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Development of an All-ceramic Module with Silica Membrane Tubes for High Temperature Hydrogen Separation

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Abstract: Heat resistant hydrogen selective membranes are desired for use as membrane reactors in low-temperature hydrogen production via the steam reforming of hydrocarbons, which are usually operated over 1000 K. In addition, developing a multi-tubular type of membrane unit that can process more reactants is becoming more and more important in order to realize the practical use of membrane reactors.

In this study, an all-ceramic module consisting of 6 silica membrane tubes with a comparatively large membrane area of around 0.04 m^2 was fabricated by a counter-diffusion chemical vapor deposition technique. As a result, the H_2/N_2 ideal separation factor and the H_2 permeance of the module were 1300 and $1.9 \times 10^{-7}\,mol \cdot m^{-2}s^{-1}Pa^{-1}$ at 873 K, respectively. In a 1000-hour thermal stability test for the silica membrane module, it was found that the H_2 permeance initially decreased by about 30% and then became steady under $\Delta P = 0.95$ MPa at 773 K.

Keywords: Ceramic, CVD, hydrogen production, module, silica membrane

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INTRODUCTION

Inorganic membranes will play a key role in future processes of hydrogen production and separation at high temperatures. Most of the presently produced hydrogen via steam-reforming technology is being operated at as high as 1000–1100 K to obtain the maximum possible conversion under equilibrium limitations. If the reaction temperature could be reduced, a considerable decrease in the heat consumption during the reactor operation would be expected. As one of the ways to lower the temperature, applications of hydrogen-permselective membrane reactors have been proposed to shift the equilibrium point, thus making it possible to decrease the reaction temperature (1–5).

For assembling the membrane reactors operating at higher temperatures, a heat resistant hydrogen selective membrane should be used. One of the most promising materials is ceramics such as alumina, silica, and zirconia. Of these, many silica based membranes for hydrogen separation have been developed by a sol-gel method (4,6–10) or a chemical vapor deposition (CVD) method (11–23). The CVD on a porous substrate can be classified into two methods according to how to supply the precursor (12). For the first one, the precursor is provided on one side of the substrate (20–21), while the other side of the substrate is usually vacuum treated to obtain a pinhole-free membrane (22). For the second method (so-called counter diffusion CVD), two kinds of reactants are separately supplied to the both sides of the support (11–16,23).

The pore size and effective membrane thickness can be controlled by changing the reactants and reaction conditions. For a single tube system, it has been reported that a very high selectivity for He with a higher He permeance can be obtained by the counter diffusion CVD method using tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS) and O_3 as the reactants (11–13). In the TMOS/O_3 system, the He permeance was $3 \times 10^{-8}\,\mathrm{mol \cdot m^{-2} s^{-1} Pa^{-1}}$ with the He/N_2 ideal separation factor of 950 at 313 K (13). As silica membrane is stable at high temperature prepared by the counter diffusion CVD method using TMOS and O_2 has also been reported (14–15), having a H_2/N_2 ideal separation factor of ca. 1000 at 873 K as well as a H_2 permeance of $1.5 \times 10^{-7}\,\mathrm{mol \cdot m^{-2} s^{-1} Pa^{-1}}$ (14).

Recently, a small module with 3 silica membrane tubes (2.7 mm diameter, 50 mm effective length, and a membrane area of $1.4 \times 10^{-3}\,\mathrm{m^2}$) has been prepared by the counterdiffusion CVD method, having a H_2/N_2 ideal separation factor of 2900 and a H_2 permeance of $4.4 \times 10^{-8}\,\mathrm{mol \cdot m^{-2} s^{-1} Pa^{-1}}$ at 873 K (16). It has been shown that the hydrogen selectivities of successfully prepared silica membranes are high enough to improve the conversion of methane steam reforming using the silica membrane reactor (23,24). To advance to the next stage, that is, for practical use, further improvement in the production rate should be made. For that, as a matter of course, the hydrogen permeance must be improved while maintaining the selectivity. A more effective and important scheme would be to develop and establish the formation process of a module with a large membrane area along with a high-temperature stability.

