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Advanced CO_2/H_2 separation materials incorporating active functional agents

Investigators

Shingo Kazama, Ph.D. Group Leader, Chief Researcher, Chemical Research Group, RITE

Katsunori Yogo, Ph.D. Senior Researcher, Chemical Research Group, RITE

Teruhiko Kai, Ph.D. Senior Researcher, Chemical Research Group, RITE

Ikuo Taniguchi, Ph.D. Senior Researcher, Chemical Research Group, RITE

Kazuya Goto, Ph.D. Senior Researcher, Chemical Research Group, RITE

Shuhong Duan, Ph.D. Researcher, Chemical Research Group, RITE

Kota Yamazaki Ph.D. Researcher, Chemical Research Group, RITE

Research Institute of Innovative Technology for the Earth (RITE)

9-2 Kizugawadai, Kizugawa-shi Kyoto 619-0292, JAPAN

Contact: kazama@rite.or.jp

1. Research Subject

Advanced CO_2/H_2 separation materials incorporating active functional agents

2. Abstract

The basic concept of a novel supercritical CO_2 (sc-CO_2) directing method was invented for preparation of an innovative CO_2/H_2 separation membrane with a CO_2 molecular gate function. In this study, The CO_2 gas separation membrane created by supercritical carbon dioxide (sc-CO_2) structure directing method was designed. The polymeric material selected was poly(ethyleneimine) (PEI), a polymer with high amine density. Formation of CO_2 permeation pathway by amino groups in polymeric membrane was investigated by sc-CO_2 structure directing method. Carbamate formation was examined as a CO_2 permeation mechanism. The sc-CO_2 treated membrane showed increased CO_2 permeance with decreased He permeance, as a result, CO_2/He selectivity was enhanced.

3. Introduction

CO_2 capture and storage (CCS) is an important option for mitigating CO_2 emission so as to suppress global warming. However, in terms of present-day technology, CCS 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, have been investigated and developed. Among these technologies, membranes require the least energy.

We have developed advanced composite materials having a functional agent by nano-architecture controlling technologies in polymeric and inorganic materials. For example, selective extraction of CO_2 from CO_2 and H_2 gas mixture was enabled by introducing amine, which interacted to CO_2 preferentially. The materials consist of the 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. Our research is expected to provide insights for production of effective and promising separation materials.

One objective of this research is to develop 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. The pathway for gas molecules is occupied solely by CO_2, which acts as a gate to block the sorption of other gases. Consequently, permeation of H_2 is greatly limited and high concentrations of CO_2 can be obtained in the permeate. The molecular gate membrane realizes CO_2 separation over smaller H_2 in reverse molecular sieving mechanism. Figure 1 (b) explains details of the preferential CO_2 separation with amine compounds, such as poly(amidoamine) (PAMAM) dendrimers. A carbamate ion pair is formed with one CO_2 molecule and two amine moieties of the dendrimer. The carbamate ion pair works as a quasi cross-linkage that inhibits H_2 permeation through the membrane. On the other hand, because formation of carbamate ion pairs are in equilibrium with free CO_2 and amine moieties, the CO_2 in carbamate form can diffuse into the membrane to form another carbamate ion pair with free amine moieties next to the carbamate. As a result, CO_2 molecules can permeate the membrane preferentially.

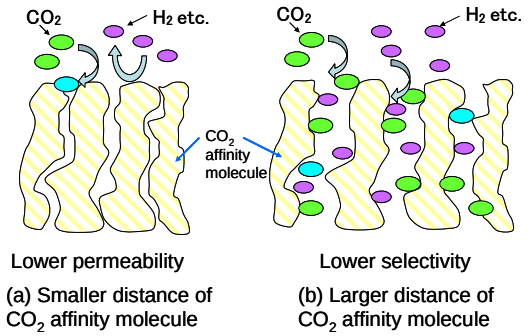


Figure 1: Concept of the CO_2 molecular gate membrane.

