Novel Fixed-Carrier Membranes for CO_2 Separation

Ying Zhang, Zhi Wang, Shichang Wang

Chemical Engineering Research Center, School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, People's Republic of China

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ABSTRACT: A new membrane material having two kinds of CO_2 carriers was obtained. Composite membranes were prepared with the material and support membranes. The facilitated transport of CO_2 through these membranes was performed with pure CH_4 and CO_2 as well as CH_4/CO_2 mixtures containing 50 vol % CO_2. The results show that the membranes possess better CO_2 permeance than that of other fixed carrier membranes reported in the literature. In the measurements with pure gases, at 26°C, 0.013 atm of CO_2 pressure, the membrane with polysulfone support displays a CO_2 permeance of 7.93×10^{-4} cm^3 /cm^2 s cmHg and CO_2/CH_4 ideal selectivity of 212.1. In the measurements with mixed gases, at 26°C, 0.016 atm of CO_2 partial pressure, the membrane displays a CO_2 permeance of 1.69×10^{-4} cm^3 /cm^2 s cmHg and CO_2/CH_4 selectivity of 48.1. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2222–2226, 2002

Key words: gas permeation; facilitated transport; fixed-carrier membranes; carbon dioxide

INTRODUCTION

Separation and removal of carbon dioxide is an important subject in view of environment and energy. Gas separation based on membrane has an advantage over the conventional separation methods because of low capital and high-energy efficiency. The commercially available polymeric membranes often have either high permeability or high selectivity, but not both.[1] Facilitated transport membranes [including supported liquid membranes (SLMs), ion-exchange membranes and fixed carrier membranes] selectively permeate a substance by means of the reversible reaction between the substance and the carriers in the membranes, and they possess high permeability as well as high selectivity. The fixed carrier membranes are generally favorable compared with SLMs and ion-exchange membranes because of their superior durability. Therefore, in recent years, the fixed-carrier membranes for CO_2 separation, especially the membranes having amine moiety, have been investigated extensively.[2–4]

We think it is beneficial for the facilitated transport of CO_2 to introuduce more than one kind of carriers in a membrane. On the basis of this idea, we developed a membrane material having secondary amine and carboxyl groups, which can act as the carriers of CO_2, by the hydrolysis of polylvinylpyrrolidone (PVP), and prepared fixed-carrier composite membranes for CO_2 separation using this material. In this article, the method to obtain the material and the methods to prepare and evaluate the membrane will be introduced.

EXPERIMENTAL

Materials

The PVP was synthesized through radical polymerization in 20% N-vinylpyrrolidone (NVP, it was purified by fractional distillation under reduced pressure) aqueous solution by using azobisisobutyronitrile (AIBN) (it was twice recrystallized from ethanol) as the initiator at 60°C in the inert atmosphere of nitrogen gas.[5] The PVP was hydrolyzed in an alkali solution at boiling temperature (as shown in Fig. 1). The resulting polymer was precipitated by using acetone, then the polymer was dissolved in water. This aqueous solution was purified with ion-exchange resin to remove low-molecular-weight impurities and the purified polymer solution was used as the membrane-casting solution.

Analysis

The content of active carriers (secondary amine and carboxyl groups) was measured by titration method.

Correspondence to: Z. Wang (wangzhi@tju.edu.cn).

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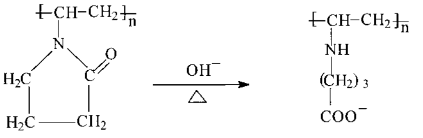

Figure 1 The hydrolysis reaction of polyvinylpyrrolidone (PVP).

The molecular weight of resulting polymer was calculated from that of PVP and the hydrolysis reaction conversion. The viscosity molecular weight of PVP (M) was calculated from intrinsic viscosity (η) according to the equation:[6] $[\eta] = 1.4 \times 10^{-2} \times M^{0.7}$.

