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Gas Permeation through Microporous Alumina Membranes Containing Highly Dispersed Metal Particles

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Hydrogen gas permeation through sol-gel derived microporous alumina membranes was strongly promoted in the presence of metal particles highly dispersed in the pore structure. The separation factor of hydrogen for ruthenium-dispersed membranes exceeded the limitation of the Knudsen diffusion mechanism.

Inorgnic microporous membranes attract much of attention for the application to high-temperature gas separation processes and catalytic membrane reactors.[1-4] For these practical applications membrane materials have to be much improved in the following two points. First, the conventional inorganic membrane materials can be hardly used for the high temperature above 800 ℃ due to crack formation caused by sintering. We have already reported the new membrane materials based on BaO- and La2O3-Al2O3 systems, which could be used above 1000 ℃ without thermal deterioration.[5] Secondly, the problem is to enhance the rate and the selectivity of permeation of particular gas species. Since only the Knudsen mechanism is not enough to attain high selectivities, other mechanisms, such as surface diffusion, capillary condensation, and/or molecular sieving, need to be brought about by the chemical modification of membrane materials. In this study, we report the marked enhancement of the selectivity of hydrogen permeation by introducing metal fine particle deposits into the microporous structure of alumina membranes.

Microporous membranes of alumina were prepared by repeated dip-coating of a coarse porous substrate (Al2O3 76%, SiO2 23%, pore size 500 nm, porosity 45%, Nippon Kagaku Togyo) with alkoxide-derived sol prepared by the following procedure.[5] Aluminium iso-propoxide, Al(OC3H7)3, was introduced into excess hot water (80 ℃, 100 mol/mol-alkoxide) under vigorous stirring. After a clear sol was obtained by introducing dilute HCl (0.1 mol/ mol-alkoxide), aqueous solutions of four types of metal salts (Pd(NH 3)Cl2, H2PtCl6, RhCl3, and RuCl3) was added to the sol. The dip-coated membranes were dried at room temperature in air and calcined at 500 ℃ for 5 h after single dip-coating process. The dip-coating was repeated 15 times, resulting in the formation of membranes with the thickness of ca. 10 μm. Prior to the gas permea-

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tion measurement, the metal-dispersed membranes were treated in a H_2 stream at 500 ℃ to reduce the dispersed metal salt to the metallic state.

Microstructural parameters of the membrane were evaluated by means of N_2 adsorption at 77 K as follows: surface area, 150 m^2/g; the peak of pore size distribution, ca.1-5 nm; and pore volume, 0.13 cm^3/g. No microstructural difference was observed between metal dispersed and neat membranes. Transmission electron microscopic observation was performed on the 1.33 wt% Ru-dispersed alumina membrane (Fig. 1). The sample consists of fine particles of metastable alumina (γ-phase) and uniformly deposited Ru particles. The particle size of Ru metal is about 5 nm.

Fig. 1. Transmission electron micrograph of the 1.33 wt% Ru-dispersed Al_2O_3 membrane.

The permeation selectivity of gaseous mixture through the membrane was measured in a conventional flow system.[2] Figure 2 shows the schematic diagram of the experimental apparatus. The membrane was bound to the end of the nonporous alumina tube with a glass paste. An equimolar mixture of H_2 and N_2 was fed to the membrane and argon was introduced to the permeation side to sweep the permeated gas. Pressure drop (P-P', the difference of total pressure between both sides of the alumina membrane), gas permeation rate, and the composition of permeation gas were measured several times. Here, the permeation selectivity is defined as a separation factor, α,

