Fabrication of supported Si₃N₄ membranes using the pyrolysis of liquid polysilazane precursor

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Abstract

The fabrication process is described of supported microporous Si₃N₄ membranes, prepared by pyrolytically decomposing organo-substituted polysilazane precursor. The membrane had a composite asymmetric structure consisting of a mechanically strong porous Si₃N₄ support which had 42 vol% pores between 0.4 and 0.52 μm, coated with an intermediate and one or two thin active top layers. The individual layers were fabricated by the conventional dip-coating technique.

Permeation experiments with He, N₂ and CO₂ have been performed to determine the gas transport characteristics and separation performance of the processed membranes. The permeation is pressure-independent, indicating no viscous flow in the supported top layer. The proposed process has made it possible to prepare membranes with He permeation rates of ≥5.3×10⁻¹⁴ mol m⁻² s⁻¹ Pa⁻¹ and He/N₂ permeselectivities of ≥2.0, even in the membrane with one top layer. It is also demonstrated from separation experiments, that the membrane with high quality top layer has the separation factors of 4.7 for He/N₂ and of the theoretical of Knudsen flow for CO₂/N₂. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Ceramic membrane; Pyrolysis; Silicon nitride; Gas separation

1. Introduction

Microporous ceramic membranes recently have been attracting a good deal of attention resulting from the important applications of such membranes in separation industries where their organic counterparts fail to function [1–3]. Silicon nitride membranes do offer potential advantages, particularly in high-temperature gas separation and reactor applications because of their unique combination of better high-temperature mechanical properties, wear-resistance, and thermal shock resistance [4]. For making use of these characteristics, pure Si₃N₄ has to be densified. Si₃N₄ powders are normally sintered under high-temperature conditions with sintering additives, which form a second phase along grain boundaries during the sintering process, and commonly impair the mechanical and physical properties of the original material.
New processing routes are in progress to fabricate pure Si$_3$N$_4$ ceramics by using thermal decomposition of organo-substituted polysilazane [5,6]. These routes enable high-yield pure Si$_3$N$_4$ to be synthesized at unusually low-temperatures without sintering aids. Since the pyrolysis products show some blistering of the solid, reasonably so, due to the release of gaseous by-products during pyrolysis [7,8], polysilazane cannot be directly transformed into dense Si$_3$N$_4$ ceramics.

Nevertheless, the fact that Si$_3$N$_4$ porous bodies can be prepared using the pyrolysis of polysilazane reasonably suggests an application in the fabrication of Si$_3$N$_4$ membrane system [9]. A major concern is therefore to develop a technology to form well-tailored microstructures by controlling the gas release during pyrolysis. In a previous paper [10] we have proposed a process fabricating porous Si$_3$N$_4$ compacts from a mixture of Si$_3$N$_4$ powders and polysilazane. In that process it is quite feasible for the pore size of the compacts to be controlled in the range 1–1000 nm, under the process conditions: adequate control of the firing temperature and the amount of doped polysilazane. The results again imply that the process conditions which enable pore size to be tailored in the order of nanometer should be applicable in the development of separation layer of membrane as well as membrane-support systems.

The objective of the present study is to develop a fabrication technology of supported Si$_3$N$_4$ membranes with well-controlled microstructures, based on the pyrolysis mechanism of polysilazane. Asymmetric membrane usually consists of a thin top-layer responsible for separating components, and a porous ceramic-support with single or multiple intermediate layers imparting the required mechanical strength to the membrane composite. In all cases, the top-layer must be defect-free and has preferably a narrow pore-size distribution, whose indispensability sets severe demands on the quality of the intermediate layer and the support. It should be noted that the support system including intermediate layers can have different morphologies and microstructures. The present paper discusses the feasibility of fabricating supported Si$_3$N$_4$ membranes by applying dip-coating process, in which process porous Si$_3$N$_4$ supports are dipped into toluene-containing thick syrups of polysilazane and then subjected to the thermal decomposition of polysilazane. It should be mentioned that liquid polysilazane pre-cursor is capable of serving as a binder for Si$_3$N$_4$ powders during the formation of intermediate layers, as well as being used to surface-coat and yielding Si$_3$N$_4$ on pyrolysis.

