

Article

Gas permeation Property of Silicon Carbide Membrane Synthesized by Counter Diffusion Chemical Vapor Deposition

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Abstract: An amorphous silicon carbide (SiC) membrane with H_2 permeance of $1.2\text{E-}7 \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ and excellent H_2/CO_2 selectivity of 2600 at 673 K was successfully synthesized on a Ni- γ -alumina-coated γ -alumina porous support by counter diffusion chemical vapor deposition (CDCVD) using silacyclobutane (SCB) at 788 K. The dominant permeation mechanism for He and H_2 in the temperature range 323–673 K was activated diffusion. The SiC active layer was formed in Ni- γ - Al_2O_3 intermediate layer. The thermal expansion coefficients mismatch between SiC active layer and Ni- γ - Al_2O_3 -coated γ - Al_2O_3 porous support was eased by the low decomposition temperature of SiC source and membrane structure.

Keywords: hydrogen, amorphous, silicon carbide, alumina, chemical vapor deposition

1. Introduction

Silicon carbide (SiC) membrane with high strength and high chemical stability can be used under high pressure and corrosion atmosphere at elevated temperatures. The synthesis of SiC membranes have been reported in precursor polymer pyrolysis and chemical vapor deposition (CVD)/chemical vapor infiltration (CVI).

In the polymer precursor pyrolysis, many researchers have reported gas permeation behavior. Polycarbosilane (PCS) is converted to amorphous SiC by the heat treatment at $> 1073 \text{ K}$. Therefore, PCS has been used as a pre-ceramic polymer. Shelekhin and co-workers synthesized polymer/inorganic composite membrane on porous Vycor glass by the pyrolysis of PCS at 743 K and reported hydrogen/nitrogen permeance ratio (H_2/N_2) of 14.3 [1]. Kusakabe and co-workers reported polymer/inorganic composite/ γ - $\text{Al}_2\text{O}_3/\alpha$ - Al_2O_3 membrane with H_2 permeance of $4\text{E-}8 \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ and H_2/N_2 of 20 at 773 K by the pyrolysis of PCS [2]. Lee and co-workers reported Si-O-C membrane with H_2 permeance of $2.7\text{E-}9 \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ and H_2/N_2 of 20 at 473 K by pyrolysis of polydimethylsilane (PMS) [3]. These membranes were cured in oxygen atmosphere to form Si-O-Si cross-linking into a network polymer. The oxygen introducing in Si-C network affected to the stability in hydrothermal exposure [4, 5].

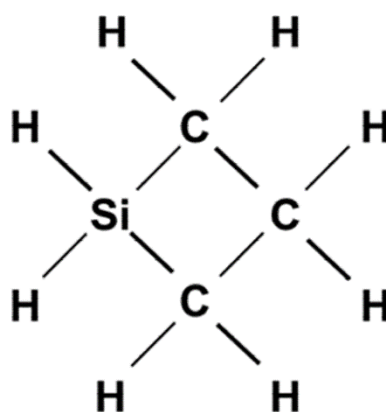
On the other hand, some researchers reported PCS-derived membranes without oxygen curing process. Suda and co-workers reported that SiC membranes synthesized by using p-diethynylbenzene and $\text{Pt}_2(1,3\text{-divinyltetramethyldisiloxane})_3$ as a catalyst possessed H_2 permeance of $3\text{E-}8 \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ and H_2/N_2 of 150 at 373 K [6, 7]. Authors reported that SiC/ γ - $\text{Al}_2\text{O}_3/\alpha$ - Al_2O_3 membrane synthesized by PCS without oxygen curing process possessed H_2 permeance of $1.3\text{E-}7 \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ and H_2/N_2 of 8.5 at 873 K [8]. The thermal expansion coefficient difference between SiC active layer and γ - $\text{Al}_2\text{O}_3/\alpha$ - Al_2O_3 porous support was large. Therefore, the improving of H_2/N_2 was difficult due to the crack formation at thin SiC active layer. Takeyama and co-workers investigated the synthesis of SiC/ γ - $\text{Al}_2\text{O}_3/\alpha$ - Al_2O_3 by exposing to electron beam irradiation in Helium (He) at room temperature and reported H_2 permeance of $3.1\text{E-}7 \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ and H_2/N_2 selectivity of 51 at 523 K [9].