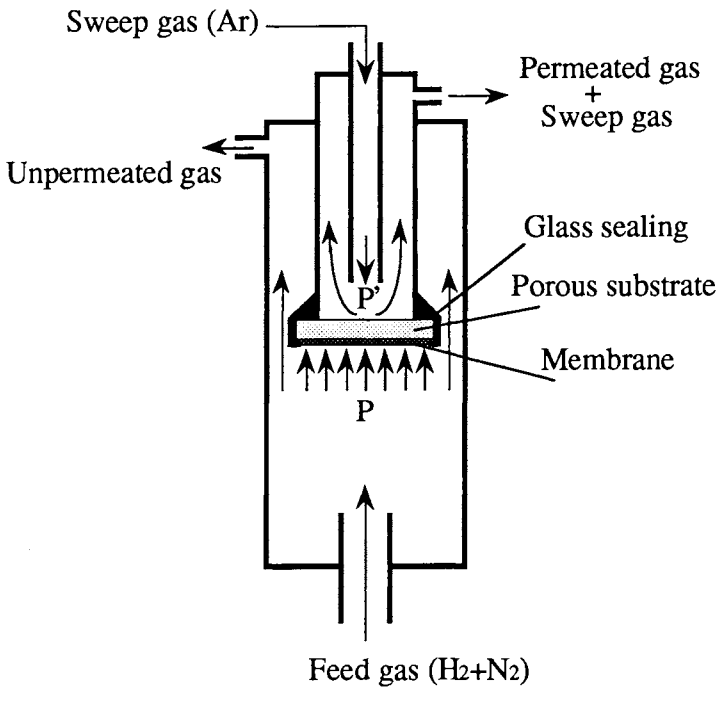

Fig.2. Schematic diagram of the experimental apparatus. P'=1.01x10^5 Pa

$$\alpha = (p'(H2)/p'(N2))/(p(H2)/p(N2))$$

where p and p' are partial pressures in the feed and in the permeation gas, respectively.

Figure 3 shows the temperature dependence of the separation factor, α, for the hydrogen/nitrogen mixture (p(H2)/p(N2)=1.0) at P-P'= $1.4X10^4$Pa. The flow rate of the sweep gas was 10 cm^3/min. The separation factor for a hydrogen/nitrogen mixture of the neat alumina membrane at room temperature, α=3.36, was within a limitation of the ideal Knudsen diffusion (α=3.74) for which the separation factor is determined by the ratio of the reciprocal square root of the molecular weight of the gaseous species. It should be noted that the four types of metal-dispersed membranes showed higher separation factors than that of the neat alumina membrane. The highest selectivity was attained by the use of the Ru-dispersed membrane, of which α values exceeded those expected from the ideal Knudsen flow in the whole temperature range examined. One of the most promising features of this Ru-dispersed membrane is to enhance the separation factor and permeation rate of hydrogen simultaneously. The hydrogen permeability of the Ru-dispersed membrane, ca. 2 X 10^{-12} mol m s^{-1} m^{-2} Pa^{-1}, is twice as large as that of the neat membrane. However, nitrogen permeabilities of the two types of membranes were almost the same in the whole temperature range.

The deviation from the Knudsen diffusion was more obviously observed in the effect of flow rate of sweep gas (Ar) on the separation factor as shown in Fig. 4. The separation factor of the neat and Ru-dispersed alumina membranes increased with an increase in flow rate of Ar. This is because the gas permeation through the membrane depends on the concentration gradient of gaseous species in the membrane. The high sweep gas rate keeps the low H2 concentration at the permeation side of the membrane, providing the large concentration gradient of H2. In spite of this effect, the separation factor of the neat alumina membrane was found to saturate at α = 3.7, because the gas separation is governed by the Knudsen diffusion. The separa-

