Gas Permeable Mixed Matrix Membranes Composed of a Polymer of Intrinsic Microporosity (PIM-1) and Surface-modified Pearl-necklace Silica Nanoparticles: Effect of Expansion of Nano-space on Gas Permeability

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Gas permeable mixed matrix membranes (MMMs) based on a polymer of intrinsic microporosity (PIM-1) was studied focusing on the effect of the expansion of nano-space formed by surface modification on non-porous silica nanoparticles on gas permeability. The silica nanoparticles modified with different generations dendritic moieties were successfully synthesized and characterized by FT-IR and TGA measurements. The CO₂ permeability of the MMMs significantly increased with an increase of loading of the particles and addition of the particles with high modification ratio was more effective in improving gas permeability. The expansion of nano-space formed by the surface modification on silica nanoparticles would improve gas diffusion coefficient in MMMs. This was supported by the correlation between the diffusion coefficient in the MMMs and the peaks observed by ¹²⁹Xe NMR spectroscopy.

Keywords: Mixed matrix membrane, Surface modification, Silica particle, PIM-1, Gas permeability, Xe NMR

1. Introduction

Controlling CO₂ emissions is an urgent issue as a countermeasure against global warming, and practical application of CO₂ capture and storage (CCS) would be one of the most important approaches [1]. Since energy consumption of CO₂ separation process from emission sources is quite large, improving the efficiency of the separation process is one of the issues for practical use of CCS. Therefore, development of a gas separation membrane with excellent energy efficiency is eagerly desired. However, it is known that there is a trade-off relationship between gas permeability and gas selectivity of gas separation membranes [2]. Numerous polymer membrane studies suggested that it would be difficult to overcome this relationship. In recent years, studies on mixed matrix membranes (MMMs) composed of inorganic materials and polymer materials have been conducted.

MMMs containing porous materials, such as zeolite [3–6] and metal organic frameworks (MOF) [7,8], have been studied to improve gas permeability and gas selectivity. Several studies have succeeded in developing gas permeation properties exceeding Robeson's upper bound [9,10]. On the other hand, it has been reported that MMMs with non-porous particles have also improved gas permeability [11–13]. Regardless of the type of porous and non-porous particles used, the addition of low-concentration particles improved gas permeability of the MMMs, while the addition of high-concentration particles caused particle aggregation, resulting in a significant decrease in gas selectivity of the MMMs [6,12].

We have succeeded in significantly improving gas permeability without decreasing CO₂/N₂ selectivity by adding surface-modified non-porous silica nanoparticles to a polymer of intrinsic microporosity (PIM-1) [14,15]. PIM-1 is a...
spirobisindane ladder-type polymer as shown in Fig. 1, with rigid polymer backbone and large free volume elements, and is frequently used as a matrix for MMMs. As mentioned above, however, increasing the particle concentration in MMMs causes a significant decrease in gas selectivity of MMMs. The gas selectivity was maintained in the MMMs we developed, even when the particle concentration was high. We believe that the organic moiety modified on the nanoparticle surface acts as a high gas permeation path with gas selectivity. Furthermore, the MMMs using surface-modified pearl-necklace silica nanoparticles showed a significant improvement in gas permeation properties, because particles with shape anisotropy created effective gas transport channels [15]. As shown in Fig. 2, the space formed by the modification is defined as “nano-space”. The expansion of the nano-space as shown in Fig. 2 would improve gas permeation characteristics of MMMs. In this study, the effect of expansion of the nano-space caused by increasing the number of generations of surface modification on gas permeation characteristics of MMMs was studied using pearl-necklace silica nanoparticles.