The supported membrane is so designed to have microstructure with a gradual change in pore size and consist of the same material through the membrane/support system, thereby insuring the stability of the processed membrane either thermal or chemical. Another important aspect of the proposed process is that the feasibility of controlling pore size exactly depends on the control of the pyrolysis [10]. This is very advantageous from a technological point of view, since the reproducibility of pore size control is easily ensured by controlling the firing temperature–time schedule, compared with another processing methods such as sol–gel processes, which commonly contain a large number of process parameters and accompany the difficulty of conserving a reasonable reproducibility, stemming from the chemical instability involved basically [11].

The characterization of the processed membranes is discussed based on results from single-component gas permeation and binary gas separation experiments. Emphasis is laid mainly on the influence of preparation conditions of dip solutions on the separation factor, along with the gas transport mechanism. The performance of the processed membrane is also compared with that of sol–gel derived supported membrane with high-quality top-layer.

2. Experimental

The finally determined sequence of steps in preparing supported Si$_3$N$_4$ membranes is shown in Fig. 1, where the membranes were prepared by a dip-coating process of α-Si$_3$N$_4$ supports (closed-end tubes of 80 mm length, with an outer and inner diameters of 13 and 9 mm, respectively) in dip solution containing polysilazane.

2.1. Preparation of supports

Porous Si$_3$N$_4$ supports were prepared by slip casting in the conventional process. Casting slips were prepared by dispersing Si$_3$N$_4$ powders (SN-E10, Ube,
Fig. 1. Preparative procedure of supported Si₃N₄ membranes by thermal decomposition of polysilazane.

with an average diameter of 300 nm) in deionized water with the dispersant (1 wt% triethanol-amine, supplied by Chukyo) in a solids content of 35 vol%.

The slips were homogenized by ball-milling for 16 h using Si₃N₄ balls in a polyethylene bottle. Drain casting was performed in gypsum molds. The slip-cast supports were allowed to dry in a stream of nitrogen at room temperature for 24 h and then at 105°C for 24 h. The dried supports were fired at 1800°C for 4 h under the atmosphere of 0.1 MPa nitrogen, according to the predetermined firing-program [10]. The prepared supports had 42 vol% pores between 0.4 and 0.52 μm, the values of which were observed by mercury-penetration porosimetry.

2.2. Preparation of intermediate layers

The intermediate layer must prevent the penetration of the precursor of top-layer material into the pores of the support during the coating, and the collapse of the thin top-layer (the proper separation layer for gas separation) into the large pores of the support. This set severe demands on the quality of the support if the formation of the top-layer is mainly determined by capillary action on the support. The prepared supports generally have a feasibility of much lower surface quality, and will consequently need additional intermediate layers of better quality before modification can be successfully performed [11]. In order to form a well characterized intermediate layer, the Si₃N₄ sup-
ports were modified by a dip-coating process. The dip solution was prepared from the mixture of $\alpha$-$\text{Si}_3\text{Na}_4$ powders and toluene-containing thick syrups of polysilazane (SILACERAM-NCP-201, Chisso Corporation, with average molecular weight of 1250) by ball-milling for 1 h, and then by ultrasonically dispersing for 5 min. To gain insight into the optimal modification conditions, the volumetric ratio of $\text{Si}_3\text{Na}_4$ powders to polysilazane was adjusted to 160/100 or 120/100 for $\text{Si}_3\text{Na}_4$/polysilazane. The total concentration of $\text{Si}_3\text{Na}_4$ and polysilazane in a dip solution was also changed in the range 2.5–10% by weight, because the thickness of coating layer in dip-coating process depends strongly on the viscosity and hence the total concentration of the dip solution [11]. The dipping was performed manually in one step in an open beaker and the standard dipping time was 1 s. The obtained specimens were allowed to dry in a stream of 0.1 MPa-nitrogen at room temperature for 48 h, and then fired at 1350°C for 4 h with a heating rate of 3°C min$^{-1}$. The results for the preparation of porous fired $\text{Si}_3\text{Na}_4$ compacts using the pyrolysis of polysilazane, as have been shown in the previous paper [10], suggest that mean pore sizes of the compacts fired at 1350°C are 9 and 18 nm for 160/100- and 120/100-specimens, respectively. It is also noted that, in this modification process, polysilazane is capable of serving as a binder for $\alpha$-$\text{Si}_3\text{Na}_4$ powders.

