

Hydrogen selective nanoporous SiC membrane at high temperature

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ABSTRACT: Ceramic membranes having nano sized pores have great potential for gas separation at high temperature due to their good thermal stability. Moreover, nanoporous silicon carbide membrane has potential application under hydrothermal condition at high temperature. In this research, nanoporous SiC membrane has been developed on the porous alumina plate using a chemical vapour technique. The average thickness of the SiC membrane is ranged from 1 μm to 10 μm . SiC coated porous alumina possesses asymmetric pore size distribution. There are micropores originated from porous alumina substrate and nanopores derived from amorphous state of SiC membranes. Pore size distribution measurement shows that the sample contains 1-2 nm sized nano pores. The hydrogen permeability and selectivity toward nitrogen gas were measured using a single gas method. The produced SiC membranes showed hydrogen permeances in the range of $0.43 \times 10^{-6} \sim 1.7 \times 10^{-6}$ mol/m²·s·Pa and selectivity for H₂ gas is 3.09 ~ 117.5 toward N₂ gas. The developed nanoporous hydrogen selective SiC membrane shows promise for the applications in hydrogen separation from water electrolysis at high temperature or steam reforming reaction of natural gas since SiC membrane is stable at hydrothermal condition.

Keywords: Hydrogen, Separation, High Temperature, Nanoporous SiC Membrane

1. INTRODUCTION

In recent years there has been considerable interest in the development of inorganic membranes for the separation of hydrogen from a mixed gas stream. Because of concerns about global warming, hydrogen is rapidly becoming one of the alternatives to fossil hydrocarbon fuels. [1~7] Inorganic membranes can be used under conditions such as high temperature and reactive environments where organic membranes are not usable. Amongst the inorganic

membranes for the separation of hydrogen, nanoporous inorganic membranes offer many advantages over dense palladium membranes and ion-transport membranes. Nanoporous inorganic membranes that can be used at higher pressures can be fabricated from a variety of materials and are relatively cheaper as compared to palladium membranes. Thus, there have been attempts to produce nanoporous inorganic membranes of alumina, silica, zeolite, silicon carbide, etc. However, silica and alumina membranes show instability at high

temperature especially in the presence of steam. The main advantage of silicon carbide is a combination of strength, thermal and chemical stability at high temperatures, especially under hydrothermal conditions.

For highly efficient gas separations, the control of effective mean pore diameter is very important. As a very small pore size preferably less than 1 nm is required for hydrogen separation, the membrane must be very thin. There are relatively few reports discussing the control of effective mean pore diameter.

In this study, for the purpose of hydrogen separation from CO₂, SiC membrane on the porous alumina support having less than 1nm pore size has been developed by chemical vapour deposition technique.

2. EXPERIMENT

2.1 Preparation of nanoporous SiC membrane

Nanoporous SiC membrane was prepared by hot wall type CVD reactor using methyltrichlorosilane as a precursor at the temperatures between 950°C and 1100°C.

A porous α -Al₂O₃ disk type support (average pore size: 100nm, diameter: 25mm, thickness: 2mm, supplied by Nanopore materials Co.) was used as a substrate for coating. To maintain constant concentration of precursor in reactor, graphite susceptor which is sample holder was tilted about 10°. Ar and H₂ mixed gas was bubbled through methyltrichlorosilane at 25 °C and precursor was introduced into CVD reactor. During the experiment, pressure inside of reactor was 3 torr. To neutralize silane gas as by-product after deposition, alkali trap was placed between reactor and mechanical pump.

HITACHI, S-4100 scanning electronic microscopy was used for morphology observation of SiC nanoporous membrane. The pore size was determined by argon

physisorption using a Micromeritics ASAP 2010.

2.2 Gas Separation measurement

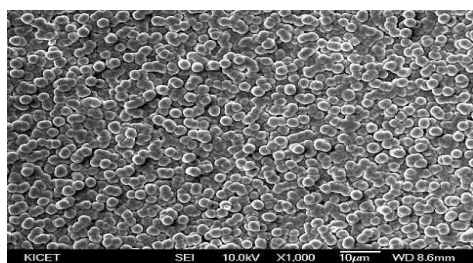
Gas permeation experiments were performed at room temperature using single component hydrogen and nitrogen gases measurement apparatus. Each flow rate was measured with soap film flow meter. Applied pressure was 6 psi.

