metal ions, covalently bound compounds, or as tiny crystals, could increase stability under hydrothermal conditions. Doped cobalt might reduce the attack of water vapor and prevent thermally induced movement of silanol groups, such as rotation, followed by reduced recombination, as has been suggested for carbonized-template silica membranes by Duke et al.[27,28]

Temperature dependency of gaseous permeance through microporous silica membranes

The temperature dependency of helium and hydrogen permeance was evaluated for a silica membrane before and after hydrothermal treatment. Figure 5 shows the Arrhenius plot of gaseous permeance during the hydrothermal treatment of a silica membrane that was prepared by firing in dry air at 500°C. The permeance ratio of He over N_2 before

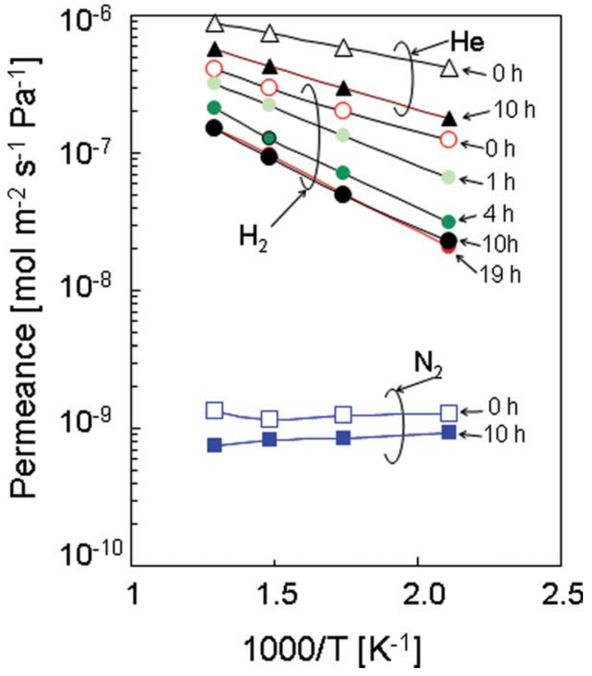

Figure 5. Arrhenius plot of helium, hydrogen, and nitrogen permeation through silica membrane during hydrothermal treatment (Mem-Si-1, steam partial pressure = 90 kPa).

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hydrothermal treatment was ~700, with a He permeance of 0.89×10^{-6} mol m^{-2} s^{-1} Pa^{-1}. After hydrothermal treatment of a steam partial pressure at 90 kPa for 10 h, which is a much milder hydrothermal condition compared with that in Figure 4, He and H_2 permeance decreased to approximately one-half and one-third, respectively, although nitrogen permeance remained practically constant. The enhanced hydrothermal stability of metal-doped silica membranes prepared under hydrothermal conditions was again suggested. As shown in Figure 5, the permeance shows a linear dependency on reciprocal temperature for helium and hydrogen, indicating an activated diffusion mechanism.

Permeation mechanisms through porous membranes can be categorized as the viscous flow (molecular diffusion), Knudsen, surface diffusion, and molecular sieving, based on the size ratio of the molecules permeating a membrane pore, as well as the interaction between permeating molecules and membrane pore walls.[34–37] In viscous flow, permeating molecules collide with one another more frequently than with the wall, resulting in no separation properties for mixed gases. On the other hand, permeating molecules collide with pore walls more frequently than with one another in Knudsen diffusion, resulting in separation ability based on the Knudsen diffusivity, that is, the square root of the reciprocal ratio of molecular weights of the permeating molecules. The permeance in the Knudsen mechanism (P_K) is formulated as follows, using porosity (ε) pore radius (r_p) membrane thickness, L:

$$P_K = \varepsilon \frac{2r_p}{3} \left(\frac{8RT}{\pi M} \right)^{1/2} \frac{1}{RTL} \tag{1}$$

