

Development of Innovative Gas Separation Membranes through Sub-Nanoscale Material Control

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Abstract

New membrane types with well-controlled sub-nanostructures were developed from both polymeric and inorganic materials: carbon-based membranes, functionalized mesoporous oxide membranes and molecular sieving zeolite membranes. Regarding the carbon membranes, a novel carbon membrane with enhanced CO₂ affinity was developed. The prepared membrane had a higher separation performance than that of the original carbon membrane in the separation of CO₂/N₂ mixtures under humid conditions. In addition, a method to control the sizes of subnano/nano pores of the carbon membrane was developed. Regarding the inorganic membranes, we proposed a novel method for the synthesis of the composite layer of zeolite and the porous substrate; i.e., a melt-filling method. It was revealed that CO₂ separation selectivity increased after the treatment.

Introduction

Carbon dioxide capture and storage (CCS) could allow the utilization of abundant fossil fuel reserves, while significantly decreasing emissions of CO₂ to the atmosphere. However, the cost of CCS, especially of CO₂ capture, is still too expensive for CCS to be considered as a cost effective technique. This project intends to develop a variety of efficient, low-cost polymeric and inorganic CO₂ separation membranes as a game changing technology. Material structure engineering on the scale of gas molecules will be used to increase the permeability and selectivity of the membrane. Regarding the polymeric based materials, a cardo polymer-based carbon membrane incorporating molecules or atoms having strong CO₂ affinity has been prepared. CO₂ affinity materials will be optimized and the preparation method modified to improve the separation performance further. Regarding the inorganic materials, zeolite membranes have been prepared. The preparation of ultra-thin, defect-free membranes will be investigated.

Background

Membrane separation of CO₂ from other gases is an active field of study, but the best membrane today is still considered too energy intensive and expensive to be implemented on a large scale. Gas separation in membranes is driven by a pressure difference across the membrane. To obtain a sufficiently pure stream of CO₂, the selectivity for CO₂ must

be high. In addition, high permeability is required to produce a compact membrane facility. Many current systems require a large membrane area and cascading for the gas to permeate through multiple membrane stages to achieve the desired flow rate and purity. As such, new membrane types are required to have high permeability and selectivity, as well as long-term durability. Two areas of current gas separation membrane research are the development of polymeric and inorganic membranes. Polymeric membranes are relatively easy to manufacture and are well-suited for low temperature applications. The polymer morphology and mobility determine the gas permeability and selectivity. In addition, by carbonizing these polymeric materials it is possible to obtain a molecular sieve capability. Inorganic membranes on the other hand, have much greater thermal and chemical stability. Inorganic materials including zeolites and silicas have appropriately-sized pores that can act as molecular sieves to separate gas molecules by effective size. Surface adsorption and diffusion inside the pores can also play a role in separating gas molecules. Since the effective sizes of CO₂, N₂, H₂, and other gases present in fossil fuel conversion systems are very similar, the membrane pore spaces must be controlled on a scale comparable to the size differences among these gas molecules. This will be achieved for a variety of membrane types using several different techniques. In this paper, we describe the development of new membrane types with well-controlled sub-nanostructures prepared from both polymeric and inorganic materials: carbon-based membranes, functionalized mesoporous oxide membranes and molecular sieving zeolite membranes.

Results

(1) Carbon membrane

(1.1) Concept of the membrane structure

In the concept of molecular gate separation, originally proposed by Sirkar et al. [1], CO₂ absorbed in organic materials (e.g., the poly(amidoamine) (PAMAM) dendrimer) blocks the permeation of other permanent gases such as N₂ and H₂; thus high separation performance is obtained. So far, we have developed new dendrimer materials that have a higher separation performance than the conventional PAMAM dendrimer has [2]. In addition, we have successfully developed dendrimer composite membrane modules using this PAMAM dendrimer. These PAMAM dendrimer composite membrane modules have high CO₂ separation performance under realistic operating conditions (i.e., a pressure difference between the feed and permeate sides) [3, 4]. However, the separation performances of current dendrimer membranes were strongly dependent on the relative humidity (water uptake in the dendrimer). To control water uptake, excess water uptake should be suppressed by the porous matrix around the dendrimer.

