다단계 기공구조개선을 통한 알루미나 막의 수소분리 특성

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Preparation of Alumina Membrane for Hydrogen Separation by Multistep Pore Modification

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1. INTRODUCTION

In last decades, gas separation by membrane was developed from experimental scales to plant scales that can be used in practical use, because membrane separation has many advantages such as energy savings and easy operational conditions. In the membrane separation processes, the permeability and selectivity are the very important factors. Polymer membranes show the performance improvement limit as a limiting line for selectivity - permeability plot[1]

Although inorganic membranes are still in developing stage, it has a lot of advantages and large potential, therefore much researches are carried on. Compared to polymeric membranes, inorganic membranes are thermally and structurally stable, can be easily cleaned and has high resistance to chemical reagents. But they have disadvantages such as brittleness and high cost. Porous materials, such as alumina membranes and Vycor glasses, are practically used separation processes because they have high permeability. Alumina membranes that have microporous structure, show relatively high gas permeability and thermal resistance in gas separation processes

In the mechanism of gas separation by porous alumina membrane, Knudsen diffusion is dominant, but when the molecular weight difference is small the selectivity is not much high. So many researches is continued to improve the selectivity by surface modification.[2,3,4] Lee. S. J. *et al.*[4] impregnated Pd particles into γ-alumina membrane by direct mixing of alumina sol and palladium precursor. Lee. S. Y. *et al.*[5] made Pd intermediate layer in alumina membrane by Soaking and Vapor Deposition. These membranes showed high hydrogen selectivity in the low and moderate pressure difference. By these pore densification and modification, surface diffusion becomes dominant and overcomes Knudsen Limit.

2. EXPERIMENTAL

To prepare membrane which is effectively operated at high pressure and shows high selectivity, we adopt the *in-situ* hydrolysis of TEOS and H_2O. The Experiments are composed of three steps.

First, we applied Sol-Gel technique onto the α-Al_2O_3 support(Noritake Co. Limited) which has an asymmetric structure and pore size of 80 nm. In this technique, γ-Al_2O_3 sol was

prepared by Yoldas's optimum condition, and γ-Al_2O_3 sol impregnated with Pd. After sonication, γ-Al_2O_3 sol is coated onto the α-Al_2O_3 support using dip-coating method followed by calcination at 500 °C. The dip-coating and calcination procedure was repeated 7-8 times.

After applying the Sol-Gel procedure several times, we employed *in-situ* hydrolysis of TEOS and H_2O in the cylindrical pores of the membrane. In this method, TEOS vapor is driven to the outside of the membrane with water vapor driven to the inside of the membrane. N_2 was used here as a carrier gas. The two vapors react in the pores of the support and, as a result, membrane pores are plugged with SiO_2. [Fig 1]
This method is very effective in narrowing the pores of the membrane and the membrane prepared by this method is very effective especially when the transmembrane pressure between the outer and inner side of the tube-type membrane is relatively high.

Finally, to enhance the hydrogen selectivity of the membrane, we applied, what we call, Soaking and Vapor Deposition(SVD) method onto the membrane. In SVD, the metal source, palladium(II) acetate, was decomposed in pores in nitrogen atmosphere. During SVD, temperature is gradually increased from room temperature to 180 °C under reduced pressure. By this method, we can form an intermediate layer of palladium in the vicinity of the interface between the two layers of the support.

The gas permeate rate was measured by the mass flow controller (UFC-1500A, Unit Co.) in the permeate side and the transmembrane pressure ΔP by the differential pressure gauge (7354 Series. Cole Parmer Inc.)

3. Result and Discussion

In this present work, the permeability F of a membrane is defined as

$$F = \frac{Q}{2\pi r L(\Delta P)}$$

where Q is the volumetric flow rate at the standard state, and r and L denote the outer radius and the length of the support respectively. We measured the permeabilities of hydrogen and nitrogen as functions of temperature T and transmembrane pressure ΔP. And the ideal hydrogen selectivity defined as the ratio of hydrogen to nitrogen permeability. The permeability and selectivity change is shown in Fig 2. and Fig 3.

As shown in Fig 2. and Fig 3. pore modification by Sol-Gel method is valid only in the ranges of low transmembrane pressure difference. ($\Delta P = 1 \sim 5$ psi) After Sol-Gel method had been carried out 8 times, the *in-situ* Hydrolysis of TEOS and H_2O was done twice. By this step, it seems that the pore modification is performed at the separation layer of the alumina support microstructure, therefore alumina membrane can be used in a very high transmembrane pressure difference.($\Delta P = 35$ psi) But, as SiO_2 is less than Pd in hydrogen adsorption, the hydrogen selectivity is low relative to the Sol-Gel driven membrane. It can be explained that the gas permeate mechanism of Sol-Gel driven membrane is surface diffusion dominant, but that of hydrolysis adopted membrane is Knudsen diffusion dominant. From the permeability measurement, we can confirm that three consecutive

experiments plugged the membrane pore effectively. Especially, hydrolysis of TEOS and H_2O gave strong plugged pore structure to membrane layer.
Therefore, after effective pore densification by the *in-situ* Hydrolysis of TEOS and H_2O, to improve high hydrogen selectivity, Soaking and Vapor Deposition(SVD) method was carried out. As the size of palladium acetate(II) particles are nanometer scale, it can be easily deposited onto the pore structure of the hydrolysis modified membrane. After 7 times SVD method was carried, hydrogen selectivity was enhanced to 7, and permeability of each gas was much decreased. This reflects that by the SVD method, hydrogen selective effect of Pd was become dominant. The membrane prepared by these multistep pore modification methods shows a good hydrogen selectivity at high temperature and at high transmembrane pressure(ΔP), and also shows relatively high permeability compared to polymeric membrane.

