EFFECTIVE HYDROGEN SEPARATION THROUGH SILICA BASED MEMBRANES

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ABSTRACT.

Solar energy is one of the promising energy sources. However, optimum places for solar energy is limited. Therefore, production of energy carries such as hydrogen or ammonia should be developed. The effective hydrogen separation technique is important for efficient hydrogen production. Silica membranes have been developed for the hydrogen permselective membranes. Alkoxysilane such as tetramethoxy-silane (TMOS) have been used for the silica sources of the membranes. We have been developing silica based membranes by introducing organic functional groups to silica source to improve the hydrogen permeances. The membrane preparation method was a counter diffusion chemical vapor deposition (CVD) method. The organic functional groups such as alkyl group or phenyl groups have been investigated to control the pore sizes of the silica membranes. The hexyltrimethoxysilane (HTMOS) derived membrane showed the high hydrogen permeance of 2.1 x 10^{-6} mol m^{-2} s^{-1} Pa^{-1}. However, the pore sizes cannot be predicted before the membrane preparation. In this study, the pore sizes of the silica based membranes were evaluated both from the silica sources and the single gas permeances. The pore size evaluation from the silica sources is based on the calculation of the sizes of the organic functional groups in the silica precursors. The pore size evaluations from the single gas permeances were conducted by using the normalized Knudsen-based permeation (NKP) method. These pore sizes were compared by changing the silica sources of the membranes. The pore sizes evaluated by the NKP method showed the positive correlation with those by the silica sources indicating that the silica sources are the one of the key factors to determine the pore sizes of the deposited membranes.

1. INTRODUCTION

Recently, hydrogen is expected as a clean energy and an energy carrier. Membrane reactors are known as effective devices to enhance chemical equilibriums by extracting specific reactants from a reaction field. The membrane should have thermal stability, high H_2 permeance and high H_2 selectivity. Many researchers for hydrogen permselective ceramic membranes for efficient hydrogen separation. Silica hybrid membrane were developed as the H_2 permeselective membranes by using a sol-gel method (M. de Vos, 1999, Nair, 2000 and Kanezashi, 2006) or a CVD method (e.g. Gavalas and Okubo, 1989). In this paper, we discussed about the silica membranes prepared by using a CVD method. The geometries of the CVD methods are important. There are two methods classified by the geometries of the provide direction of the reactants. All the reactants are provided from the one side of a porous substrate for the one-side CVD method, and two reactants are provided at the opposite side of the porous substrates for the counter diffusion CVD method. The H_2/N_2 permeance ratio of 880 through the membrane prepared by the one-side CVD method (Nam, 1993). Nakao et al. (2000) reported that the silica membrane was prepared by the counter diffusion CVD of TEOS/ O_3 at 150－200°C. This membrane was obtained the He permeance of 3×10^{-8} mol m^{-2} s^{-1} Pa^{-1} with the He/N_2 permeance ratio of 950. Gapalakrishman et al. (2007) reported that the H_2 permeance of 6.4×10^{-7} mol m^{-2} s^{-1} Pa^{-1} with a H_2/N_2 permeance ratio of 2343 at 600°C through the membrane prepared by the counter diffusion CVD method of the $TMOS/O_2$ systems. They also obtained the three membranes module by using the counter diffusion CVD method (Gopalakrishnan, 2006). Such a complex shape modules can be prepared by the CVD method that indicates a practical application of a membrane reactor. Nomura et al. (2007) used propyltrimethoxysilane (PrTMOS) as a silica precursor for the counter diffusion CVD method. The H_2 permeance of 1.3×10^{-7} mol m^{-2} s^{-1} Pa^{-1} was obtained with a H_2/N_2 permeance ratio of 30. The pore size of the silica hybrid

membranes can be controlled by changing the deposition conditions due to the part of decomposition of the propyl groups in the silica precursor. However, the pore size evaluation has not done. Hence, the deposited silica membranes were evaluated by the silica precursors and by the single gas permeances. The pore sizes were predicted by the model pore size considering the size of the organic functional groups in the silica precursors. The pore sizes were also evaluated by the single gas permeances based on the NKP method.

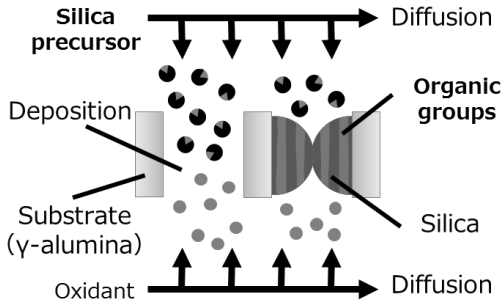

Fig. 1 Schematic diagram of a counter CVD method.

2. EXPERIMENT

2.1 Membrane preparation

Porous γ-alumina substrates (φ3 mm, effective length 40 mm, pore size 4 nm) were provided by NOK Co. TMOS, ethyltrimethoxysilane (ETMOS), propyltrimethoxysilane (PrTMOS), HTMOS, phenyltrimethoxysilane (PhTMOS) or diphenyldimethoxysilane (DPhDMOS) were used as silica sources (Shin-Etsu Chem. Co.). Silica precursor were provided through N_2 bubbler kept at 45-125°C and the vapor was introduced to the outside of the γ-alumina substrate. O_3 was produced by using an O_3 generator (SOW-5000R or ZOS-YB-20G, SYOKEN Co.) O_3 of 0.2 L min^{-1} was introduced into the inside of the substrate.

