Influence of Chemical Modification on CO2 Permeability of Polymers of Intrinsic Microporosity / Silica Nanoparticles Composite Membranes

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High gas permeable polymer membranes are required to achieve carbon dioxide capture and storage with high efficiency. In this study, novel mixed matrix membranes (MMMs) based on a chemically modified polymer of intrinsic microporosity and silica nanoparticles were fabricated, and their gas permeation properties were evaluated. The methyltetrazole-modified polymer of intrinsic microporosity (MTZ-PIM) showed higher CO2/N2 selectivity than the pristine PIM membrane, and their composite membrane with the surface-modified silica nanoparticles achieved improved CO2 permeability and good selectivity.

Keywords: Carbon dioxide, Gas separation, Mixed matrix membrane, Polymers of intrinsic microporosity, Silica nanoparticle

1. Introduction
Carbon dioxide capture and storage (CCS) technology has been strongly desired to reduce CO2 emissions and to prevent global warming [1]. CO2 separation is one of the most important processes in CCS technology. Polymer membrane-based gas separation process with low cost, low energy consumption, and simple operation is more effective than the conventional chemical or physical CO2 adsorption methods [2,3]. In order to realize the CCS with gas separation membranes, many efforts have made to improve the CO2 permeability of membranes by synthesizing novel polymers or fabricating newly structured membranes [4].

Mixed Matrix Membranes (MMMs) consisting of polymer and nano-sized additives have been actively studied for gas separation to improve the gas permeability and/or selectivity [5-7]. In our previous study, we synthesized silica nanoparticles bearing aromatic dendritic structures on the nanoparticle surface to form a high gas permeable pathway. The MMMs composed of high CO2 permeable fluorinated polyimide (FPI) [8,9] or polymers of intrinsic microporosity (PIM-1) [10] and the surface-modified nanoparticles showed enhanced CO2 permeability with maintaining their selectivity (e.g., CO2/N2 selectivity) [11-13].

In this study, a new polymer, methyltetrazole-modified polymer of intrinsic microporosity (MTZ-PIM), was attempted as the polymer matrix for the MMMs to achieve good CO2 separation performance (Fig. 1). It is reported that the MTZ-PIM membrane showed higher CO2/N2 selectivity due to the interaction among the MTZ groups [14]. In addition, the MTZ-PIM is known to show better resistance against the aging process that often becomes a significant issue of PIMs to decline their permeability over time. The novel MMMs using MTZ-PIM are expected to achieve not only high CO2 permeability by the high gas permeable surface-modified nanoparticles but also good CO2/N2 selectivity.
due to the MTZ moieties in the matrix polymer.

Fig. 1. The concept of this study: Fabrication and gas permeability evaluation of MMMs composed of MTZ-PIM and the surface-modified silica nanoparticles.

2. Experimental

3,3′,3′-Tetramethyl-1,1′-spirobiindan-5,5′,6,6′-tetroil (TMSBT) and tetrafluoro terephthalonitrile (TFTPN) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and were purified by recrystallization and sublimation, respectively. 3-Aminopropyl triethoxysilane (APTES), and 1H-benzotriazol-1-ylxytris (dimethylamino) phosphonium hexafluoro phosphate (BOP) were purchased from Tokyo Chemical Industry. 3,5-Diaminobenzoic acid (DABA) was purchased from Aldrich (St. Louis, United States). Sodium azide, zinc chloride, potassium carbonate, methyl iodide, hydrochloric acid (HCl), triethylamine (TEA), N-methyl-2-pyrrolidone (NMP), N,N-dimethyl acetamide (DMAc), and tetrahydrofuran (THF) were purchased from Kanto Chemical (Tokyo, Japan). Silica nanoparticles with 10-15 nm diameters were provided by Nissan Chemical Corporation. All the chemicals were used as received unless otherwise specified.