In CVD/CVI process, Takeda and co-workers synthesized that SiC/ γ -Al₂O₃/ α -Al₂O₃ membrane by CVI with alternating gas supply of H₂+SiH₂Cl₂ and H₂+C₂H₂ in the temperature range 1073-1173 K [10]. Their membrane possessed H₂ permeance of 1.4E-8 mol·m⁻²·s⁻¹·Pa⁻¹ and H₂/N₂ of 3.36 at 623 K. Pages and co-workers synthesized SiC membranes inside asymmetric porous alumina tube by plasma-enhanced CVD. Their permeation mechanism was Knudsen diffusion [11]. Sea and co-workers synthesized SiC membrane in the macropores of α -Al₂O₃ support tube by CVD using triisopropylsilane (TPS) in the temperature range 973-1023 K with a forced cross-flow through the porous wall [12]. The permeation mechanism except H₂O was Knudsen diffusion in the temperature range 323-673 K. Ciora and co-workers synthesized microporous SiC/ γ -Al₂O₃/ α -Al₂O₃ by CVD using 1, 3-disilabutane (DSB) and TPS. The TPS-derived membranes were hydrothermally stable [13]. Authors also tried the improving of H₂/N₂ selectivity in PCS-derived SiC/ γ -Al₂O₃/ α -Al₂O₃ membrane by chemical vapor infiltration (CVI) using H₂+SiH₂Cl₂ and H₂+C₂H₂ [14]. However, the improving of H₂ permselectivity was affected by the densification of Si-C network during surface modification at elevated temperatures.

Generally, inorganic membranes except zeolite are composed of an active layer for separating gas, an intermediate layer for suppressing the formation of pinhole defects on the active layer and a porous support. In the preparation of a microporous membrane by CVD and CVI, gas permeation property strongly depended on the mesoporous intermediate layer structure [15]. The hydrothermal stability of γ -Al₂O₃ intermediate layer was also important for membrane durability [16]. Authors improved the hydrothermal stability of γ -Al₂O₃ by 5 mol% Ni doping [17].

α -Al₂O₃ porous support is the most popular for inorganic membranes. However, there is a large thermal expansion coefficient difference between Al₂O₃ (7.2E-6/K) and SiC (3.7E-7/K). Recently, Dabirs and co-workers synthesized asymmetric porous SiC tube [18]. However, the controlling of SiC membrane structure using polystyrene was not easy. Besides, the commercial supply of SiC tubes have been limited.

In this study, we synthesized SiC/Ni-doped γ -Al₂O₃/ α -Al₂O₃ membrane by counter diffusion chemical vapor deposition (CDCVD) using silacyclobutane (SCB) with the decomposition temperature of 448 K, as shown in Fig. 1. The thermal expansion coefficients mismatch can be solved by lowering CVD temperature and minimizing of SiC volume inside γ -Al₂O₃/ α -Al₂O₃ porous support.



Silacyclobutane (SCB)

Figure 1. CVD Source for SiC membranes.

2. Experimental procedure

α -Al₂O₃ porous capillary tube (150 nm in mean pore diameter, 2.9 mm in outer diameter, 2.1 mm in inner diameter, 400 mm in length, NOK Corporation, Tokyo, Japan) was used as the substrate. The effective membrane area with a length of 5 cm was at the center of the substrate. The dip-coating

solution for γ - Al_2O_3 was prepared by reacting 0.05 M of aluminum-tri-sec-butoxide ($\text{Al}(\text{O}-\text{s-Bu})_3$ = ATSB, 97 %, Aldrich, USA) and 0.1 M isopropyl alcohol (Kanto chemical Co., Inc., Japan) with double-distilled water at 363 K. After the addition of ATSB, the mixture was maintained at 363 K for at least 1 h to evaporate off the isopropyl alcohol and the butanol that formed. The mixture was subsequently cooled down to room temperature and peptized with 1 M HNO_3 at a PH of about 3. During the synthesis, the sol was stirred vigorously. The peptized mixture was refluxed at 363 K for 15 h, yielding a very stable 0.05 M boehmite sol with a clear whitish-blue appearance. Doping of this sol was performed by mixing it with an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Ltd., Japan). The amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was 5 mol%.

The dip-coating solution for γ - Al_2O_3 was obtained by diluting boehmite sol (γ - AlOOH) with a 3.5 wt% solution of polyvinyl alcohol (PVA, mean molecular weight = 72,000: Kanto Kagaku Co., Ltd., Tokyo, Japan) at 363 K. The end of the α - Al_2O_3 substrate was plugged. The outer surface of the substrate was dipped in the solution for 10 s, whereas the inner surface of the capillary was evacuated to obtain a pinhole free membrane using a vacuum pump. After dipping, the membrane was dried for 2 h in air. It was then calcined at 1123 K for 1 h at a heating/cooling rate of 1 K/min. This dipping–drying–firing sequence was repeated twice [17].

The pore size distribution of the $\text{Ni-}\gamma$ - Al_2O_3 intermediate layer on the α - Al_2O_3 substrate was analyzed using a nanoporometer (TNF-3WH-110ME: Seika Sangyo Co., Tokyo, Japan). Nitrogen was used as a noncondensable gas, and the liquid used as condensable vapor was water. Specimens were set in the apparatus after annealing at 393 K for 1 h.

