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Nickel-Doped Silica Membranes for Separation of Helium from Organic Gas Mixtures

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Abstract: One of the problems in the use of inorganic silica membranes is their instability against water or water vapor, a problem that results from the dissolution and rearrangements of silica networks. In this work $Ni(NO_3)\cdot 6H_2O$ was added to silica sol for fabrication of Ni-doped silica membranes by sol-gel techniques in order to prevent the densification of amorphous silica networks in a humid atmosphere at 50–300°C. A fresh Ni-doped silica membrane ($Si/Ni = 2/1$) fired at 500°C showed a large He permeance of about 2.6×10^{-5} [m^3 (STP)/($m^2 \cdot s \cdot kPa$)] with a selectivity of 600 (He/CH_4) at 300°C. After the Ni-doped silica membrane was left in humid air (40°C, 60% RH) for 4 days, the He permeance decreased slightly (by 5%) with a larger selectivity of 800 (He/CH_4) at 300°C. However, little change was observed in the activation energy of He permeation, suggesting that nickel oxides added to silica can preferably prevent the densification of silica networks through which only H_2 and He can permeate. Humid He and CH_4 showed smaller permeabilities, especially at temperatures below 150°C, than those of dry gases because of condensed and/or adsorbed H_2O molecules in silica networks and on grain boundaries.

Separation of He/CH_4 mixtures with the fresh Ni-doped silica membrane ($Si/Ni = 2/1$) at 300°C gave relatively good results and coincided well with the predicted values with the ideal permeance ratio, 600.

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INTRODUCTION

The conventional processes to recover helium from natural gases containing 0.2–5% He comprise mainly partial condensation and adsorption processes, which require a large amount of separation energy and an extremely large physical installation for practical separation and purification of helium.

Membrane separation, on the other hand, is considered quite attractive as a simple and energy-conserving separation method and offers many advantages, especially for gas separation without any phase change. Many researchers, therefore, have tried to develop gas separation membranes using various materials such as organic polymers, zeolite, silica, and alumina. Stern et al. (1) developed several kinds of organic membranes, such as Teflon FEP, a copolymer of tetrafluoroethylene and hexafluoropropylene, for separation of helium from organic mixtures. In general, however, organic membranes were found to have quite low He fluxes and poor thermal and chemical stability. On the other hand, inorganic materials, such as porous silica and alumina, offer substantial advantages (e.g., high flux and good thermal and chemical stability). Silica is one of the most attractive inorganic membrane materials because of its possible amorphous structures in a wide temperature range and its pore sizes of less than 1 nm, features that are quite useful for high permselectivity in gas separation. At the end of the 1980s, dense silica membranes prepared by sol-gel techniques or chemical vapor deposition (CVD) methods were found to show some excellent separation performance for hydrogen or helium at high temperature (2–5). Uhlhorn et al. (6) developed a modified silica membrane for separation of H_2 and CO_2 from the CH_4 mixture. Applying sol-gel techniques, Asaeda et al. (7) developed silica membranes of high flux with high helium and hydrogen selectivity in a temperature range of 50–300°C. The high flux and high selectivity of helium at a moderate temperature should offer advantages in helium recovery from natural gases and in the subsequent purification via membrane separation. However, dense and porous silica membranes were found to be unstable against water vapor at high temperature (>400°C) (8–10). As reported by de Lange et al. (11), micropores of sol-gel derived from silica membrane were densified by the exposure to lean water vapor in the temperature range 250–300°C. Even at room temperature, the permeability of He and H_2 decreased drastically (to 1/10 of the initial level) after the porous silica membrane was left in humid air (40°C, 60% RH) for several days. The activation energy of H_2 permeation increased from 3 to 14 kJ/mol because of the densification of amorphous silica networks (7). Further improvements in the stability of silica membranes are crucially important for their practical use in industry.

In this work, nickel oxides were added to silica to obtain Ni-doped silica membranes via sol-gel techniques in attempts to improve the stability of the membranes against water or water vapor. Some gas permeation measurements with the Ni-doped silica membranes were performed to study the permeation characteristics of He, N_2, and CH_4. The membrane was applied to the separation of He from organic gas mixtures to study the separation performance. Further, the effects of moisture on the gas permeation were studied in the temperature range 50–300°C. The stability of membranes was also examined by observing the changes of gas permeation characteristics before and after exposure to humid air (40°C, 60% RH) for several days.