PIM-1 was synthesized by polycondensation of TMSBT and TFTPN according to the literature [10] and characterized by 1H NMR (Bruker AVANCE III 500; (CDCl3, δ in ppm) 6.8 (s, 2H, Ph), 6.5 (s, 2H, Ph), 2.3 (br, 4H, -CH2-), 1.3 (s, 12H, -CH3). MTZ-PIM was also synthesized based on the paper [14]. A typical synthetic procedure of MTZ-PIM is as follows: First, in a 500 mL three-neck round bottom flask, PIM-1 (0.92 g, 2.0 mmol), DMAc (200 mL), sodium azide (1.04 g, 16.0 mmol), and zinc chloride (1.09 g, 8.0 mmol) were added and stirred at 120 °C for 8 days. After the reaction, diluted HCl was added to obtain a solid precipitate, which was subsequently filtered and washed with diluted HCl, water, and acetone. After drying under vacuum, the crude product (0.49 g, 0.9 mmol) was dissolved in DMAc (20 mL), and potassium carbonate (0.74 g, 5.4 mmol) and methyl iodide (0.77 g, 5.4 mmol) were added. The solution was stirred at 120 °C for 24 hours. A diluted HCl was added and stirred at 70 °C for 1 hour to precipitate solid. The solid was filtered and washed with diluted HCl, water, and acetone. After drying under vacuum at 120 °C for 24 hours, MTZ-PIM was obtained as a brown powder. Characterizations of the polymers were

Scheme 1. Synthesis of the PIM-1 and MTZ-PIM.
performed by \(^1\)H NMR spectroscopy ((CDCl\(_3\), \(\delta\) in ppm) 6.5 (s, 2H, Ph), 6.1 (s, 2H, Ph), 4.5 (br, 3H, -CH\(_3\)), 4.1 (br, 3H, -CH\(_3\)), 2.2 (br, 4H, -CH\(_2\)-), 1.3 (s, 12H, -CH\(_3\))) and gel-permeation chromatography (GPC, detector: JASCO 860-RI monitor) using Shodex SB-806HQ and SB-804HQ columns.

The surface-modified silica nanoparticles (NP) were obtained according to the previous papers [11-13]. The surface of nanoparticles was first modified with APTES and was reacted with DABA. The modification ratio was estimated by thermogravimetric analysis (TGA, DTG-60H, Shimadzu, Kyoto, Japan). The weight percent of the organic component in NP was determined to be 89 wt%.

MMMs composed of the surface-modified silica nanoparticles and MTZ-PIM were prepared by a solvent casting method. A typical procedure is as follows: First, an appropriate amount of the DABA-modified silica nanoparticles (NP, 10 or 15 wt% vs. total MMMs) were dispersed in THF by ultrasonication for 1 h. MTZ-PIM (2.5 wt% vs. THF) was added to the suspension and stirred at room temperature for 24 h. The MTZ-PIM/NP mixture suspension 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 MTZ-PIM/NP membrane was peeled from the petri dish and was further dried at 80 °C for another 18 h in a vacuum oven. For comparison, an MTZ-PIM membrane without nanoparticles and a PIM-1/NP membrane were also prepared in a similar manner. The thicknesses of the obtained membranes were in the range of 30-50 \(\mu\)m. The tensile test was performed by a precision universal tester (AGS-X5kN, Shimadzu) at 25 °C and 60% RH.

The gas permeability of the MMMs was measured on a series with pure gasses (\(N_2\), \(O_2\), \(CO_2\), \(CH_4\)) 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:

\[
P = D S
\]

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

using the time lag, \(\theta\)[11].

3. Results and discussion

3.1. Synthesis of MTZ-PIM and the surface-modified silica nanoparticles

PIM-1 is known as its high CO\(_2\) permeability and has been actively studied as the polymer matrix for gas separation [10]. The chemical modification of nitrile groups into MTZ group was reported to improve the selectivity and membrane stability. Both PIM-1 and MTZ-PIM were synthesized according to the literatures [10, 13] and were obtained with high molecular weights (PIM-1: \(M_n=328,000\), \(M_n/M_n=10.6\), MTZ-PIM: \(M_n=454,000\), \(M_n/M_n=8.6\) after purification. The \(^1\)H NMR spectroscopy revealed the successful synthesis of PIM-1 and MTZ-PIM with the expected chemical structures, where the nitrile groups of the PIM-1 were quantitatively converted to the MTZ groups.

The surface-modified silica nanoparticle (NP) was successfully obtained according to our previous study [11-13]. The progress of the surface-modification reaction was analyzed by the TGA measurement to reveal that the DABA was reacted with the APTES groups with the modification ratio [DABA]/[APTES] = 0.81 on the nanoparticle surface.

