PLASMA POLYMERIZATION OVER POROUS INORGANIC MEMBRANES AND THE PERMEABILITY OF THE MEMBRANES (II)

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Plasma polymerization of tetraethoxysilane or perfluoro-n-hexane/hydrogen was investigated in order to reduce the pore size of NaA and ZSM-5 zeolite membranes and improve the gas selectivity through the membrane. Plasma polymerization was carried out in a bell-jar type of reactor with an inductive coupled rf (13.56 MHz) power source. The effect of plasma condition on the deposition rate of plasma polymer was examined and the structure of plasma polymers was characterized by IR. The gas permeation through zeolite membranes modified by plasma polymerization was also investigated. Modified ZSM-5 zeolite membrane shows an improvement of the selectivity of gases by the reduction of the size of defect pore of the membrane.

1. Introduction

Plasma polymerization is an unique method to prepare an ultra thin film with unique characters. One of the main advantage of plasma polymerization is the ability to prepare films with thicknesses in the range from several nanometers to several hundreds of nanometers, where conventional polymer coating methods are difficult or impossible. Moreover, the plasma-polymerized films which are uniform and pinhole-free can be deposited onto any substrates from almost all organic compounds. Thus, many studies have been made on application of plasma polymerization to membrane separations such as reverse osmosis, gas separation, pervaporation and so on [1,2]. However, up to now very few studies have been reported the plasma polymer was deposited onto a microporous inorganic membrane to control the pore size of the membrane and to prepare a gas separation membrane. In our previous paper [3], we reported that plasma polymer from perfluoroalkanes was deposited onto the porous inorganic and organic membranes and the gas permeability of the membranes was examined. In this work, plasma polymerization of tetraethoxysilane(TEOS) and perfluoro-n-hexane(PFH) was carried out to further evaluate plasma polymerization to control the pore size of zeolite membranes.
2. Experimental

Tetraethoxysilane (TEOS) obtained from Shin-etsu Co. and perfluoro-n-hexane (PFH) obtained from Tokyo Kasei Co. were used as a monomer without further purification. NaA and ZSM-5 zeolite polycrystalline membranes were grown hydrothermally on the surface of a porous cylindrical substrate of alumina by following a published method \[4,5\]. The porous substrate has a mean pore diameter of 1 μm with a porosity of about 50% and its dimensions are 0.01 m in outer diameter, 0.002 m in thickness and 0.15 m in length.

A bell-type of reactor was used for plasma polymerization. Figure 1 shows a schematic diagram of the apparatus. Plasma was generated by an inductive coupled rf (13.56 MHz) power source. After the reactor was evacuated to 0.01 Torr, the monomer gas adjusted to a fixed flow rate was introduced into the reactor. The plasma polymerization was carried out at 0.1 and 0.2 Torr and discharge power of 20-50 W for a certain period. The deposition rate of plasma polymerization was determined by weighing of substrates before and after plasma polymerization. FTIR spectra of monomer and plasma polymer deposited on KBr crystal were recorded on Horiba-FT200 spectrometer.

Gas permeation was carried out at 35-200°C using single-component H\(_2\), He, CO\(_2\), N\(_2\), CH\(_4\) and SF\(_6\) gases with the apparatus described elsewhere \[5\]. Feed gas was introduced to the outer side of the cylindrical membrane in the stainless-steel cell that was placed in a thermostated air bath. The permeation rates were measured with a capillary bubble flowmeter after the membrane was evacuated at 200°C for at least one day in the case of ZSM-5 membrane or one week for NaA membrane.