2. Experimental

All reagents were purchased from commercial sources and used as received without any mention. Non-porous pearl-necklace-like silica nanoparticle (SNOWTEX® ST-PS-SO) was provided from Nissan Chemical Corporation (Tokyo, Japan). The particle size of SNOWTEX® ST-PS-SO was estimated to be 92 nm (D1) by dynamic light
scattering method and 15 nm (D2) by nitrogen adsorption method. Particle size ratio D1 / D2 = 6.1 reflects shape anisotropy of the particles [15]. (3-Aminopropyl)triethoxysilane (APTES), 3,5-diaminobenzoic acid (DABA), and 1H-benzotriazol-1-yl-oxytris(dimethylamino) phosphonium hexafluorophosphate (BOP) were purchased from Sigma-Aldrich Co. (St. Louis, MO, United States). Potassium carbonate, triethylamine (TEA), anhydrous aluminum chloride (AlCl3), 5,5',6,6'-Tetrahydroxy-3,3',3'-tetramethyl-1,1'-spirobiindan (TTSBI) with a purity of 96% was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and was purified by recrystallization. Deionized and distilled water was obtained using a water purifier (WG250, Yamato Scientific Co., Tokyo, Japan).

Polymer of intrinsic microporosity, PIM-1, was prepared according to the literatures [16,17]. Synthesis of PIM-1 was characterized by 1H NMR spectroscopy (AVANCE III 500, Bruker BioSpin K.K.). The number-average molecular weight (Mn) and weight-average molecular weight (Mw) were estimated with polystyrene standards by gel-permeation chromatography (detector: UV-2075, JASCO Co., Tokyo, Japan) using a Shodex KF-805L column with an eluent of THF at a flow rate of 1.0 mL min⁻¹.

Surface-modified silica nanoparticles were prepared by APTES modification step and DABA modification steps (Scheme 1) as previously reported [15]. The APTES-modified particles are represented as G0. G1 and G2 represent the first generation DABA modified particles and the second generation DABA modified particles, respectively. The surface-modified silica nanoparticles were characterized by thermogravimetric analysis (TGA, STA7000, Hitachi High-Tech Science, Tokyo, Japan) and Fourier transform infrared spectroscopy (FT-IR, 6100V, JASCO, Tokyo, Japan).

3. Results and discussion
3.1. Characterization of surface-modified silica nanoparticles
The surface modification on silica nanoparticles was confirmed using FT-IR spectroscopy. The changes in the FT-IR spectrum due to the surface modification were similar to those reported previously [15]. Figure 3 shows an enlarged...
spectrum of the part where the change due to modification can be most clearly confirmed. In the spectrum for G0 that is the APTES–modified silica nanoparticles, a peak at 1480 cm\(^{-1}\), which is assigned to the NH\(_2\) deformation mode of the amine group [18], could be observed. The presence of amine groups provides proof of successful APTES modification. Furthermore, when comparing the G1 spectra with the G0 spectrum, differences in absorbance and peak positions were observed. The peak at 1547 cm\(^{-1}\) and the shoulder observed around 1600 cm\(^{-1}\) suggest the presence of a phenylamine group or an aromatic ring [19]. In addition, the increase in absorbance at 1630 cm\(^{-1}\) assignable to the C=O stretching mode indicates the formation of an amide bond between the amine group of APTES and the carboxylic acid group of DABA. The spectrum of G2 was basically the same as that of G1 except for the intensity ratio.

Figure 4 shows the TGA curves of G0, G1 and G2. The weight loss ratios of G0, G1, and G2 after heating to 1000 °C were 6.2, 11.0 and 36.4 wt%, respectively. The modification ratio of APTES to the hydroxyl group on the unmodified pearl-necklace shape silica nanoparticles was calculated to be [APTES]/[OH] = 0.67 (mol/mol). This value was higher compared to our previous report [15].

The modification ratio of DABA of G1 and G2 was estimated to be [DABA]/[APTES] = 0.37 and 3.16 (mol/mol), respectively. The modification ratio of G2 is sufficiently large compared to that of G1. This means that the nano-space formed by the organic moiety was successfully expanded in G2. No change in particle shape due to the surface modification process for G1 production have been reported [15]. Therefore, we believe that shape anisotropy of the silica nanoparticle is maintained in G2, because G2 production process is the same as G1 production process.