3. RESULT AND DISCUSSION

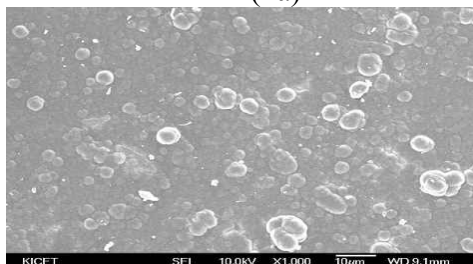
Fig. 1~4 are the FE-SEM data of the cross-section and the top surface of the SiC membranes prepared at different temperatures. The thickness of the SiC membrane layer is ranged from 1 μ m to 10 μ m and the membrane thickness entirely depends on deposition temperatures. Energy Dispersive x-ray analysis of the membranes revealed the membrane is composed of Silicon and Carbon only. As we see in Fig. 1a and 1b, the SiC membrane prepared at 1100°C covered with crystallite SiC particulates and the membrane thickness is about 10 μ m. However, the SiC membrane prepared at 1050°C covered with amorphous SiC particulates and the membrane thickness is about 1 μ m. The SEM microstructure prepared at 1000°C shows especially SiC whisker shape on the top surface. The SiC membrane prepared at 950°C covered with amorphous SiC particulates but it is not fully covered α -Al₂O₃ support. And the membrane thickness is less than 1 μ m.

For highly efficient gas separations, the membrane has to be very uniform without any defect such as crack. Also, the control of effective mean pore diameter is very important. As a very small pore size preferably less than 1 nm is required for hydrogen separation.

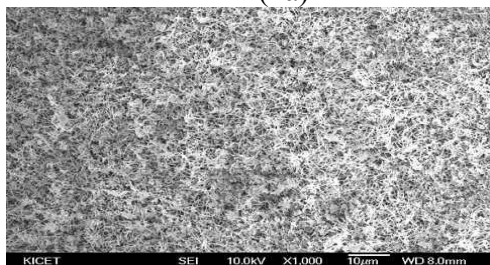
Among above 4 samples, the membrane prepared at 1050°C shows most uniform membrane thickness less than 1 μ m.



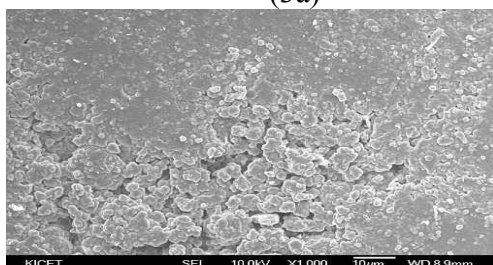
(1a)



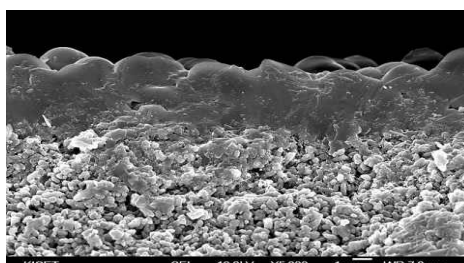
(2a)



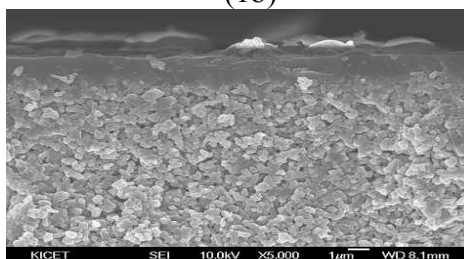
(3a)



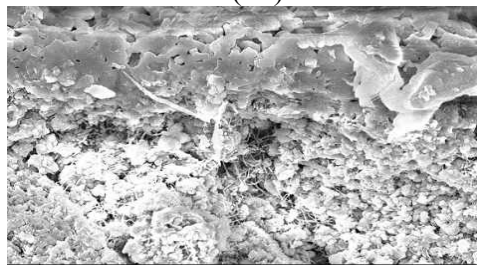
(4a)



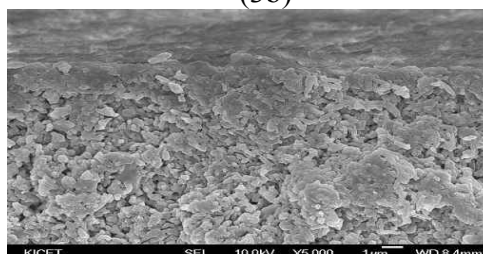
(1b)



(2b)



(3b)



(4b)

Fig. FE-SEM data of top surface SiC membranes prepared at 1a:1100°C, 2a: 1050°C, 3a: 1000°C and 4a: 950°C.

Pore size distribution measurement by BET method of this sample shows that the sample contains around 1 nm sized nano pores. SiC coated porous alumina possesses asymmetric pore size distribution.

Fig. FE-SEM data of cross section of SiC membranes prepared at 1b:1100°C, 2b: 1050°C, 3b: 1000°C and 4b: 950°C.

There are micropores originated from porous alumina substrate and nanopores derived from amorphous state of SiC membranes. And nanopores exist in SiC membrane is known to selectively permeable more H₂ gas than CO, CO₂, N₂ gases.