The CO_2 molecular gate requires fine morphological alignments of the compounds. In Figure 1, the distance between two amine moieties should be controlled to express the CO_2 molecular gate function. If the distance is shorter than an appropriate distance, the hydrogen bonding formed can be much stronger, which suppresses CO2 moving. As a result, the membrane will not have sufficient CO_2 permeability (Figure 2(a)). On the other hand, if the distance is far, a quasi cross-linkage to prevent H_2 permeation will not be achieved. Precise control of the molecular alignments will be thus required as represented in Figure 2(b).

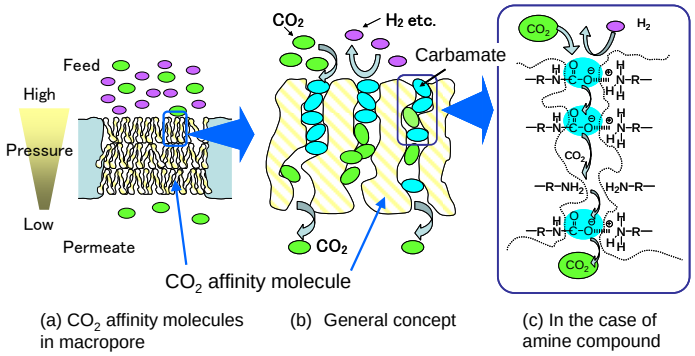


Figure 2: Morphological deformation and the molecular gate function.

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

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

Bicarbonate ion was formed with one mole of CO_2, H_2O and amine moiety. On the other hand, carbamate ion pair was with one mole of CO_2 and two moles of amine moieties. The bicarbonate formation requires H_2O, while the carbamate formation does not. Our recent results suggest that humidity is crucial to determine the CO_2 separation properties, which means bicarbonate ion is dominant of CO_2 permeation species in an amine containing membrane. On the other hand, when CO_2 permeates in the carbamate ion form, H_2O will not give any effect on CO_2 permeation.

Thinking of actual use of the CO_2 separation membrane, the membranes insensitive to humidity will be preferable, especially, that works under dry operation is more sought. Thus, carbamate ion transportation is required in comparison to current bicarbonate ion transportation.

The reason why the carbamate ion transportation was not attained in membrane permeation is the difficulty to precisely controlled conformations of adjacent amino moieties for the carbamate ion transportation. The suitable conformation to form carbamate ion readily accepts rapid hopping of CO_2 in carbamate form.

Gas separation membrane showed the CO_2 permeance Q_{CO_2} = 1.0 x 10^{-10} (m^3(STP)/m^2 s Pa) and selectivity CO_2/H_2 = 30 at higher relative humidity condition (RH 80 %). This membrane needs water to exhibit the higher CO_2 separation performance. If the gas separation membrane with high CO_2 gas permeability and high CO_2/H_2 selectivity under dry condition would be prepared, this membrane would

be useful in a wide area such as in CO_2/CH_4 separation.

Our methodology

A promising way of creating the best morphology for the hopping of carbamate ion is the rearrangement of amine moiety in the membrane to form the ion hopping channel using structure directing agent. We select super critical CO_2 (sc-CO_2) as a structure directing agent for rearranging conformation of amino moiety for carbamate ion hopping. Sc-CO_2 would be one of the promising candidates for the agent. Sc-CO_2 can readily penetrate and diffuse into the pre-formed membrane to act as a structure directing agent to form carbamate ion.

Figure 3 shows a conceptual image of sc-CO_2 treatment of membrane for CO_2 transport pathway. 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 the carbamate ion to rearrange the morphology. Because of the near-zero surface tension, after removing sc-CO_2, the rearranged morphology would be maintained for serving the suitable channel for carbamate ion hopping.

The selection of membrane materials and tuning the sc-CO_2 treating condition would be critically important to create a channel of carbamate ions hopping.