In this project, the concept of molecular gates is applied to subnano/nano porous materials. The concept of the membrane structure for high separation performance is shown in Figure 1.

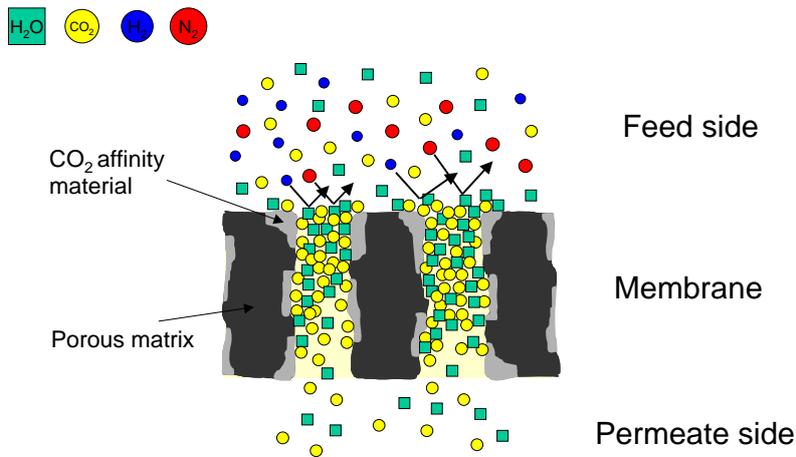


Figure 1. Concept of the membrane structure for high separation performance.

The pore surface of a subnano/nano porous material is modified with CO₂ affinity materials to produce ideal CO₂ molecular gates; i.e., high separation performance regardless of relative humidity. CO₂ affinity materials can be blended with precursor, or can be inserted into the pores of the carbon membrane. The CO₂ adsorbed in the porous material blocks the permeation of other permanent gases.

The design of the novel CO₂ affinity-enhanced carbon membrane is shown in Figure 2.

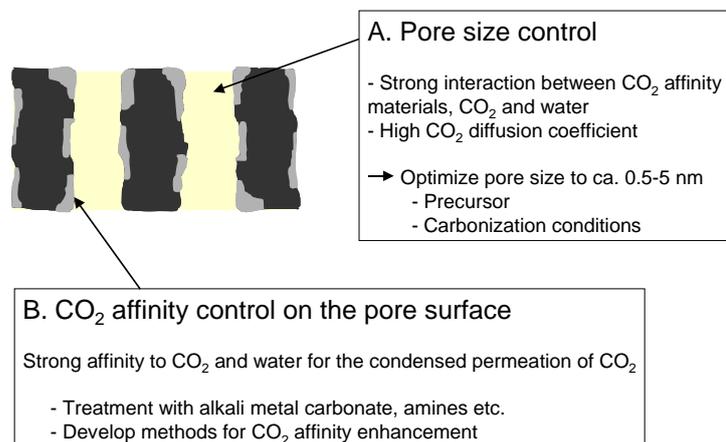


Figure 2. Design of the novel CO₂ affinity-enhanced carbon membrane.

To obtain ideal molecular gate separation, there are two important parameters to control: (a) pore size and (b) CO₂ affinity on the pore surface. The pore size should be small enough to obtain a strong interaction between the CO₂ affinity materials and CO₂ even at the center of a pore.

At the same time, if CO₂ affinity materials are to be inserted into the pores, the pore size should be sufficiently large. From these considerations, the optimum pore size is from 0.5 to 5 nm. To control the CO₂ affinity on the pore surface, a method to incorporate CO₂ affinity materials into the pores should be developed. In addition, the selection of CO₂ affinity materials for high CO₂ separation performance is also important.