3. Results and Discussion

Plasma Polymerization

The amount of polymer deposition from TEOS was found to be linear with duration time of plasma polymerization. Figure 2 shows the effect of discharge power on the deposition rate of plasma polymerization of TEOS at different monomer pressure. The rate of polymer deposition
obtained at a monomer pressure of 0.2 Torr is faster
than that of 0.1 Torr, which indicates that the
deposition rate is controlled by the concentration of
monomer. Furthermore, it is seen that the
deposition rate at both 0.2 and 0.1 Torr increased
with increasing discharge power up to a value of 30
W and then sharply decreased with further
increasing discharge power. Generally, there are
two competitive reactions in plasma poly-
merization: polymer formation which leads to the
deposition of material, and ablation which leads to
the removal of material. Which of the above
reactions is predominant depends upon the plasma
polymerization conditions. When the discharge
power exceeded 30 W, the ablation was a pre-
dominant reaction and then the deposition rate
decreased. A similar phenomenon have been
observed for many monomers [1,2]. In the case of
the plasma polymerization of PFH, the deposition
rate increased with increasing discharge power up to
a value of 40 W and then sharply decreased and the
deposition rate of the PFH + H₂ system was about
two times faster compared to the pure PFH
polymerization because of hydrogen scavenging of
fluorine atoms as described in a previous paper[3].

IR spectra of the plasma-polymerized TEOS and
TEOS monomer are shown in Figure 3. TEOS
monomer shows absorptions at 3000-2800 cm⁻¹,
1500-1300 cm⁻¹, 1200-1100 cm⁻¹, 795 cm⁻¹ and 500 cm⁻¹, denoting CH₃ and CH₂ stretching,
CH₃ and CH₂ deformation, Si-O-C stretching, SiO₄ stretching and Si-O bending, respectively [6].
IR spectra of the plasma-polymerized TEOS were similar to those of the monomer except for the
broadening of various bands and the decrease in the band intensities at 3000-2800 and 1500-1300
cm⁻¹ assigned to CH₃ and CH₂ groups, and at 795 cm⁻¹ due to SiO₄ stretching. This indicates
that the fragments of CH₃ or CH₃CH₂ groups were removed out from the plasma polymer and
then the plasma polymer containing the main SiOₓ components was obtained through plasma
polymerization of TEOS.
Gas Permeation

Useful transport mechanisms for gas separation through the porous membrane rely on the following four mechanisms: Knudsen diffusion, surface diffusion, selective condensation (capillary condensation or micropore-filling) and molecular sieving. The dependence of gas permeation rates through NaA zeolite polycrystalline membrane on the inverse of square root of molecular weight of gases and the ability of SF6 gas, whose kinetic diameter (55 nm) is larger than the NaA zeolite pore diameter (40 nm) [7], to still permeate through the membrane indicate the Knudsen diffusion of gases through defect pores between grains of NaA zeolite crystals [3]. Thus, selectivities of the membrane is small and is limited by the square root of the molecular weight ratios of the gases being separated.

In order to reduce the size of defect pores and improve the selectivity, plasma polymer of TEOS or PFH+H2 was deposited on the membrane. Figure 4 shows an example of the variation of gas permeation rates through the NaA zeolite membrane modified by plasma polymerization of TEOS. Although permeation rates decreased with an increase of the duration time of plasma polymerization, the gas transport was still controlled by Knudsen diffusion. In the NaA zeolite membrane modified by plasma polymerization of PHF+H2, the gas transport mechanism was also Knudsen diffusion and there was no improvement in selectivity.

Judging from the reduction of gas permeation rates, the pore size was reduced to some extent. However, plasma polymerization of TEOS or PFH+H2 at room temperature could not effectively control the pore size of NaA zeolite membrane. Furthermore, plasma polymer of PFH+H2 exhibited considerable cracking at the long duration time of plasma polymerization, suggesting high stress due to the highly crosslinked structure as described in a previous paper [3], while plasma polymer of TEOS adhered well to the underlying zeolite membranes.

Figure 5 shows gas permeation rates at 105°C through original ZSM-5 zeolite membrane and modified ZSM-5 membrane prepared by plasma polymerization of TEOS. For these membranes, the deviation from ideal Knudsen behavior was observed. High permeation rates for condensable gases such as CO2 and CH4 indicate the transport of the gases is enhanced by surface diffusion,
as suggested by Hwang and Kammermeyer [8] in a microporous Vycor glass where transports of He, N₂, O₂, Ar and CO₂ are controlled by a combination of Knudsen diffusion and surface diffusion and show a temperature minimum of the adjusted permeability corrected for temperature (T) and molecular weight of permeated gas (M), \( Q(MT)^{1/2} \) where Q means of original permeability of gases. The observation that the adjusted permeation rates for gases through original and modified ZSM-5 zeolite membranes show the temperature minimum further supports the presence of surface diffusion.

