Gas Permeation of SiC Membrane Coated on Multilayer γ -Al₂O₃ with a Graded Structure for H₂ Separation

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Abstract A promising candidate material for a H₂ permeable membrane is SiC due to its many unique properties. A hydrogen-selective SiC membrane was successfully fabricated on the outer surface of an intermediate multilayer γ -Al₂O₃ with a graded structure. The γ -Al₂O₃ multilayer was formed on top of a macroporous α -Al₂O₃ support by consecutively dipping into a set of successive solutions containing boehmite sols of different particle sizes and then calcining. The boehmite sols were prepared from an aluminum isopropoxide precursor and heated to 80°C with high speed stirring for 24 hrs to hydrolyze the precursor. Then the solutions were refluxed at 92°C for 20 hrs to form a boehmite precipitate. The particle size of the boehmite sols was controlled according to various experimental parameters, such as acid types and acid concentrations. The topmost SiC layer was formed on top of the intermediate γ -Al₂O₃ by pyrolysis of a SiC precursor, polycarbosilane, in an Ar atmosphere. The resulting amorphous SiC-on-Al₂O₃ composite membrane pyrolyzed at 900°C possessed a high H₂ permeability of 3.61×10^{-7} mol·m⁻²·s⁻¹·Pa⁻¹ and the H₂/CO₂ selectivity was much higher than the theoretical value of 4.69 in all permeation temperature ranges. Gas permeabilities through a SiC membrane are affected by Knudsen diffusion and a surface diffusion mechanism, which are based on the molecular weight of gas species and movement of adsorbed gas molecules on the surface of the pores.

Key words boehmite sol, polycarbosilane, SiC membrane, H₂/CO₂ separation.

1. Introduction

The increased demand for pure hydrogen (H₂) as a clean, renewable and environment friendly future energy source has led to a wide interest in separation methods for H₂.¹⁾ An important step in producing pure H₂ is separating it from CO containing gas mixtures (H₂, CO, CO₂ and steam) produced by high temperature reforming of hydrocarbons in industrial chemical processes. Development of inorganic membranes which have excellent properties under severe operational conditions holds the key to the successful economical production of molecular hydrogen.

There are various membranes such as silica, zeolite, Pd, carbon molecular sieves and so on.¹⁻²⁾ A Pd-dense membrane can separate high-purity H₂ by ionic conduction mechanism; however, it has a low permeability.³⁻⁴⁾ Porous membranes using zeolite and silica have high gas permeability and selectivity;⁵⁻⁸⁾ however, the structure of the membranes becomes rapidly unstable at high temperature and under steam condition. Non-oxide ceramics such as silicon carbide (SiC) - and silicon nitride (Si₃N₄) - based

materials are promising for high temperature gas separation due to its high thermal and chemical stability. Therefore, we have studied SiC membrane, which is a covalent material with high mechanical strength, resistance in acidic and alkaline environments, chemical inertness and thermal stability. Thus, SiC is a promising candidate material for H₂ permeable membrane applications at high temperature.

Several works on SiC-based membrane have been carried out. Takeda et al.⁹⁾ synthesized SiC membrane coated on γ -Al₂O₃ tube by CVI (chemical vapor infiltration) technique using SiH₂Cl₂ and C₂H₂ gases. The H₂ permeability of the membrane was 10⁻⁸ mol·m⁻²·s⁻¹·Pa⁻¹ at 350°C, the H₂/N₂ selectivity was 3.36, which was lower than the theoretical Knudsen value of 3.74. Pages et al.¹⁰⁾ fabricated SiC membrane coated on α -Al₂O₃ tube using PECVD technique inducing SiH₂(C₂H₅)₂ gas and they obtained the H₂ permeability of 10⁻⁷-10⁻⁶ mol·m⁻²·s⁻¹·Pa⁻¹, the H₂/N₂ selectivity of 3-4. CVI/CVD techniques can be applied at very high temperature and are difficult to control the quality of final products.¹¹⁾ To overcome these problems, preceramic method has been employed due to low cost, heat-treatment at relatively low temperature and easiness of synthesis.¹²⁻¹³⁾ Interrante et al.¹⁴⁾ measured the He permeability using SiC membrane obtained via the pyrolysis of a partially allyl-