High separation factors can be achieved by the surface diffusion and molecular sieving mechanisms. In the case of activated diffusion, molecules permeate through micropores as being exposed to repelling force from the pore walls, and molecules that have enough kinetic energy to overcome the repelling force can permeate the pores. Permeance in the activated diffusion has been formulated based on several models. The most frequently used formulation of activated diffusion permeation is shown below:

$$P = P_0 \exp\left(-\frac{E_1}{RT} \right) \tag{2}$$

where E_1 indicates the activation energy of permeation. Pre-exponential (P_0) is permeance at infinite temperature where permeating gases have enough kinetic energy and permeate through micropores with no permeation barrier, and, therefore, P_0 reflects the pore structure including pore area and volume in the silica matrix. This rather simple transport equation was originally derived for dense polymeric membranes and is based on the concept that solution and diffusion are kinetic processes. By considering the heat of adsorption (ΔH), that is, the interaction between permeating molecules and a membrane material, and the activation energy of diffusion (ΔE_d), the activation energy of permeation can be interpreted as $E_1 = -\Delta H + E_d$. The solubility of permeating molecules and the diffusivity of a membrane can be interpreted as $c_{eff} = C_0 \exp(\Delta H/RT)$ and $D_{eff} = D_0 \exp(-E_d/RT)$, respectively, and fulfills $P_0 = C_0 D_0$. Therefore, the activation energy of permeation can be determined by the pore structure (size and shape) and interaction between silica and permeating molecules, although permeance is reflected in other factors such as membrane thickness. In other words, the activation energy can be considered an intrinsic property of silica microporous membranes.

The following permeation equation,[35,36] which is referred to as the activated Knudsen or gas-translation model, has been derived for microporous inorganic membranes.

$$P = \frac{k_0}{\sqrt{MRT}} \exp\left(-\frac{E_2}{RT} \right) \tag{3}$$

where E_2 is the activation energy of H_2 permeation, k_0 is the structural parameter, M is the molecular weight of the permeating molecules, and R is the gas constant. Equation 3 covers the activated diffusion ($E_2 > 0$), surface diffusion ($E_2 < 0$), and Knudsen diffusion ($E_2 = 0$). The activation energy can be determined by interactions between permeating molecules and the pore wall, based on the Lennard-Jones potential using the size (membrane pore size, molecular size of permeating molecules) and the interaction parameters.[35,36]

Recently, Oyama et al.[43,44] applied a different type of permeation equation, which was originally proposed by Barrer and Vaughan,[45] to the analysis of gaseous permeance through microporous silica membranes prepared by the CVD technique. Although the physical meaning of this permeation equation is clear, at least three parameters are required. In this study, Eqs. 2 and 3, which require two parameters, were applied for simplicity. In Figures 6a, b, fitted curves of helium and hydrogen permeances using Eqs. 2 and 3 are summarized together with the pre-exponential parameters of P_0 and k_0 (Table 1). The activation energy obtained using the two equations was approximately the same, although activation energy values obtained by Eq. 3 were slightly larger than those obtained by Eq. 2. The pre-exponential parameters, P_0 and k_0, which indicate the structural factors of amorphous silica networks, were approximately the same for He and H_2, irrespective of hydrothermal treatment. Therefore, a decrease in permeance after hydrothermal treatment can be explained by an increase in activation energy of permeation. In this study, Eq. 3, which can cover permeation mechanisms from Knudsen, surface diffusion and activated diffusion, was used to obtained activation energy. The activation energy of helium was lower than that of hydrogen because the kinetic diameter of hydrogen (0.289 nm) is smaller than that of helium (0.26 nm). It should be noted that nitrogen showed a decreased permeance with increased temperature. This can be explained by the Knudsen diffusion mechanism through permeation of large pores left in porous membranes, such as pinholes.

As Figure 5 shows, the longer the hydrothermal treatment time, the larger the permeance slope, that is, the larger the activation energy of permeance. The time course of the activation energy of helium and hydrogen through a silica membrane together with the permeance ratio of He over H_2 are summarized in Figure 7. The activation energy gradually increased with time. The increase in the activation energy can be explained by the reduction of pore structure caused by hydrothermal treatment under a steam partial pressure of 90 kPa. Because helium and hydrogen are small molecules that show no, or a quite small interaction with silica, the activation energy of permeation is mostly determined by that

