Gas Separation Membrane Composed of Polyimide and Surface-modified Nanoparticles: Influence of Surface-modification Structures on Gas Permeation Properties

Hiroto Mikami¹, Azusa Osawa¹, Manabu Tanaka¹,², and Hiroyoshi Kawakami¹,²*

¹ Department of Applied Chemistry for Environment,  
² Research Center for Hydrogen Energy-based Society (ReHES),  
Tokyo Metropolitan University,  
1-1, Minami-osawa, Hachioji, Tokyo 192-0397, Japan  
*kawakami-hiroyoshi@tmu.ac.jp

Polymer membranes with high gas permeability have been strongly desired for energy- and environmental-applications. In this study, novel mixed matrix membranes (MMMs) composed of fluorinated polyimide and silica nanoparticles modified with various organic moieties were fabricated, and their gas permeation properties were evaluated. The influence of surface-modification structures, especially the length and density of linker molecules, on gas permeation properties of the MMMs were investigated. The modification structures affected the formation of high CO₂ permeable space on the nanoparticle surface, and appropriate structures effectively enhanced the CO₂ permeability of the MMMs.

Keywords: Carbon dioxide, Fluorinated polyimide, Gas separation, Mixed matrix membrane, Silica nanoparticle

1. Introduction

Carbon dioxide capture and storage (CCS) technology has attracted attention to reduce greenhouse gas emissions and to prevent global warming [1]. The CO₂ separation is one of the most important processes in the CCS technology. Compared to the conventional CO₂ separation methods including the adsorption method with amine solutions, polymer membrane-based gas separation process has been recognized as the most effective method because of its low cost, low energy consumption, simple operation, and environment adaptability [2,3]. The recent study revealed that achieving higher CO₂ permeability is more useful for the polymer membranes than attaining higher permselectivity to reduce the cost of CO₂ capture from flue gases [4]. Therefore, many efforts have made to improve the CO₂ permeability of membranes by synthesizing novel polymers or fabricating newly structured membranes [5].

Recently, novel polymer composite membranes, so-called “Mixed Matrix Membrane (MMM),” consisting of polymeric materials and submicron-/nano-sized particles, have been actively studied for gas separation to improve the gas permeability and/or selectivity [6-8]. In our previous study, we synthesized nanoparticles having gas permeable nano-space formed by introducing aromatic dendritic structures onto the surface of non-porous silica nanoparticles. The MMMs composed of high CO₂ permeable fluorinated polyimide (FPI) [9-11] and the surface-modified nanoparticles showed enhanced CO₂ permeability without the significant decreasing of their permselectivity (e.g., CO₂/N₂ selectivity).

In this study, in order to discuss the influence of surface-modification structures on gas permeation properties of the MMMs, a series of nanoparticles modified with linker molecules bearing different length and density were synthesized. The gas permeation properties of the fluorinated polyimide-based MMMs containing...
the novel surface-modified nanoparticles were investigated (Fig. 1).

Fig. 1. The concept of this study: Fabrication and gas permeability evaluation of MMMs containing surface-modified silica nanoparticles bearing different linker length and density.

2. Experimental

2,2’-Bis(3,4-dicarboxyphenyl)hexafluoropropene dianhydride (6FDA) was purchased from Central Glass Co. (Saitama, Japan) and purified by sublimation before use. 2,4,6-Trimethyl-1,3-phenylenediamine (3MPA) was purchased from Tokyo Chemical Industry Co., LTD (Tokyo, Japan) and recrystallized from hexane before use. 3-Aminopropyl triethoxysilane (APTES), 3-(2-aminoethyl)aminopropyl triethoxysilane (AEAPTES), and 1H-benzotriazol-1-yloxytris(dimethylamino)phosphonium hexafluoro phosphate (BOP) were purchased from Tokyo Chemical Industry. 3,5-Diaminobenzoic acid (DABA) was purchased from Aldrich (St. Louis, United States). Triethylamine (TEA), N-methyl-2-pyrrolidone (NMP), and tetrahydrofuran (THF) were purchased from Kanto Chemical (Tokyo, Japan). Colloidal silica nanoparticles, PL-1, with 10-15 nm diameters were obtained as a water dispersion (silica content of 12 wt%) from Fuso Chemical Co., LTD (Osaka, Japan). All the chemicals were used as received unless otherwise specified.