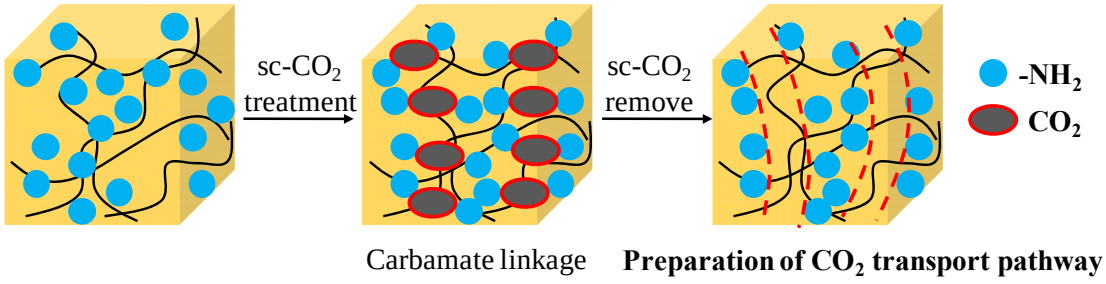


Figure 3: Conceptual image of sc-CO_2 treatment of membrane for CO_2 transport pathway.

The amino groups are effective for CO_2 gas separation membrane application. However, the CO_2 gas separation membrane did not show higher CO_2 separation performance at low relative humidity condition, which would be due to the random distribution of the amino group. To obtain high CO_2 permeance and CO_2/H_2 separation, it is required to control of amino group arrangements. In other words, formation of CO_2 transport pathway of is needed. The CO_2 transport pathway will be organized by fine alignments of an amino group in the membrane by sc-CO_2 treatment.

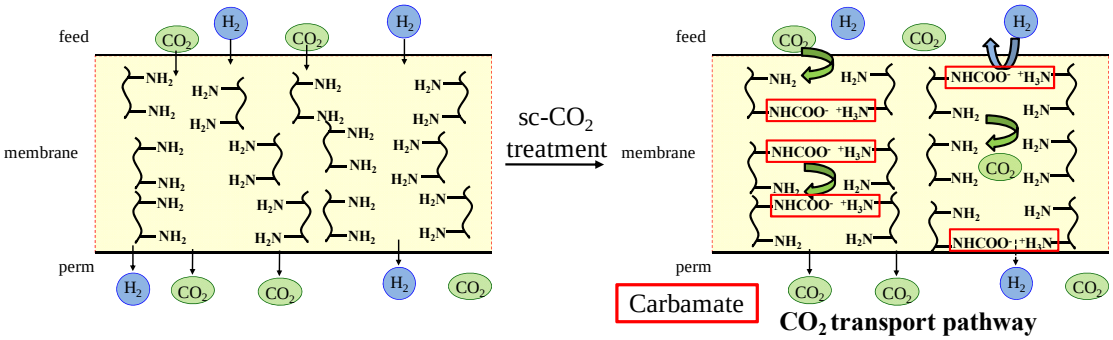


Figure 4: Schematic image of sc-CO_2 treatment of membrane.

4. Background

Creation of a CO_2/H_2 separation membrane is a topic in gas separation membrane research. RITE has been leading the CO_2 separation technologies and developed PAMAM dendrimer containing membranes for CO_2 separation. Quite high CO_2 separation performance of PAMAM dendrimer membrane was first reported by Sirkar and coworkers 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. With the 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 morphological control of the dendrimer channel is required.

Freeman et al. 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]. Ho et al. at Ohio State University has reported a cross-linked

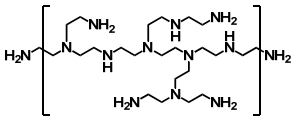
poly(vinyl alcohol) membrane containing amine compounds [4]. Matsuyama et al. at Kobe University in Japan has also reported a gel membrane, which consists of poly(vinyl alcohol)/poly(acrylic acid) co-polymer and an amine as CO_2 carrier [5]. Those membranes exhibit very good CO_2/H_2 selectivity at an elevated temperature with low CO_2 partial pressure.

