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Advanced CO_2/H_2 separation materials incorporating active functional agents

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1. Research Subject

Advanced CO_2/H_2 separation materials incorporating active functional agents

2. Abstract

The concept for a novel supercritical CO_2 (SC-CO_2) structure directing method was invented and tried for preparation of an innovative CO_2/H_2 separation membrane possessing a CO_2 molecular gate function. Poly(amidoamine) (PAMAM) dendrimer was selected as the CO_2 molecular gating material, held within a polymeric matrix of polyethylene glycol dimethacrylate (PEGDMA) and X. SC-CO_2 may work as a structure directing agent for creating the CO_2 molecular gate channel. CO_2 molecules would form carbamate ion pairs with the amino moieties of the PAMAM dendrimer under the SC-CO_2 atmosphere to regulate PAMAM dendrimer morphology for ideal CO_2 molecular gating channels. The resulting membrane had increased CO_2/H_2 selectivity and CO_2 permeability.

3. Introduction

CO_2 capture and storage (CCS) is an important option for mitigating global warming. However, CCS in terms of present-day technology consumes a large amount of energy and is costly, especially in CO_2 capture. Several CO_2 capture technologies such as chemical and physical absorption, adsorption and membranes are under research and development. Among these, membranes are the least energy intensive method.

We have been developing advanced composite materials possessing molecular interaction forces with specific molecules using nanoscale control technologies in polymeric and inorganic materials. For example, such forces can selectively extract CO_2 from CO_2 and H_2 mixed gas. The materials consist of active functional agents in the nanopores of a porous substrate or polymeric matrix. We control the configurations, surface atoms/molecules and the compositions of the pore/matrix and functional compounds to create the desired molecular interaction forces. Our research is expected to provide detailed insight into molecular dynamics in nanoscale structures and result in the future production of superior separation materials.

One objective of this research is to realize the development of an improved CO_2 separation membrane for CCS. Such an innovative material will greatly reduce energy consumption and costs in the separation process.

Basic concept of CO_2 molecular gate membrane

Figure 1 shows the basic outline of the CO_2 molecular gate membrane. In Figure 1 (b), the pathway for gas molecules is occupied solely by CO_2, which acts as a gate to block the passage of other gases. Consequently, the amount of H_2 permeating to the other side of the membrane is greatly limited and high concentrations of CO_2 can be obtained. The molecular gate membrane can achieve reverse size separation of CO_2 and H_2. Figure 1 (c) shows further detail of the amine compounds, such as polyamidoamine (PAMAM) dendrimers. In the figure, one CO_2 molecule is shown to form a carbamate ion pair with two amino moieties from the membrane material. The carbamate ion pair works as a quasi cross-linkage that restricts H_2 permeation through the membrane. On the other hand, because carbamate ion pairs are in equilibrium with free CO_2 and amine moieties, CO_2 can release from the original carbamate ion pair and jump down to the next pair of amine moieties via the CO_2 concentration gradient in the membrane. As a result, only CO_2 molecules permeate the membrane.

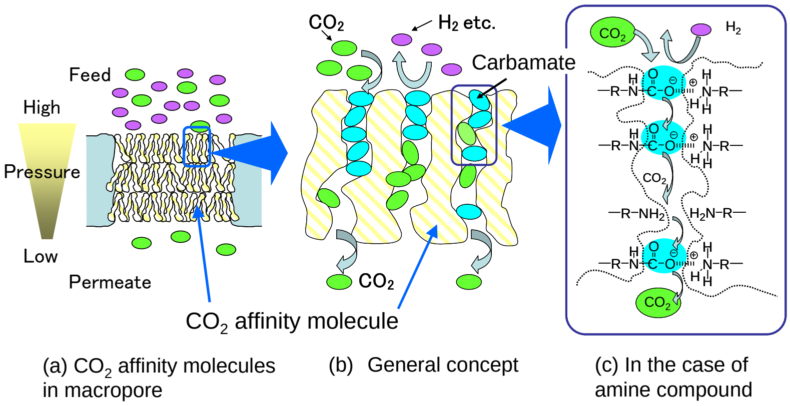

Figure 1: Concept of the CO_2 molecular gate membrane

The CO_2 molecular gate requires strict morphological arrangement. In Figure 1 (c), a strict morphological control of the distance between two amine moieties is required for the perfect CO_2 molecular gate. If the distance is too small and allows strong hydrogen bonding of the amine moieties, the membrane will not have sufficient CO_2 permeability (Figure 2(a)). On the other hand, if the distance is too large, there will not be enough carbamate ion pairs for the gate to function. It is critical that this is avoided for better CO_2 selectivity (Figure 2(b)).