In this study, therefore, a large-scale membrane module including the arrangement of the membrane tubes was designed. The CVD conditions of preparing the silica membrane module were then intensively examined to realize the higher hydrogen production per unit module. In addition, the thermal stability of the silica membrane module was tested at high temperature.

EXPERIMENTAL

Preparation of Multi-tube Module

Support

A porous α-alumina tubular support (6 mm diameter, 400 mm long, 40% porosity, and 700 nm pore size) was prepared as previously described in detail (6). The membrane module was prepared by fixing six alumina tubular supports on dense alumina endplates using a glass-based sealant at around 1473 K. The thermal expansion coefficient of the selected glass sealant was nearly same as that of alumina. It was confirmed by leakage tests that a good seal was attained.

A photograph of the membrane module together with the tube arrangement is shown in Fig. 1. The all-ceramic module has a peripheral volume of about 800 ml and weighs about 300 g. The membrane area/peripheral volume ratio of the module was $60\,m^2 \cdot m^{-3}$. Next, an α-alumina intermediate layer having a 60 nm pore diameter and 39% porosity was coated on the above base support using a slurry casting technique. Finally, a γ-alumina layer with a thickness of about 2 μm and an average pore diameter of 4 nm was formed by dip coating using a boehmite sol. The hydrogen permeance of the module type of support coated with γ-alumina was higher than $1 \times 10^{-6}\,mol \cdot m^{-2}s^{-1}Pa^{-1}$ at 873 K.

Membrane Formation

Figure 2 represents the cross-sectional view of the assembled module. A schematic diagram of the counter diffusion CVD apparatus for the

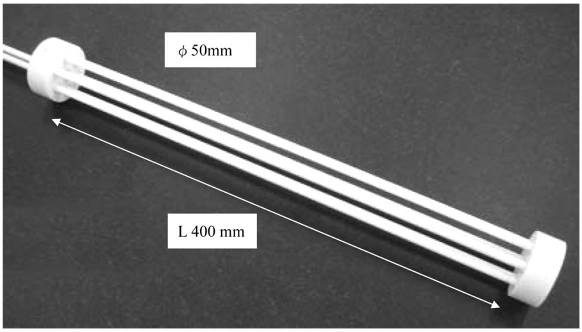

Figure 1. Photograph of the 6-tube support for the membrane module.

module is presented in Fig. 3. TMOS in a vaporizer kept at 318 K was evaporated by controlling the N_2 flow rate as the carrier gas, which could be varied between 200 to 1000 ml · min^{-1} using a mass flow controller in which the TMOS vapor pressure was 9 kPa. The TMOS vapor was supplied to the outside of the support, the temperature of which was maintained at 873 K. Oxygen gas was introduced into the inside of the support by controlling the O_2 flow rate between 100 to 200 ml · min^{-1} using a mass flow controller. The CVD process time was varied between 15 to

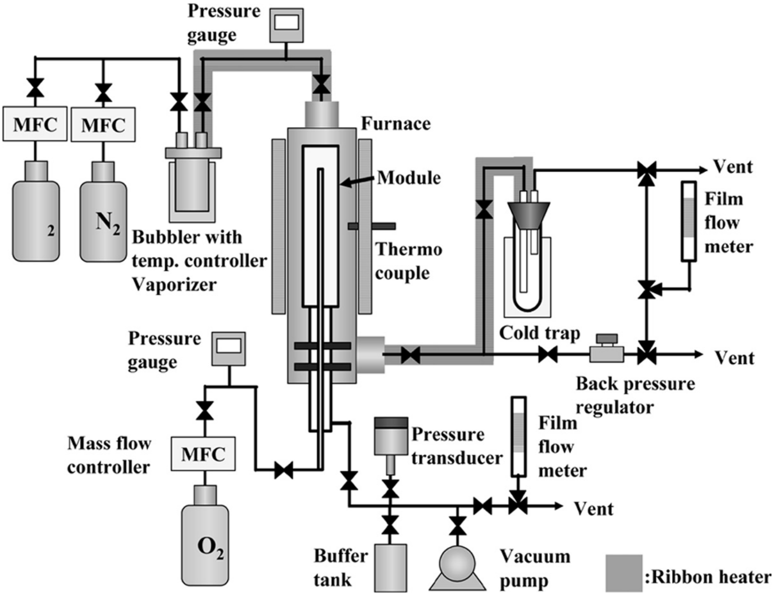

Figure 2. Schematic diagram of the counter diffusion CVD apparatus.