The word "molecular gate" is sometimes used in the field of separation membranes. The term was proposed by Sirkar, however, the concept in his reports 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 humidified condition. Ideal CO_2 molecular gate membrane would also show excellent CO_2 separation properties under a dry or less humid condition.

In this research, the ideal CO_2 transportation by carbamate ion hopping has been investigated. Sc-CO_2 has been selected as the structure directing agent of the CO_2/H_2 separation membrane for the reasons given above.

The novel CO_2 separation membrane has been prepared by an amine polymer with high density of amino groups such as polyethyleneimine (PEI). The pretreatment amine polymer was prepared by solution-casting method with crosslinking. Operating temperature and gas pressure of the sc-CO_2 treatment condition are fixed to 50 °C and 10 MPa, respectively. The sc-CO_2 treatment time is varied for 1 to 4 h to confirm the effect of sc-CO_2 directing method on gas separation performance.

Table 1: Properties of PEI amine polymer.

	Amine polymer
	Polyethyleneimine (PEI)
Chemical structure	
Molecular weight of repeat unit	**533 g/mol**
Amine content	**~37%**
Tg	**-40 °C**

5. Results

We have developed CO_2 separation membrane created by sc-CO_2 structure directing method using PEI polymer. Figure 5 shows preparation of PEI polymer membrane.

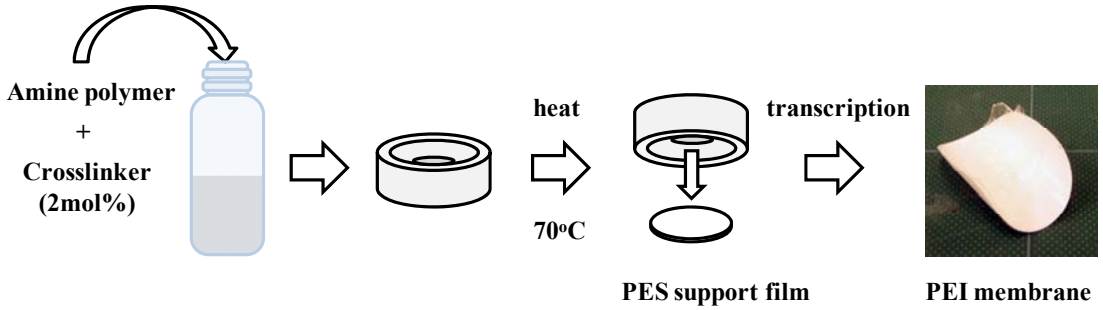


Figure 5: Preparation of PEI membrane.

