

Preparation and Characterization of SiC membranes for High Temperature Hydrogen Separation

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Aiming at development of high temperature hydrogen separation membranes, silicon carbide (SiC)-based membranes were prepared by the pyrolysis of polymeric precursor and characterized. To reduce the contamination of siloxane bonds in the SiC membrane, a polymeric precursor was prepared by hydrosilylation cross-linking of commercial polycarbosilane with *p*-diethynylbenzene, instead of conventional oxidation cross-linking with air. The present preliminary study implied that the SiC-based membranes obtained by pyrolysis under argon after coating and drying had micropore structure by which selective gas permeation could be expected. As an example, the SiC-based amorphous membranes pyrolyzed at 873 K exhibited excellent H₂/CO separation performance; the ideal separation factor measured at 373 K for the gas pair was larger than 100.

Key words: Inorganic membrane, Hydrogen separation, Polycarbosilane, Silicon carbide, Hydrosilylation

1. INTRODUCTION

There is growing interest in application of inorganic materials to practical gas separation membranes, in view of increasing need for separation of gases under severe conditions like high temperature. Purified hydrogen supply to a fuel cell is one of the examples, whose gas should be separated in-situ from CO containing gas mixture (H₂, CO, CO₂, and steam) produced by high temperature reforming of hydrocarbons. Development of inorganic membranes with excellent severe condition-proof holds the key to the success. Non-oxide ceramics like silicon carbide and silicon nitride are expected to be used as inorganic materials for gas separation membranes. We have started the research which aimed at establishment of the basic technology for applying the silicon carbide-based materials to gas separation membranes. Such membranes can be fabricated by controlled pyrolysis of a polymeric precursor coated on a porous ceramic substrate as in the past¹⁻⁷.

In view of membrane fabrication, ceramic synthesis from a polymeric precursor is advantageous compared to a conventional powder sintering method. Improvement of ceramic yield, membrane coating without any defects, and appropriate micropore formation, however, needs investigation on modification (curing and cross-linking processes) of a polymeric precursor in advance.

Although air oxidization¹⁻⁵ is a simple method for curing, the drawback is that the method introduces much amount of siloxane bonds in the structure of a product, which may make lower the high temperature stability.

UV irradiation method^{6,7} is alternative for curing without introduction of any oxygen, however, this method gives only a limited modified structure as in the case of air oxidation.

Our approach is different from the others, and it is to cross-link a polymeric precursor with non-oxygen bond, by using the hydrosilylation reaction of an unsaturated compound. This curing method based on organic chemistry has a possibility to give a wide variety of precursor with modified structure compared with the other methods.

In this study, aiming at development of high temperature hydrogen separation membranes, silicon carbide-type membranes were prepared by the pyrolysis of polymeric precursor cross-linked with organics, and quality of coating, porosity, and gas permeation properties are investigated. Polycarbosilane powder was used as a precursor after cross-linking with a non-oxygen bond for the purpose of lessening the percentage of siloxane bonds in the membrane structure.

2. EXPERIMENTAL

2.1. Preparation of SiC-based membranes

Commercial polycarbosilane powder was used as a polymeric precursor of silicon carbide. In the cross-linking reaction, *p*-diethynylbenzene (*p*-DEB) and Pt₂(dvs)₃ (dvs: 1,3-divinyltetramethyldisiloxane) was used as a cross-linking agent and as a hydrosilylation catalyst, respectively. Porous alumina tube (purity: 99.99 % α -Al₂O₃, average pore size: 150 nm,

average porosity: 40 %, and outer diameter: 2.9 mm, inner diameter: 2.2 mm, supplied by NOK Corp.) was used as a substrate for coating.

Coating and pyrolysis conditions are as follows; the alumina substrate tube was dipped into a solvent containing 10 or 20 wt% of the cross-linked or non cross-linked (original) polycarbosilane precursor, followed by drying at room temperature and pyrolysis in a tube furnace at higher temperatures. Precursor membranes were pyrolyzed at 673–1073 K for 2 hours with heating rate of 5 K/min under argon gas flow after holding at 473 K for 1 hour. All the membranes were allowed to cool to room temperature under argon atmosphere (Fig.1). Exception is that, for comparison to the literature¹⁻⁵, non cross-linked polycarbosilane membranes were cured in air at 473 K for 1 hour, and allowed to cool to room temperature in air (dotted curves in Fig.1) prior to the same pyrolysis procedure as that for cross-linked membranes.