Figure 5 also shows that the gas permeation rates through modified ZSM-5 membrane were reduced, while the selectivities of modified membrane were increased. Ideal separation factors (permeation rate ratios) of gases through original and modified ZSM-5 zeolite membranes are shown in Table 1. Compared with the original membrane, the membrane prepared by plasma polymerization showed higher selectivities, which implies that the pore size of the membrane was reduced by plasma polymerization.

The dependence of the permeation rates on the differential pressure was also investigated at 105°C. The H₂, CO₂ and N₂ permeation rates increased with increasing differential pressure. This is consistent with the results that the surface diffusion is expected to be operative at lower temperature. Increasing pressure would increase surface coverage and the surface diffusion flux up to the saturation pressure of the adsorption isotherm at the temperature and pressure corresponding to the permeation measurement. If surface diffusion is a predominant process of gas transport at the certain temperature, gas permeability depends on differential pressure. On the other hand, surface diffusion should decrease with increasing temperature because the interaction between the gas molecules and the membrane surface decreases and so desorption increases as temperature increases. As shown in Table 1, separation factors determined at 200°C was close to

<table>
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<tr>
<th>Membrane</th>
<th>Temp [°C]</th>
<th>CO₂/N₂</th>
<th>CO₂/N₂</th>
<th>H₂/N₂</th>
<th>H₂/SF₆</th>
<th>He/SF₆</th>
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</thead>
<tbody>
<tr>
<td>Original</td>
<td>35</td>
<td>1.36</td>
<td>0.71</td>
<td>1.54</td>
<td>34.6</td>
<td>15.8</td>
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<td>105</td>
<td>1.72</td>
<td>0.90</td>
<td>1.96</td>
<td>11.6</td>
<td>5.83</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.39</td>
<td>0.83</td>
<td>2.86</td>
<td>8.85</td>
<td>5.62</td>
</tr>
<tr>
<td>Modified</td>
<td>35</td>
<td>2.15</td>
<td>1.19</td>
<td>2.01</td>
<td>81.4</td>
<td>39.4</td>
</tr>
<tr>
<td></td>
<td>105</td>
<td>2.19</td>
<td>1.45</td>
<td>4.35</td>
<td>30.0</td>
<td>18.9</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.34</td>
<td>0.82</td>
<td>3.84</td>
<td>22.1</td>
<td>15.9</td>
</tr>
</tbody>
</table>

Knudsen diffusion: 0.80 | 0.60 | 3.72 | 8.48 | 6.04

Feed pressure: 2 atm, Permeate pressure: atmospheric
the values that would be expected from a Knudsen diffusion mechanism with the exception of separation factors of H$_2$/SF$_6$ and He/SF$_6$ for the modified membrane.

The permeation rates as a function of the gas kinetic diameter at 200°C are shown in Figure 6. It can be seen that the significant decrease in the permeation rates through modified ZSM-5 membrane was observed for SF$_6$, which has the largest kinetic diameter in all gases measured. Thus, the separation factor of H$_2$/SF$_6$ and He/SF$_6$ through modified membrane at 200°C (Table 1) greatly exceed the values of original one which are close to the ideal Knudsen values. Although the size correlation is not perfect because the lack of the pore size distribution data, molecular sieving appears to be contributing to the permeation of SF$_6$ through modified membrane.

In conclusion, the results of gas permeation through modified ZSM-5 zeolite membrane suggest the possibility of improving the separation property by plasma polymerization. After the modification, molecular sieving appears to be the dominant mechanism at high temperature. More work is needed to understand the microstructure and transport mechanism in the modified membrane.

References