(1.2) Membrane preparation

We examined two methods for incorporating CO₂ affinity material into the pores, as shown in Figure 3.

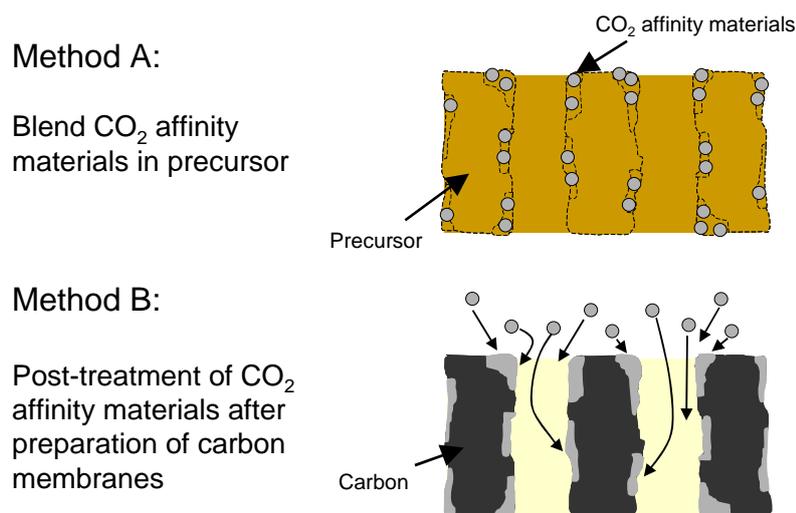


Figure 3. Methods to incorporate CO₂ affinity materials into the pores.

In method A, CO₂ affinity materials were blended with precursor solution. After drying, CO₂ affinity materials were dispersed in the precursor and hence dispersed also in the carbon matrix. The CO₂ affinity materials must withstand high temperatures (ca. 600 °C), so heat-resistant materials were used in this method. In method B, CO₂ affinity materials were incorporated into the carbon membrane by post-treatment. This method allows the use of non-heat-resistant CO₂ affinity materials in addition to alkali metal carbonate. However, CO₂ affinity materials might be incorporated only near the surface.

A type of polyimide was chosen as the precursor for preparing subnano/nano porous carbon membranes.

A tubular-type porous alumina membrane (pore diameter of 150 nm) was used as the porous support. The precursor solution was coated on the outer surface of the alumina support by the dip-coating method. After drying, the precursor-coated membrane was carbonized under a N_2 atmosphere.

Figure 4 is a photograph of a precursor-coated membrane and a carbon membrane. As seen in the figure, a yellow precursor layer was formed on the alumina support by dip-coating. Pyrolysis of the precursor layer resulted in the formation of the black carbon layer. The thickness of the carbon membrane was around 3 μm .

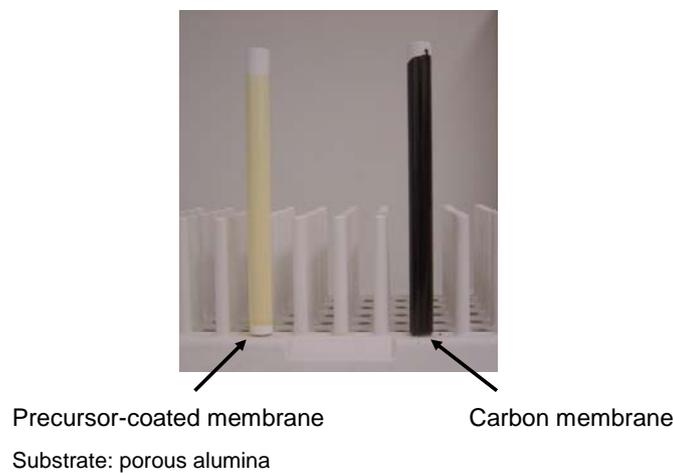


Figure 4. Photograph of a precursor-coated membrane and pyrolyzed carbon membrane.