FPI was synthesized by polycondensation of...
6FDA and 3MPA monomers and was characterized according to our previous papers [10-12]. The conventional APTES-modified silica nanoparticle, APTES<sub>100</sub>(G0), was prepared by using an excess amount of APTES as a linker. The APTES-modified silica nanoparticle with low APTES modification density, APTES<sub>50</sub>(G0), was prepared by using a limited amount of APTES (50 mol% of the theoretically required amount that can be fully modified the hydroxyl groups on the surface of silica nanoparticles). The DABA-modified (1st generation) silica nanoparticle, APTES<sub>100</sub>(G1), was synthesized by the condensation reaction of amine groups on the APTES<sub>100</sub>(G0) with DABA in the presence of BOP and TEA in NMP under inert conditions based on our previous study [12]. The DABA-modified (2nd generation) silica nanoparticle with low linker density, APTES<sub>50</sub>(G2), was also prepared through the twice DABA-condensation reactions on APTES<sub>50</sub>(G0). A series of silica nanoparticles using AEAPTES as a linker, AEAPTES<sub>100</sub>(G0), AEAPTES<sub>50</sub>(G0), and AEAPTES<sub>50</sub>(G2), were similarly prepared. After each reaction, excess unreacted or unmodified reagents and by-products were eliminated by washing the nanoparticles with appropriate solvents for many times. The progress of modification reactions was confirmed by thermogravimetric analysis (TGA, DTG-60H, Shimadzu, Kyoto, Japan). The silica compositions (wt%) of G0 nanoparticles were estimated by the residual weight of the nanoparticles after heating to 1000 °C, in which all the organic moiety decomposed. Based on the silica and APTES compositions of the G0 nanoparticles, the DABA composition (diaminophenyl amide moiety) of the G1 and G2 nanoparticles were also estimated by the TGA measurements.

MMMs composed of the surface-modified silica nanoparticles and FPI were prepared by a solvent casting method. A typical procedure is as follows: First, an appropriate amount of the surface-modified silica nanoparticles (10 or 20 wt% vs. total MMMs) were dispersed in THF by ultrasonication for 1 h. FPI (2.5 wt% vs. THF) was added to the suspension and stirred for 24 h at room temperature. The FPI/nanoparticle mixture solution was cast into a petri dish, and the solvent was slowly evaporated in a vacuum oven at 40 °C for 4 h. After cooling, the MMM was peeled from the petri dish and was further dried at 80 °C for another 18 h in a vacuum oven. For comparison, the FPI membrane without nanoparticles was also prepared in a similar manner. The thicknesses of the obtained membranes were in the range of 30-50 μm.

Gas permeability measurements were performed on a series of MMMs with pure gases (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>) at 35 °C and 76 cmHg using a differential pressure type high vacuum apparatus (Rika Seiki, Inc., K-315-H, Tokyo, Japan). The gas permeability coefficient (P), diffusion coefficient (D), and solubility coefficient (S) of the membranes were calculated from the following equations:

\[
P = DS
\]

\[
D = \frac{L^2}{6\theta}
\]

using the time lag, \(\theta\) [12].

### 3. Results and discussion

#### 3.1. Synthesis of the surface-modified silica nanoparticles

A series of surface-modified nanoparticles, which were composed of non-porous silica nanoparticles with 10-15 nm diameters and aromatic dendritic structures conjugated to nanoparticle surface with linkers, were synthesized according to Scheme 1. As a new linker, AEAPTES was first selected along with the conventional linker, APTES, to discuss the influence of the linker length on gas permeation.