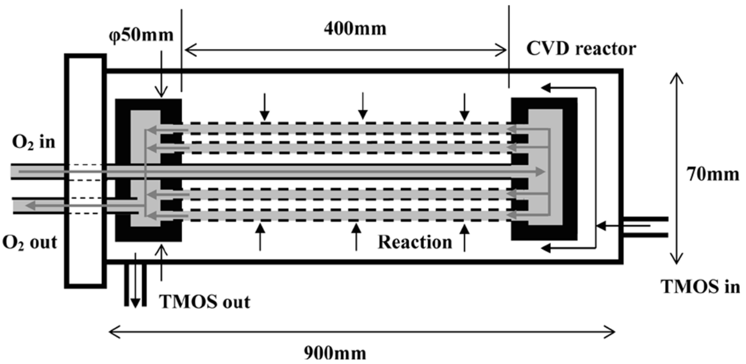

Figure 3. Schematic diagram of the counter-diffusion CVD reactor for preparing the membrane module.

120 minutes. The microstructure of the surface and the cross-section of the silica membranes were observed by a transmission electron microscopy (TEM, TOPCON EM-002B) and a scanning electron microscope (SEM, JEOL JSM-6490LA).

Gas permeation measurements were carried out using the same apparatus for the CVD. The gas permeance was determined on the basis of the pressure difference method, which was suitable when the permeance was less than $1 \times 10^{-8} \mathrm{mol \cdot m^{-2} s^{-1} Pa^{-1}}$. In this method, the outside of the membrane tube was filled with pure gas (H_2 or N_2) at atmospheric pressure while the inside of the membrane was evacuated using a vacuum pump. When the valve between the membrane container and the vacuum pump was closed, the pressure on the inside of the membrane tube started to increase. From the change in the pressure with time, the gas permeance could be calculated using to the following equation.

$$\begin{aligned}\text{Permeance} =& [\{(P_{2f} - P_{2s})/P_0\}(T_0/T_2)V_0/22400]/[A\{(P_1 - P_{2s}) \\ &+ (P_1 - P_{2f})\}/2\Delta t]\end{aligned} \tag{1}$$

P_0: atmospheric pressure [Pa], P_1: initial gas pressure on the shell side [Pa], P_{2s}: initial pressure on the membrane side [Pa], P_{2f}: final pressure [Pa], T_0: atmospheric temperature [K], T_2: cell temperature [K], V_0: total volume on the permeate side [ml], A: membrane area [m^2], Δt: time [s].

Also, it is important to obtain information on the hydrogen selectivity in the gas separation process. To know that, a H_2/N_2 ideal separation factor is defined as follows.

$$H_2/N_2 \text{ ideal separation factor} = (H_2 \text{ Permeance})/(N_2 \text{ Permeance}) \tag{2}$$

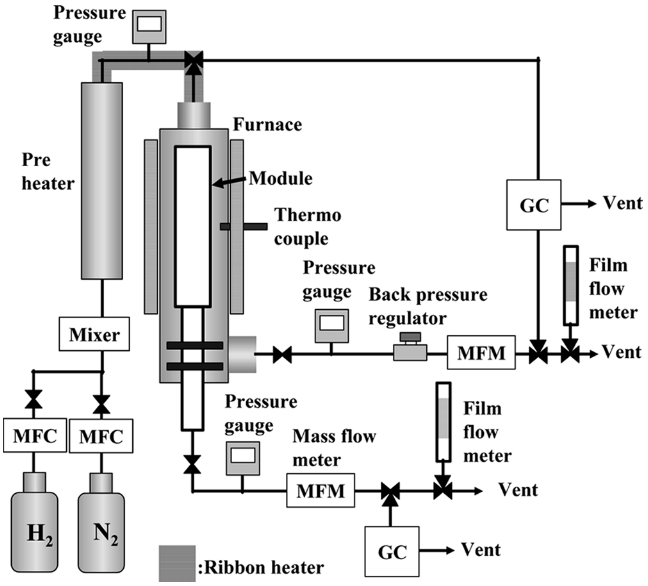

Figure 4. Schematic diagram of the apparatus specially designed for thermal stability test.