EXPERIMENTAL

Preparation of Porous Ni-Doped Silica Membranes

Porous Ni-doped silica membranes were prepared by sol-gel techniques. First, four kinds of Ni-doped silica colloidal sols were prepared; the hot coating methods were then applied to form a thin layer of Ni-doped silica membrane on a porous ceramic substrate.

Preparation of Colloidal Sols

The most important consideration in preparation of metal-doped colloidal sols is to obtain homogeneous metal oxide–silica composite sols. Otherwise, there would be a high possibility of phase segregation during drying and firing in the sol-gel procedures. In this work, Ni-doped silica colloidal sols ($Si/Ni = 2/1$) were prepared by hydrolysis and condensation reactions of tetraethoxysilane (TEOS) in ethanol with $Ni(NO_3)_2 \cdot 6H_2O$ and water. The preparation procedures are as follows: a specified amount of TEOS (e.g., 7.5 g) was added to ethanol (50 g) with nickel nitrate (5.23 g). The solution was then stirred for a sufficient period of time for hydrolysis and condensation reactions to occur at room temperature. After a specified amount (2 g) of nitric acid (61 wt%) and a large amount of water (500 g) were added, the solution was boiled for about 10 h for 1.5 wt% colloidal sol. The total amount of the solution was kept constant, and the organic chemicals initially contained were removed during the boiling. Four kinds of colloidal sols (containing 2, 1.5, 1, and 0.5 wt% of equivalent TEOS in the final sol) were prepared.

Membrane Fabrication

Porous α-alumina tubes (porosity: 50%, average pore size: 1 μm, outside diameter: 10 mm, length: 100 mm) were used as the supports for the Ni-doped silica membranes. Before coating, glass tubes were connected to both ends of cylindrical α-alumina supports for easy handling and gas permeation measurements. Fine α-alumina particles (average particle diameter: 0.2–1.9 μm) were coated on the outer surface of a porous support and fired at 500°C for 10–20 min to make the surface smooth. These procedures were repeated several times to remove large pinholes that might remain in the final membrane. Before coating with Ni-doped silica colloidal sols, silica-zirconia (Si/Zr = 1/1) colloidal sols were coated on the substrate by the hot coating methods (12). In this procedure, the substrate (module) was first heated to around 180°C. It was then coated by contacting the module quickly with a wet cloth with the sol. This hot coating method makes the sol dry instantly and prevents it from penetrating deep into the pores. Four kinds of Ni-doped silica colloidal sols were subsequently coated on the substrate by the hot coating method. The coating and firing procedures were repeated several times with each colloidal sol prepared.

Gel Preparation for N_2-Adsorption Characteristics and XRD Observation

In order to examine the gel characteristics, some powdered samples of Ni-doped silica gel were prepared from the colloidal sols by quick drying or by dripping colloidal sols on a hot platinum plate at 180°C and by firing at 500°C for 30 min.

Gas Permeation Measurements and Separation Tests

Figure 1 shows a schematic diagram of the experimental apparatus. A single gas (He, N_2, or CH_4) was fed on the outside (upstream) of a cylindrical membrane module at 0.2 MPa, keeping the downstream pressure constant at the atmospheric pressure. In the case of moist gas permeation, a single gas was fed to the permeation cell through an evaporator of H_2O at room temperature. The partial pressure of H_2O was kept constant at the saturation vapor pressure at 25°C. The temperature of the separation cell was kept constant at a specified temperature between 50 and 300°C. The permeation rate was measured by a soap-film flowmeter. After using a fresh membrane to measure the permeance dependency of various gases on temperature, the membrane was kept in humid air at 40°C and 60% RH for a specified period. The gas permeabilities were observed again in the same temperature range.

Gas separation tests were performed at 50–300°C with gas mixtures of He and CH_4, which were fed on the outside (upstream) of the cylindrical membrane module at 0.2–0.4 MPa, keeping the downstream pressure constant at the atmospheric pressure. The upstream and downstream flow rates were measured via soap-film flowmeters, and the gas compositions were analyzed via gas chromatography with a thermal conductivity detector (activated carbon column).