The silicon carbide coating of a $\text{Ni-}\gamma$ - Al_2O_3 -coated α - Al_2O_3 substrate was performed by CDCVD, as shown in Fig. 2. The substrate was coaxially fixed in a stainless tube and placed in an electric tubular furnace. The temperature of SCB was controlled to 298 K with a mantle heater. SCB was supplied through the outer surface of the substrate by controlling the Ar flow rate at 7.2 ml/min. The source gas was diluted with Ar at the flow rate of 64.3 ml/min. Hydrogen (H_2) was introduced into the inner surface of the substrate at a flow rate of 275 ml/min. Pattern of source gas supply, reaction gas supply and vacuum inside tube are shown in Fig. 3. Furnace temperature and deposition time were 788 K and 9 min, respectively.

SEM specimens were prepared using a focused ion beam (FIB) system (Model FB-2100, Hitachi Co., Tokyo, Japan) at acceleration voltages of 40 to 10 kV. The specimen surface was coated with Platinum to suppress charge up. The thickness of platinum layer was 60 nm. Tungsten was deposited on the surface of the sampling area in the FIB system to protect the top layer of the membrane from gallium ion sputtering during FIB milling. The membrane was dug out by FIB milling and small specimens ($3 \times 25 \times 15 \mu\text{m}$) were prepared. The specimens were lifted out using a tungsten needle and transferred to TEM grids. The specimens were then fixed onto the TEM grids by FIB-assisted deposition and thinned by FIB milling.

The top surfaces and cross-sectional structure of $\text{Ni-}\gamma$ - Al_2O_3 -coated α - Al_2O_3 capillaries were observed by scanning electron microscopy (SEM; Model S-8000, Hitachi, Tokyo, Japan). The composition of the top layer was analyzed by energy-dispersive X-ray spectroscopy (EDS) with SEM.

X-ray photoelectron spectroscopy (XPS) analysis was performed using (PHI 1800, ULVAC PHI, Inc., Chigasaki, Japan) to evaluate SiC membrane structure. The X-ray source was an Al $\text{K}\alpha$ (1253.6 eV) anode kept 350 W. Analyzer pass energy of 23.5 eV was used. The Shirley model was used for establishing the background.

Single gas permeance (P) was evaluated by a constant-volume manometric method [19]. Permeance data can be measured from $1\text{E-}5$ to $1\text{E-}12 \text{ mol} \cdot \text{m}^2 \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ by changing experimental conditions. The outside of the membrane was filled with pure gas under atmospheric pressure conditions. The inside of the membrane was evacuated using a vacuum pump. After terminating evacuation, the rate of pressure increase at the inside of the membrane was measured five times to calculate permeance. The average of the third, fourth and fifth measurements was accepted as permeance data. The gas permeance at each temperature was evaluated in the order of He , H_2 , CO_2 , Ar , and N_2 . Permselectivity was defined as the permeance ratio of the two gases. For example, the H_2/N_2 permselectivity is given by the ratio $P_{\text{H}_2}/P_{\text{N}_2}$.