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substituted hydridopolycarbosilane. The He permeability was 10^{-8} – 10^{-7} mol·m⁻²·s⁻¹·Pa⁻¹ at 200°C, the He/N₂ selectivity was 20. Suda et al.¹⁵⁾ synthesized SiC membrane on α -Al₂O₃ tube support by dip-coating technique through the pyrolysis of polycarbosilane with added polystyrene to form pores of the membrane. The H₂ permeability was 1 – 3×10^{-8} mol·m⁻²·s⁻¹·Pa⁻¹ at 100°C, the H₂/N₂ selectivity was 90–150. Morooka et al.¹⁶⁾ fabricated SiC membrane by the pyrolysis of polycarbosilane using γ -Al₂O₃ as intermediate layer on porous α -Al₂O₃ tube. The H₂ permeability of the γ -Al₂O₃ was 2.25×10^{-6} mol·m⁻²·s⁻¹·Pa⁻¹ at 25°C, the that of the SiC membrane was 1.32×10^{-6} mol·m⁻²·s⁻¹·Pa⁻¹. Nagano et al.¹⁷⁾ synthesized SiC membrane by the pyrolysis of polycarbosilane using γ -Al₂O₃ intermediate layer with twice dip-coating. The H₂ permeability was 9×10^{-6} mol·m⁻²·s⁻¹·Pa⁻¹ at 600°C, the H₂/N₂ selectivity was lower than the theoretical Knudsen value.

The membranes for gas separation need to satisfy the following requirements to have effective gas separation properties of high permeability and selectivity; (a) thin thickness, (b) a defect-free and continuous structure, (c) small and uniform pore sizes, (d) support without permeation resistance and (e) chemical stability.¹⁸⁾ Therefore, the membranes for gas separation consist of three parts; they are macroporous support having high mechanical strength, mesoporous intermediate layer being easy to control pore sizes and having thermal stability, and finally microporous separation layer having high chemical stability.

In general, intermediate layers with small and uniform pore size can be obtained by dipping into the solutions containing sol particles. If the particle size of sol is too small compared with the pore size of support, sol particles will easily infiltrate into the pores of support and do not form bridges between pores. On the other hand, if the particle size of sol is too large, sol particles will necessarily have interstitial spaces and not cover the surface uniformly. Therefore, the effective intermediate layer with a graded structure can be obtained by using a large particle and then sequentially coating particles of smaller size on top.¹⁸⁾

In this study, we successfully synthesized amorphous SiC membrane on intermediate multilayer γ -Al₂O₃ with graded layers of total thickness $\sim 2 \mu\text{m}$ by the pyrolysis of polycarbosilane. The γ -Al₂O₃ layer was formed on top of a macroporous α -Al₂O₃ support by successively dipping into a series of solutions containing boehmite sols of different particle sizes and then calcining.

2. Experimental Procedure

A porous α -Al₂O₃ disk (diameter 30 ϕ , thickness 2 mm) with 100 nm macropores was used as the supporter. Boehmite (γ -AlOOH) sols were prepared using sol-gel method.^{18–19)} Aluminum isopropoxide (98+%, Al(^oC₃H₇)₃,

Aldrich) was added to distilled water, which was kept at 80°C and stirred for 24hrs to hydrolyze isopropoxide and form boehmite precipitate. The molar ratio of water/alkoxide was 90 : 1. To control the particle size of boehmite sols, the precipitate was peptized using a quantity of acetic acid (99.7%, CH₃COOH, Aldrich) or nitric acid (70%, HNO₃, Aldrich) with a molar ratio of acid/alkoxide in the range of 0.10–0.70. The boehmite sol was refluxed at 92°C for 20hrs to get clear or slightly translucent sol. pH meter and dynamic light scattering (DLS, Model: ELS-8000, Otsuka Electronics Co. LTD) were used to measure pH and particle size distribution of the boehmite sols, respectively.

Intermediate γ -Al₂O₃ multilayer was prepared on a macroporous α -Al₂O₃ support by dipping-calcining method. Dipping solutions were prepared with a polyethylene glycol (PEG, MW: 10,000, Fulka) as the binder. After the α -Al₂O₃ disk was dipped into the dipping solution, the support was dried overnight in air and calcined at 650°C for 2hrs. The γ -Al₂O₃ multilayer with a graded structure was prepared using the particle size-controlled boehmite - 500 nm, 250 nm and 50 nm - sols. The dipping-drying-calcining process was repeated three times.