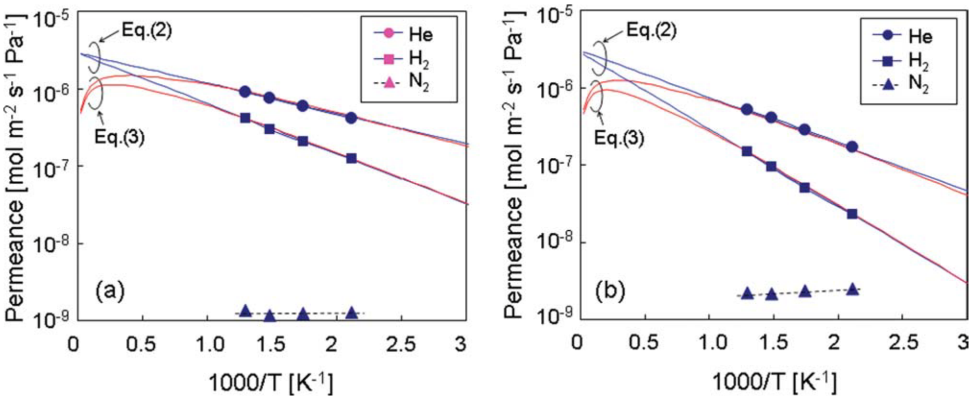

Figure 6. (a and b) Arrhenius plot of helium and hydrogen though a silica membrane before (a) and after (b) hydrothermal treatment under a steam pressure of 90 kPa for 18 h (Mem-Si-1, curves were calculated using Eqs. 2 and 3).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of diffusion. It should be noted that a theoretical model that considers the interactions between permeating molecules and pore walls, using the Lennard-Jones potential together with the size (membrane pore size, molecular size of permeating molecules) and interaction parameters, predicts that the smaller the pore size, the larger the activation energy.[35–37] Oyama and coworkers[46] recently reported ab initio calculation of the activation energy of H_2 permeance through $H_{2n}Si_nO_n$ ($n = 4$–8) cyclosiloxane n-membered rings, which correspond to the pore sizes of silica networks. They clearly showed that activation energy increased with a decrease in silica member rings. Because the repelling force increases as pore size decreases, the activation energy of H_2 permeance corresponds with the pore size that is effective for H_2 permeation. The top figure in Figure 7 shows the time course of the permeance ratio of He/H_2, indicating increased He/H_2. The kinetic diameters of He and H_2 are 0.26 nm and 0.289 nm, respectively, and, therefore, densification of the silica network was also confirmed from the view point of permselectivity; that is, permeance of H_2, a larger molecule, decreased more rapidly that that of He, a smaller molecule. Therefore, the activation energy can be interpreted as a measure of the pore sizes of silica networks; the smaller is the pore size, the larger is the activation energy. Therefore, an increase in the activation energy of hydrogen can be attributed to the densification of the silica network under hydrothermal treatment.

Permeation of hydrogen through silica membranes

Permeation of gases through microporous silica membranes can be explained based on the assumption of a bimodal pore size distribution consisting of intraparticle pores and interparticle pores.[3] Small molecules such as helium and hydrogen can permeate through the intraparticle pores, that is, an amorphous silica network, in activated diffusion. On the other hand, large molecules such as nitrogen can permeate through relatively large pores or pinholes in the Knudsen diffusion mechanism. Therefore, small molecules such as helium and hydrogen can permeate through both intraparticle and interparticle pores. Roughly speaking, the approximate sizes of silica networks available for He and H_2 permeation could be from 0.25 to 0.3 nm, based on the kinetic diameters of permeating molecules. Because the permeation through interparticle pores obeys the Knudsen mechanism, it is possible to obtain permeance through silica network pores. Therefore, to discuss the permeation mechanism through silica networks, the following correction (Eq. 4) was made for Knudsen diffusion through relatively large pores through which nitrogen can permeate. Although correction of Knudsen flow was made in this study, the activation energy without correlation was approximately the same as that without correction when the permeance ratio was greater than 100, due to the small contribution of permeation through large pores.

$$P - \sqrt{14}P_{N_2} = \frac{k_0}{\sqrt{MRT}}\exp\left(-\frac{E_2}{RT}\right) \tag{4}$$