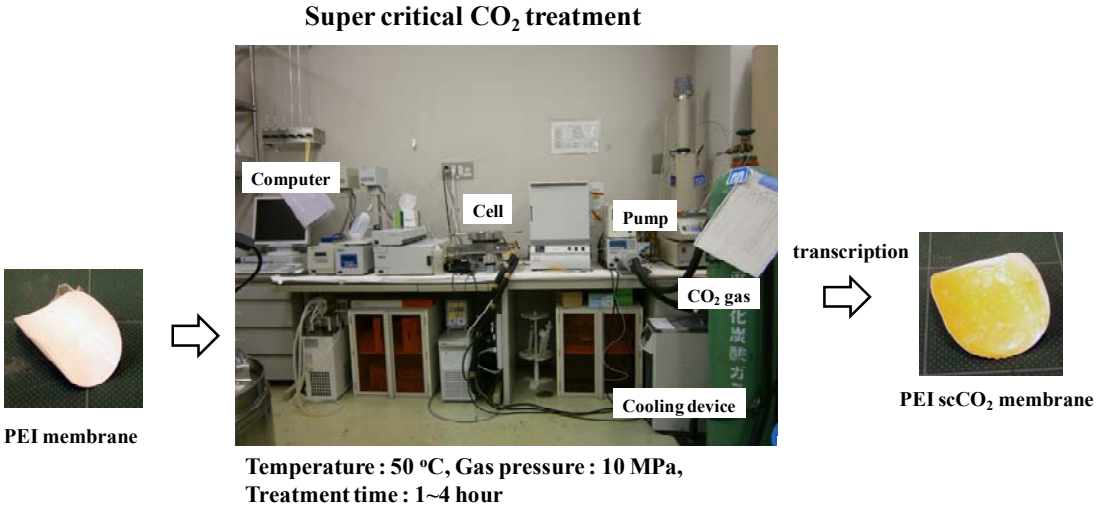
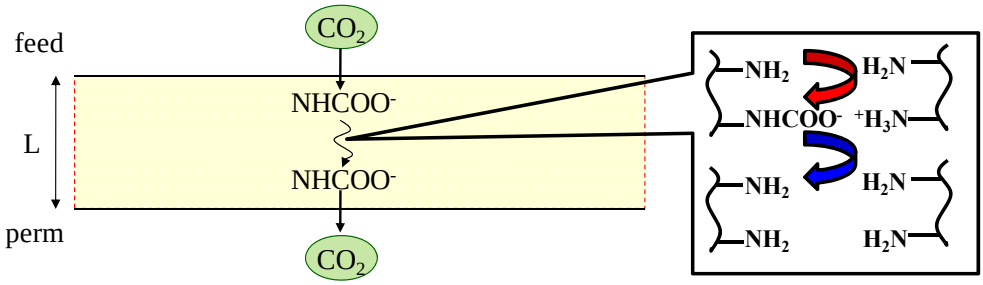


Figure 6: Membrane preparation by sc-CO_2 structure directing method.

The CO_2 separation membrane has been prepared by an amine-bearing polymer with high density such as PEI. The pretreatment amine polymer was crosslinked after solution-casting. Operating temperature and gas pressure of the sc-CO_2 treatment condition are fixed to 50 °C and 10 MPa, respectively. The sc-CO_2 treatment time varied from 1 to 4 h to confirm the effect of sc-CO_2 direct method on gas separation performance.



$R\text{-}NH_2 + CO_2 + R\text{-}NH_2 \rightarrow R\text{-}NHCOO^- + {}^+H_3N\text{-}R$: k = 6000 s^{-1}

$R\text{-}NHCOO^- + {}^+H_3N\text{-}R \rightarrow R\text{-}NH_2 + CO_2 + R\text{-}NH_2$: k = 30 s^{-1} **Rate determining step**

$D = k[R\text{-}NHCOO^-]$ k = 30 s^{-1} **Assumption :** $[R\text{-}NH_2]=[R\text{-}NHCOO^-]$ ⇒ $D = 9.5 \times 10^{-6}$ m^2/s

Assumption : S_{CO_2} **is** CO_2 **solubility in water** ⇒ $P = 7.5 \times 10^{-15}$ $[m^3(STP)\ m/(m^2\ s\ Pa)]$

Membrane thickness = 500 μm ⇒ $Q = 1.5 \times 10^{-11}$ $[m^3(STP)/(m^2\ s\ Pa)]$

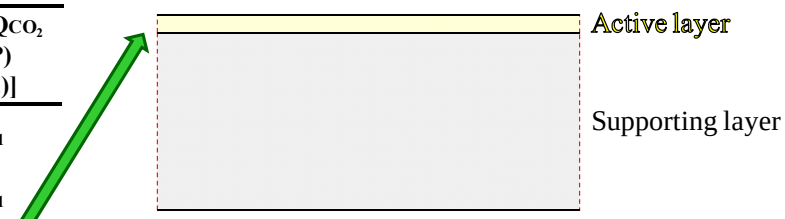
The CO_2 gas transport mechanism in carbamate form was studied to confirm a feasibility of the concept of carbamate gas transport pathway created by sc-CO_2 structure directing method. Several assumptions are taken in these calculations.