(1.2.1) Subnano porous carbon membranes with enhanced CO_2 affinity formed using method A

Energy dispersive X-ray (EDX) spectra of the surfaces of the carbon membranes are shown in Figure 5.

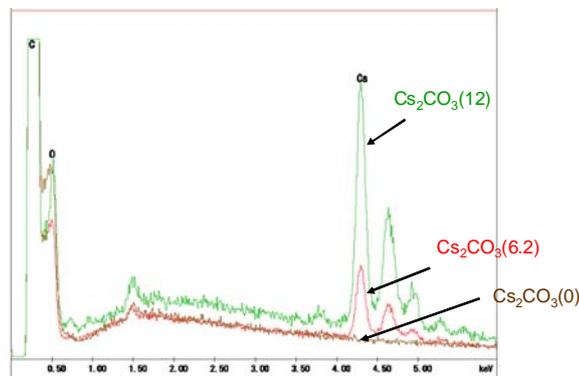


Figure 5. EDX spectra of the surfaces of the carbon membranes (method A). The values in the parentheses are weight percentages of Cs_2CO_3 in the precursor.

The Cs peak is at 4.3 keV. No Cs peak was observed for the carbon membrane without Cs_2CO_3 incorporation. On the other hand, there was a Cs peak for the carbon membrane prepared from Cs_2CO_3 -containing precursor solution. The Cs peak became more intense as the Cs_2CO_3 content in the precursor solution increased. EDX analysis suggested the amount of incorporated Cs_2CO_3 could be controlled by the Cs_2CO_3 concentration in the precursor solution.

Results for the water vapor sorption isotherm using carbon samples at 40 °C are shown in Figure 6.

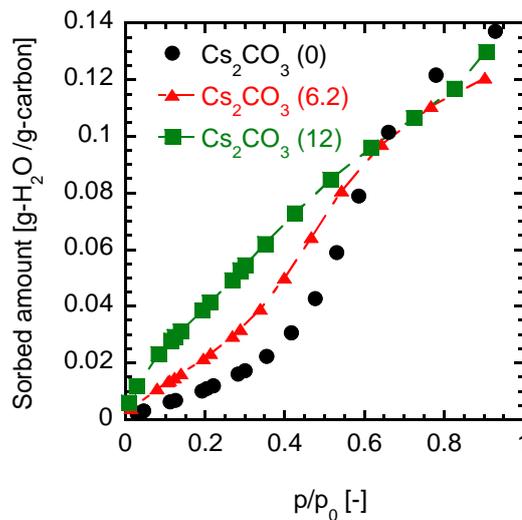


Figure 6. Water vapor sorption of carbon films (method A).

The values in the parentheses are weight percentages of Cs_2CO_3 in the precursor.

The carbon film without Cs_2CO_3 incorporation had a sigmoid sorption isotherm. The shape of sorption isotherm changed as the Cs_2CO_3 concentration in the precursor increased; when the relative humidity or p/p_0 was lower than ca. 0.6, the sorbed amount of water increased as the Cs_2CO_3 concentration in the precursor solution increased. On the other hand, when the relative humidity or p/p_0 was higher than ca. 0.6, the sorbed amounts of water were almost the same for the three samples. These results suggest the pores of the carbon became more hydrophilic but the total pore volume of carbon did not change significantly with the incorporation of Cs_2CO_3 .

(1.2.2) Subnano porous carbon membranes with enhanced CO_2 affinity formed using method B

A carbon membrane was treated with Cs_2CO_3 using method B. The cross-sectional distribution of carbon and cesium from the surface in a Cs_2CO_3 -incorporated carbon membrane determined by an X-ray photoelectron spectroscopy (XPS) depth profile measurement is shown in Figure 7.