Thermal Stability Test

The apparatus for the thermal stability test of the membrane module is shown in Fig. 4. The hydrogen-nitrogen (3:7) mixture was used as the test gas in which hydrogen composition was selected to be 30% based on the product gas in the methane steam reforming. Practically, the test gas was generated by mixing H_2 at 16 $1\,min^{-1}$ and N_2 at 37 $1\,min^{-1}$ using a mass flow controller, in which the gases other than H_2 such as CH_4, CO, CO_2, H_2O were replaced with nitrogen. The pressure of the mixture was maintained at 0.95 MPa using a backpressure regulator and the temperature was maintained at 773 K for 1000 hours. The compositions of the supply gas, the retentate, and the permeate were analyzed by gas chromatography.

RESULTS AND DISCUSSION

Membrane Module Formation

Basic Procedure

The CVD technique developed for a single tube (14,16), in which the TMOS and O_2 are counter-wise diffused and reacted to form a silica layer in the porous support, has been extended to the multi-tube type from the

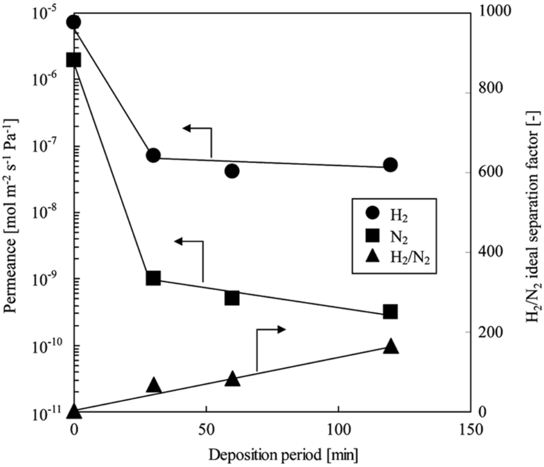

Figure 5. Permeances of the module by changing deposition period at 873 K.

viewpoint of scale-up. The flow rate of the N_2 gas as the carrier gas for generating the TMOS vapor was 1000 ml min^{-1}, which was determined in order to coincide with the linear velocity of the reactant in the single tube (200 ml min^{-1}). On the other hand, the O_2 gas flow rate was initially fixed at 200 ml min^{-1} to clearly determined the influence of the TMOS supply rate. For the CVD process time varied between 30 and 120 minutes, the module performances are shown in Fig. 5. The silica membrane module after a 2-hour deposition showed a H_2/N_2 ideal separation factor of 160 and a H_2 permeance of 5.2×10^{-7} mol $m^{-2}s^{-1}Pa^{-1}$ at 873 K. It can be seen that the H_2 and N_2 permeances decreased rapidly in the first 30 minutes, and then the changes became small. The selectivity, i.e., the H_2/N_2 ideal separation factor, was quite low, so that the following improvement was attempted.

Since the capacity of the bubbler, 500 ml, was not very large, it was possible that the carrier gas was not thoroughly saturated with the TMOS vapor, and this should lead to the incomplete formation of the silica layer. The N_2 flow rate was then decreased from 1000 to 200 ml. min^{-1}. After 2 hours of deposition at 200 ml min^{-1} of N_2, the silica membrane module showed a H_2/N_2 ideal separation factor of 1800 and a H_2 permeance of 2.8×10^{-8} mol $m^{-2}s^{-1}Pa^{-1}$ at 873 K. This selectivity was found to be fairly improved whereas the H_2 permeance decreased.