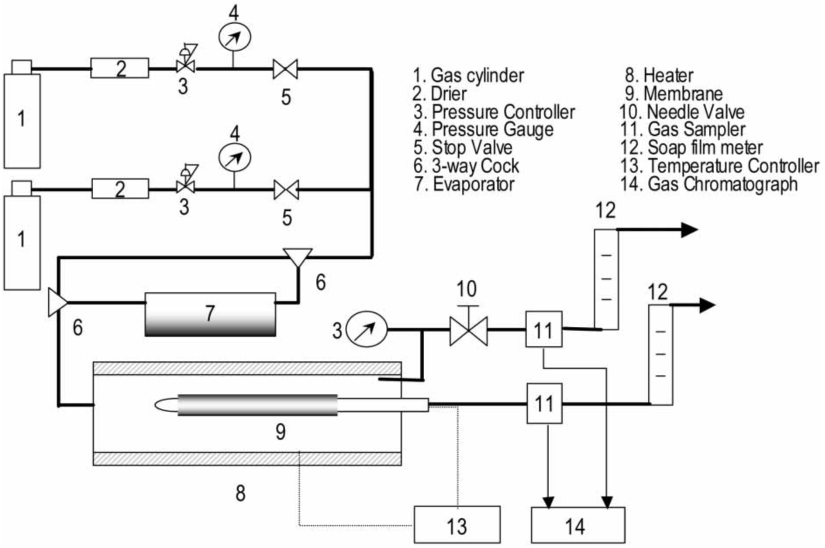

Figure 1. Schematic diagram of experimental apparatus.

RESULTS AND DISCUSSION

Membrane Characterization

Figure 2 shows a scanning electron micrography (SEM) photo of a typical cross-section of a Ni-doped silica membrane ($Si/Ni = 2/1$). A thin active layer of Ni-doped silica for selective He permeation can be seen at the top just above the SiO_2/ZrO_2 layer. The thickness of this separation layer (i.e., the Ni-doped silica layer) is observed to be less than 1 μm. It is naturally

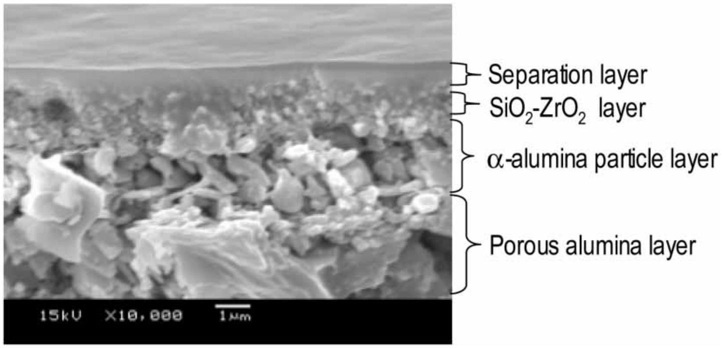

Figure 2. Cross-section of Ni-doped silica membrane ($Si/Ni = 2/1$).

preferable to make the separation layer thin enough for high permeability without any pinhole.

Gel Characterization

The segregation of metal oxides seems to cause structural heterogeneity in membranes, resulting in instability against water and water vapor. Therefore, the preparation of homogeneous gel structures of well-dispersed NiO in silica networks is extremely important in this work. Some observed X-ray-diffraction (XRD) patterns of Ni-doped silica gels are shown in Fig. 3. For the SiO_2-NiO composite gel (Si/Ni = 2/1), the figure shows broad peaks of NiO, which are quite different from those for a simple mixture of SiO_2 and NiO (Si/Ni = 2/1). This result suggests that the segregation of NiO in SiO_2-NiO composite gel can be prevented comparatively well, considering that a simple mixture of SiO_2 and NiO powders (Si/Ni = 2/1) or a sample from a simple mixture of silica sol and $Ni(NO_3)_2$ after sol preparation shows a pattern with sharp peaks. Figure 4 shows a large difference in pore-size distributions obtained by N_2 adsorption methods for powdered samples of pure silica gel, a simple mixture of SiO_2 and NiO powders, gel from colloidal sol with $Ni(NO_3)_2$, and SiO_2-NiO composite gel. The SiO_2-NiO composite gel sample shows a quite different pore-size distribution from the one for the simple mixture of SiO_2 and NiO powders (Si/Ni = 2/1). However, the pore-size distribution of the latter