2.3. Preparation of top layers

The top layer was applied on the previously prepared intermediate layer by dip coating in a dip solution of toluene-containing polysilazane. The concentration of polysilazane in the dip solution was 1%, 5%, and 10% by weight. The dipping in this step was also carried out manually in an open beaker for 1 s. The top layers were dried for 48 h in the same manner as the intermediate layers, followed by firing at 800°C for 4 h with a heating rate of 3°C min$^{-1}$ under 0.1 MPa nitrogen. In order to demonstrate the effects of multiple modification on the separation performance, the second modification step (dipping, drying, and then firing) was performed for the case of 1 wt% dip solution.

2.4. Characterization of membranes

The processed membranes were characterized by gas permeation measurements using helium, nitrogen, and carbon dioxide, with equipment as shown in Fig. 2. The gases used had a purity >99.99%. The specimens were placed in a stainless-steel cell, with the microporous top-layer at the feed side. The gas flow through the membrane was controlled by mass flow controllers placed parallel. The feed pressure and pressure difference over the membrane were measured using pressure transducers. The gas flow rates were recorded as a function of gas pressure difference across the membranes. The flow rate, measured by timing the rise of a soap bubble in a graduated column, was recorded at room temperature.

Gas separation experiments were also performed using binary gas mixtures of He/N$_2$ and CO$_2$/N$_2$, in equipment as shown in Fig. 2. The feed composition was 50:50 (vol%) with a flow rate of 400 ml min$^{-1}$. The influence of back-diffusion was avoided by introducing vacuum at the low-pressure side. Both the retentate and the permeate composition were analyzed using a gas chromatograph. The separation factor ($\alpha$),

![Fig. 2. Experimental configuration for gas permeation and separation experiments.](image-url)
3. Results and discussion

Fig. 3(a)–(d) are typical SEM micrographs of the cross-sections of the membranes after applying the second modification procedures for top layer. It is demonstrated that the top layer follows the contours of the surface of intermediate layer, is approximately 2 μm thick, and has no visible cracks. The microstructure of the underlying support tube is uniform and highly porous. The fracture surface of the support is shown in Fig. 3(b), in which some longer grains can be seen in contrast to the irregular and equiaxed starting α-Si3N4 particles. These grains should be β-Si3N4 as defined as the enrichment factor of one component in the permeate compared to the feed composition, is calculated by [12]:

\[
\alpha = \frac{y \cdot 1 - x}{1 - y \cdot x}
\]

where \( y \) is the molar fraction of the faster permeating component in the permeate and \( x \) is the molar fraction of this component in the feed. In order to determine the process conditions for the intermediate layer, within the limits of this paper, the supports coated with intermediate layer were also subjected to gas permeation and gas separation experiments using He and N2.

Fig. 3. Scanning electron micrographs of fabricated supported Si3N4 membrane: cross-sections of (a) supported membrane, (b) underlying support, (c) intermediate-layer/ support interface, and (d) top-layer/ intermediate-layer interface.
have been shown previously [10]. From Fig. 3(c) and (d), one can see that the pyrolysis product of poly- 
silazane effectively bridged or covered Si$_3$N$_4$ particles through the intermediate layer, resulting in the 
formation of extended network structure and hence in the 
reduction in pore size. The top layer shows a more 
dense structure and successfully forms a percolation 
system of pores at the membrane/support interface. 
From the results of XRD analysis [10], the products 
pyrolyzed at 1350°C and 800°C should be α and 
amorphous phases, respectively.