Improvement in the CVD Process (Change in Oxygen Feed Rate)

Although the selectivity was improved, a decrease in the H_2 permeance was observed. In addition, it was observed that the silica powder was situated at the bottom of the CVD reactor. This is assumed to be due to the gas-phase reaction of TMOS with the bulk flow of oxygen from the membrane tube side to the TMOS side driven by the pressure difference. Such an occurrence was thought to be possibly reduced by decreasing the inner pressure of the membrane tubes, this could be done by decreasing the flow rate of oxygen. When the O_2 flow rate decreased to $100\,\mathrm{ml\ min^{-1}}$, the silica membrane module after a 2 hour-deposition showed a H_2 permeance of $3.2 \times 10^{-8}\,\mathrm{mol\ m^{-2}s^{-1}Pa^{-1}}$ with a H_2/N_2 ideal separation factor as 5800 at 873 K. Unfortunately, the permeance had not significantly increased, but no silica powder was then observed, meaning that the O_2 flow rate was appropriate. The silica particle formation was found over the entire membrane tube as shown in Fig. 6.

According to these results, it can be said that the CVD process should be diffusion controlled, whereby depressing the one-sided bulk flow of TMOS or O_2 completely and therefore making possible to form a reaction interface in the support layer (see Appendix). Let us see the CVD process in the porous layer in more detail but qualitatively. The CVD temperature is usually selected as the CVD reaction rate is too high to be limited by the gas phase diffusion. The initial deposition of silica from TMOS may take place in the porous γ-alumina layer of the support (4 nm in average pore diameter) because the O_2 diffusion is faster than that of the TMOS in the Knudsen regime and the O_2 reaches the γ-alumina pores on the TMOS side. It is considered that the reaction interface formed initially is important to obtain a uniform and firm silica

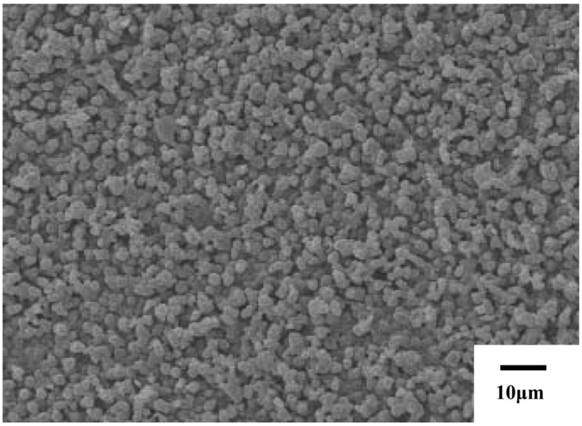

Figure 6. SEM image of the silica particles formed on the module surface after deposition for 2 hours at 873 K.

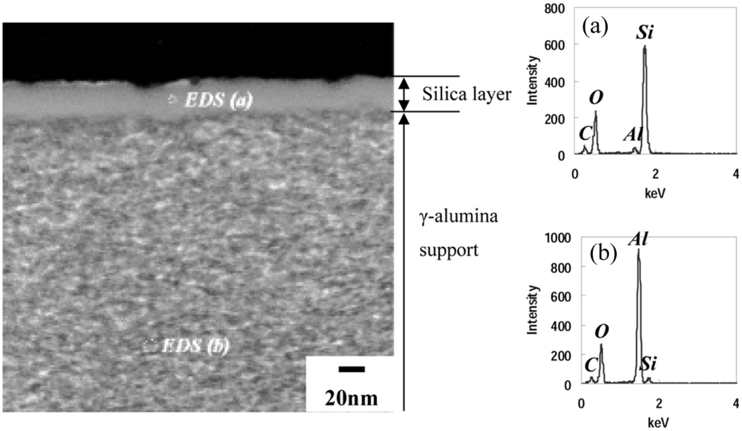

Figure 7. Cross-sectional TEM image and EDS spectra of the silica membrane deposited for 5 min.

deposited layer. After that, the silica layer will grow only in the direction of the TMOS side because the diffusion of TMOS with a large molecular volume in the silica layer is restricted. Finally, the silica formation will terminate automatically when no more O_2 can diffuse through the pores in the silica layer.