Figure 8 shows the permeance ratio of He/H_2 as a function of the activation energy of H_2 for microporous silica membranes prepared by sol–gel,[17,22] CVD,[24,47–49] and vitreous silica[9] using various materials including silica and silica composite oxides with Zr, Ni, and Co. It should be noted

Table 1. Activation Energy (E_1, E_2) and Pre-exponential Parameters (P_0, k_0) Fitted with Eqs. 2 and 3

Hydrothermal treatment		Equation 2 P_0 (mol m^{-2} s^{-1} Pa^{-1})	E_1 (kJ mol^{-1})	Equation 3 k_0 (kg$^{0.5}$ J$^{0.5}$ m^{-2} s^{-1} Pa^{-1})	E_2 (kJ mol^{-1})
Before	He	2.9×10^{-6}	7.5	2.20×10^{-5}	10.0
	H_2	2.9×10^{-6}	12.5	1.41×10^{-5}	14.5
After 18 h	He	3.04×10^{-6}	11.0	2.20×10^{-5}	14.0
	H_2	2.9×10^{-6}	19.0	1.41×10^{-5}	21.0

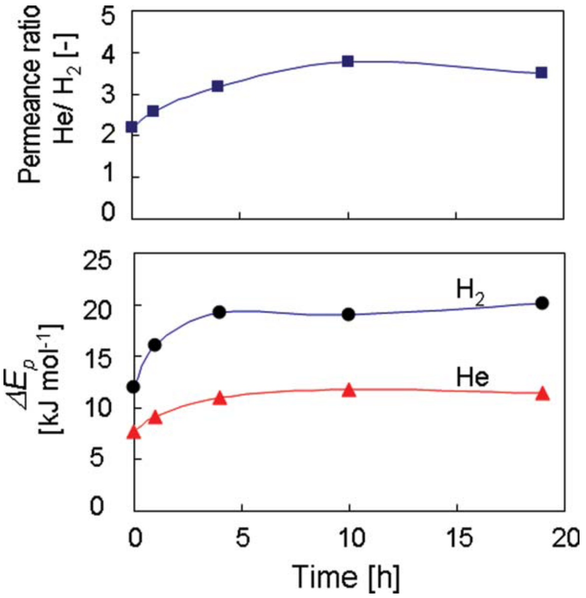

Figure 7. Time course of He/H$_2$ permeance ratio (500°C) and activation energy of He and H$_2$ during hydrothermal treatment at 500°C and a steam partial pressure of 90 kPa (Mem-Si-1, steam partial pressure = 90 kPa).

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that each point corresponds with one membrane. The activation energy of permeance was obtained from 300–500°C, whereas the separation factor was at 500°C. Because the molecular size of He is smaller than that of H$_2$, the pore size effective for permeation is larger for He than it is for H$_2$. Therefore, the permeance ratio of He/H$_2$ can be considered as a measure of the pore size distribution of a silica network.

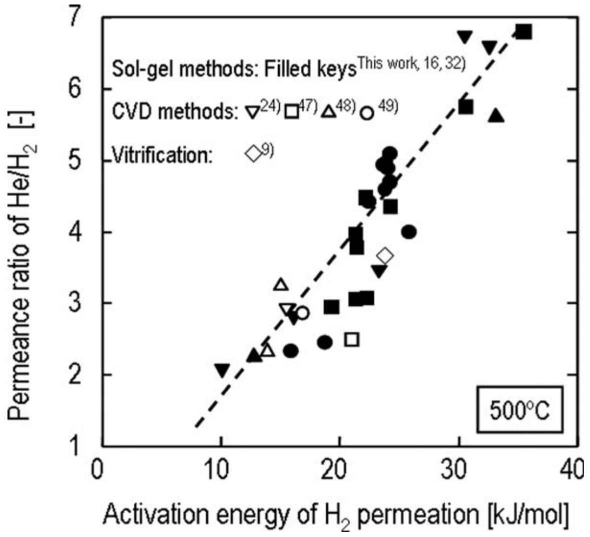

Figure 8. Permeance ratio of He/H$_2$ (500°C) as a function of activation energy of hydrogen for various types of silica membranes prepared by sol–gel, CVD, and vitreous silica using different types of materials.