The typical measured He and N$_2$ flows (in 
m$^3$ m$^{-2}$ s$^{-1}$) through the support system (fabricated 
intermediate layer and Si$_3$N$_4$-support), are given as a 
function of pressure difference over the support system 
in Fig. 4. As can be seen from Fig. 4, the He and 
N$_2$ flow rates are linearly dependent on the pressure 
difference, which means that the permeation (in 
mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$), defined as the transport rate 
divided by the pressure difference, is pressure-inde- 
pendent. It is also demonstrated that the permeation 
depends on both the polysilazane/Si$_3$N$_4$ volumetric 
ratio and the total concentration of a mixture (poly- 
silazane+Si$_3$N$_4$ particles) in dip solution. The results 
of single gas permeation data have been summarized 
in Table 1 for the supports coated with different wt% 
dip solutions, in combination with separation perfor- 
mance. The data represents the average values 
obtained from five samples. The permeation data 
for the specimens where leaks due to some defects 
were clearly recognized, are excluded from the table. 
The dip solution with higher viscosity and concentra- 
tion of Si$_3$N$_4$ particles did not form an uniform inter-
mediate layer at the entrance of the pores in the 
support, resulting in the formation of macroscopic 
defects.

The permselectivity for He/N$_2$, defined as the ratio 
of permeation rates of the two gases, was calculated 
from the measurements of mass flow rate of each gas. 
If the permeation rate is independent of pressure level, 
as in this case, the separation factor can be calculated 
from measurements for individual gases [12]. As can 
be clearly seen in Table 1, the permeation rates for He 
are approximately twice as high as those for N$_2$, which 
is reasonably caused by the difference in the molecular 
weight. The permselectivity for He/N$_2$ does not change 
significantly with the concentration of dip solution and is around 1.8, although the permeation 
rate changes by almost a factor 2. The permselectiv- 
ities for He/N$_2$ were not close to the theoretical limit, 
suggesting that the prepared support system would 
contain some defects. These defects were, however, 
reasonably repaired during the next dipping procedure 
for the top-layer, due to the lower resistance against 
liquid transport than that at the defect-free site on the 
intermediate layer. In the case where the total con- 
centration in dip solution is 2.5 wt%, the 120/100 dip- 
solution results in higher permeation rate, compared 
with the 160/100 dip-solution. This result reasonably 
 stems from the difference in the size of formed pores. 
In the previous paper [10], the feasibility was inves- 
tigated of controlling pore sizes of porous fired Si$_3$N$_4$ 
 compacts prepared from a mixture of Si$_3$N$_4$ powders 
and polysilazane. The experimental results have 

![Fig. 4. Gas flow rate as a function of pressure difference for the support with an intermediate layer: polysilazane/Si$_3$N$_4$ volumetric ratio and total concentration of a mixture (polysilazane+Si$_3$N$_4$ particles) in a dip solution: 120/100, 2.5 wt% ( ), 160/100, 2.5 wt% ( ), 160/100, 7.5 wt% ( ). (a) Gas flow rates for nitrogen. (b) Gas flow rates for helium.](image-url)
shown that the median pore size can be controlled in the range 1–1000 nm, under the process conditions: adequate control of the firing temperature and the amount of doped polysilazane. These results suggest that the 160/100 dip-solution would structure pores around 9 nm, while the 120/100 dip-solution would result in the formation of pores of approximately 18 nm and reduce the permselectivity accordingly.

The results of separation experiments for the processed support system have also been summarized in Table 1. The observed separation factor is around 2.0 and slightly higher than the permselectivity (in Table 1) determined from the measurements of flow rate of each gas. A value from these measurements greater than 1 indicates gas separation. When the measured values are close to the ideal values (2.65 for He/N₂), the separation reaches the Knudsen separation limit.

In order to finally determine the conditions for preparing dip solution, further work should be in progress to address the details of the influence of solids concentration in the dip solution on the performance of intermediate layer, as well as the dip-coating process conditions involved. In the present study, the process condition was used for the preparation of intermediate layer, that the polysilazane/Si₃N₄ volumetric ratio is 160/100 and the total concentration of polysilazane and Si₃N₄ in a dip solution is 5 wt%, which would result in higher permeation performance.