From the TEM observation shown in Fig. 7, it was clarified that such a particle layer was formed during the initial stage of the CVD process, that is, within 5 minutes, which might become an impedance to the H_2 permeation.

Change of Timing in Oxygen Supply

To eliminate as much as possible the silica particles on the TMOS side, the timing of the oxygen supply was changed. After TMOS (with 200 ml min^{-1} of N_2) was supplied for 10 minutes, the oxygen was started at 100 ml min^{-1}. The total deposition time was defined as the TMOS supply period. Fig. 8 shows the performance of the silica membrane module, the H_2/N_2 ideal separation factor and the H_2 permeance were 3700 and 7.4×10^{-8} mol m^{-2} s^{-1} Pa^{-1}, respectively, at 873 K. Although being about two times greater than the result described in section "Improvement in the CVD process", the H_2 permeance was found to be still lower than that obtained in the single tube, i.e. 1.5×10^{-7} mol m^{-2} s^{-1} Pa^{-1} with a 1100 H_2/N_2 ideal separation factor (14).

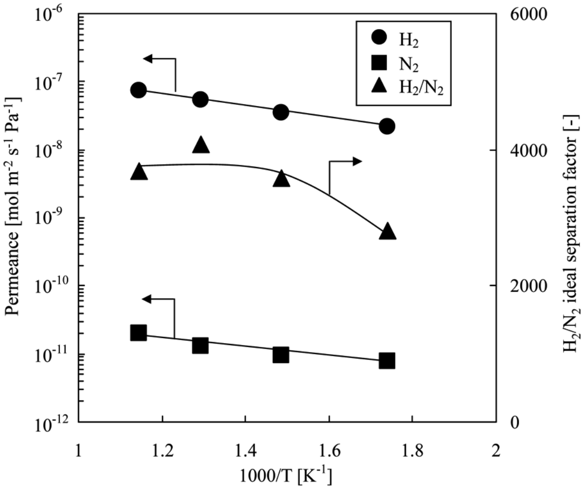

Figure 8. Arrhenius plots of the silica membrane module deposited for 2 hours at 873 K.

Change in the CVD Process Time

The CVD process time was varied between 15 to 120 minutes in order to improve the H_2 permeance. These results are shown in Fig. 9. The deposition period significantly affects the permeance as well as the separation factor. The N_2 permeance considerably drops for 30 minutes, then tends to approach to a plateau. Therefore, 15 minutes was selected as the most appropriate deposition period in this study.

The silica membrane module obtained in 15 minutes. Which had the H_2 permeance of 1.9×10^{-7} mol $m^{-2} s^{-1} Pa^{-1}$ and H_2/N_2 ideal separation factor of 1300 at 873 K, could outperform the single tube (1.5×10^{-7} mol $m^{-2} s^{-1} Pa^{-1}$ and 1100). Figure 10 shows the temperature dependence of the pemeance and separation factor. The activation energy of the H_2 permeation was 14 kJ mol^{-1}.

High-temperature Durability

Figure 11 shows the silica membrane module durability at 773 K. The H_2 permeance initially decreased by about 30% and then became steady during the 1000-hour treatment for $\Delta P = 0.95$ MPa at 773 K. Also, the N_2 permeance was almost unchanged. As a result, the H_2/N_2 separation factor slightly declined during the initial 100 hours.

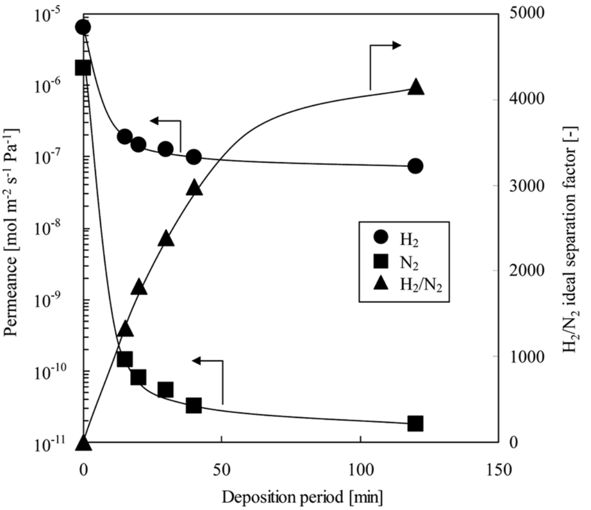

Figure 9. Permeances of the module by changing deposition period at 873 K.