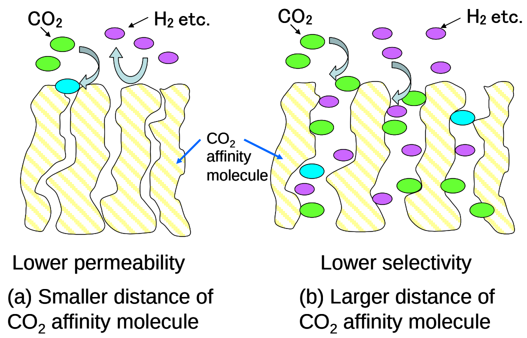

Figure 2: Morphological deformation and the molecular gate function

As for CO_2 affinity molecules, amine compounds were preferably selected. Amine compounds react with CO_2 to form both bicarbonate and carbamate ions as follows:

Bicarbonate: $CO_2 + H_2O + R\text{-}NH_2 = HCO_3^-$(Bicarbonate) + $R\text{-}NH_3^+$

Carbamate: $CO_2 + 2(R\text{-}NH_2) = R\text{-}NHCOO^-$(Carbamate) + $R\text{-}NH_3^+$

As shown in the equation, bicarbonate was formed with one molar of CO_2, H_2O and amine moiety. On the other hand, carbamate was formed with one molar of CO_2 and two molars of amine moieties. Accordingly, a formation of bicarbonate needs a H_2O, not for carbamate.

Actually, a polyamidoamine (PAMAM) dendrimer was observed to form both bicarbonate and carbamate ions by NMR observation. In the molecular gate membrane using PAMAM dendrimer, CO_2 would exist as bicarbonate and carbamate ions. And those ions could move in the membrane. Figure 3 shows a conceptual diagram of those ions transportation through membrane.

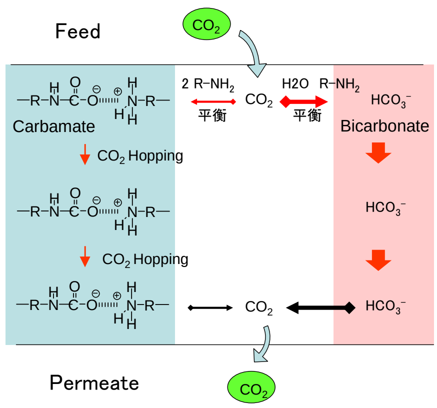

Figure 3: Expected CO_2 permeation through membrane via carbamate and bicarbonate.

In the figure, the transportation of bicarbonate essentially requires the existence of an equal mole of H_2O. On the other hand, the CO_2 transportation via carbamate does not need a water existence.

Existing molecular gate membranes containing PAMAM dendrimer work well under a highly humid feed gas condition. For example, a CO_2/H_2 selectivity of the membrane shows a maximum value at 80-90 %RH (relative humidity) of a feed gas. Lower relative humidity decreases CO_2/H_2 selectivity of the membrane drastically. Stable selectivity over a wide rage of moisture content in a feed gas would be favorable performance for CO_2 separation from various gas mixtures.

From the strong influence of moisture content in a feed gas on CO_2 permselectivity, bicarbonate ions seem to be dominant species of CO_2 permeation in the conventional PAMAM dendrimer membrane.

If carbamate ions are dominant species for CO_2 permeation of membranes, no water existence would be required. In addition, smaller moisture influence on CO_2 permeation would be observed. Therefore, dry or less humid gas feed would be acceptable to the membrane separation system. The mechanism of CO_2 permeation via carbamate ions should be preferable to that of bicarbonate ion transportation for CO_2 separation. However, the dominant transportation via carbamate ion was not achieved until now. Actually, bicarbonate ions are the dominant species for CO_2 permeation in various facilitated membranes.