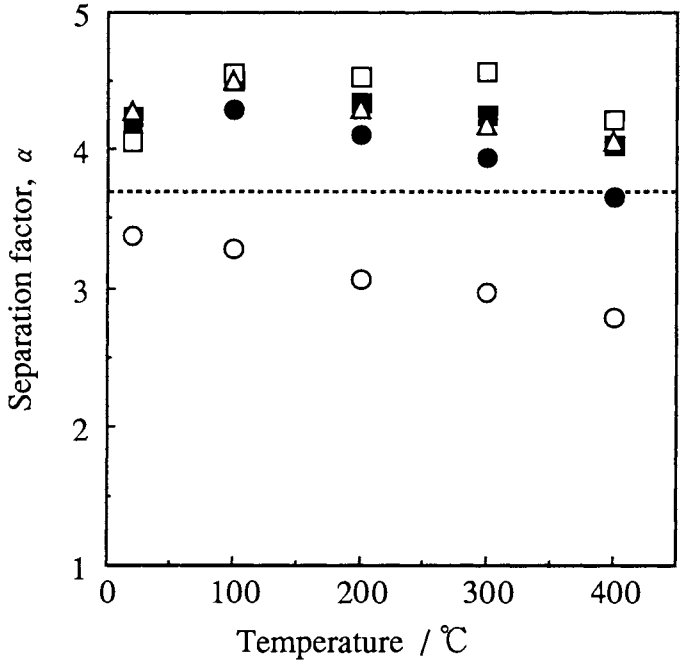

Fig. 3. The separation factor for a hydrogen-nitrogen mixture as a function of temperature. The broken line is the theoretical value from the Knudsen diffusion mechanism.
○ Al_2O_3, □ Ru - Al_2O_3, △ Pd - Al_2O_3,
■ Rh - Al_2O_3, ● Pt - Al_2O_3
P-P'= $1.4X10^4$ Pa, $p(H_2)/p(N_2)=1.0$

tion factor of Ru-dispersed membrane increased with an increase in the rate of sweep gas, further exceeding the limitation of Knudsen flow. These results indicate that highly dispersed Ru particles promote the selective permeation of hydrogen through the microporous alumina membrane. This effect, being much more strongly observed at elevated temperatures (Fig. 4), shows that diffusion mechanisms other than the Knudsen flow should come into play. Since the promotion of H2 permeation took place above 200 ℃, at which the hydrogen chemisorption occurred significantly, the effect is probably related to chemisorption of H 2 on the Ru particles.

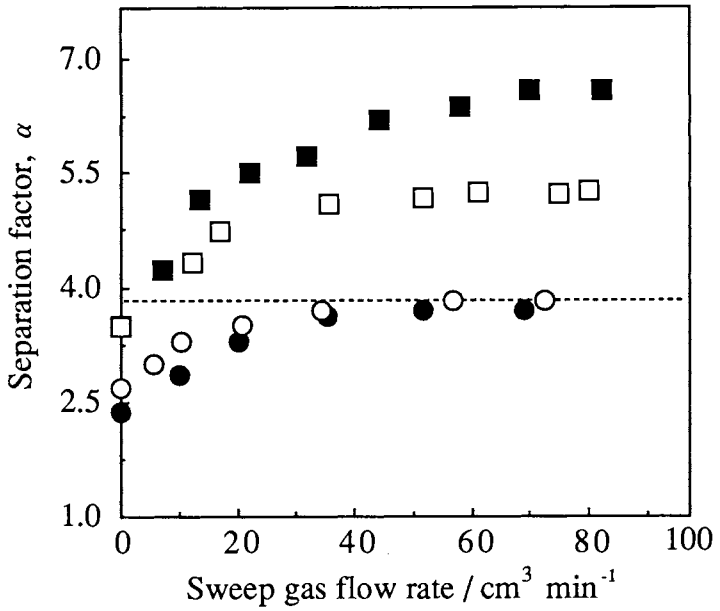

Fig. 4. Effect of the flow rate of sweep gas (Ar) on the separation factor. The broken line is the theoretical value from the Knudsen diffusion mechanism.
○ Al_2O_3, 20℃, ● Al_2O_3, 400℃,
□ Ru-Al_2O_3, 20 ℃, ■ Ru-Al_2O_3, 400℃
P-P' = $1.4X10^4$ Pa, $p(H_2)/p(N_2)=1.0$

Among conventional inorganic membranes, dense Pd membranes are known to be permeable only to hydrogen.[6] However, their low permeabilities and ease of hydrogen embrittlement will not lead to the separation applications. On the contrary, the metal dispersed microporous membrane in this study attained high selectivity and permeation rate for H2 simultaneously, being one of possible designs of inorganic membranes for gas separation processes.

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