<table>
<thead>
<tr>
<th>Silica / wt%</th>
<th>Linker / wt%</th>
<th>DABA / wt%</th>
<th>DABA/Linker</th>
</tr>
</thead>
<tbody>
<tr>
<td>APTES&lt;sub&gt;100&lt;/sub&gt;(G0)</td>
<td>89.3</td>
<td>10.7</td>
<td>0.0</td>
</tr>
<tr>
<td>APTES&lt;sub&gt;100&lt;/sub&gt;(G1)</td>
<td>74.9</td>
<td>9.0</td>
<td>16.1</td>
</tr>
<tr>
<td>APTES&lt;sub&gt;50&lt;/sub&gt;(G0)</td>
<td>95.3</td>
<td>4.7</td>
<td>0.0</td>
</tr>
<tr>
<td>APTES&lt;sub&gt;50&lt;/sub&gt;(G2)</td>
<td>78.6</td>
<td>3.9</td>
<td>17.5</td>
</tr>
<tr>
<td>AEAPTES&lt;sub&gt;100&lt;/sub&gt;(G0)</td>
<td>87.6</td>
<td>12.4</td>
<td>0.0</td>
</tr>
<tr>
<td>AEAPTES&lt;sub&gt;100&lt;/sub&gt;(G1)</td>
<td>79.2</td>
<td>11.2</td>
<td>9.6</td>
</tr>
<tr>
<td>AEAPTES&lt;sub&gt;50&lt;/sub&gt;(G0)</td>
<td>93.1</td>
<td>6.9</td>
<td>0.0</td>
</tr>
<tr>
<td>AEAPTES&lt;sub&gt;50&lt;/sub&gt;(G2)</td>
<td>80.5</td>
<td>6.0</td>
<td>13.5</td>
</tr>
</tbody>
</table>
properties of the MMMs. In addition, in order to investigate the effect of the linker density, silica nanoparticles modified with APTES or AEAPTES with low modification densities were also prepared by controlling the feeding amounts of the linkers on the surface-modification reactions. The progress of the surface-modification reaction was quantitatively analyzed by the TGA measurement.

As shown in Table 1, the surface-modified nanoparticles prepared by using an excess amount of APTES or AEAPTES comprehended 10.7 or 12.4 wt% of organic moieties, respectively, indicating that the surface of nanoparticles was fully modified with the linker molecules. Here we name these nanoparticles APTES100(G0) and AEAPTES100(G0). On the other hand, the nanoparticles modified with 50 mol% APTES or AEAPTES showed 4.7 or 6.9 wt% of organic moieties, denoting these nanoparticles as APTES50(G0) and AEAPTES50(G0), respectively.

Then, the aromatic dendritic structures were introduced onto the G0 nanoparticles. The first-generation (G1) silica nanoparticles, APTES100(G1), APTES50(G1), AEAPTES100(G1), and AEAPTES50(G1), were synthesized by the condensation reaction of the surface amino groups of the corresponding G0 nanoparticles with 3,5-diamino benzoic acid (DABA). The APTES50(G1) and AEAPTES50(G1) nanoparticles were further reacted with DABA to obtain the second-generation (G2) silica nanoparticles, APTES50(G2) and AEAPTES50(G2), respectively. The progress of each surface modification reaction was similarly analyzed by TGA. The molar ratios of DABA per linker (APTES or AEAPTES) on the G1 and G2 nanoparticles were calculated from the composition of APTES and DABA (Table 1). Each G1 and G2 nanoparticle showed reasonable DABA/linker ratios (relatively close values to 1 and 3 for G1 and G2 nanoparticles, respectively). These results indicate that the modification of DABA proceeded successfully, although some amino groups remained unreacted, maybe due to the steric hindrance on the surface of nanoparticles.