The reason why the CO_2 transportation via carbamate ion was not attained in membrane permeation is the difficulty to precisely conformational control of adjacent amino moieties for the transportation. The suitable conformation of precisely controlled adjacent amino moieties would enable to form carbamate ion easily and accept the rapid hopping movement of CO_2 via carbamate.

Our methodology

A promising way of creating the best morphology for the CO_2 hopping via carbamate is the rearrangement of amino moiety to form an ion hopping channel by using a structure directing agent. We select supercritical CO_2 (SC-CO_2) as a structure directing agent for rearranging amino moiety conformation for the CO_2 hopping channel. SC-CO_2 can penetrate easily into a pretreated membrane to act as the structure directing agent to form carbamate ion pairs.

Figure 4 shows conceptual diagram of our methodology. A membrane containing amine compound was treated under SC-CO_2 atmosphere. SC-CO_2 can easily penetrate into the membrane and swell it. And spontaneously SC-CO_2 would form carbamate ion pairs to rearrange the morphology of amino moieties for the CO_2 hopping channel. Because of their having near-zero surface tension, after removing SC-CO_2, the rearranged morphology would be kept for serving the best channel for CO_2 hopping.

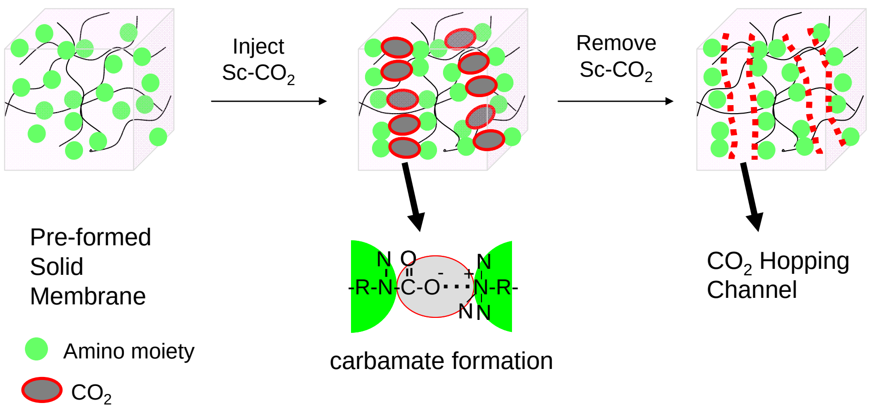

Figure 4: Concept of creation of CO_2 hopping channel via carbamate ion

The selection of membrane materials and tuning the SC-CO_2 treatment condition would be critically important to create the best channel of CO_2 hopping.

Another strong point of SC-CO_2 treatment is that this method can be applied to membranes in a module formation. It means membranes in a module would gain the molecular gate function by our method. Figure 5 shows a conceptual image of SC-CO_2 treatment of a membrane module for CO_2 molecular gating. A membrane module containing nascent membranes is set in a high pressure vessel, followed by treated by SC-CO_2 to create a CO_2 molecular gating layer.