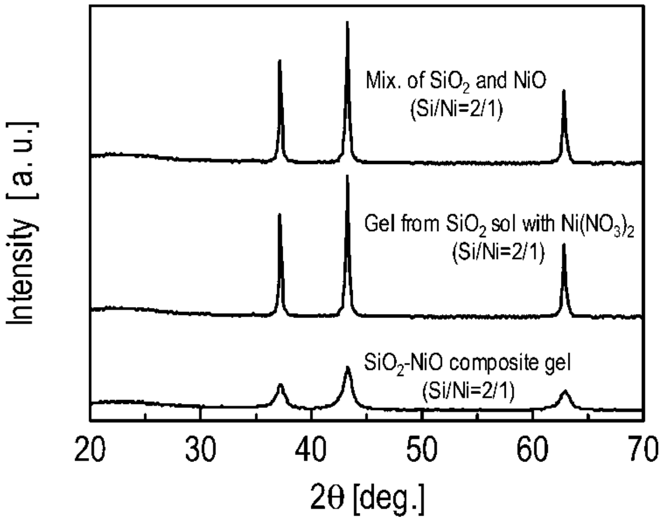

Figure 3. Observed XRD patterns of Ni-doped silica gels (Si/Ni = 2/1).

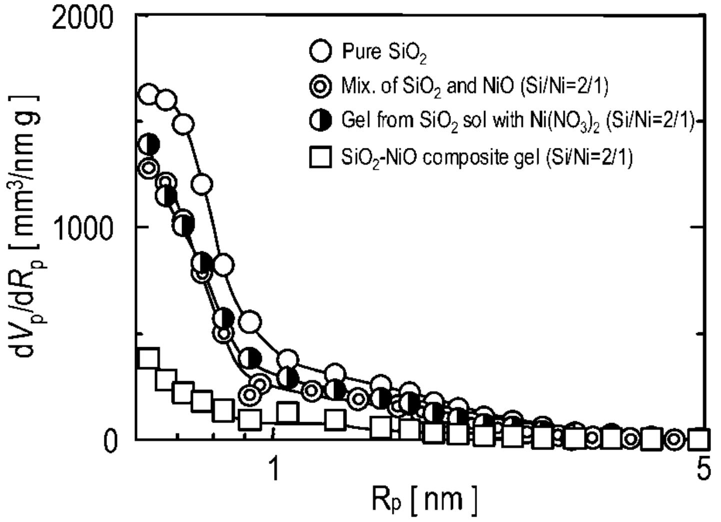

Figure 4. Observed pore-size distributions of Ni-doped silica gels (Si/Ni = 2/1).

mixture is similar to that for pure silica. Moreover, the simple addition of $Ni(NO_3)_2$ to colloidal SiO_2 sol (Si/Ni = 2/1) also shows a pore-size distribution quite close to that for the simple mixture of SiO_2 and NiO (Si/Ni = 2/1). These results suggest that some of NiO must be well dispersed in micropores, in grain boundaries, and also in the silica amorphous networks to form rather homogeneous composite structures.

Gas Permeation Characteristics and Stability

Figure 5 shows a schematic image of pore structures. In general, silica membranes prepared by sol-gel techniques show rather wide pore-size distributions comprised of pores in silica networks and interparticle pores or pores due to grain boundaries. While He and H_2 can be considered to permeate through silica networks primarily via activated diffusion or permeation, a slightly larger molecule (e.g., N_2, CH_4, and SF_6) can permeate only through grain boundaries mostly via a Knudsen diffusion mechanism. One of the important problems in fabrication of inorganic separation membranes by sol-gel techniques is determining how to create a sharp pore-size distribution or how to eliminate the interparticle pores for noble He separation membranes.

Figure 6 shows some observed permeances of He, N_2, and CH_4 in the temperature range of 50–300°C for a fresh Ni-doped silica membrane (Si/Ni=2/1) under dry conditions (closed symbols on solid lines). In the same figure are shown the gas permeances observed after the membrane was left

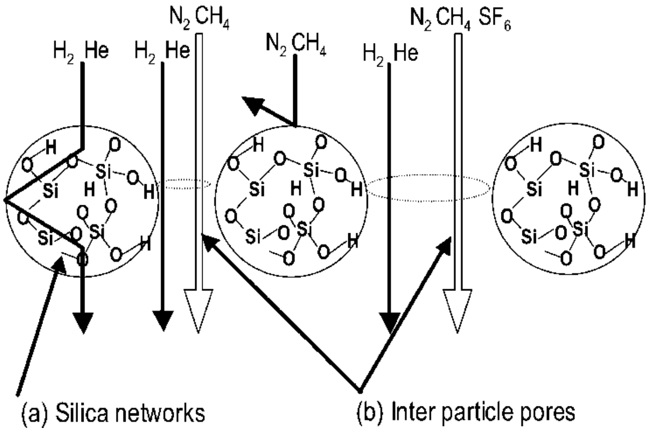

Figure 5. Schematic image of pore structures.