4. CONCLUSION

1. The membrane prepared by the three consecutive pore densification steps (Sol-Gel technique, *in-situ* hydrolysis of TEOS and H_2O, and Soaking and Vapor Deposition(SVD)) shows a good hydrogen selectivity at high temperature and at high transmembrane pressure(ΔP). The separation factor of hydrogen and nitrogen is above the Knudsen limit(3.74) up to $\Delta P = 35$ psi.

.2. The *in-situ* hydrolysis of TEOS and H_2O gave the effective pore densificatiion, but because of the silica character that is low hydrogen selectivity, the membranes driven by this method exhibit low hydrogen selectivity. .

3. Additional modification of membrane surface by SVD contributed to enhance surface diffusion at high transmembrane pressure(ΔP) as the particle size of palladium acetate(II) is very small and easily deposited onto the asymmetric porous membrane structure, which is formed palladium intermediate layer.

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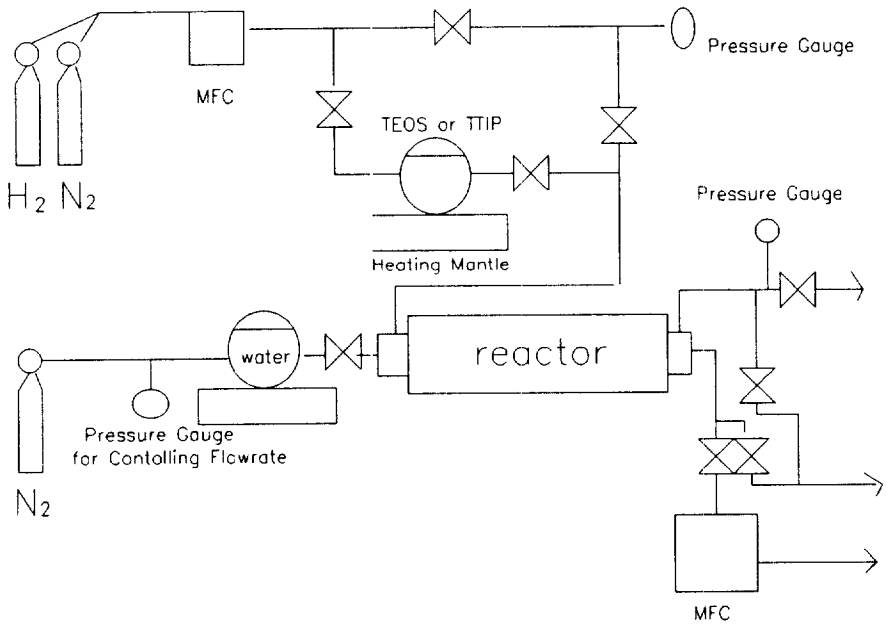

Fig. 1. Experimental apparatus of the *in-situ* Hydrolysis of TEOS and H_2O

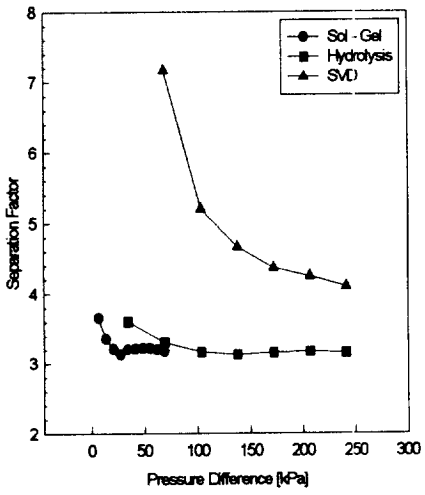

Fig 2. The permeability change by three consecutive pore densification steps. (T = 400°C)

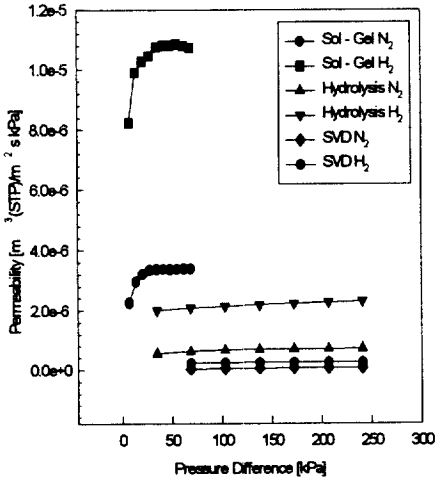

Fig 3. The separation factor change by three consecutive pore densification steps. (T = 400°C)