Polycarbosilane (NIPUSI Type A, Nippon Carbon Co.) was used for the synthesis of amorphous SiC membranes.^{12,20)} Polycarbosilane precursor was dissolved in toluene (99.8%, C₆H₅CH₃, Aldrich) to make the polycarbosilane 20wt% solution. The γ -Al₂O₃ intermediate layer coated on the macroporous α -Al₂O₃ support was dipped into the polycarbosilane solution. After overnight drying, the membrane was cured at 200°C for 1hr in the air for high yield of SiC ceramics.²¹⁾ The membrane was heated from 200°C to 900°C with rate of 5°C/min and then pyrolyzed at 900°C for 2hrs under Ar atmosphere.

Thermal decomposition of the polycarbosilane up to 1000°C in nitrogen with a heating rate of 5°C/min was measured by thermogravimetry-differential thermal analysis (TG-DTA, Model: Diamond TG/DTA 6300 Lab System, Perkin Elmer). Heat treatment of boehmite powder causes the formation of a number of phase transition, and transition phase was investigated through X-ray diffraction (XRD, Model: DMAX-2500, Rigaku) using CuK α radiation. Changes in the chemical structure during pyrolysis process of the polycarbosilane were determined by a Fourier transform infrared spectroscopy (FT-IR, Model: VERTEX 80V, Bruker). KBr disk was prepared by compressing a finely ground mixture with a weight ratio of KBr/sample powder in 40 : 1. Cross-sectional structure of the amorphous SiC membrane on the γ -Al₂O₃-coated α -Al₂O₃ porous support was observed by a scanning electron microscope (SEM, Model: S-4300, Hitachi). The gas permeation properties of the resultant membranes were investigated using H₂, CO, N₂ and CO₂ single-component gases at permeation temperature of 25–700°C.

3. Results and Discussion

3.1 Crystalline phase analysis of boehmite

Fig. 1 shows the typical XRD patterns of the powders peptized with acetic acid with acid/alkoxide molar ratio of 0.10 at various heat-treatment temperatures. The XRD peaks of the powder dried at 80°C for 24hrs appeared at $2\theta = 14^\circ$ (020), 28° (120), 38° (031), 49° (200), 65° (080). These peaks agree with the crystalline peaks of the boehmite phase. The intensity of boehmite peaks of the powder heat-treated at 350°C for 2hrs was extremely weak due to the transformation of boehmite to γ - Al_2O_3 phase. The crystalline peaks of the powder calcined at 650°C for 2hrs appeared at $2\theta = 37^\circ$ (311), 46° (400), 67° (440). From these results, it is apparent that the boehmite to γ - Al_2O_3 transformation is complete.²²⁾

3.2 Effects of synthesis parameters on particle size of boehmite sols

The formation of stable colloidal boehmite sols strongly depends on various experimental variables such as alkoxide-water ratio, hydrolysis temperature and time, acid concentration, acid type and aluminum source. Table 1 and Fig. 2 show pH and particle size distribution of boehmite sols peptized with acetic acid or nitric acid with various molar ratios of acid/aluminum alkoxide ($R = 0.10$ – 0.70) at 92°C for 20hrs. Fig. 2 is the particle size distribution of boehmite sols peptized with different acid types and concentrations. While the aluminum alkoxide was hydrolyzed and polymerized, aluminum oxy hydroxide precipitate was formed simultaneously. When the acetic acid or nitric acid was added to the precipitates, boehmite sol became a transparent and stable suspension by peptization. H^+ of acid charges the surface of the precipitates of sol causing them to repel each other, allowing the larger precipitates to

Table 1. The pH of boehmite sols peptized with different acid types and concentrations.

Sample	Peptization agent (acid)	Molar ratio of acid/alkoxide	pH
1	CH_3COOH	0.10	4.1
2	CH_3COOH	0.70	3.6
3	HNO_3	0.20	3.3

Fig. 2. The particle size distribution of boehmite sols peptized with different acid types and concentrations. In BS-X (Y) notation, BS stands for boehmite sol, X is molar ratio of acid/alkoxide and Y is peptization agent.

break up and form smaller particles through hydrolysis and condensation reactions.¹⁸⁾ First, the effect of acid type was investigated. It was found that strong nitric acid gives much smaller particle size (50 nm) compared to weak acetic acid (500 nm). Also, acetic acid with different molar ratios of H^+ /alkoxide ($R = 0.1$ and 0.7) displayed considerable differences in the particle sizes, i.e., 500 nm and 250 nm respectively. Thus, lower acetic acid concentration produces larger size particles. Since the pore size of the bare Al_2O_3 support is 100 nm, a large particle size is required as the first layer of Al_2O_3 support.