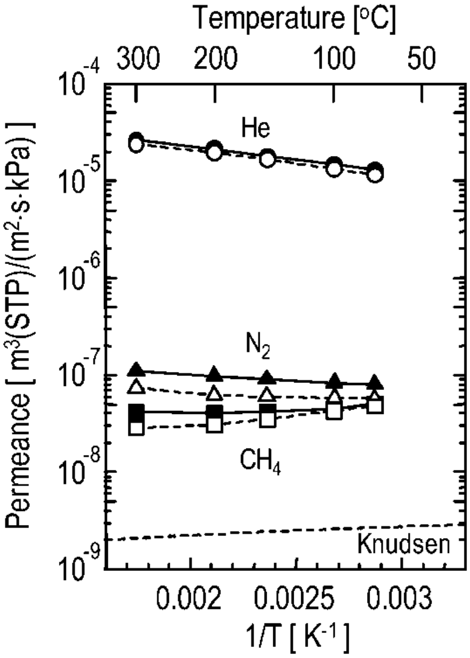

Figure 6. Observed gas permeances for Ni-doped silica membrane (Si/Ni = 2/1). Closed symbols on solid lines: fresh membrane; open symbols on broken lines: membrane after 4 days in humid air.

in humid air (40°C, 60% RH) for 4 days (open symbols on broken lines). The fresh Ni-doped silica membrane (Si/Ni = 2/1) shows a relatively large He permeance at around 2.6×10^{-5} [m^3 (STP)/($m^2 \cdot s \cdot kPa$)] with a selectivity of 600 (He/CH_4) at 300°C and shows (to a limited extend) the characteristics of the activated permeation. The CH_4 permeance increases at lower temperatures showing characteristics somewhat like Knudsen permeation. Considering that the selectivity of He/CH_4 is larger than that of Knudsen's ratio, the pore-size distribution of this Ni-doped silica membrane seems to be sufficiently sharp. After the membrane was left in humid air for 4 days, the He permeance decreased slightly (by about 5%), while the permeances of N_2 and CH_4 decreased by about 30%. These phenomena resulted in a larger He selectivity of 800 (He/CH_4) at 300°C. The temperature dependency of He permeance showed little change after the membrane was left in humid air for 4 days. The activation energy of gas permeation, ΔE, can be obtained by applying the following equation [Eq. (1)] (13) to the observed temperature dependency of permeance, P, with a small correction applied for the contribution of the Knudsen flow based on N_2 permeation:

$$P = \frac{k_0}{\sqrt{MRT}} \exp\left(-\frac{\Delta E}{RT}\right) \tag{1}$$

where k_0 is a characteristic constant of the porous membrane, M is the molecular weight of the permeating gas, R is the gas constant, and T is the temperature. The fresh Ni-doped membrane (Si/Ni = 2/1) showed 7.1 kJ/mol of activation energy for He permeation. Smaller activation energy of He permeation is naturally preferable for a He-separation membrane to be effectively applied even at lower temperatures. The activation energy of He permeation showed little change after the membrane was left in humid air for 4 days. Since larger activation energy of gas permeation suggests more dense membrane structures, this fact suggests that well-dispersed NiO and homogeneous composition can prevent the densification of amorphous silica networks and that Ni-doped membranes (Si/Ni = 2/1) are relatively stable against water.

In order to examine the effect of H_2O on gas permeation characteristics, some gas permeances were observed in moist conditions. The results are shown in Fig. 7. Clear differences in gas permeation characteristics were observed below around 150°C in moist conditions, in which the permeances of He and CH_4 decreased drastically compared with those in dry conditions. This can be considered due to the condensed and/or adsorbed H_2O molecules in silica networks and on grain boundaries. Moreover, the decrease in He permeability was larger than that of CH_4, resulting in a smaller selectivity of 30 (He/CH_4) at 50°C. This is probably because H_2O molecules can enter the silica networks to prevent He permeation. These results suggest that He can be preferably separated from CH_4 mixtures with