On the other hand, hydrogen activation energy corresponds to the membrane pore sizes through which H$_2$ permeates, as discussed in the previous section. The correlation between the activation energy of permeation and the selectivity of gaseous molecules, both of which are intrinsic properties of microporous silica, is newly proposed in this study, and the applicability can be examined using various types of silica membranes, including sol–gel derived membranes, CVD, and vitreous glass silica. Surprisingly, irrespective of preparation methods and types of membrane materials, all types of membranes can be expressed with one correlation curve; Figure 8 shows that the permeance ratio of He/H$_2$ increased with an increase in the activation energy of hydrogen for any type of silica membrane. Oyama and coworkers discussed the activation energy of hydrogen through *n*-membered cyclosiloxane.[46] Based on their ab initio calculation, the activation energy of 30, 20, and 10 kJ corresponds to pore sizes of 0.25, 0.30, and 0.35 nm, respectively.

The reason that no effect of membrane materials was observed can be explained as follows. When compared with some metals, including Si, oxygen is electronegative and attracts electrons showing a larger size than other metals.[38] In other words, the pore walls of silica and silica composite oxides are assumed to be covered by oxygen. Another important point that should be emphasized is that no dependency on the preparation method was observed in the correlation curve. We can conclude that amorphous silica networks have similar pore size distributions, irrespective of membrane materials and preparation technique.

Figure 9 shows the activation energy of He permeation through silica membranes prepared by sol–gel, CVD, and vitreous glass, as a function of that of H$_2$, showing an approximately linear correlation between them. The larger is the activation energy of helium, the larger is that of hydrogen. The difference in activation energy between helium and hydrogen is 5 and 10 kJ/mol for silica membranes having H$_2$ activation energy of 20 and 30 kJ/mol, respectively, suggesting that with a decrease in pore size, the activation energy of hydrogen increases more rapidly than that of He due to

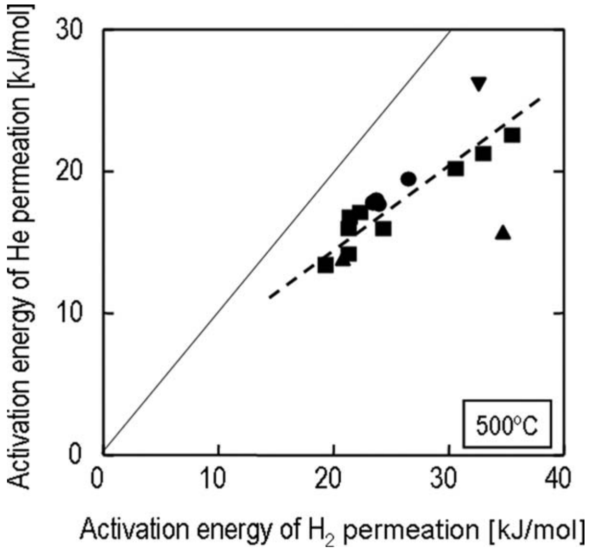

Figure 9. Correlation of activation energy of He and H$_2$ through microporous silica membranes.

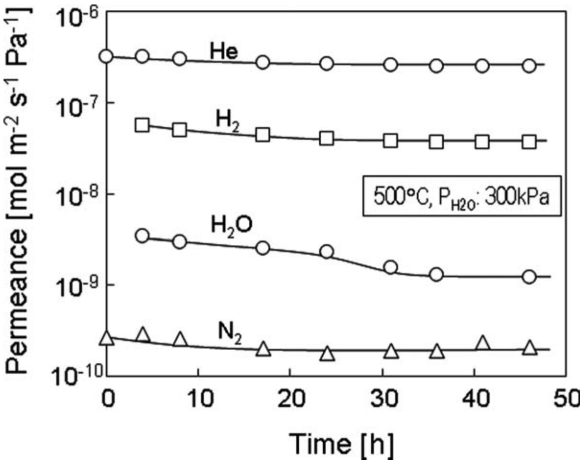

Figure 10. Time course of permeance through a Co-doped silica membrane (Si/Co = 1/1) in steam atmosphere (Mem-CoSi-2, steam partial pressure of 300 kPa).