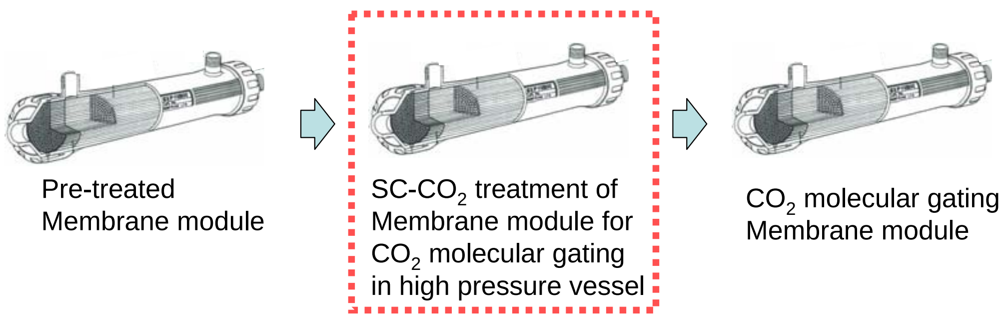

Figure 5: Concept of SC-CO_2 treatment of membrane module

4. Background

Creation of a CO_2/H_2 separation membrane is a very hot topic in gas separation membrane research. RITE is a leading research institute on CO_2 separation technologies and has studied polyamidoamine (PAMAM) dendrimer membranes for CO_2 separation (Figure 6). A PAMAM dendrimer membrane was first reported by Professor Sirkar's group at the New Jersey Institute of Technology as an immobilized liquid membrane for CO_2/N_2 separation [1]. A liquid state dendrimer has been successfully and stably fixed in a polymeric matrix as a composite hollow fiber membrane at RITE [2]. RITE's membrane holds the world record for CO_2/H_2 separation properties (CO_2/H_2 selectivity: 30) at an elevated CO_2 pressure. In this membrane, PAMAM dendrimer was incorporated into a cross-linked polymeric matrix, whereby a continuous channel of PAMAM dendrimer through membrane was formed. Further improvement of the dendrimer membrane and morphologic regulation of the dendrimer channel is required.

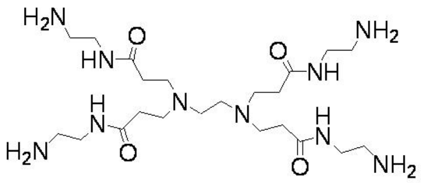

Figure 6: Chemical structure of PAMAM dendrimer (conventional).

Professor Freeman's group at the University of Texas at Austin also attains very good CO_2/H_2 separation membranes of cross-linked poly(ethylene glycol) (PEG) network, which show a selectivity of 10 at 30 °C and an elevated CO_2 pressure, as well as a good CO_2 permeability [3]. Professor Ho's group at Ohio State University has reported a cross-linked poly(vinyl alcohol) membrane containing amine compounds [4]. Professor Matsuyama's group at Kobe University in Japan has also reported a gel membrane, which consists of poly(vinyl alcohol)/poly(acrylic acid) co-polymer and an amine as CO_2 carrier [5]. Both membranes exhibit very good CO_2/H_2 selectivity at an elevated temperature and a low CO_2 partial pressure.

The word "molecular gate" is sometimes used in the field of separation membranes. The term is also used by Sirkar's group but its concept in their paper was not clear [1]. The concept of a CO_2 molecular gate mentioned above was developed at RITE and the concept is now being confirmed. Conventional RITE's molecular gate membranes work well at highly humid condition. Ideal CO_2 molecular gate membrane should also work under a dry or less humid condition.

In this GCEP research, the creation of the ideal CO_2 molecular gate channel using CO_2 hopping via carbamate is studied. SC-CO_2 has been selected, for the first time, as the structure directing agent of the CO_2/H_2 separation membrane for the reasons given above.

5. Results

We have developed CO_2 molecular gate membranes using poly(amidoamine) (PAMAM) dendrimer immobilized in a polymer matrix network. Typical dendrimer immobilized membrane was prepared with PAMAM dendrimer and polymer matrix of polyethylene glycol dimethacrylate (PEGDMA) and X.

The ethanol solution containing these three materials was casted on a glass plate. A just casted film containing solvent was photo cured and evaporated the solvent. Figure 7 shows the schematic image of PAMAM dendrimer immobilized membrane in a polymer matrix network of PEGDMA and X. Photo of the membrane is also shown in the Figure.

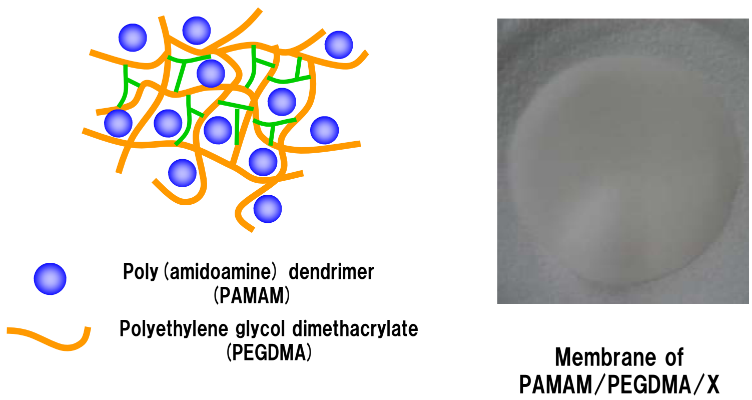

Figure 7: Schematic image and photo of PAMAM dendrimer immobilized membrane.