(1) The reaction rate of carbamate formation and carbamate hydrolysis are k_f = 6000 s^{-1} and k_h = 30 s^{-1}, respectively. So, carbamate hydrolysis is substituted the reaction rate of carbamate transport.

(2) Amine concentration [$R\text{-}NH_2$] is equivalent to carbamate concentration [$R\text{-}NHCOO^-$].

(3) Solubility of CO_2 (S_{CO_2}) is CO_2 solubility in amine solution. As a result, the gas permeability P was calculated to 7.5 x 10^{-15} [m^3(STP) m/(m^2 s Pa)].

Apparent thickness (μm)	Apparent Q_{CO_2} [m^3(STP) /(m^2 s Pa)]
500	1.51 x 10^{-11}
100	7.54 x 10^{-11}
10	7.54 x 10^{-10}



Active layer — High gas permeance and CO_2/H_2 selectivity

Supporting layer — Handling of gas separation membrane

Figure 8: Theoretical calculation of Q_{CO2} in PEI thin membrane.

The gas permeance Q is calculated Q = P / L, where P is gas permeability and L is membrane thickness. Apparent Q_{CO_2} decreased with decreasing the apparent thickness. The apparent Q_{CO_2} shows 7.54 x 10^{-10} [m^3(STP) m/(m^2 s Pa)] at the 10 μm of apparent thickness. However, thin membrane of 10 μm in thick would be brittle and can not tolerate under high pressure gas condition. The novel gas separation membrane designed consists of an active layer with higher gas permeance and

selectivity obtained by the sc-CO_2 treatment and a supporting layer.

Table 2: Thickness and gas permeance of CO_2 separation membrane.

sc-CO_2 treatment time (h)	Thickness (μm)	Q_{CO_2} [m^3(STP) /(m^2·s·Pa)]	Q_{He} [m^3(STP) /(m^2·s·Pa)]	$\alpha_{CO_2/He}$
0	300	7.16E-12	4.03E-13	17.7
1	489	1.78E-11	1.11E-12	16.1
2	480	1.73E-11	1.05E-12	16.5
3	509	2.21E-11	9.03E-13	24.4
4	492	1.48E-11	5.97E-13	24.8

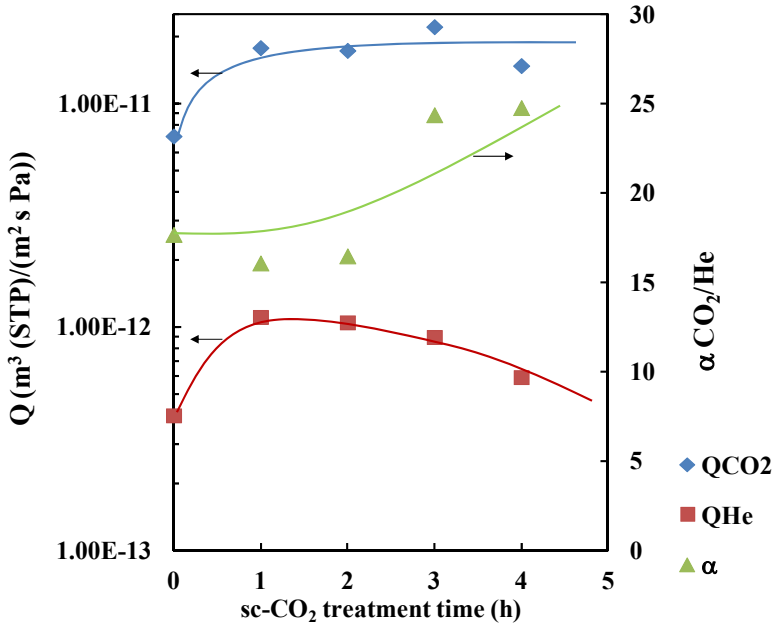


Figure 9: Gas permeance and selectivity of CO_2 separation membrane with sc-CO_2 treatment.