The initial decrease in the H_2 permeance is probably due to the silica densification, which can be identified from the fact that the activation energy for the hydrogen permeation increased from 14 kJ mol^{-1} to 16 kJ mol^{-1}. The stability of the silica layer against steam is considered

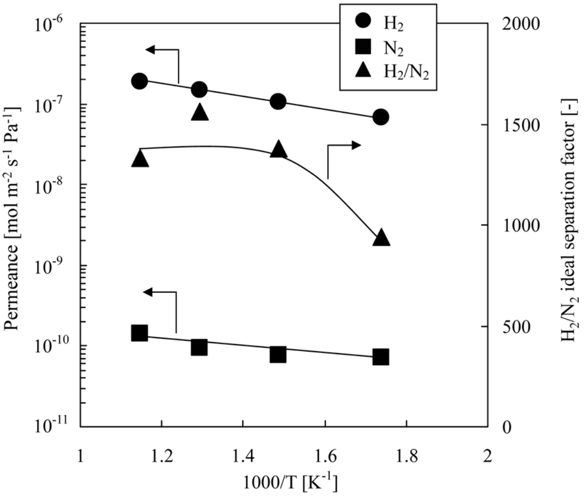

Figure 10. Arrhenius plots of the silica membrane module deposited for 15 minutes at 873 K.

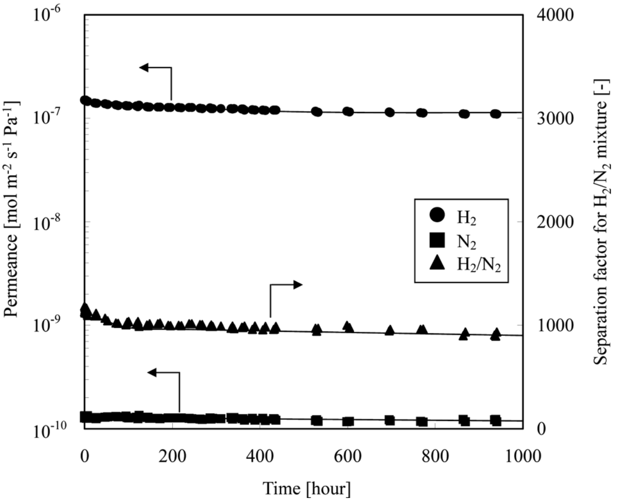

Figure 11. Performance of the silica membrane module durability for 1000 hour at 773 K ($\Delta P = 0.95$ MPa) using a mixture of 30% H_2 and 70% N2.

to be important property when the membrane module will be applied for steam reforming using membrane reactors (10,14–15). It is, therefore, scheduled to clarify the influence of steam in a future work.

CONCLUSIONS

The counterdiffusion CVD technique using tetramethoxy orthosilicate (TMOS) and oxygen was used to prepare an all-ceramic module type of silica membrane supported by porous γ-alumina tubes.

As a result, a thin silica layer could be successfully formed on the support tubes by adjusting the flow conditions for TMOS vapor and oxygen to be diffusion controlled. The membrane module showed a high H_2/N_2 separation factor of about 1300 and a H_2 permeance of 1.9×10^{-7} mol m^{-2} s^{-1} Pa^{-1} at 873 K. The thermal stability test for the module was carried out at 0.95 MPa and 773 K using a mixture of 30% H_2 and 70% N_2. Though the H_2 permeance was initially decreased about 30%, the change thereafter was small during the 1000-hour test.

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APPENDIX

When the reaction is assumed to be infinitely fast in the porous support, the thickness of the reaction zone will be reduced to that of a plane situated at a distance t_i from the TMOS side as illustrated in Fig. A1. In the TMOS zone ($t = 0 \sim t_i$), the concentration of TMOS, C_{TM}, varies between C^b_{TM} and zero while in the zone between t_i and t_s O_2 varies between zero and C^b_{O2}. The location of the reaction interface is dictated by the concentrations C^b_{TM} and C^b_{O2}, but also by the diffusion rates.