### 3.2. Fabrication of MMMs

The surface of all MMMs obtained was smooth. The MMMs containing 30 wt% of particles were translucent and light brown. The color is attributed to surface-modified nanoparticles and the slight turbidity signifies the presence of aggregates of submicron particles. Some distortion was observed in the MMMs containing 30 wt% of particles, but there was no particular problem with all measurements.

Figure 5 shows typical cross-sectional SEM images of PIM-1 and the MMMs. These SEM images reveal that all the membranes were dense.
without any identifiable voids. Aggregation of particles could not be clearly confirmed in the MMM with G1 and G2. High surface modification ratio would have improved the dispersibility of particles in PIM-1 and suppressed the formation of large aggregates.

3.3. Gas permeation properties of MMMs

Gas permeability and selectivity for N\textsubscript{2} and CO\textsubscript{2} of the MMMs were summarized in Table 2. The permeability of the gases increased with the addition of the surface-modified silica nano particles. This was a similar trend to results of the MMMs containing G1 reported [15]. Compared to the previously reported results, this value was slightly smaller. There are two possible reasons for this. First, the gas permeability of PIM-1 as a matrix was different due to the different molecular weight and molecular weight distribution. The second is that the modification ratio of the surface-modified particles was different.

Furthermore, the gas permeability of the MMM containing G2 was higher than that of the MMM containing G1 at higher loading. This suggests that addition of G2 with expanded organic moiety is more effective in increasing gas permeability of the MMMs. In the low particle concentration, the effect of the nano-space was limited. PIM-1 synthesized in this study showed an extremely high gas permeability ($P_{CO2} = 4520$ Barrer). This value is larger than that of MMM containing G1 of 10 wt% reported previously [15]. The high gas permeability of this matrix relatively reduces the gas permeability of the particles. As a result, differences between G1 and G2 might be difficult to observe in a small amount of addition.

It is important to emphasize that the nanoparticle loading significantly increased the gas permeabilities in the MMMs without a significant decrease in selectivity. If the gas permeable nano-space has not gas selectivity, then the gas selectivity in MMMs would be greatly reduced when the particle concentration is high. In addition,

Table 2. Gas permeability and selectivity $\alpha$ of MMMs composed of surface-modified silica nanoparticles, at 35 °C and 1 atm.

| Loading/ wt% | $P_{N2}$ / Barrer | $P_{CO2}$ / Barrer | $\alpha$ ($P_{CO2}$/ $P_{N2}$) |
|-------------|-----------------|-----------------|-----------------|
| PIM-1       | 0               | 249             | 4520            |
|             | 10              | 326             | 4980            |
| PIM-1/G1    | 30              | 440             | 6196            |
|             | 10              | 317             | 5040            |
| PIM-1/G2    | 30              | 563             | 8090            |

$1$ Barrer $= 1 \times 10^{-10}$ cm$^3$ (STP) cm/(cm$^2$ s cmHg).
expansion of nano-space did not reduce gas selectivity in the MMMs.

Gas permeation in non-porous membranes is explained by a dissolution-diffusion model. The gas permeability $P$ is expressed as follows:

$$P = S \cdot D$$  \hspace{1cm} (3)

where, $S$ is solubility coefficient and $D$ is diffusion coefficient. The $D$ value could be evaluated by the time lag method, and the $S$ value was obtained by dividing the $P$ value by the $D$ value. Figure 6 shows the dependence of CO$_2$ diffusion coefficient and solubility coefficient of the MMMs on the particle loading. The $D$ value increased with the addition of the particles. Furthermore, the addition of G2 particles increased the diffusion coefficient more than that of G1 particles, suggesting that the diffusion of gas was improved by the expansion of the nano-space. On the other hand, the solubility coefficient decreased slightly with the addition of particles. Since silica nanoparticles do not dissolve CO$_2$, the solubility coefficient of CO$_2$ in MMMs decreases with the addition of silica particles [20]. The surface density of amine group increases as the surface modification generation from G1 to G2. However, no difference was observed in the solubility coefficient of CO$_2$ in the MMMs containing G1 and G2. This suggests that the nano-space has little effect on solubility of gas but improves diffusivity of gas in the MMMs.