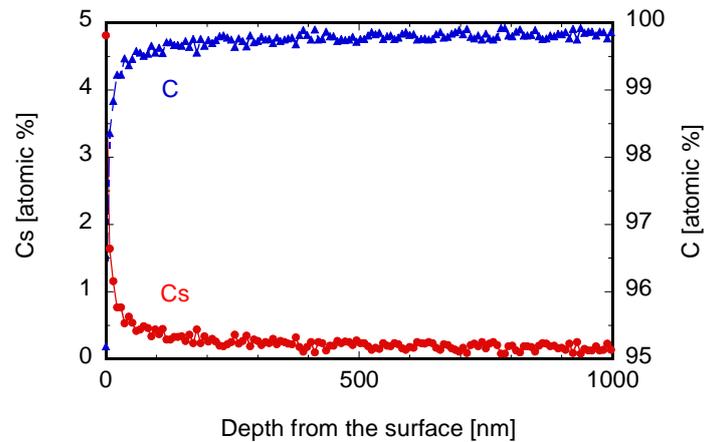


Figure 7. Cross-sectional distribution of carbon (C) and cesium (Cs) in a Cs_2CO_3 -incorporated carbon membrane determined by an XPS depth profile measurement. The pretreatment condition was dipping in saturated Cs_2CO_3 aqueous solution while evacuating the permeate side at room temperature for 1 hour.

The intensity of the Cs peak was a maximum at the surface and decreased monotonically with depth from the surface, reaching the background noise level at around 300 nm. Considering the thickness of carbon membrane was around 3 μm , it is suggested that Cs_2CO_3 could only be incorporated into the pores of the carbon membrane near the surface using method B.

The relationships between the relative humidity in the feed gas and permeance, Q , and separation factor, $\alpha_{\text{CO}_2/\text{N}_2}$, for (a) the original carbon membrane and (b) the CO_2 affinity-enhanced carbon membrane prepared using method B are shown in Figure 8.

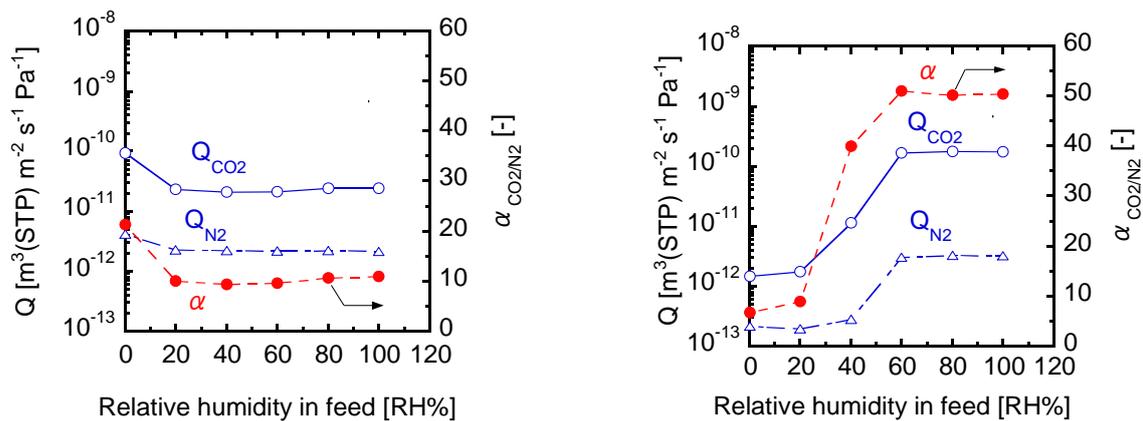


Figure 8. Effect of humidity on the separation performance. (a) Original carbon membranes, (b) CO_2 affinity-enhanced carbon membrane (method B, Cs_2CO_3 +DAPA). Gas separation conditions: temperature of 40 $^\circ\text{C}$, feed gas composition of CO_2/N_2 (5/95 vol/vol), relative humidity of ca. 100%, feed pressure of 0.1 MPa, permeate pressure of 0.1 MPa (He sweep method).