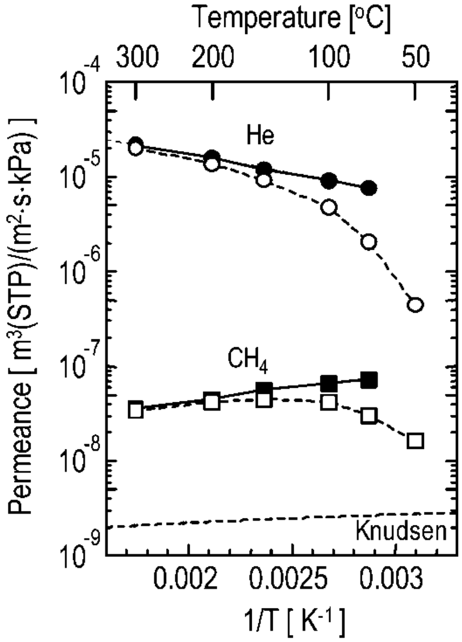

Figure 7. Observed gas permeance changes in moist condition for Ni-doped silica membrane (Si/Ni = 2/1). Closed symbols on solid lines: dry condition; open symbols on broken lines: moist condition.

this kind of membrane in the separation temperature range of 150–300°C, regardless of the presence of saturated water vapor at 25°C.

Gas Separation

Separation performance for gas mixtures depends on the operating conditions: the pressure ratio, Pu/Pd [i.e., feed (upstream) pressure/permeate side (downstream) pressure], and on the ideal selectivity or permeability ratio, α. The larger the pressure ratio Pu/Pd and the value of α, the higher the permeate concentration becomes.

Figure 8 shows the observed separation results of He/CH_4 at 300°C for the Ni-doped silica membrane (Si/Ni = 2/1) before the membrane was left in humid air. The predicted separation curves in this figure were obtained by the following equation [Eq. (2)] (3, 14):

$$Y_A = \frac{\beta - \sqrt{\beta^2 - 4\gamma(\alpha - 1)\alpha X_A}}{2\gamma(\alpha - 1)} \tag{2}$$

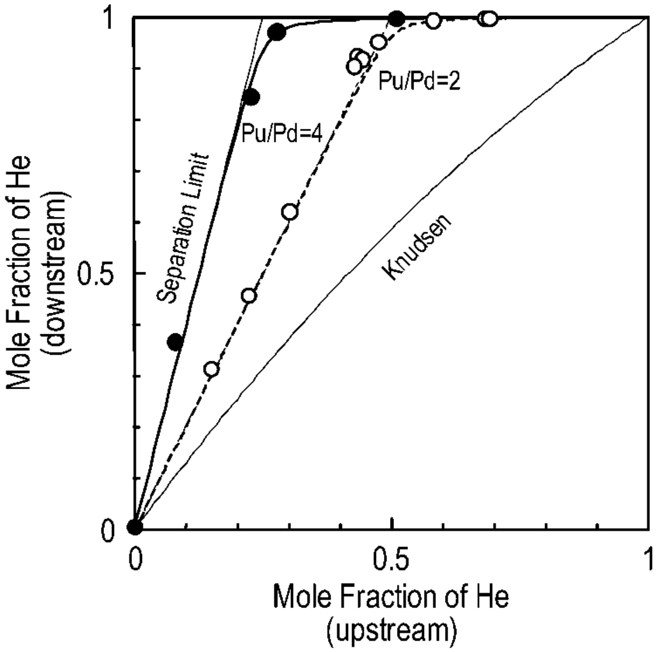

Figure 8. The effect of Pu/Pd ratio on separation performance of He/CH_4 at 300°C for Ni-doped silica membrane ($Si/Ni = 2/1$) (for $\alpha = 600$). Closed symbols on solid line: $Pu/Pd = 4$; open symbols on broken line: $Pu/Pd = 2$.

where Y_A is the mole fraction of gas A in permeates (downstream), X_A is the mole fraction of gas A in the feed (upstream), α is the permeability ratio, $\beta = (\alpha - 1)(X_A + \gamma) + 1$, and $\gamma = Pd/Pu$. The observed results can be seen to be in good agreement with the predicted separation curves for $Pu/Pd = 2$ and $Pu/Pd = 4$ with $\alpha = 600$. In the case of purification of He (relatively high feed concentration), there is little appreciable difference in separation performance for $Pu/Pd = 2$ and 4, except in the permeation flux of He. However, separation performance of He recovery from natural gas (low feed concentration) is greatly affected by the Pu/Pd ratio, as can be seen in Fig. 8. Since the concentration of He in natural gas is quite low (0.2–5%), it may be preferable to perform the He recovery operation under conditions of a larger Pu/Pd ratio if a large flux with relatively high He concentration in the permeates is required by one stage of membrane separation. This can be done either by reducing the downstream pressure or by raising the upstream pressure.