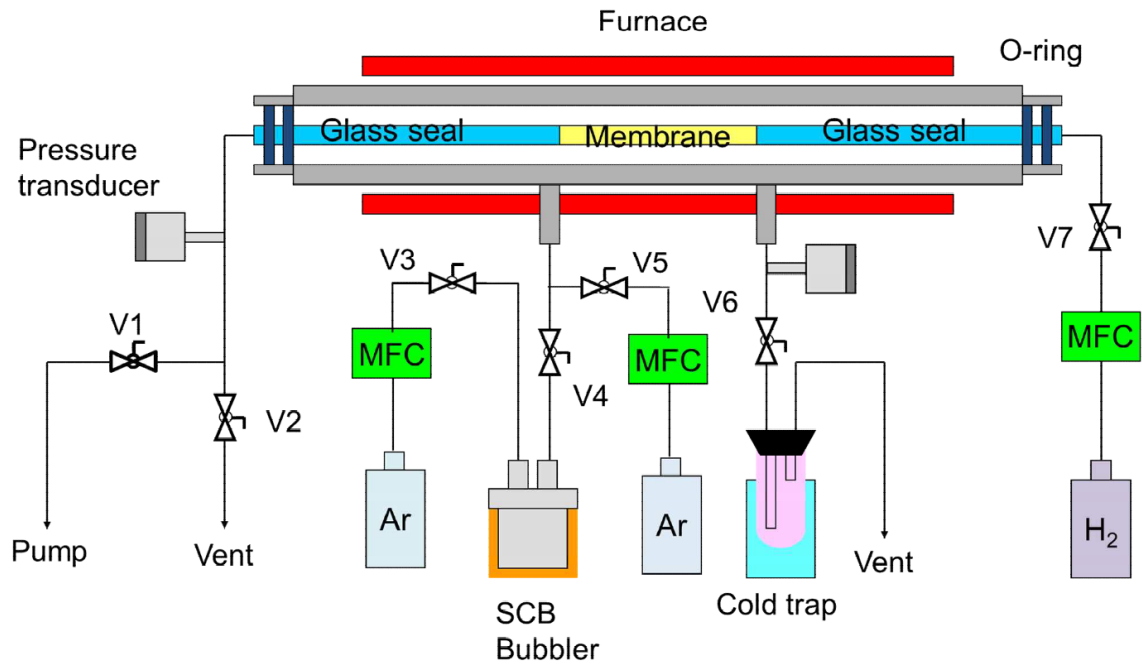


Figure 2. Schematic figure of counter diffusion chemical vapor deposition apparatus.

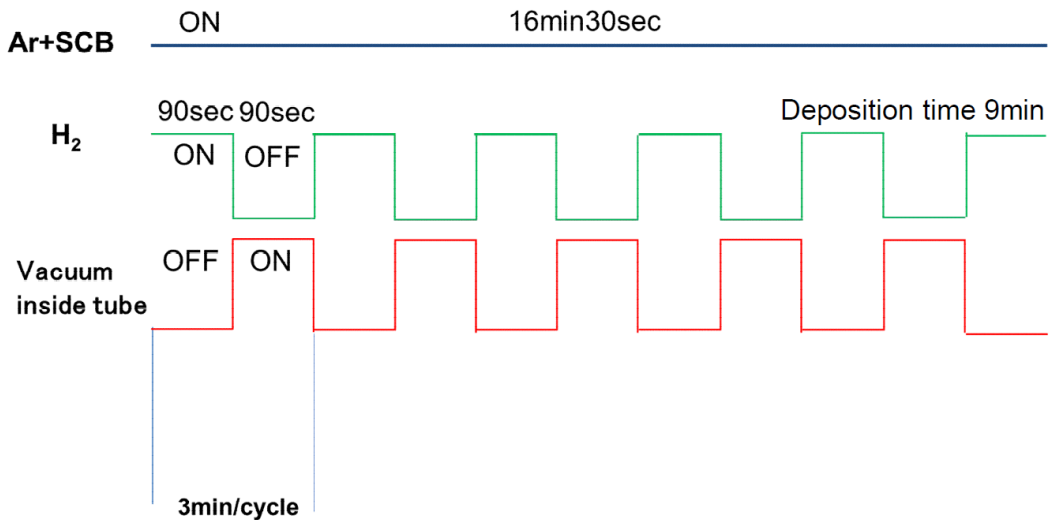


Figure 3. Pattern of source gas supply, reaction gas supply and vacuum inside tube.

3. Results and discussion

3.1. Microstructure of SiC membrane

The pore size distribution of the Ni- γ -Al₂O₃ intermediate layer is shown in Fig. 4. The pore sizes of the sample calcined at 1123 K for 1 h were almost distributed between 4 and 8 nm. The average pore size was 5.9 nm.

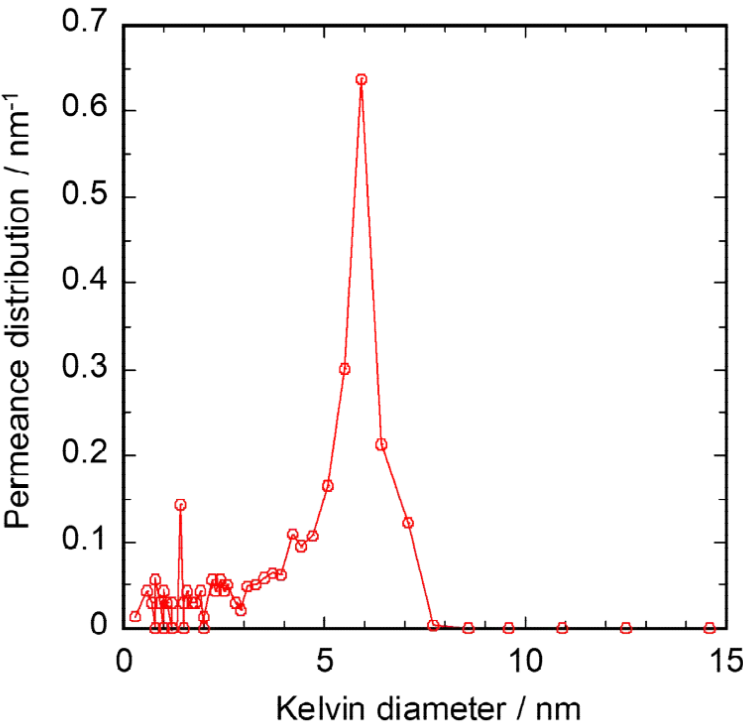


Figure 4. Pore size distribution of Ni- γ -Al₂O₃ intermediate layer.