3.2. Fabrication of MMMs

FPI that is known as its high CO2 permeability and moderate permselectivity was selected for the polymer matrix [10-12]. The polycondensation reaction of 6FDA and 3MPA yielded the target FPI with high molecular weight and narrow molecular weight distribution ($M_w = 4.9 \times 10^5$, $M_w/M_n = 1.8$, calibrated with the standard polystyrene samples).

According to our previous study [12], all the MMMs composed of FPI and a series of surface-modified nanoparticles were obtained as defect-free dense membranes by the solvent-cast method. To investigate the effect of nanoparticle contents in MMMs on gas permeation properties, MMMs containing 10 or 20 wt% surface-modified nanoparticles were fabricated.

3.3. Gas permeation properties of the MMMs

Gas permeation properties of the MMMs were measured by the differential pressure method. The CO2 permeability coefficient ($P_{CO2}$), diffusion coefficient ($D_{CO2}$), solubility coefficient ($S_{CO2}$), and their selectivity against nitrogen ($P_{CO2}/P_{N2}$, $D_{CO2}/D_{N2}$, and $S_{CO2}/S_{N2}$) of the MMMs are summarized in Table 2. The $P_{CO2}$ and $P_{CO2}/P_{N2}$ of the original FPI were 610 barrer ($1 \times 10^{-10}$ [cm3(STP)cm / (cm2 sec cmHg)]) and 20, respectively (Table 2, run 1), which were good agreement with the values reported in the previous paper [12]. As apparent from Table 2, all

<table>
<thead>
<tr>
<th>run</th>
<th>membrane</th>
<th>$P_{CO2}$</th>
<th>$P_{CO2}/P_{N2}$</th>
<th>$D_{CO2}$</th>
<th>$D_{CO2}/D_{N2}$</th>
<th>$S_{CO2}$</th>
<th>$S_{CO2}/S_{N2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FPI</td>
<td>610</td>
<td>20</td>
<td>13</td>
<td>1.3</td>
<td>45</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>FPI / APTES100(G1) 10wt%</td>
<td>770</td>
<td>19</td>
<td>18</td>
<td>1.2</td>
<td>42</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>FPI / APTES100(G1) 20wt%</td>
<td>1000</td>
<td>18</td>
<td>26</td>
<td>0.9</td>
<td>39</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>FPI / APTES50(G2) 10wt%</td>
<td>840</td>
<td>19</td>
<td>19</td>
<td>1.4</td>
<td>43</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>FPI / APTES50(G2) 20wt%</td>
<td>1100</td>
<td>18</td>
<td>25</td>
<td>1.1</td>
<td>45</td>
<td>16</td>
</tr>
<tr>
<td>6</td>
<td>FPI / AEAPTES100(G1) 10wt%</td>
<td>690</td>
<td>19</td>
<td>18</td>
<td>1.0</td>
<td>38</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>FPI / AEAPTES100(G1) 20wt%</td>
<td>770</td>
<td>18</td>
<td>19</td>
<td>1.1</td>
<td>40</td>
<td>16</td>
</tr>
<tr>
<td>8</td>
<td>FPI / AEAPTES50(G2) 10wt%</td>
<td>770</td>
<td>20</td>
<td>15</td>
<td>1.1</td>
<td>50</td>
<td>17</td>
</tr>
<tr>
<td>9</td>
<td>FPI / AEAPTES50(G2) 20wt%</td>
<td>1100</td>
<td>18</td>
<td>30</td>
<td>1.0</td>
<td>37</td>
<td>19</td>
</tr>
</tbody>
</table>

$P = 1 \times 10^{-10}$ [cm3(STP)cm / (cm2 sec cmHg)], $D = 1 \times 10^{-8}$ (cm2 / sec), $S = 1 \times 10^{-2}$ [cm3(STP) / cm3 cmHg]
the MMMs containing the surface-modified nanoparticles showed higher CO₂ permeability than the original FPI membrane with maintaining their permselectivity. In addition, all the MMMs containing higher particle contents (20 wt%) showed higher permeability coefficients than the corresponding lower ones (10 wt%).