In the case of the original carbon membrane (Figure 8(a)), the CO₂ permeance and separation factor were $9.3 \times 10^{-11} \text{ m}^3(\text{STP})\text{m}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ and 21, respectively, when the dry feed gas was used (i.e., relative humidity of 0%). When the feed gas mixture was humidified (20RH%), the CO₂ permeance and separation factor dropped to $2.3 \times 10^{-11} \text{ m}^3(\text{STP})\text{m}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ and 10, respectively. The CO₂ permeance and separation factor did not change significantly when the relative humidity in the feed gas was increased from 20 to 100%, having values of $2.4 \times 10^{-11} \text{ m}^3(\text{STP})\text{m}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ and 11 at 100RH%, respectively. Therefore, the separation performance of the original carbon membrane became worse under the humidified conditions. On the other hand, in the case of the CO₂ affinity-enhanced carbon membrane (Figure 8(b)), the CO₂ permeance and separation factor were $1.5 \times 10^{-12} \text{ m}^3(\text{STP})\text{m}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ and 6.7, respectively, when the dry feed gas was used (i.e., relative humidity of 0%). Both CO₂ permeance and N₂ permeance increased as the relative humidity in the feed gas increased and reached constant values for 60-100 RH%. Since CO₂ permeance increased much more than N₂ permeance did, the separation factor increased as the relative humidity in the feed gas increased and reached a constant value for 60-100 RH%. The CO₂ permeance and separation factor were $1.8 \times 10^{-10} \text{ m}^3(\text{STP})\text{m}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ and 51, respectively. As designed, both the CO₂ permeance and separation factor of the CO₂ affinity-enhanced carbon membrane were higher than values for the original carbon membrane under humidified conditions.

(1.2.3) Control of subnano/nano pores in carbon membranes

We developed a method to control the subnano/nano pore size in carbon membranes. Results of the pore size distribution using nanoporometry are shown in Figure 9.

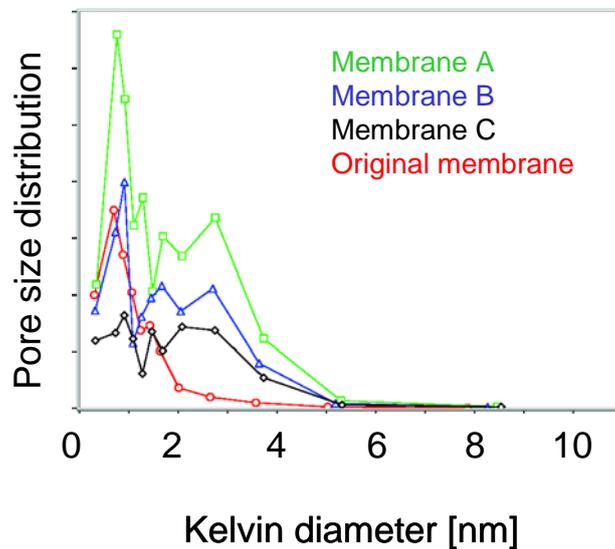


Figure 9. Pore size distribution of the prepared carbon membranes.

Membranes A-C were prepared by the developed method. The principle of nanoporometry is as follows. He gas permeance is measured under a constant

operating pressure, while the vapor pressure of a condensable gas (H_2O) is varied in the He carrier gas. He permeance decreases as the H_2O vapor pressure increases, because the H_2O condenses and plugs some of the membrane pores by capillary condensation. Since the relationship between the pore diameter and H_2O vapor pressure when capillary condensation occurs is described by the Kelvin equation, the pore diameter distribution can be evaluated.

In the case of original carbon membranes, the pore diameter of the pores contributing to the He permeation is limited to the sub-nano order. Therefore, relatively large dendrimers (molecular size > 1 nm) cannot be inserted into the original carbon membrane. On the other hand, the new carbon membranes have nanopores ranging 1-5 nm in size, in addition to the subnano pores, and the dendrimer can be inserted into these pores. Research into inserting dendrimers into the pores of these nanoporous carbon membranes is ongoing.