Fig. 5 shows a representative gas permeation plot for a supported membrane after the first or second modification steps for top-layer. The gas permeation of the membranes is calculated by dividing the flow rate through the membrane by the product of measurement area and pressure difference over the membrane. The permeation is pressure-independent, indicating no viscous flow in the supported top layer. The transport of gas component for such a top layer is contributed mainly by Knudsen flow [11] within the error of the measurements. In Table 3 permeation results are summarized for prepared membranes with finished top-layer. The permeation data represents the average

<table>
<thead>
<tr>
<th>Gas</th>
<th>Polysilazane/Si₃N₄ volumetric ratio in dip solution</th>
<th>Total concentration of (polysilazane+Si₃N₄) in dip solution wt%</th>
<th>Permeation (10⁻⁵ mol m⁻² s⁻¹ Pa⁻¹)</th>
<th>Permeability selectivity for He/N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>160/100</td>
<td>7.5</td>
<td>1.5</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>160/100</td>
<td>5.0</td>
<td>2.3</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>160/100</td>
<td>2.5</td>
<td>1.2</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>120/100</td>
<td>2.5</td>
<td>1.8</td>
<td>1.6</td>
</tr>
<tr>
<td>N₂</td>
<td>160/100</td>
<td>7.5</td>
<td>0.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td>160/100</td>
<td>5.0</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>160/100</td>
<td>2.5</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120/100</td>
<td>2.5</td>
<td>1.1</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Polyzilazane/Si₃N₄ volumetric ratio in dip solution</th>
<th>Total concentration of (polysilazane + Si₃N₄) in dip solution wt%</th>
<th>Permeation (10⁻⁵ mol m⁻² s⁻¹ Pa⁻¹)</th>
<th>Separation factor for He/N₂</th>
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<tbody>
<tr>
<td>160/100</td>
<td>7.5</td>
<td>1.3</td>
<td>0.63</td>
</tr>
<tr>
<td>160/100</td>
<td>5.0</td>
<td>2.1</td>
<td>0.94</td>
</tr>
<tr>
<td>160/100</td>
<td>2.5</td>
<td>1.1</td>
<td>0.56</td>
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<tr>
<td>120/100</td>
<td>2.5</td>
<td>1.7</td>
<td>0.96</td>
</tr>
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</table>
values from three determinations for each sample. The number of employed sample is five for each dip solution. According to molecular weight, the permeation for He should be the highest, and the permeation for CO₂ is comparable to that for N₂, as seen in Fig. 5. It can be seen in Table 3 that the supported top layer with high quality has been successfully prepared by applying single modification procedure, with He permeation rates of $5 \times 10^{-6}$ mol m⁻² s⁻¹ Pa⁻¹ and He/N₂ permselectivity of ≥2.0. From the CO₂ permeation data it is also shown that the high permselectivity for CO₂/N₂ has been achieved (ideal value for CO₂/N₂ is 0.798). The permeation result is also shown in Table 3, for the top layer prepared by applying the modification procedure twice using 1 wt% dip-solution. The second modification step has improved the permselectivity for He/N₂ to 2.3. This result reasonably indicates that an effective modification has been performed for preparing a multiple separation layer.

The forming mechanism of supported thin films is characterized by linear increase of the layer thickness as a function of the square root of dipping time [3]. Since the viscosity of dip solutions containing 1–10 wt% polysilazane is almost constant (2.1 MPa s), the thickness of the formed top layer might independent of polysilazane concentration in the dip solution. The slight change in the observed permeation is probably caused by the difference in the formed microstructure through the top layer. The viscosity of dip solution did not change with the concentration.

Table 3

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration of polysilazane in dip solution (wt%)</th>
<th>Permeation⁺ (10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹)</th>
<th>Permselectivity⁺ for X/N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1</td>
<td>6.9 (3.5)</td>
<td>2.0 (2.3)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>5.3</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6.8</td>
<td>2.2</td>
</tr>
<tr>
<td>CO₂</td>
<td>1</td>
<td>2.7 (1.4)</td>
<td>0.89 (0.95)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.0</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.0</td>
<td>0.97</td>
</tr>
<tr>
<td>N₂</td>
<td>1</td>
<td>3.3 (1.5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.1</td>
<td></td>
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</table>

⁺Values between parentheses represent the data after the second modification.
of polysilazane to 12 wt% but increased abruptly at 15 wt%. When the 15 wt% dip solution was used, the fabricated top layer had the worse adherence to the support system, thus forming large defects, such as wide cracks or large pinholes. It will be concluded that only within an appropriate viscosity range can the dip solution convert to a top layer with uniform thickness.