The steady-state diffusive flux for TMOS, N_{TM}, in the zone $t = 0$ to $t = t_i$ can be given by

$$N_{TM} = \frac{D_{TM}}{t_{ti}} C^b_{TM} \quad (A-1)$$

where D_{TM} is the diffusion coefficient of TMOS. The flux of O_2, N_{O2}, is obtained in a similar way using the diffusion coefficient of oxygen, D_{O2}, as follows.

$$N_{O_2} = \frac{D_{O_2}}{t_s - t_i} C^b_{O_2} \quad (A-2)$$

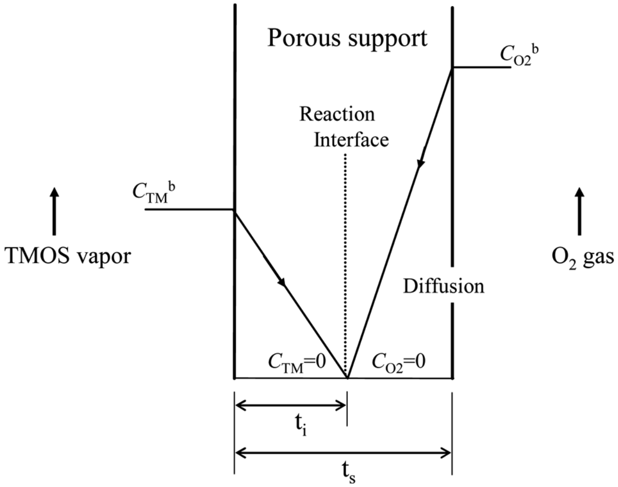
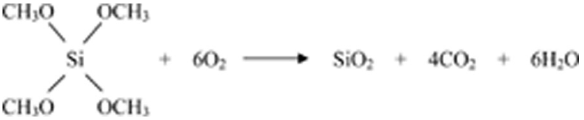


Figure A1. Concentration profile for TMOS and O_2 in the porous support, in which the TMOS is reacting with O_2 at the reaction interface.

where the following stoichiometric relation holds at the reaction interface.

$$\frac{N_{TM}}{a} = \frac{N_{O_2}}{b} \tag{A−3}$$

Here, the complete decomposition of TMOS with O_2 is represented by



so that a = 1 and b = 6 in Eq. (A–4). Putting Eq. (A–2) and (A–3) into Eq. (A–4), one obtains

$$\frac{D_{TM}}{t_i} C_{TM}^{b} = \frac{D_{O_2}}{6(t_s - t_i)} C_{O_2}^{b} \tag{A−4}$$

Eq. (A–4) can be rearranged as

$$\frac{t_i}{t_s} = \frac{1}{1 + \frac{1}{6} \frac{D_{O_2}}{D_{TM}} \frac{C_{O_2}}{C_{TM}}} \tag{A−5}$$

Here, since the porous support with an average diameter of 4 nm is the Knudsen-flow controlled, the diffusion coefficients, D_{O2} and D_{TM}, can be given as

$$D_j = \frac{1}{3} \left(\frac{8RT}{\pi M} \right)^{1/2} d \tag{A−6}$$

Consequently, Eq. (A–5) becomes

$$\frac{t_i}{t_s} = \frac{1}{1 + \frac{1}{6} \left(\frac{M_{TM}}{M_{O_2}} \right)^{1/2} \frac{C_{O_2}}{C_{TM}}} \tag{A−7}$$

From the experimental condition, i.e., $C_{O2} = 1.40 \times 10^{-2}$ mol/l, $C_{TM} = 1.24 \times 10^{-3}$ mol/l, $M_{TM} = 124$ g/mol, and $M_{O2} = 32$ g/mol, t_i/t_s is calculated as 0.21, meaning that the reaction interface locates within the support.

This result suggests that the silica deposition can properly occur in the support.

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