(2) Inorganic membrane

(2.1) Synthesis of novel zeolite membranes for CO_2 separation

In collaboration with the Tohoku University, we have been undertaking a simulation forecast of the optimum pore structure for CO_2 separation and investigating the synthesis method for a new type of porous material effective in CO_2 separation. Based on the simulation results, we have selected a number of candidate zeolite structures for use in CO_2 separation studies and have begun synthesis of new zeolite membranes. In addition, we are continuing to prepare several zeolite seed crystals, from which several new zeolite membranes are anticipated. In this study, we newly prepared various high silica zeolites. These have not previously been reported as a membrane (Figure 10).

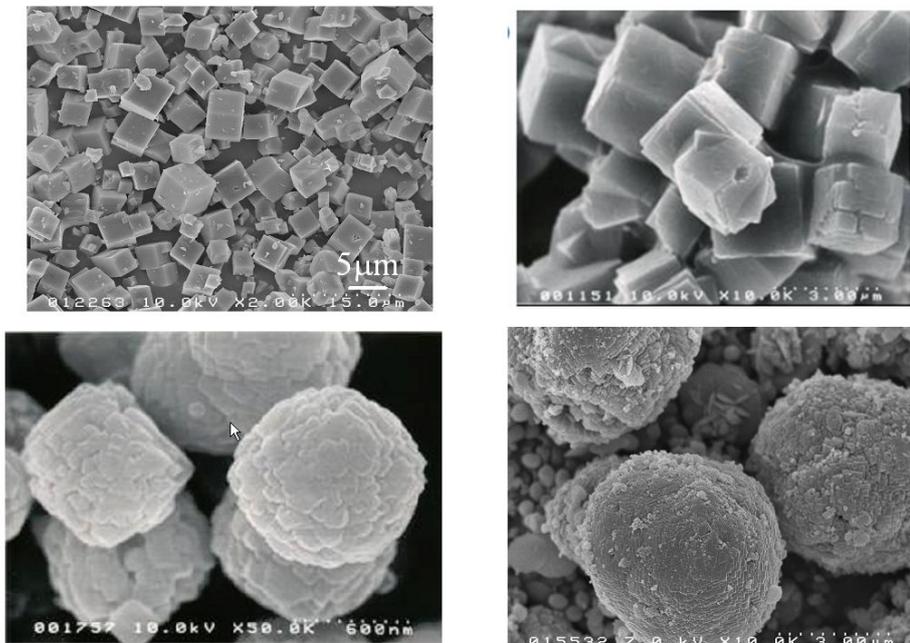


Figure 10 SEM images of prepared zeolite crystals

(2.2) Challenges in the development of a zeolite membrane without defects

We have demonstrated the novel synthesis of a defect-free zeolite membrane suitable for CO₂ separation. The porous substrate has been filled with zeolite crystals. The gas permeability measurements of the zeolite membrane prepared by the melt-filling method are currently in the process of evaluation. (Figure 11).