3.2. Fabrication of MMMs

According to our previous study [13], the MMMs composed of MTZ-PIM and the surface-modified nanoparticles were obtained as

![Fig. 2. Photographs of (left) PIM-1, (center) MTZ-PIM, and (right) MTZ-PIM/NP (10 wt%).](image)
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 15 wt% surface-modified nanoparticles were fabricated. Although higher particle contents, such as 20 and 30 wt%, were attempted for the MMMs, the membranes were too brittle to handle and evaluate their permeability. Figure 2 shows the photographs of the PIM-1, MTZ-PIM, and MTZ-PM/NP (10 wt%). All of them showed good membrane formability. The mechanical strength of the membranes was evaluated by the tensile tests. The MTZ-PM/NP (10 wt%) membrane showed higher maximum stress and Young’s modulus, and lower elongation at break (47 MPa, 390 MPa, and 1.7%, respectively) than the MTZ-PIM membrane (29 MPa, 340 MPa, and 3.7%, respectively). It is considered that incorporation of the surface-modified nanoparticles into the polymer matrix could enhance the mechanical strength because of the rigid characteristics of the silica nanoparticles themselves and the high affinity to form a dense interface between the nanoparticle and the polymer matrix.

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 PIM-1, MTZ-PIM, MTZ-PIM/NP membranes at 35 °C and 76 cmHg are summarized in Table 1. The $P_{CO2}$ and $P_{CO2}/P_{N2}$ of the PIM-1 were 2900 Barrer ($1 \times 10^{-10}$ [cm³(STP)cm / (cm² sec cmHg)]) and 19, respectively (Table 1, run 1), which were reasonable values compared to the previous paper [10]. The MTZ-PIM showed lower permeability and higher selectivity ($P_{CO2} = 1360$ Barrer and $P_{CO2}/P_{N2} = 23$) than the PIM-1 membrane, indicating the MTZ groups affected the packing and free volume of the membrane. As apparent from Table 1, the MMMs containing the surface-modified nanoparticles showed higher CO₂ permeability than the pristine MTZ-PIM membrane with maintaining their selectivity. In addition, the MMMs containing higher particle contents (15 wt%) showed higher permeability coefficients than the corresponding lower ones (10 wt%).

It is known that the gas permeability ($P$) is determined by the product of gas diffusivity ($D$) and gas solubility ($S$). The MMMs showed higher $D_{CO2}$ values than the MTZ-PIM membrane, although the $S_{CO2}$ values were slightly lower than the MTZ-PIM membrane (Table 1). A potential reason for the decrease of $S_{CO2}$ values on the MTZ-PIM/NP membrane could be the slight morphological (packing structural) change of the polymer matrix by the composition of the NPs. These results indicate that the enhancement of $P_{CO2}$ on MMMs was mainly originated from the improvement of gas diffusion properties by introducing the surface-modified nanoparticles. It is expected that the surface-modified nanoparticles had high gas permeable spaces on the nanoparticle surfaces. However, the CO₂ permeability enhancement was limited compared to our previous study [11-13]. It is considered that the strong interaction among the MTZ groups in the polymer matrix may disturb the formation of the continuous high gas permeable pathway. A further detailed study is required to achieve higher CO₂ permeability of the MMMs based on MTZ-PIM.

| run | membrane     | $P_{CO2}$ | $P_{CO2}/P_{N2}$ | $D_{CO2}$ | $D_{CO2}/D_{N2}$ | $S_{CO2}$ | $S_{CO2}/S_{N2}$ |
|-----|--------------|-----------|-----------------|-----------|------------------|-----------|------------------|
| 1   | PIM-1        | 2900      | 19              | 32        | 1.3              | 91        | 15               |
| 2   | MTZ-PIM      | 1360      | 22              | 20        | 1.2              | 66        | 19               |
| 3   | MTZ-PIM/NP (10 wt%) | 1570      | 22              | 29        | 1.0              | 53        | 24               |
| 4   | MTZ-PIM/NP (15 wt%) | 1630      | 20              | 29        | 1.0              | 57        | 21               |

$P = 1 \times 10^{-10}$ [cm³(STP)cm / (cm² sec cmHg)], $D = 1 \times 10^{-8}$ (cm² / sec), $S = 1 \times 10^{-2}$ [cm³(STP) / cm³ cmHg].

Table 1. 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 PIM-1, MTZ-PIM, MTZ-PIM/NP membranes at 35 °C and 76 cmHg.
higher CO$_2$ permeability (1630 barrer) than the MTZ-PIM membrane (1360 barrer). Further study has the potential to improve the gas separation performance of the MMMs.

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