The cross-sectional SEM image and EDS line analysis for SiC/Ni- γ -Al₂O₃/ α -Al₂O₃ membrane are shown in Fig. 5. α -Al₂O₃ was uniformly coated with Ni- γ -Al₂O₃ layer and the thickness of the Ni- γ -Al₂O₃ layer was approximately 2.3 μ m. The contrast in Ni- γ -Al₂O₃ layer was originated from the heat history. EDS analysis showed that the entire top layer was composed of silicon, carbon, aluminum and oxygen. The content of C was not constant in Ni- γ -Al₂O₃ intermediate layer. Therefore, the effective membrane thickness was estimated to be less than the thickness of Ni- γ -Al₂O₃ surface layer.

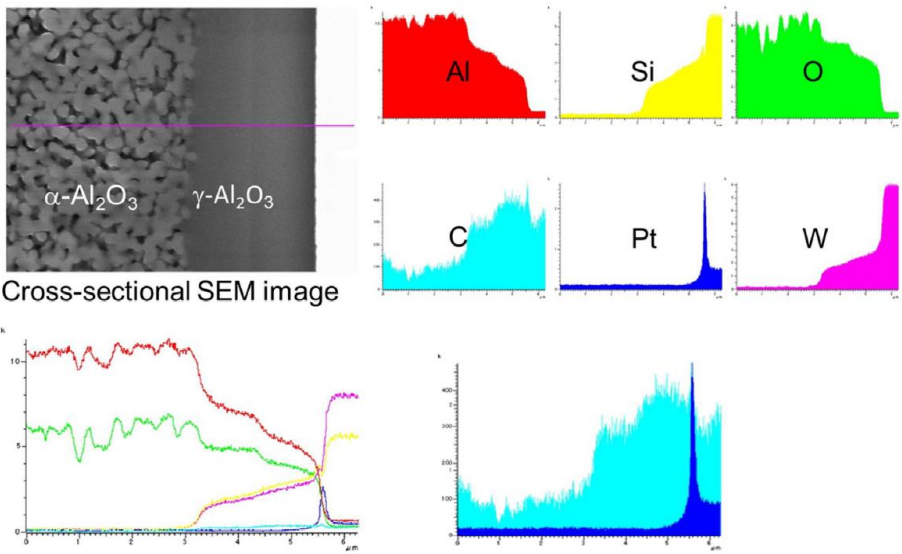


Figure 5. EDS line analysis for SiC/Ni- γ -Al₂O₃/ α -Al₂O₃ membrane.

Accordingly, the synthesized sample was considered to be composed of two layers, namely, the α -Al₂O₃ porous support and the Ni- γ -Al₂O₃ intermediate layer gradually modified with SiC.

Result of XPS analysis for SiC/Ni- γ -Al₂O₃/ α -Al₂O₃ membrane is shown in Fig. 6. The peak profile of SiC membrane was broad in comparison with that of α -SiC polycrystalline powder. The binding energy of C_{1s} showed that this active layer was composed of Si-C and C-C bonding. On the other hand, the binding energy of Si_{2p} showed that the active layer was composed of Si-Si, Si-C, SiO_x and SiOC bonding. The oxygen contamination was thought to come from source gas or minor leaks. The C/Si atomic ratio for the active layer was 1.05. Therefore, a part of C-C bonding in SCB was thought to be decomposed with H₂ during CDCVD.

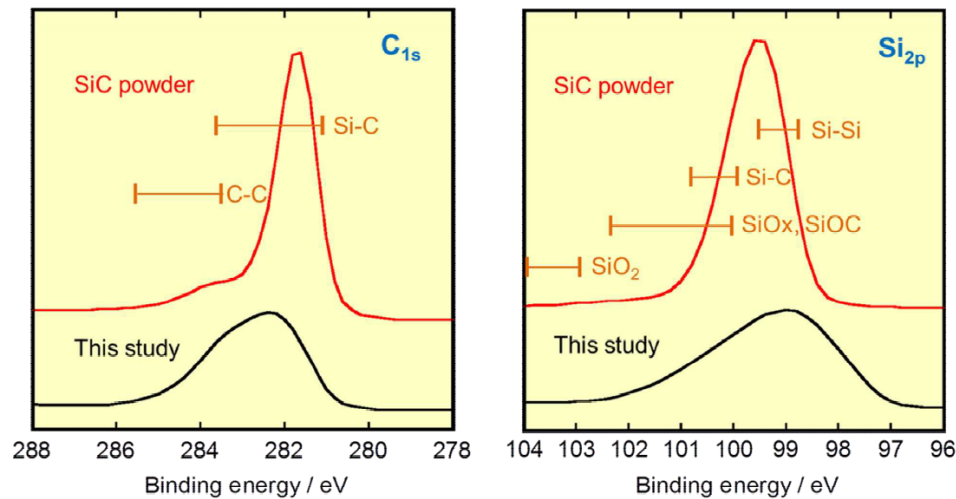


Fig. 6 Result of XPS analysis for SiC/Ni-g-Al₂O₃/ α -Al₂O₃ membrane.