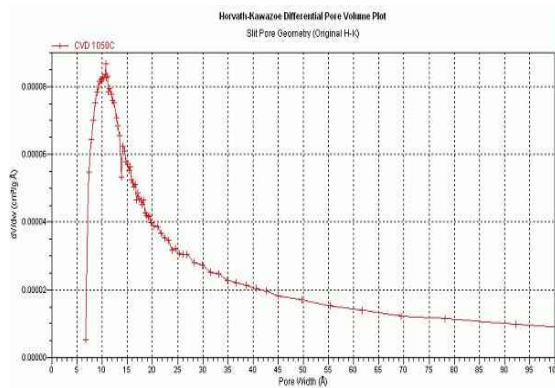


Fig. 5 Pore size distribution of SiC membrane prepared at 1050°C

Gas permeation experiments were performed at room temperature using single component hydrogen and nitrogen gases measurement apparatus. Each flow rate was measured with soap film flow meter. Applied pressure was 6 psi and permeance rate and selectivity were obtained from the following equations.

Permeance Rate $Q_1 = A_i / (P_{ri} - P_{pi}) * S * t$,
Selectivity $\alpha = Q_{H_2} / Q_{N_2}$

Q: Permeance Rate ($\text{mol}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$),

A: Permeate mole (mol),

Pr: Feed Pressure (Pa),

Pp: Permeate pressure (Pa)

S: Membrane area (m^2),

T: Time (seconds),

i: H_2 , N_2

As shown in table 1, the hydrogen gas permeance of SiC membrane prepared at 950°C was $1.7 \times 10^{-6} \text{ mole}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$ and hydrogen selectivity toward N_2 gas was 3.09. And this value is similar to the Kundsens diffusion selectivity for H_2/N_2 , which is 3.74. It is attributed that the quality of membrane prepared at this temperature was not appropriate for gas separation. As shown in fig. 4a, SiC membrane was not covered fully $\alpha\text{-Al}_2\text{O}_3$ support since the deposition rate of SiC was low at 950°C.

SiC membrane prepared at 1000°C was appeared as whisker shape and the hydrogen gas permeance was $0.6 \times 10^{-6} \text{ mole}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$

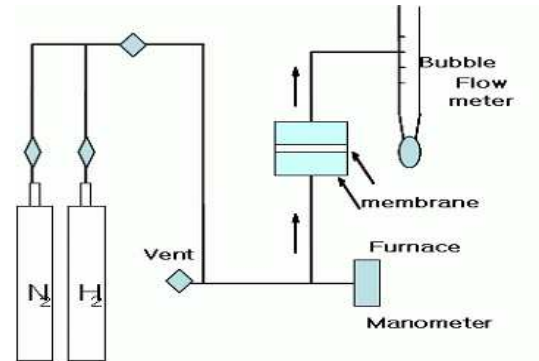


Fig. 6 Single gas permeability measurement apparatus

and hydrogen selectivity toward N_2 gas was 17.5. The best hydrogen selectivity was achieved at the SiC membrane prepared at 1050°C. The SiC membrane prepared at 1050°C covered with amorphous SiC particulates and the membrane thickness is about 1 μm . The hydrogen gas permeance was $0.43 \times 10^{-6} \text{ mole}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$ and hydrogen selectivity toward N_2 gas was 117.5.

However, As shown in Fig. 1a and 1b, the SiC membrane prepared at 1100°C covered with crystallite SiC particulates and the membrane thickness is about 10 μm . In this case, neither N_2 nor H_2 does not through the membrane. It is attribute that the thickness of the membrane is too thick to pass through gas molecules.

Table 1 H_2 Permeance and Separation Factor of Nanoporous SiC Membranes prepared by CVD technique.

Synthetic Temp.	Applied pressure	H_2 Permeance $\text{mole}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$	N_2 Permeance $\text{mole}/\text{m}^2 \cdot \text{s} \cdot \text{Pa}$	Separation Factor
950°C	6 psi	1.7×10^{-6}	0.55×10^{-6}	3.09
1000°C	6 psi	0.60×10^{-7}	$>0.37 \times 10^{-8}$	>17.5
1050°C	6 psi	0.43×10^{-6}	$>0.37 \times 10^{-8}$	>117.5
1100°C	6 psi	0.0	-	-

4. CONCLUSION

Nanoporous SiC membrane having less than 1nm pore size was fabricated on porous alumina substrate. To prepare SiC nanoporous membrane, chemical vapor deposition was carried out using methyltrichlorosilane as a precursor at the temperatures between 950°C and 1100°C.

SiC coated porous alumina possesses asymmetric pore size distribution. There are micropores originated from porous alumina substrate and nanopores derived from amorphous state of SiC membranes. The hydrogen gas permeance of prepared SiC membrane at 1050°C was 0.43×10^{-6} mole/m²·s·pa and hydrogen selectivity toward N₂ gas was 117.5. And nanopores exist in SiC membrane is known to selectively permeable more H₂ gas than CO, CO₂, N₂ gases. The developed nanoporous hydrogen selective SiC membranes show promise for application in hydrogen separation from coal gasification such as Integrated Gasification Combined Cycle (IGCC)

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