Figure 8 shows the setup for the SC-CO_2 structure directing method. The setup consists of a syringe pump, high pressure view cell with a sapphire window, a back pressure regulator and a monitoring camera. The resulting solid membrane containing PAMAM dendrimer was placed on a glass plate in a high-pressure cell. CO_2 was injected gradually into the cell with a high pressure pump to produce a supercritical condition at 20-60 °C. Pressure was maintained for four hours at 10 MPa and then decreased at a rate of 0.1 MPa/min to create channels for CO_2 hopping via carbamate ion pairs.

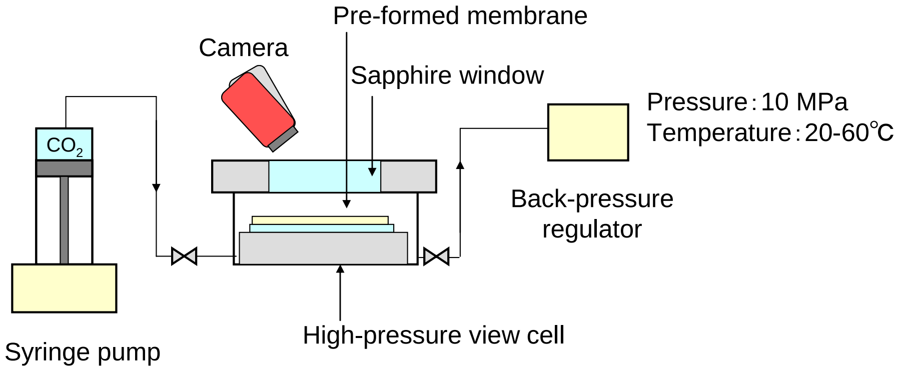

Figure 8: Setup for the SC-CO_2 structure directing method.

Structural control on a nanometric scale is critically important to attain the ideal molecular gating channel with specific amine compounds. In our new research in GCEP, CO_2 itself will be used as the structure-directing agent for producing an ideal channel of CO_2 hopping via carbamate ion.

Figure 9 shows a membrane in a high pressure cell for SC-CO_2 treatment. A membrane containing PAMAM dendrimer was placed on a glass plate.

As mentioned above in Figure 4, SC-CO_2 would work as a structure-directing agent for controlling the dimensional accuracy of amino moieties of PAMAM dendrimers for the CO_2 transporting channel, due to the formation of carbamate ion pairs that bridges the amino moieties. SC-CO_2 would cause negligible deformation of the formed structure during the treatment, due to the near-zero surface tension of SC-CO_2. As a result, the SC-CO_2 directing method will offer an ideal channel structure of CO_2 hopping via carbamate for the CO_2 molecular gate.

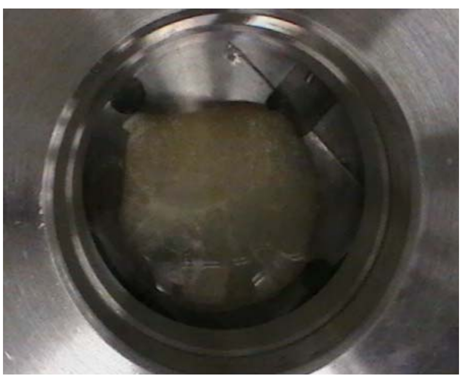

Figure 9: Membrane in a high pressure cell for SC-CO_2 treatment.

In preliminary experiments, several kinds of membranes were treated under various SC-CO_2 conditions. Cellulose tri-acetate, polyimide and various cross linked polymeric materials containing dendrimers were tested. From these results, some data indicates the effectiveness of SC-CO_2 treatment for improving CO_2 permeance and CO_2/H_2 selectivity.