3.3 Changes of physical/chemical structure of polycarbosilane with various heat treatments

Fig. 3 shows the TG-DTA graphs of the as-received polycarbosilane under N_2 atmosphere. The weight loss up to 240°C associated with an endothermic in the DTA trace occurred due to volatilization of the low molecular weight oligomers such as Si-H, C-H, Si- CH_3 bonds and water. The weight increase from 250°C to 550°C was caused by the oxidation of as-received polycarbosilane containing O_2 and dehydrogenation or dehydrocarbonation condensation reaction. Above 550°C , organic side groups in the polycarbosilane decomposed, resulting in weight loss. After Si- CH_2 -Si in the polycarbosilane started to convert into SiC at 800°C , amorphous SiC was formed around 900°C

Fig. 1. The XRD patterns of the powders peptized with acetic acid and then heat-treated at different temperatures.

Fig. 3. The TG-DTA traces of as-received polycarbosilane in nitrogen atmosphere with a heating rate of 5°C/min.

with no significant weight loss.²⁰⁻²¹⁾

Fig. 4 shows the FT-IR spectra of the polycarbosilane heat-treated at various temperature conditions. The IR spectrum of an as-received polycarbosilane presented typical absorption peaks due to Si-CH₃ bending at 830 cm⁻¹, CH₂ bending of Si-CH₂-Si at 1020 cm⁻¹, Si-CH₃ stretching at 1250 cm⁻¹, Si-H stretching at 2100 cm⁻¹ and C-H stretching of Si-CH₃ at 2950 cm⁻¹. The spectrum of the polycarbosilane cured at 200°C for 1hr in the air showed absorption peaks due to Si-O stretching at 1020 cm⁻¹, C=O stretching at 1710 cm⁻¹. During the cross-linking process in the air, mainly the Si-H and C-H groups having low bond energies in the polycarbosilane were attacked by oxygen, creating Si-O-Si and Si-O-C bonds as indicated by the decrease in the intensity of the Si-H, C-H and Si-CH₃ bands. The spectrum of the polycarbosilane, which was cured at 200°C for 1hr in the air and then pyrolyzed at 500°C for 2hrs under Ar atmosphere, shows that Si-C bond due to decomposition of residual organic side groups did not yet occur. Finally, the spectrum of the polycarbosilane, which was cured at 200°C for 1hr in the air and pyrolyzed at 900°C for 2hrs under Ar atmosphere, shows that Si-C bond formation is complete as evidenced by the amorphous SiC absorption peak^{17,21)} around 790 cm⁻¹.

3.4 Microstructures of γ -Al₂O₃ multilayer and SiC composite membranes

Fig. 5 shows the cross-section of γ -Al₂O₃ intermediate multilayer prepared by gradually changing particle size-controlled boehmite sols such as 500 nm, 250 nm and 50 nm, sequentially coated on the macroporous α -Al₂O₃ support. The top γ -Al₂O₃ layer had a finer structure than the other two layers below because of the use of a solution with smaller sol particles. Thickness of the membrane for gas separation greatly affects gas permeation properties. If

Fig. 4. The FT-IR spectra of as-received polycarbosilane heat-treated at various temperature conditions.

Fig. 5. The SEM image (magnification = 6,000×) of cross-section of γ -Al₂O₃ intermediate layer coated on the macroporous α -Al₂O₃ support.

it is very thick, delamination of obtained separation layer occurs or gas permeability decreases. On the other hand, if it is very thin, gas selectivity decreases. Therefore, various dip-coating conditions of boehmite sols were tried and the following conditions were found to be optimal; withdrawal speed = 0.5 mm/s, PEG concentration = 1wt%, contact time = 10s. The total thickness of the γ -Al₂O₃ membrane on the macroporous α -Al₂O₃ support was around 1.6 μ m. Fig. 6 shows the cross-section of the SiC membrane cured at 200°C and pyrolyzed at 900°C on the graded structural γ -Al₂O₃ through high magnification. A boundary between the graded structural γ -Al₂O₃ and the SiC membrane was clear and the thickness of the SiC membrane was about 300 nm.