The CO_2 separation membrane was prepared by the sc-CO_2 treatment using amine polymer. Table 2 summarizes the membrane thickness and gas permeance of CO_2 separation membranes. The sc-CO_2 treated membranes would be swollen in sc-CO_2.

The CO_2 permeance increased with sc-CO_2 treatment time, and then it remains unchanged. On the other hands, the He permeance also increased in sc-CO_2 treatment time for 1 h. In Table 2, the pristine membrane without the sc-CO_2 structure directing method showed Q_{CO_2} of 7.16 x 10^{-12} and Q_{He} of 4.03 x 10^{-13} m^3(STP)/(m^2 s Pa), respectively. On the other hand, the membrane treated by sc-CO_2 for 1 h shows Q_{CO_2}

of 1.78 x 10^{-11} and Q_{He} of 1.11 x 10^{-12} m^3(STP)/(m^2 s Pa), respectively. However, the He permeance decreased with sc-CO_2 treatment time. The membrane with sc-CO_2 treating for 4 h shows Q_{CO_2} of 1.48 x 10^{-11} and Q_{He} of 5.97 x 10^{-13} m^3(STP)/(m^2 s Pa), respectively. We considered that the membrane was swollen by the sc-CO_2 treatment in a short treatment time, then the mobility of an amine groups because of decreasing in glass transition temperature (T_g), so the CO_2 gas transport pathway was formed. As a result, CO_2/He selectivity was increased.

The sc-CO_2 treatment improved CO_2 permeability of the membrane. However, at the present moment, the effect is not as significant as expected. The reason of the insufficient improvement might be low T_g of PEG matrix. Lower T_g might cause distortion of favorable topology of the amine moiety formed by sc-CO_2 treatment.

The sc-CO_2 treatment of a membrane containing amine moiety would induce rearrangement of the moiety for an ideal CO_2 molecular gating. Moreover, forming a favorable morphology in the membrane under sc-CO_2 would be also important for the purpose of this study.

6. Progress

CO_2 separation membranes will take an advantage for CO_2 capture from a pressurized gas stream in such as the Integrated Coal Gasification Combined Cycle (IGCC) plant with CO_2 capture and storage (CCS). CO_2 separation membranes would be one of the most powerful candidates of CO2 removal from higher CO_2 content natural gases. In addition, CO_2 separation membranes are considered as an example of CO_2 capture from a flue gas of coal-power plant.

An IGCC power plant of 300 MW would emit about one million metric tons of CO_2 a year. Assuming 90% CO_2 recovery by 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 the membrane system is installed in 100 IGCC plants, annual CO_2 reduction can be 90 million metric tons. Additionally, the GCEP outcomes by the CO_2 membrane research might be applicable to the existing power plants such as coal-fired thermal power plants. A 1000 MW coal-fired power plant emits about five million metric tons of CO_2 a year. Significant improvement of CO_2 permeability is required for effective CO_2 membrane separation from those power plants, however, when it comes, more than four million metric tons of CO_2 would be captured annually from a 1 GW coal-fired power plant. Our final goal is the creation of a game-changing CO_2 separation membrane, which can be applied in the existing power plants and steel works, as well as the next generation plants such as IGCC.

7. Future Plans

The following research will be conducted into an ideal CO_2 separation membrane with carbamate transport pathway.

- Improvement of the sc-CO_2 directing method
- Applying the sc-CO_2 directing method to higher Tg polymeric materials such as polyallylamine
- Investigation of the structure of the sc-CO_2 treated membrane
- Elucidation of the mechanism of the sc-CO_2 directing method

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Contact

Shingo Kazama: kazama@rite.or.jp