In Table 4 permeation results measured from separation experiments are summarized for the processed membranes. As can be seen in Table 4, the membrane with He/N₂ permselectivity of 4.7 has been successfully prepared from the 10 wt% dip solution. The permselectivity for He/N₂ are generally said to be higher, compared to the actually found selectivities from the separation experiments, because separation experiments are much more sensitive towards defects in the membrane than single gas permeation measurements [12]. In the present study, however, separation factors higher than those calculated from permeation experiments have been observed. Further work is in progress to address the details of relationship between separation experiments and permeation measurements, in relation to the defect involved. It is also demonstrated that the membrane has the theoretical CO₂/N₂ permselectivity for Knudsen flow.

The He/N₂ permselectivities observed from permeation measurements are plotted as a function of He permeation in Fig. 6, where the data for sol–gel derived supported-SiO₂ membranes are also shown for the comparison. The sol–gel derived membranes have been prepared by applying conventional dip-coating process, in which the number of modification proce-

<table>
<thead>
<tr>
<th>Gas system</th>
<th>Concentration of polysilazane in dip solution wt%</th>
<th>Permeation* (10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹)</th>
<th>Separation factor* for X/N₂</th>
</tr>
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<tbody>
<tr>
<td>He–N₂</td>
<td>1</td>
<td>5.9 (3.1)</td>
<td>2.6 (1.8)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.9</td>
<td>3.3</td>
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<tr>
<td></td>
<td>10</td>
<td>7.2</td>
<td>4.7</td>
</tr>
<tr>
<td>CO₂–N₂</td>
<td>1</td>
<td>2.0 (1.5)</td>
<td>0.79 (0.88)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.3</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.7</td>
<td>0.78</td>
</tr>
</tbody>
</table>

*Values between parentheses represent the data after the second modification.

Fig. 6. He/N₂ permselectivity for Si₃N₄ membrane with top-layer: concentration of polysilazane in a dip solution: 10 wt% (○), 5 wt% (△), 1 wt%, dipped (□) once and (■) twice; (●) are data for sol–gel derived supported-SiO₂ membranes. Values between parentheses show the numbers of repeated modification procedures.
tion factor by applying the subsequent modification procedures. There is of course another feasibility to improve the membrane performance by controlling the firing temperature, processing conditions concerning dip coating process, and the preparation conditions of dip solutions.

Sol–gel process has been practically applied as a feasible way to prepare microporous membrane. The characteristics of sol–gel derived membranes are determined by a large number of process parameters, and it is therefore important that the effects of these parameters are well understood to make sol–gel process a reliable and practical technology for membrane fabrication [11]. As compared with sol–gel process, the proposed technique utilizes the thermal decomposition of organo-substituted polysilazane, where the pore size of membrane is mainly controlled by the firing conditions. This is very advantageous from a technological point of view, since the proposed technique makes it possible to prepare the microstructure with gradual change in pore size through the separation layer only by controlling the firing temperature.

4. Conclusions

Fabrication process of supported microporous Si₃N₄ membranes have been developed by applying the conventional dip-coating technique, in which process a liquid polysilazane precursor is infiltrated into the pores of Si₃N₄ supports for surface-coat and then allowed to yield Si₃N₄ on pyrolysis.

It has been found from gas permeation experiments, that the permeation is pressure-independent, indicating no viscous flow in the top layer. This result also implies that the defect-free separation layers have been successfully prepared, through which the transport of gas component is contributed solely by Knudsen flow. The proposed process should make it possible, by applying single modification step, to prepare membranes with He permeation rates of ≥5×10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹, which are one order of magnitude higher than those for supported-SiO₂ membranes previously possible by sol–gel modification techniques, with undergoing no significant change in permselectivity (≥2.0).

It has also been demonstrated from separation experiments, that the separation factors for He/N₂ are as high as 4.7 for high quality membranes with He permeation rate of 7.2×10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹. The combination of high permeation rates and separation factors make these membranes very attractive for gas separation applications and/or incorporation in membrane reactors.

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