3.3. Gas permeation property

The gas permeation behavior of the γ -Al₂O₃ intermediate layer on the α -Al₂O₃ porous capillaries was confirmed that the transport of the gases is induced mainly by Knudsen diffusion. Therefore, the pores on α -Al₂O₃ porous support were controlled finely and homogeneously.

Reaction gas flow rate dependence on single gas permeance of SiC membranes at 673 K is shown in Fig. 7. The H₂ flow rate had a large effect to the permeance for CO₂, Ar and N₂. In CDCVD method, the balance of gas pressure difference between source gas and reaction gas is important to plug the pores in intermediate layer. In the membrane synthesized at H₂ flow rate of 300 sccm, membrane defect was thought to be formed by the lack of source gas in intermediate layer.

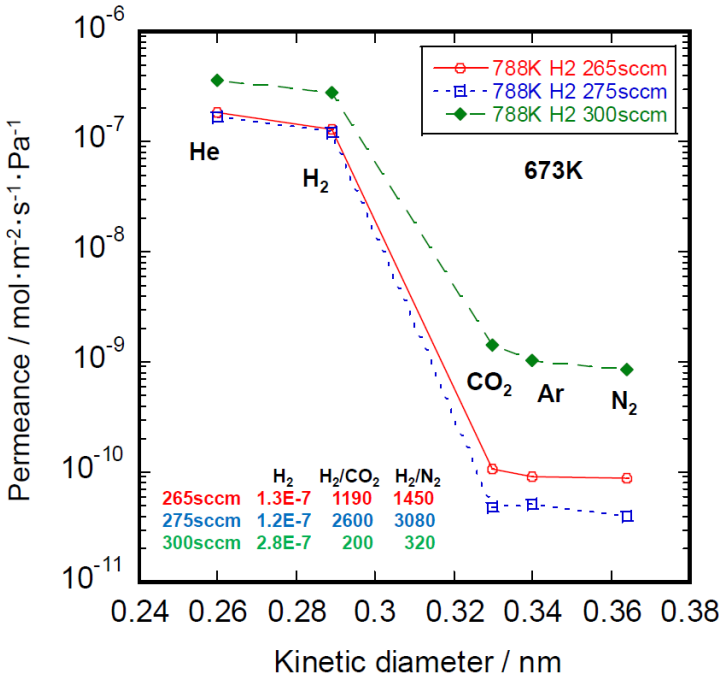


Fig. 7 Reaction gas flow rate dependence on single gas permeance of SiC membranes.

Deposition time dependence on single gas permeance of SiC membranes at 673 K is shown in Fig. 8. The increasing of deposition time brought about the membrane thickness increasing and the plugging of pores. At the deposition time for 9 min, the permeance for CO₂, Ar and N₂ was almost same. Hydrogen permeance and H₂/N₂ permselectivity was well-balanced at the deposition time for 9 min.