### 3.4. Relationship between diffusion coefficient and nano-space

$^{129}$Xe NMR spectroscopy is used to estimate an average pore size in membranes and helps understanding of gas permeation properties for many polymer membrane and MMMs [21–24]. On the other hand, the chemical shift of $^{129}$Xe adsorbed in a zeolite used as a probe in the sum of several terms characteristic of the various factors such as a crystallinity and an electric field in cavities [25]. We have reported that the peak shape in $^{129}$Xe NMR spectrum of PIM-1 with added particles was asymmetric [15]. A broad peak has been observed in low magnetic field for the peak of the original PIM-1. The new broad peak would originate in the space affected by the nanoparticlees in MMMs, which include nano-space formed by the surface modification of the nanoparticles [15].

In this study, increasing the ratio of surface modification from G1 to G2 increased the diffusion

![Fig. 7. $^{129}$Xe NMR spectrum of PIM-1 membrane at the Xe pressure of 0.3 MPa.](image-url)

![Fig. 8. Enlarged spectra of PIM-1 and MMMs containing G2 particles. The black line represents the original spectrum and the red line shows the result of peak deconvolution analysis by Lorentzian function.](image-url)
coefficient, leading improvement of gas permeability of the MMMs. If expansion of nano-space contributes to improvement of gas diffusivity, there would be a correlation between the new peak area of $^{129}$Xe NMR spectra and the diffusion coefficient in MMMs.

Figure 7 shows $^{129}$Xe NMR spectrum of the PIM-1 original membrane at 0.3 MPa of Xe. In Fig. 7, two distinct peaks were observed in the spectrum. The peak observed in high magnetic field was assigned to free Xe in the NMR tube and the peak observed in low magnetic field was assigned to Xe sorbed in the membrane [22]. The peak derived from free Xe gas in an NMR tube is used as a reference. In the spectrum of PIM-1, a single peak was observed at 182 ppm as reported by Emmler et. al [22].

Figure 8 shows the enlarged-spectra around the peak assigned to sorbed Xe in the original PIM-1 and the MMMs. The reference for chemical shift has been changed to the sorbed Xe peak to make it easier to compare peak shapes. A single Lorentzian peak was observed in the original PIM-1 and a shoulder was observed in low magnetic field in the NMR spectrum of the MMMs. We could deconvolute the peaks of the NMR spectra shown in Figure 8 and assigned higher field peak to sorbed Xe in PIM-1 as a matrix and lower field peak to sorbed Xe in the space affected by the nanoparticles [15]. The peak area observed in low magnetic field increased with increasing particle loading. This tendency is similar to the trend of diffusion coefficient with particle addition.

Figure 9 shows the relationship between diffusion coefficient and the area of the peak assigned to the region affected by the nanoparticles in $^{129}$Xe NMR spectrum. The diffusion coefficient was positively correlated with the peak area regardless of the type of particles added. This suggests that the space affected by the addition of nanoparticles has a high diffusion coefficient and the expansion of nano-space contributes to the expansion of the space with high gas diffusivity.

4. Conclusion

Gas permeation properties of composite membranes containing non-porous silica nanoparticles surface-modified with rigid organic moiety were studied. Silica nanoparticles with different surface modification ratio were synthesized, and the MMMs could be successfully fabricated by a solvent casting method. Increasing the surface modification ratio increased the gas permeability of the MMMs without impairing gas selectivity. The improvement in the permeability of MMMs was due to an increase in the diffusion coefficient. $^{129}$Xe NMR spectroscopy revealed environmental changes in the MMMs by adding surface-modified particles. The correlation between the diffusion coefficient of the MMMs and the area of newly observed peak in $^{129}$Xe NMR spectra of the MMMs was confirmed. This supported the formation of the nano-space with excellent diffusivity. The expansion of the nano-space would be an effective means to improve gas diffusion in MMMs.

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