2.2 Single gas permeation test

Single gas permeances of H_2 (0.29 nm), N_2 (0.36 nm) and SF_6 (0.55 nm) were performed at the deposited temperatures of the membranes below the 270 °C deposition. If the membranes were deposited over 270 °C, permeances were measured at 270 °C. The permeance was measured through a pressure-change method. Each three gases were provided to the outside of the membrane. The inner side of the membrane was evacuated, and the rate of the pressure change on the inside of the membrane was measured by turning off the valve between the module and the vacuum pump.

2.3 Pore size evaluation

The pore sizes of silica hybrid membranes were evaluated by two type methods. One is the model pore size considering the size of the organic functional groups in the silica precursors. The other is the normalized Knudsen-based permeation (NKP) method evaluated by the single gas permeances based on. These pore sizes showed the similar trend indicating that pore size prediction can be available from the silica precursors.

3. RESULTS & DISCUSSIONS

Fig. 2 shows the model pore size image. In this case, we assumed silica parts are circles of 2 nm in diameter and pore sizes are circles at the gaps of the silica parts. Size of the organic functional groups are calculated by the MM2 potential (Chem Draw Ultra). According to this results, the TMOS and PrTMOS derived membrane has the pore size of 0.29, 0.40 nm, respectively. It indicates the pore size of silica hybrid membranes are larger by introducing the organic functional group to silica sources.

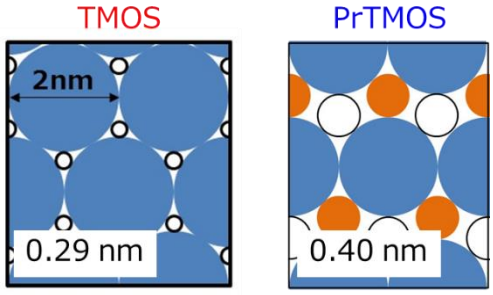

Fig. 2 Image of the model pore size.
(blue: silica part, orange: organic functional group)

Next, the pore size was evaluated by the NKP method using the three kinds of inorganic gas permeance at 270°C. Fig. 3 shows NKP plots of the TMOS and PrTMOS derived membranes. The pore sizes of the PrTMOS derived membrane are also bigger than the TMOS derived membrane. Fig. 4 shows the pore sizes of each silica hybrid membrane by the model pore size and the NKP method. The pore size evaluated by the NKP were tended to increase by larger the model pore size. Therefore, the organic functional group sizes in the silica precursors were related to the pore sizes. However, the value of the model pore size is different from the NKP pore size. Especially, the HTMOS derived membrane and the DPhDMOS derived membrane were calculated the model pore size of 0.8, 1.49 nm in diameter respectively. HTMOS has thermal stability (Matsuyama, 2014). The 270°C deposition of the HTMOS derived membrane wasn't optimized the CVD condition. Therefore, the model pore size do need to improve but this method can be calculated the pore size easily. Fig. 5 shows the H2 permeance for the silica hybrid membranes deposited 270°C. H_2 permeances increased with increasing the pore sizes evaluated by the NKP.

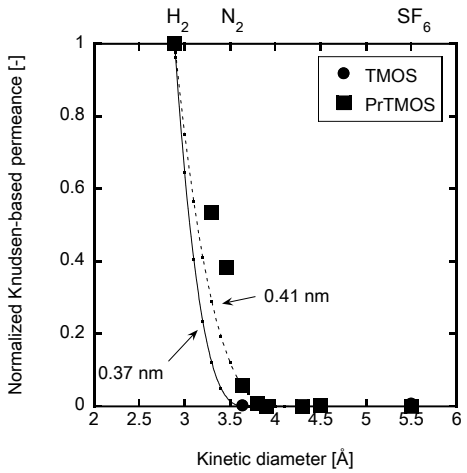

Fig. 3 NKP plots of the TMOS and PrTMOS derived membrane. (Permeation temp. 270°C)

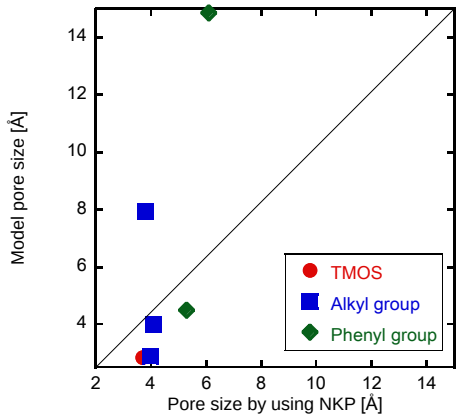

Fig. 4 Pore sizes by the model pore size and the NKP method. (Permeation temp. 270°C)

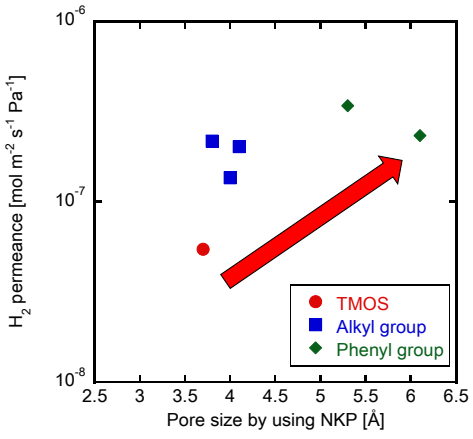

Fig. 5 H_2 permeance for the 270°C deposition silica hybrid membranes. (Permeation temp. 270°C)

CONCLUSION

The model pore size considered the size of the organic functional group in the silica precursors and the pore size evaluated by the NKP are related to positive correlation. Thus, the pore size is larger by increasing the size of the organic functional groups. Moreover, H_2 permeances increase as the pore size is bigger. From the above, H_2 permeation performance through silica hybrid membranes is expected to predict by the organic functional group size of silica sources.

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