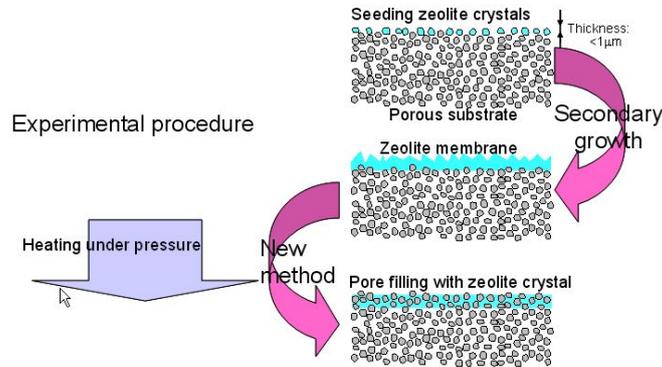


Figure 11 Concept of melt filling method

We have also prepared a zeolite membrane using this technique. As shown in Figure 12, scanning electron microscopy (SEM) images of the zeolite membrane reveal the membrane moved into the porous substrate and a composite layer was produced when using the melt-filling method. An X-ray diffraction measurement revealed the composites had the same diffraction pattern; there was no phase transition or byproducts in the melt-filling synthesis. For example, while the CO₂/N₂ separation selectivity of the zeolite Y membrane was 7, the selectivity was 25 for the melt-filling synthesized membrane. However, the separation selectivities of the membranes formed by this method tend to be low. We assume this is because of defects in the formed zeolite membranes. Therefore, the difference in the coefficient of thermal expansion between the zeolite membrane and substrate needs to be taken into consideration to solve the problem of defects in the membranes.

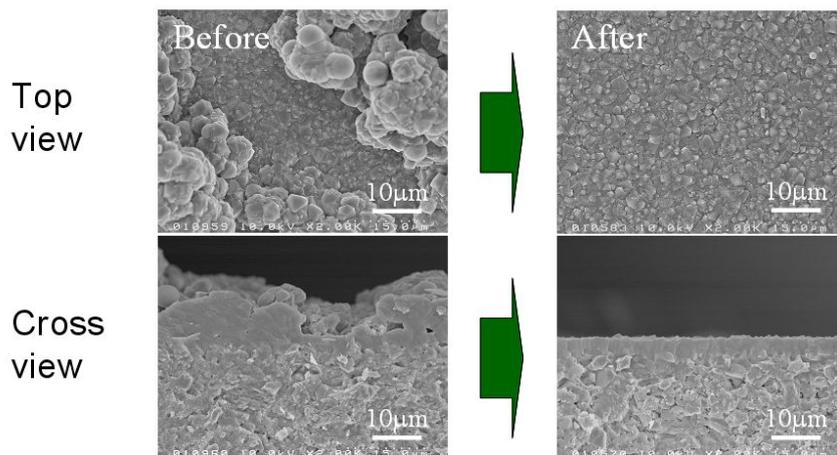


Figure 12 SEM images of the initial zeolite membrane (left) and filled zeolite crystals in porous substrate after melt-filling treatment (right).

Progress

(1) Carbon membranes

(1.1) Sub-nanoporous carbon membranes with enhanced CO₂ affinity

Novel carbon membranes with enhanced CO₂ affinity have been developed. In both methods A and B, the prepared membranes had higher separation performances than did the original carbon membranes in the separation of CO₂/N₂ mixtures at high relative humidity. Research is ongoing to improve the separation performance further based on the current progress.

(1.2) Control of subnano/nano pores in carbon membranes

We have developed a method to control subnano/nano pores in carbon membranes. Further information will be disclosed when the intellectual property issues are resolved. A study to insert dendrimers in their pores is ongoing to improve the separation performance further based on the current progress.

(2) Inorganic membranes

It was revealed that the formation of a complex layer of zeolite and the substrate improved the permeation performance when compared with the membrane prepared by arranging crystals on the substrate. A novel method for the preparation of dense complex zeolite membranes was proposed and shown to be effective.

Future Plans

(1) Carbon membranes

In the future, the CO₂ affinity materials will be optimized to improve the separation performance further. Especially, incorporation of dendrimers into the pores of carbon membranes will be examined. In addition, the preparation conditions will be optimized. Detailed characterization and separation performance measurements will be conducted on the prepared novel carbon membranes.

(2) Inorganic membranes

(2.1) Development of zeolite membranes

Various kinds of ultra-thin zeolite membranes with different pore diameters and pore structures will be examined in screening tests.

We will investigate the most suitable condition of the melt-filling method for attaining high CO₂ separation properties. The melt-filling method will be adapted to the newly prepared zeolite membranes, based on DMC simulation results, for improvement of CO₂ separation properties.

(2.2) Functionalized mesoporous membrane with high permeance

The optimization of the pore diameter, pore structure, and the choice of guest-material, as well as the surface functionalization of mesopores by chemical grafting of the guest-material will be examined in screening tests.

Publications

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