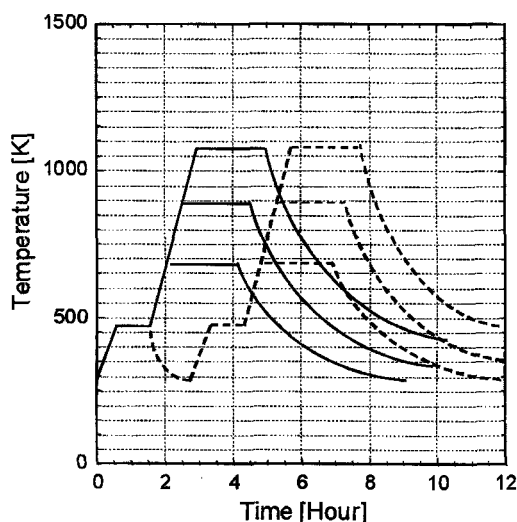


Fig.1 Heat-treatment profile for polycarbosilane membranes cross-linked with *p*-DEB (solid curves) and for those without cross-linking (dotted curves).

2.2. Characterization

Microstructure of the prepared SiC-based membranes was investigated by scanning electron microscopy (Hitachi, S900), fourier transform infra-red spectroscopy (Nicolet, Magna 550), X-ray diffractometer (MAC Science, MXP3), and gas adsorption apparatus (Nihon Bell, Belsorp 28).

Micropore was analyzed by molecular probe method from analysis of adsorption isotherms at 298 K of CO₂ probe gas with kinetic diameter of 0.33 nm⁸ by application of Dubinin-Astakhov equation⁹,

$$W = W_0 \cdot \exp \left\{ - \left(\frac{A}{E} \right)^n \right\}$$

where W is the pore volume, E is the characteristic energy of adsorption, and W_0 is the limiting pore volume whose pore size is assumed to be larger than the kinetic diameter of CO₂ probe gas. The adsorption potential A [$=RT \ln(P_s/P)$] is calculated from the saturated vapor pressure P_s , the equilibrium vapor pressure P , the gas constant R , and the measurement temperature T . The obtained adsorption data were well correlated when the

parameter n is 2. The W_0 values were obtained from y -axis intersections in the plots of $\ln W$ against $(\ln(P_s/P))^2$. Samples were degassed at 573 K for 5 hours prior to each adsorption measurement.

Gas permeance for single gases (He, H₂, CO, N₂) was measured at 323–423 K with a high vacuum time-lag method under the pressure difference of 1 atm (Fig.2). Both the feed and permeate sides of the membrane cell were evacuated ($< 10^{-5}$ torr) prior to each time-lag measurement. The rate of pressure rise on the permeate side was monitored by thermo stated Baratron sensors. The temperature of the membrane cell set in a ventilated oven was kept at a desired value. Permselectivity (ideal separation factor) is defined in the present study as the ratio of permeance of chosen gas over that of CO or N₂.

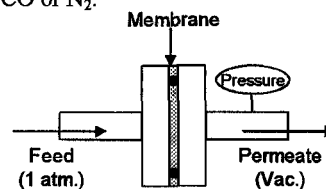


Fig.2 Schematic of high vacuum time-lag method.

3. RESULTS AND DISCUSSION

3.1. Preparation and characterization

We first investigate how the hydrosilylation reaction (addition reaction of a Si-H group to multiple bonds like C=C or C≡C, etc.) proceeds, resulting in the formation of non-oxygen cross linking moiety which can be served also as additional carbon source. Independent preliminary study implied that a model compound polymethylsilane instead of commercial polycarbosilane could be cross-linked under mild hydrosilylation reaction conditions. GLC analysis during the reaction process showed the decrease of a cross-linking agent with time. The combined analyses of the reaction by using IR, NMR, etc. suggested that this hydrosilylation reaction proceeded as shown in Fig. 3

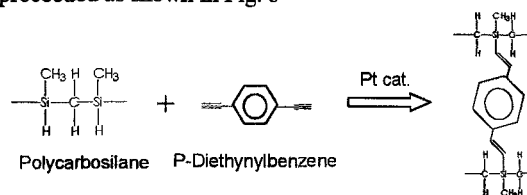


Fig.3 Scheme for the present cross-linking reaction.

3.2. Gas adsorption properties

The micropore of powdered materials which was given the same heat treatment as membranes was separately evaluated. CO₂ gas adsorption curves (Fig. 4) show that the product pyrolysed at 873 K adsorbs more CO₂ than the product pyrolysed at lower temperature of 673 K. The figure also shows that almost no CO₂ adsorption occurs for the product pyrolysed at higher temperature of 1073 K, and that cross-linking treatment makes the adsorbed amount larger, when comparing to the curves for the products pyrolysed at the same temperature of 673 K.