larger molecular size. This trend is consistent with the ab intio calculation given by Oyama and coworkers.[46]

Permeation of water vapor through silica membranes

Figure 10 shows the time courses for the permeances of He, H_2, and N_2 through a Co-doped silica membrane (Si/Co = 1/1), which were measured using pure gases after drying the membrane with nitrogen. Permeance of steam was measured using a mixture of steam and nitrogen with H_2O/N_2 of 50/50. Co-doped silica membrane again showed stable permeance under hydrothermal conditions (500°C and a steam partial pressure of 300 kPa). Permeance decreased on the order of He $>$ H_2 $>$ H_2O $>$ N_2. The permeance ratio of hydrogen to water vapor, which is an important factor for actual application to the membrane reactor of steam reforming of methane, was 30. It should be noted that the kinetic diameters, which have mostly been accepted in gas separation using porous materials such as adsorption and membrane separation, were in the order of He (0.26 nm) $<$ H_2O (0.265 nm) $<$ H_2 (0.289 nm) $<$ N_2 (0.364 nm).[38] Although water vapor is reported to be smaller than hydrogen, the permeance of water vapor was found to be lower than that of hydrogen. That is, the order of permeance does not obey that of kinetic diameters. Therefore, another possible permeation mechanism, the surface diffusion mechanism, should be examined.

Water vapor is a polar molecule that is expected to have a large interaction with silica. The effect of partial pressure on the permeance of water vapor was examined in a mixture of N_2/H_2O and H_2/H_2O systems, to determine whether the surface diffusion mechanism could be the transport mechanism. Wakabayashi and Tomozawa[50] measured diffusivity in the range of 0–20 kPa, which is much lower than the partial pressure that is required for actual applications such as steam reforming of methane, and pointed out the possible contribution of surface diffusion to the transport at high temperatures, based on the adsorption measurement. If the surface diffusion is responsible for membrane permeation, permeance should decrease with an increase in the partial pressure of water vapor. Experimental results of Co-doped silica reveal that, as shown in Figure 11a, the permeance of water vapor was approximately constant, irrespective of H_2O partial pressure in the range of 10–300 kPa at 500°C for both N_2/H_2O and H_2/H_2O systems. Moreover, no effect of the partial pressure of water vapor was observed also at 300°C for pure silica membrane, as shown in Figure 11b. No contribution of surface diffusion to permeation through silica membranes was confirmed in the range of H_2O partial pressure of 10–300 kPa at temperatures from 300–500°C. It should also be noted that hydrogen and nitrogen mixed with water vapor showed approximately the same permeance of hydrogen and nitrogen as that measured in a single gas. Decreased permeance in mixtures, compared with single