Figure 9 shows the effect of α on separation performance of He/CH_4 at 300°C. The upper part of this figure shows the total permeation flux dependency on the upstream feed concentration. If the value of α is infinity

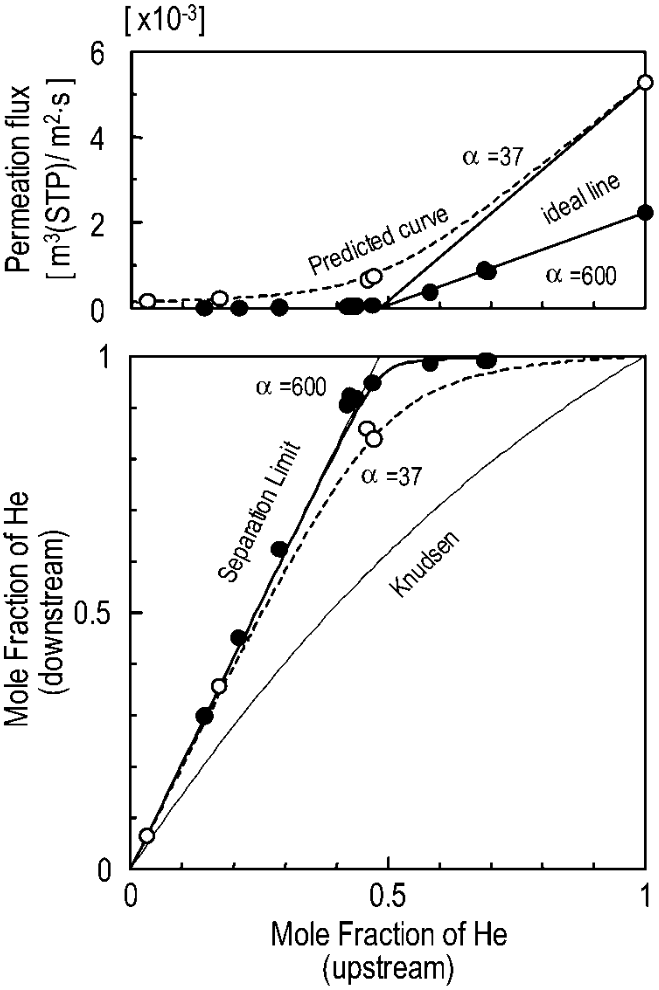

Figure 9. The effect of α on separation performance of He/CH_4 at 300°C for Ni-doped silica membrane (Si/Ni = 2/1) (Pu/Pd = 2). Closed keys on solid line: $\alpha = 600$, open keys on broken line: $\alpha = 37$.

(ideal molecular sieving), the permeation flux must not be below the He mole fraction of 0.5 for the pressure ratio $Pu/Pd = 2$, because no partial pressure difference occurs across the membrane. Although the observed flux for $\alpha = 600$ was quite small, that for $\alpha = 37$ is relatively large, due to the membrane's high permeance despite its low selectivity. When we want to obtain a larger flux with fairly large He concentration in permeates by one separation stage without reducing the downstream pressure, it would be preferable to operate with a membrane of a moderate selectivity of $\alpha = 37$, for example, instead of $\alpha = 600$. On the contrary, if we want to obtain high concentration of He (downstream) via one separation stage, it is more effective to apply a membrane of high selectivity by reducing the downstream pressure to produce a larger Pu/Pd ratio.

CONCLUSIONS

Sol-gel techniques were applied to fabricate porous Ni-doped silica membranes (Si/Ni = 2/1). The thickness of the separation layer (i.e., Ni-doped silica layer) was less than 1 μm. A fresh Ni-doped silica membrane showed high He permeability with a selectivity of 600 (He/CH_4) at 300°C. After the membrane was left in humid air for 4 days, the He permeability decreased slightly (by 5%). However, the selectivity (He/CH_4) increased to 800 at 300°C, with little change in the activation energy for He permeation. In the moist permeation condition, the permeabilities of He and CH_4 decreased drastically at temperatures below around 150°C because of condensed and/or adsorbed H_2O molecules in silica networks and on grain boundaries. Separation results for He/CH_4 mixtures at 300°C showed good agreement with the predicted results.

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