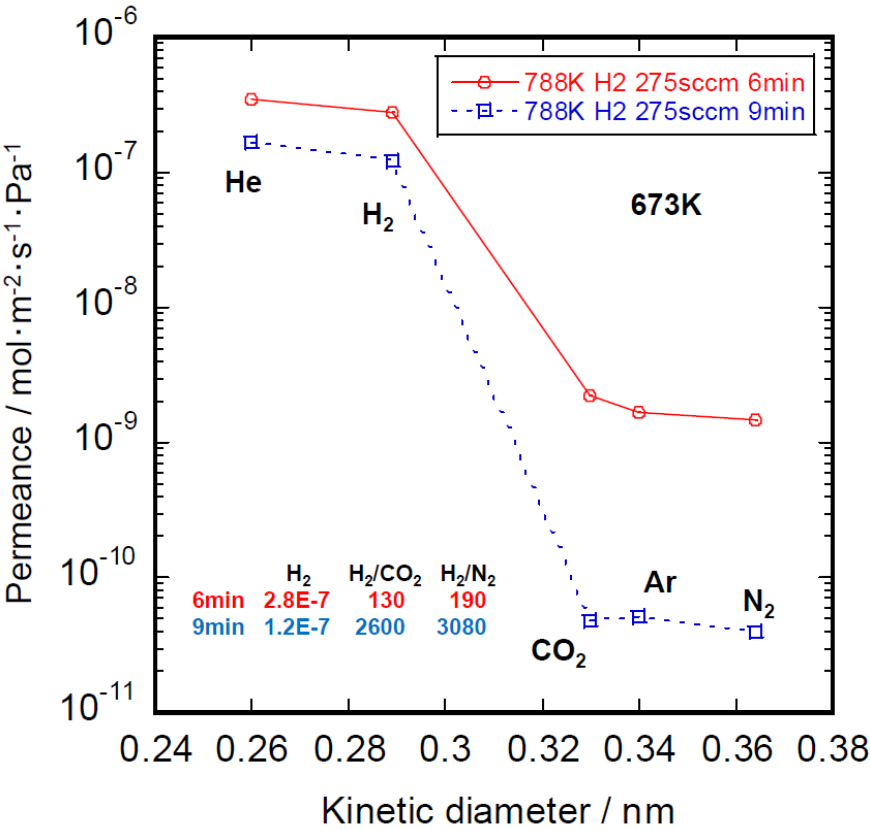


Fig. 8 Deposition time dependence on single gas permeance of SiC membranes.

Gas permeation properties through SiC/Ni- γ -Al₂O₃/ α -Al₂O₃ membrane in the temperature range 323-673 K are shown in Fig. 9. After CDCVD modification, helium and H₂ permeance tended to

increase with decreasing kinetic diameter. However, CO₂, Ar and N₂ permeance was almost same in the temperature range 323–673 K. The He, H₂, CO₂, Ar and N₂ permeance at 673 K was 1.7E-7, 1.2E-7, 4.8E-11, 5.1E-11 and 4.0E-11 mol·m⁻²·s⁻¹·Pa⁻¹, respectively. The H₂ permeance at 673 K was three orders of magnitude higher than the CO₂ permeance at 673 K, and the H₂/CO₂ permselectivity was calculated to be 2600. This membrane showed molecular sieving behavior. The pore size distribution of SiC active layer was very sharp and average pore size was considered to be about 0.3 nm between H₂ and CO₂ kinetic diameters.

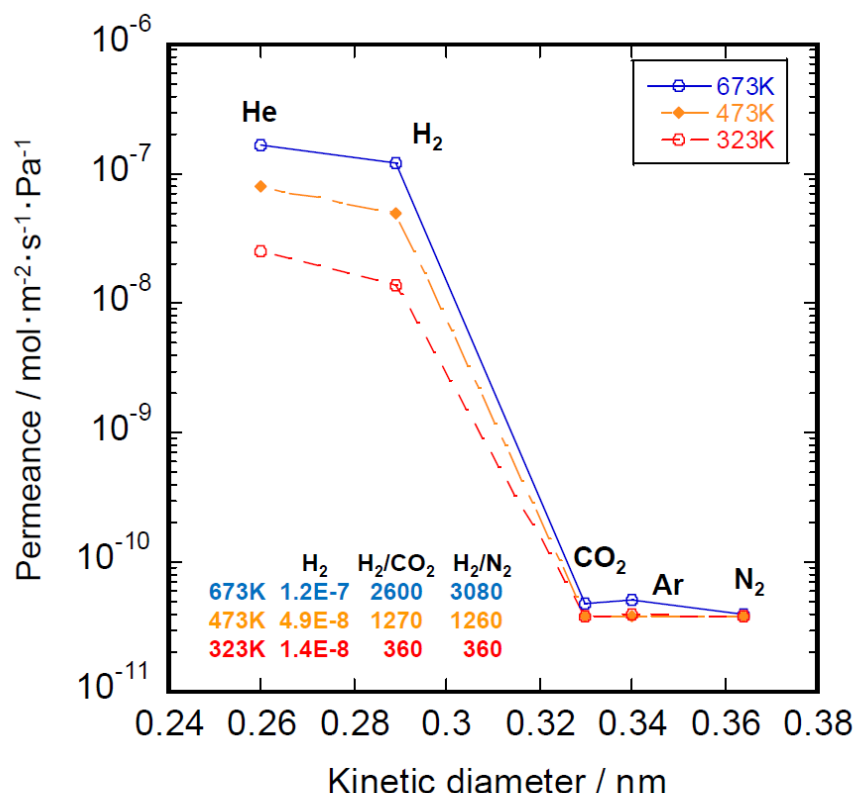


Fig. 9 Single gas permeance of SiC membrane in the temperature range 323–673 K.

The temperature dependence on each gas permeance for SiC/Ni- γ -Al₂O₃/ α -Al₂O₃ membrane is shown in Fig. 10. The permeance for He and H₂ increased with increasing permeation temperature. Accordingly, the dominant permeation mechanism for He and H₂ was considered to be activated diffusion.