Regarding the PAMAM dendrimer immobilized membrane prepared with PAMAM dendrimer, polyethylene glycol dimethacrylate (PEGDMA) and X, SC-CO_2 treatment shows positive effects. The original PAMAM immobilized membrane shows relatively good CO_2/H_2 separation properties. Table 1 shows CO_2 and H_2 permeance (Q) and CO_2/H_2 selectivity (α) of the pre- (original) and post-treated PAMAM dendrimer immobilized membrane prepared with PAMAM dendrimer, PEGDMA and X. Gas permeation data was taken at atmospheric pressure and 40 °C. A feed gas contains 80 % of CO_2 and 20% of H_2. Relative humidity in the feed was 80%RH.

Table 1: CO_2/H_2 separation properties of SC-CO_2 treated membrane.

	SC-CO_2 Treatment Temperature	QCO_2 m3 (STP) / (m2sPa)	QH_2 m3 (STP) / (m2sPa)	α CO2/H2
Reference (Pre-treated)		4.38E-12	2.98E-14	144
SC-CO_2 treated	40	8.80E-12	3.62E-14	243
SC-CO_2 treated	60	8.52E-12	4.00E-14	213

SC-CO_2 treatment condition: 10 MPa, 4 hr

In the table, the original membrane containing PAMAM dendrimer showed 4.38 x 10^{-12} m^3(STP)/(m^2 s Pa), and 2.98 x 10^{-12} m^3(STP)/(m^2 s Pa) for QCO_2 and QH_2, respectively. CO_2/H_2 selectivity (α) was 144. On the other hand, the membrane treated by SC-CO_2 at 40 °C shows 8.80 x 10^{-12} m^3(STP)/(m^2 s Pa), and 8.80 x 10^{-12} m^3(STP)/(m^2 s Pa) for QCO_2 and QH_2, respectively. And CO_2/H_2 selectivity (α) was 243. Compared with those of the pre-treated membrane, both of QCO_2 and QH_2 were increased, however, increment of QCO_2 was larger that that of QH_2. As a result, CO_2/H_2 selectivity was increased. A similar result was obtained by SC-CO_2 treatment at 60 °C. For the treatment at 60 °C, QCO_2 and QH_2 were 8.52 x 10^{-12} m^3(STP)/(m^2 s Pa), and 4.00 x 10^{-12} m^3(STP)/(m^2 s Pa), respectively.

6. Progress

Basic concept of SC-CO_2 treatment was invented, tested and modified. As a result, possibility of SC-CO_2 treatment was found. And also, the direction of attaining the ideal molecular gating with CO_2 hopping via carbamate ion pairs was obtained.

CO_2 separation membranes of the moment will be preferably employed for CO_2 capture from a pressurized gas stream such as Integrated Coal Gasification Combined Cycle (IGCC) as a means of CO_2 capture and storage (CCS). And CO_2 separation membranes will be also one of strong candidates of CO_2 removal from high CO_2 content natural gases. In addition, CO_2 separation membranes are considered as a measure of CO_2 capture from a flue gas of a coal power plant.

An IGCC power plant of 300 MW would emit roughly one million metric tons of CO_2 a year. Assuming 90% CO_2 recovery in the membrane system, the GCEP outcome will potentially contribute to a CO_2 reduction of 0.9 million metric tons per 300 MW power plant. When 100 IGCC plants employ the membrane system, the contribution to CO_2 reduction is counted as 90 million metric tons per year. Additionally, the GCEP outcomes in CO_2 membrane research might be applicable to natural gas plants and existing power plants such as coal-fired thermal power plants. Our final goal is the creation of a game-changing CO_2 separation membrane, which is applicable to existing power plants and steel works, as well as new plants such as IGCC.

7. Future Plans

The following research will be conducted into an ideal CO_2 molecular gate membrane with carbamate ion hopping in a succeeding research period.

-Improvement of the SC-CO_2 structure directing method.
- Investigating the structure of the SC-CO_2 treated membrane.
-Investigating the mechanism of the SC-CO_2 directing method.

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