The gas permeability (P) is known to be determined by the product of gas diffusivity (D) and gas solubility (S). All the MMMs showed higher $D_{\text{CO}_2}$ values than the FPI membrane, although the $S_{\text{CO}_2}$ values were almost constant among the FPI membrane and MMMs (Table 2). That is to say, the enhancement of $P_{\text{CO}_2}$ on MMMs was mainly originated from the improvement of gas diffusion properties by introducing the surface-modified nanoparticles. These results suggested that the surface-modified nanoparticles had high gas permeable spaces on the nanoparticle surfaces. We discuss the influence of surface-modification structures on the gas permeation properties of the MMMs.

First, here focuses on the differences between APTES and AEAPTES as linkers. The $P_{\text{CO}_2}$ of FPI / AEAPTES₁₀₀(G₁) 10 wt% (Table 2, run 6) and 20 wt% (run 7) were 690 and 770 barrer, respectively. These permeabilities were lower than those of the corresponding APTES-type MMMs (run 2 and 3, $P_{\text{CO}_2} = 770$ and 1000 barrer for FPI / APTES₁₀₀(G₁) 10 wt% and 20 wt%, respectively), although the permselectivities of all the MMMs were almost equal ($P_{\text{CO}_2}/P_{\text{N}_2} = 18-19$).

A similar tendency was observed in the pair of FPI / AEAPTES₅₀(G₂) 10 wt% and FPI / AEAPTES₅₀(G₂) 10 wt% (run 4 and 8). Contrary to the expectations that the longer linker, AEAPTES, can form larger high gas permeable spaces than the conventional short APTES linker, the MMMs containing AEAPTES-based surface-modified nanoparticles showed lower gas permeabilities than the conventional short APTES linker, the MMMs containing AEAPTES-based surface-modified nanoparticles showed lower gas permeabilities. This may be derived from the flexibility of the long linker molecule that could be hard to hold vertical elongated chain structures on the surface of nanoparticles.

Next, the influence of the linker density on gas permeation properties is discussed by comparing FPI / APTES₁₀₀(G₁) and FPI / APTES₅₀(G₂), in which APTES₁₀₀(G₁) and APTES₅₀(G₂) had different linker densities but had similar compositions of DABA as shown in Table 1. The $P_{\text{CO}_2}$ of FPI / APTES₅₀(G₂) 10 wt% and 20 wt% (Table 2, run 4 and 5) were 840 and 1100 barrer, which were higher than those of the corresponding MMMs with low APTES densities (run 2 and 3, $P_{\text{CO}_2} = 770$ and 1000 barrer for FPI / APTES₁₀₀(G₁) 10 wt% and 20 wt%, respectively). In the same manner, the AEAPTES₅₀(G₂) nanoparticles gave higher CO₂ permeabilities on the MMMs (Table 2, run 8 and 9) than the AEAPTES₁₀₀(G₁) nanoparticles (run 6 and 7).

Based on these results, it is considered that lower linker densities formed more high gas-permeable spaces on the surface of the nanoparticles to improve the gas permeability of the MMMs.

4. Conclusion

Novel surface-modified nanoparticles were synthesized to discuss the influence of modification structures on the gas permeation properties of the MMMs. The MMMs containing nanoparticles modified with the long linker, AEAPTES, showed lower CO₂ permeability than those with the short APTES linker. The decrease of linker density had some positive effects on the gas permeation. The length and density of the linker molecules on the nanoparticle surfaces influenced on the gas permeability of the MMMs; however, these effects were limited and other parameters, such as nanoparticle contents and generation of the aromatic dendritic moieties, influenced more drastically on the gas permeation properties. Based on this study, we are now working on the fabrication and characterization of MMMs with higher nanoparticle contents or higher modification generations.

Acknowledgment

This work was partially supported by a grant (No. P14004) from NEDO and JSPS KAKENHI Grant No. JP25281040.

References

8. M. A. Aroon, A. F. Ismail, T. Matsuda, and M.