The activation energy of permeation were obtained by fitting the experimental gas permeance data to the Arrhenius expression

$$Q = Q_0 \exp(-E_a/RT), \quad (2)$$

where Q is the permeance, Q_0 the pre-exponential factor (mol·m⁻²·s⁻¹·Pa⁻¹), E_a the activation energy (J·mol⁻¹), R the gas constant (8.314 J·mol⁻¹·K⁻¹), and T the temperature (K). The apparent activation energies in the silicon carbide membrane were roughly estimated from the experimental data. The apparent activation energy for the He and H₂ permeance in silicon carbide membrane was 9.8 and 11.2 kJ/mol in the temperature range from 323 to 673 K, respectively. Helium and H₂ through the specimen of SiC/ γ -Al₂O₃/ α -Al₂O₃ mainly permeated through the amorphous network in the temperature range 323–673 K. The activation energy of He and H₂ was close to that of SiOC membranes as shown in Table I. These values were thought to be reflected Si-O-C bonding of SiC active layer and low calcination temperature in CDCVD. On the other hand, that for the CO₂, Ar and N₂ permeance was 1.0, 1.2 and 0.1 kJ/mol in the temperature range 323–673 K, respectively. These data showed that membrane defect was little in this sample. Authors reported that the heat history during calcination and membrane thickness had an effect to the lowering of activation energy in amorphous SiC membranes [8].

Therefore, CDCVD process using precursor with Si-C bonding at low decomposition temperature is very effective to synthesize SiC membrane with molecular sieving behavior.

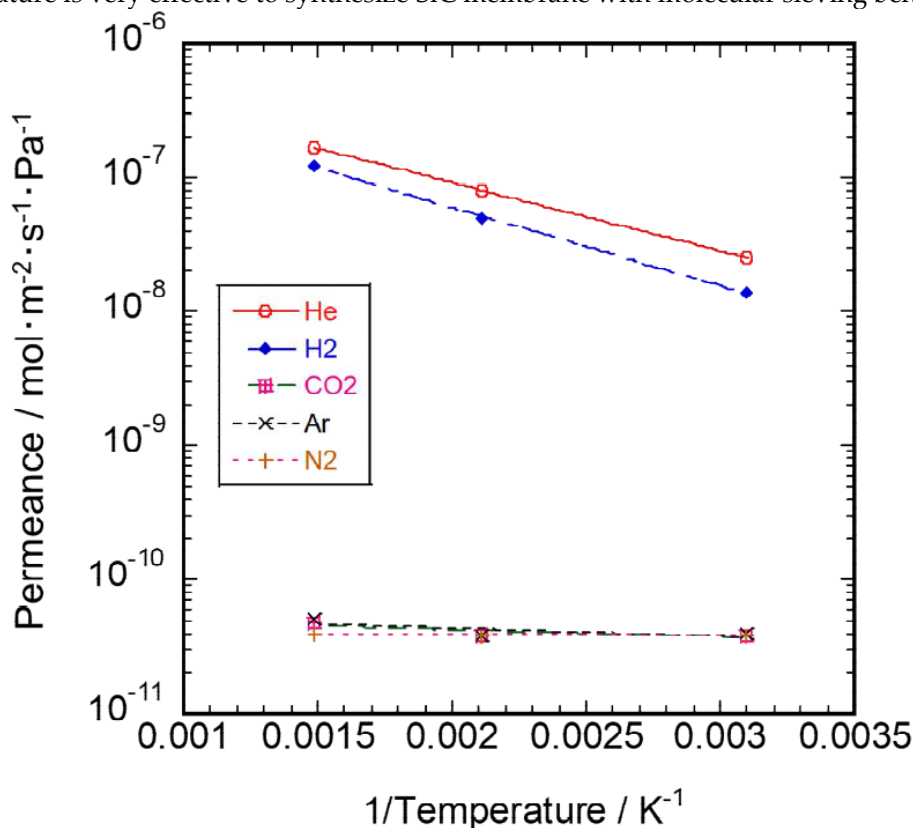


Fig. 10 Temperature dependence of single gas permeance.

4. Conclusion

Amorphous silicon carbide membranes with molecular sieving behavior were succeeded to synthesize on Ni- γ -Al₂O₃-coated α -Al₂O₃ by counter diffusion chemical vapor deposition. The dominant permeation mechanism for He and H₂ was activated diffusion. The mesoporous pores plugged with discrete SiC active layers in intermediate layer and the using of SCB with low decomposition temperature were effective to suppress thermal expansion coefficients mismatch between SiC active layer and Ni- γ -Al₂O₃/ α -Al₂O₃ porous support.

Acknowledgement

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