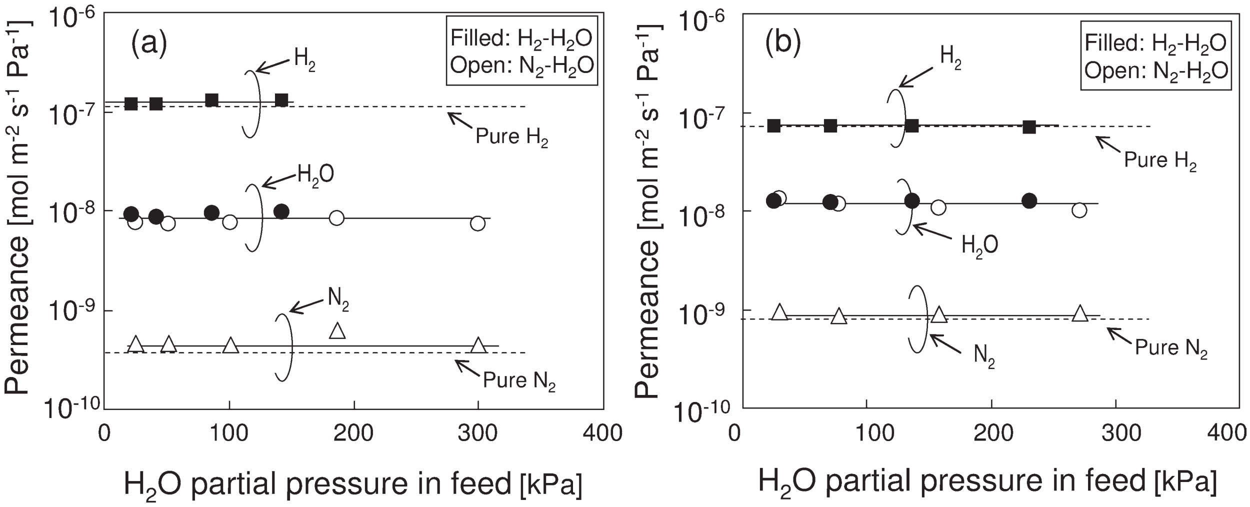

Figure 11. (a and b) Effect of the partial pressure of water on permeance through porous silica membranes in mixed H_2/H_2O and N_2/H_2O systems.

(a) Co-doped silica (Mem-CoSi-3), 500°C, and (b) silica (Mem-Si-2), 300°C.

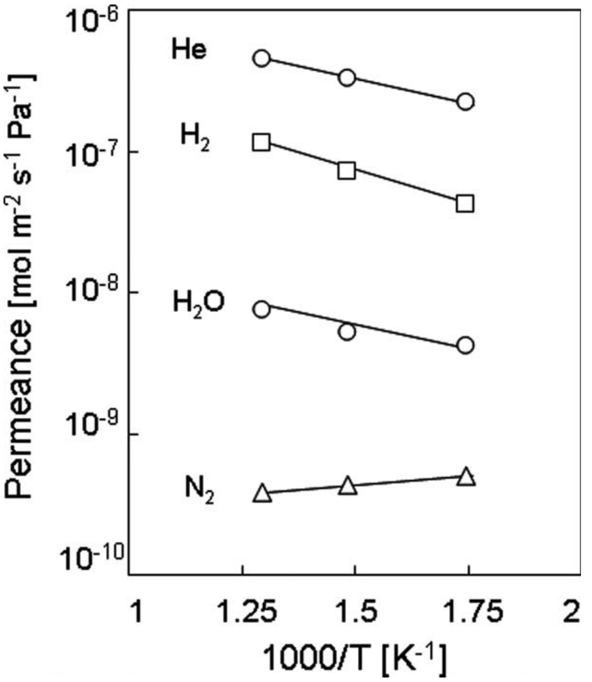

Figure 12. Arrhenius plot of permeance for a Co-doped silica membrane (Si/Co = 1/1) in a steam atmosphere (Mem-CoSi-3).

components, is reported to be due to the blocking effect of adsorptive gases on the permeation of less adsorptive gases, such as hydrogen and nitrogen, especially at low temperatures. The lack of effect of mixing the two molecules suggests a very small interaction between inorganic gases and water vapor, as well as between membrane and water vapor.

Figure 12 shows the temperature dependency of permeance, including water vapor using Mem-CoSi-3 (Si/Co = 2/1). As discussed before, the activation energy of the smaller molecule, that is He, was lower than that of H_2, whereas nitrogen showed a decreased permeance with an increase in temperature. The explanation may be that He and H_2 permeate through the small pores in the silica network, whereas nitrogen was considered to permeate through relatively large pores, such as pinholes, in the Knudsen diffusion mechanism. Water vapor appeared to follow the activated diffusion mechanism. The permeance ratio of hydrogen to water vapor was ~20, again showing that hydrogen was more permeable than water vapor. The permeance slope of water vapor is positive, but lower than that of hydrogen and higher than that of nitrogen. This intermediate tendency can be explained by the water vapor being able to permeate both the silica network (small pores) in activated diffusion and relatively large pores in Knudsen diffusion.

To date, only a limited number of papers have reported the permeance of water vapor, probably because of the difficulty of measurement and the low stability of microporous silica membranes.[6,7,17,30] Nomura et al.[7] reported permeance ratios of hydrogen to water vapor from 30 to 100 for silica membranes prepared by the CVD method. We reported that silica and silica-zirconia microporous membranes showed a higher permeance for hydrogen than for water vapor.[6,8,17,30] Therefore, the question remains, why the order of permeance follow He > H_2 > H_2O, irrespective of the order of kinetic diameter, He > H_2O > H_2. There are several possibilities: (1) a large interaction between water and the silica surface, (2) molecular shapes of water vapor and hydrogen, (3) solid vibration of the silica network, and (4) a kinetic diameter of permeating molecules through silica membranes.