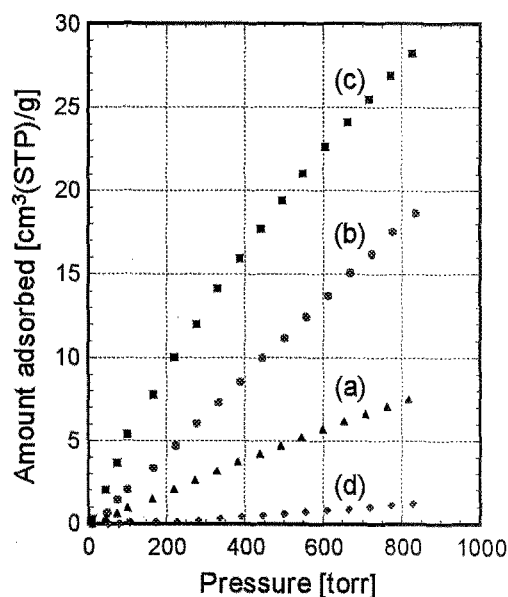


Fig.4 CO₂ gas adsorption curves for SiC-based powders (a) prepared by the pyrolysis of polycarbosilane without cross-linking at 673 K, and (b-d) those of polycarbosilane cross-linked with *p*-DEB followed by pyrolysis at (b) 673 K, (c) 873 K, and (d) 1073 K, respectively.

These findings are made clearer in figure 5, which presents how the limiting pore volume W_0 for CO₂ probe molecules varies with pyrolysis temperature. The figure shows the presence of maximum W_0 value when the pyrolysis temperature is around 750-900 K. This implies that optimum conditions exist for cross linking and pyrolysis processes to give an efficient micropore formation.

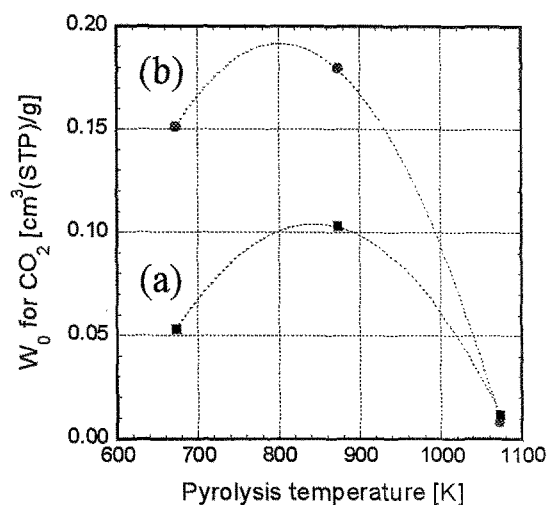


Fig.5 Dependencies of CO₂ limiting pore volume W_0 on pyrolysis temperature and cross-linking treatment of the precursor; (a) SiC-based powders prepared by the pyrolysis of polycarbosilane without cross-linking., and (b) those cross-linked with *p*-DEB.

3.3. Gas permeation properties

The SEM photograph for the fractured surface of the SiC-based membrane pyrolysed at 873 K (Fig.6) revealed that the membrane had a rather smooth surface and membrane layer with 1-2 μm in thickness. The

SiC-based amorphous membrane prepared by the pyrolysis of cross-linked polycarbosilane membrane at 873 K exhibited excellent permeation performance; at 373 K; the permeance of H₂ was 18.3×10^{-10} [mol/(m²·sec·pa)] and the permselectivity for H₂/CO gas pair exceeded over 100 (Table I).

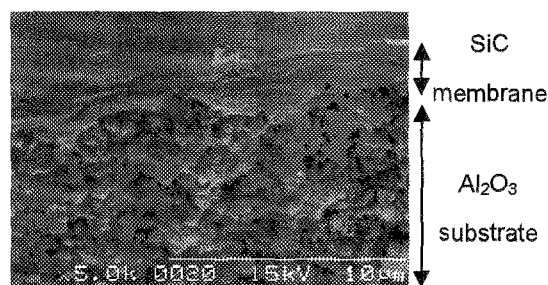


Fig.6 SEM photograph for fractured surface of the SiC-based membrane.

Table I Gas permeation properties (permeance and permselectivity for H₂/CO) measured at 373 K for (a) SiC-based membrane prepared by the pyrolysis at 873 K of polycarbosilane membrane without cross-linking, and (b) those by the pyrolysis at the same temperature of polycarbosilane membrane cross-linked with *p*-DEB.

	Permeance $\times 10^{10}$ [mol/(m ² ·sec·Pa)]				α (H ₂ /CO)
	He	H ₂	CO	N ₂	
(a)	84.1	63.5	2.88	2.63	22.0
(b)	61.8	18.3	0.16	0.13	114

4. CONCLUSION

SiC-based amorphous membranes were prepared by the pyrolysis of polycarbosilane precursor which was cross-linked with a non-oxygen bond by using the hydrosilylation reaction of an unsaturated compound. The present preliminary investigation on the coating, the micropore formation, and the gas permeation performance revealed that SiC-based amorphous membranes without any defects prepared by pyrolysis in an argon after coating and drying had microporosity by which selective gas permeation can be expected. As expected, the membrane pyrolyzed at 873 K exhibited excellent gas permeation performance. Mixture gas permeation tests under higher temperature are now in progress.

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