Fig. 6. The SEM image (magnification = 3,000 $\times$) of cross-section of the SiC membrane coated γ - Al_2O_3 intermediate layer on the macroporous α - Al_2O_3 support with high resolution (magnification = 50,000 $\times$).

Fig. 7. Gas permeabilities of the γ - Al_2O_3 intermediate layer coated on a macroporous α - Al_2O_3 support with various permeation temperatures.

3.5 Gas permeation properties of γ - Al_2O_3 multilayer and SiC composite membranes

Fig. 7 shows the H_2 , N_2 , CO and CO_2 single-component gas permeabilities of the graded intermediate γ - Al_2O_3 coated on porous α - Al_2O_3 support in the permeation temperature range 25–700°C. The H_2 gas permeability was about $1.7 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$, and the permeabilities of N_2 , CO and CO_2 gases were about $2.7 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$. The H_2 permeability value was one order of magnitude higher than those of other gases, whose permeabilities had similar values. And permeabilities of these four gases using the graded intermediate γ - Al_2O_3 membrane decreased with increasing permeation temperature. Generally, there are four transport mechanisms for gas separation of porous membrane; Knudsen diffusion, surface diffusion, molecular sieving and capillary condensation

Fig. 8. Gas permeance behavior of the γ - Al_2O_3 intermediate layer coated on a macroporous α - Al_2O_3 support.

Fig. 9. Gas permeabilities of the SiC membrane with various permeation temperatures.

with liquid flow. Among these mechanisms, the permeability of any gas via Knudsen diffusion mechanism is inversely proportional to the square root of its molecular weight and absolute temperature. So it seems that transport mechanism for the γ - Al_2O_3 membrane coated on porous α - Al_2O_3 support is Knudsen diffusion. To confirm circumstantially, gas permeation behavior of the γ - Al_2O_3 intermediate layer coated on porous α - Al_2O_3 support is shown in Fig. 8. The experimental values were plotted versus the inverse square root of molecular weight of various gases at permeation temperature of 500°C. The permeability order of the gases via the γ - Al_2O_3 membrane coated on the α - Al_2O_3 support was $\text{H}_2 > \text{CO} > \text{N}_2 > \text{CO}_2$ showing an inverse dependence on the molecular weight of the gases. Since differences in $1/M^{0.5}$ values of N_2 , CO and CO_2 gases were very small, it was considered that their permeability values shown in Fig. 7 were very similar. Therefore, these facts indicate that the permeation behavior of the γ - Al_2O_3 membrane is well explained by Knudsen diffusion mech-

anism.¹⁷⁾ The H₂/CO and H₂/N₂ selectivities were larger than 3.74, which is calculated from molecular weights of gases. Also the H₂/CO₂ selectivity was similar to the theoretical Knudsen value of 4.69.

Fig. 9 shows the H₂, N₂, CO and CO₂ single-component gas permeabilities of the SiC membrane cured at 200°C and pyrolyzed at 900°C on the graded structural γ -Al₂O₃ multilayer in the permeation temperature range 25–700°C. All gas permeabilities using SiC membrane were lower than values through γ -Al₂O₃ membrane. The H₂ gas permeability was from $3.6 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ to $3.9 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$, the N₂ and CO permeabilities were 10^{-7} – $10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ in all permeation temperature ranges. Also permeabilities of these four gases decreased with increasing permeation temperature. The CO₂ permeability was remarkably low, and the H₂/CO₂ selectivity was much higher than the theoretical value. Besides Knudsen diffusion mechanism, gas permeabilities through SiC membrane are affected by surface diffusion mechanism, which is based on movement of adsorbed gas molecules on the surface of the pores.²⁴⁾ So we suppose that chemical affinity between CO₂ gas and the pore wall of the SiC membrane was weaker than those of other species. This result is identical with that for a SiC-based membrane formed by CVD of triisopropylsilane.²⁵⁾

4. Conclusion

A H₂ permeable SiC membrane was successfully synthesized coated on the γ -Al₂O₃ intermediate layer on a macroporous α -Al₂O₃ support through pyrolysis of polycarbosilane at 900°C under Ar atmosphere. The graded structural γ -Al₂O₃ intermediate layer with a smooth and defect-free structure could be obtained from particle size-controlled boehmite sols by peptization. The H₂ and CO₂ permeabilities of SiC membrane at high permeation temperature were $\sim 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ and close to 0, respectively. Therefore, the SiC membrane is expected to effectively separate H₂ from gas mixtures.

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