Water is a polar molecule that possibly has a larger interaction with silica than does hydrogen, and therefore, the molecular motion of water vapor may be restricted on the silica surface. However, in this case, water would show the permeation characteristics of the surface diffusion, which was confirmed not to be responsible for the permeation mechanism at 300–500°C based on Figures 11a, b. The interaction with silica cannot account for the order of permeances. A water molecule consists of three atoms and forms a nonspherical structure, which may reduce its diffusivity through microporous membranes. Using CVD silica membranes, Gu and Oyama[43] reported that the order of permeance for noble gases was unusual, He > H_2 > Ne, because it followed neither the order of kinetic diameter (He: 0.26 nm, H_2: 0.289 nm, Ne: 0.275 nm) nor the molecular weight (He: 4.0, H_2: 2, Ne: 20.1). They explained the order using a theory involving jumps between solubility sites. The vibration frequency of permeating gas between the sorption sites was smallest for Ne due to its having the largest molecular weight, which also accounts for its having the lowest permeance of the three molecules. However, the applicability of the theory to polar nonspherical molecules remains unclear.

Regarding the kinetic diameters, there are several methods for determining the molecular sizes that are available for discussion of adsorption and membrane permeation in/through microporous materials, such as collision diameter and kinetic diameter. Based on the extended simple point charge (SPC/E) model proposed by Brendesen et al.,[40] water molecular size of 0.317 nm was obtained using the heat of evaporation. van Leeuwen[39] obtained the molecular size 0.2995 nm, based on the Stockmayer potential using phase-coexistence data (vapor–liquid phase). Breck and van Leeuwen used the Stockmayer potential using gaseous viscosity data and vapor–liquid equilibrium data, and obtained sizes of 0.265 nm and 0.2995 nm, respectively. Brendesen et al. also used thermodynamic data in the liquid phase. We also reported the same tendency for ammonia and hydrogen.[51] Although the kinetic diameters of ammonia and hydrogen are 0.26 nm and 0.289 nm, respectively, hydrogen showed a higher permeance than ammonia (permeance ratio: 150 at 400°C). Following Brendesen et al.[40] and van Leeuwen,[39] the order of kinetic diameters is He (0.26 nm) < H_2 (0.289 nm) < H_2O (0.2995, 0.317 nm) < NH_3 (0.3261 nm) < N_2 (0.364 nm), and agrees well with that of the permeance experimentally obtained using microporous silica membranes, which suggests that the H_2O molecular size, at 0.265 nm, may not be appropriate for silica membranes.

Conclusions

Silica and cobalt-doped silica membranes that showed high permeance, in the range of 1.8×10^{-7} mol m^{-2} s^{-1} Pa^{-1} and a H_2/N_2 permeance ratio of ~730, with excellent hydrothermal stability under steam pressure of 300 kPa, were successfully prepared, and the permeation mechanism of gaseous molecules, focusing in particular on hydrogen and water vapor, was investigated. The activation energy of H_2 permeance through cobalt-doped silica membranes with varying Co contents, which ranged from 10 to 30 kJ mol^{-1}, was found to correlate well with the permeance ratio of He/H_2 for porous silica membranes prepared by sol–gel processing as well as CVD and vitreous glasses, suggesting similar amorphous silica network structures, irrespective of preparation techniques. Co-doped SiO_2 membranes that had a sharp pore size distribution showed increased water vapor permeance with temperature and no pressure dependency, suggesting H_2O permeated through the silica network via a molecular sieving mechanism. The permeance ratios of H_2/H_2O were found to range from 5 to 40, that is, hydrogen (kinetic diameter: 0.289 nm) was always more permeable than water vapor (0.265 nm). This suggests that the H_2O molecular size of 0.265 nm may not be appropriate for permeation through amorphous silica networks.

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