Membrane preparation and evaluation

The purified polymer solution was cast on a support membrane by an applicator to form a film; then the cast film was dried at room temperature to form a composite membrane. The gas permeation experiments were carried out by using a set of test apparatus. The effective area of the composite membrane used in the test cell is 19.26 cm^2. Prior to contacting the membrane, both the feed and the sweep (H_2) gases were passed through gas bubblers containing water. The outlet sweep gas composition was analyzed by a gas chromatograph equipped with a thermal conductivity detector (HP4890, Porapak N). The fluxes of CO$_2$ and CH$_4$ were calculated from the sweep gas flow rate and its composition. The permeance is defined as the flux divided by the partial pressure difference between the upstream and downstream side of the membrane, $R_i = N_i / \Delta P_i$, and the selectivity $a$was defined as the ratio of the CO$_2$ permeance to the CH$_4$ permeance. The downstream pressure in our apparatus is one atomosphere pressure.

RESULTS AND DISCUSSION

Figures 2 and 3 show the effects of feed gas pressure on the performance of the membrane by using pure CO$_2$ and CH$_4$. Both the permeance of CO$_2$ and selectivities of CO$_2$/CH$_4$ decrease with the feed gas pressure. This is the characteristics of the facilitated transport mechanism.[7] The carriers are the secondary amine and carboxyl groups. The facilitated transport mechanism is as follows:[7,8]

$$RNH(CH_2)_3COO^- + 2H_2O + 2CO_2 \rightleftharpoons 2HCO_3^- + RNH_2^+(CH_2)_3COOH$$

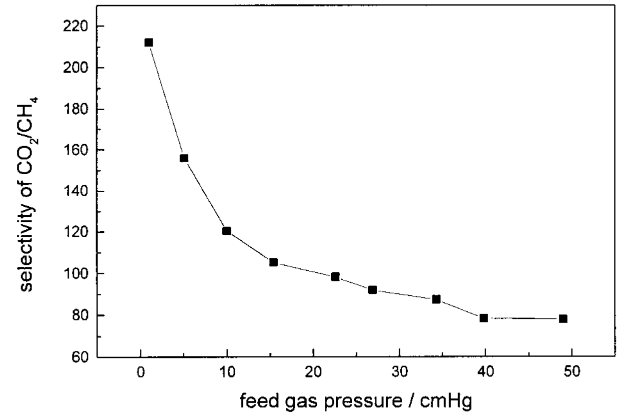

Figure 2 Effect of feed gas pressure on the selectivity of CO$_2$/CH$_4$ by using pure gases. Testing temperature: 299 K, PS support membrane.

CO$_2$ is transformed into small and easy-to-move ion HCO_3^-, the CO$_2$ transport is enhanced by the carriers. From the standpoint of the membrane structure, the high polarity in the membrane diminishes the solubility of nonpolarity component (CH$_4$), which is helpful to increase the CO$_2$ permeance and the selectivity of CO$_2$ over CH$_4$. Furthermore, the membrane is swollen by water and forms gel. Therefore, the diffusion coefficient is enhanced due to the decrement of movement resistance.

Permeation of CH$_4$ is a simple solution–diffusion process. The permeance of CH$_4$ decreases with increasing pressure, in accordance with the "dual-mode" sorption model of gas permeation through polymers.[9]

Very few studies are available in the literature that deal with the effects of the support membrane on the performance of a composite membrane. In this article, the performance of the composite membranes with different supports were studied. The results show that the polysulfone (PS) membrane (molecular weight cutoff, 50,000) is the best support membrane for CO$_2$/CH$_4$ system compared with polyethersulfone (PES) membrane (molecular weight cutoff, 30,000) and poly-

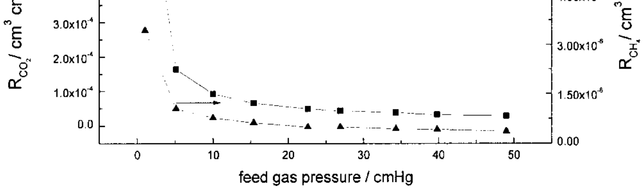

Figure 3 Effect of feed gas pressure on the permeance of CO$_2$ (■) and CH$_4$(▲) by using pure gases. Testing temperature: 299 K, PS support membrane.

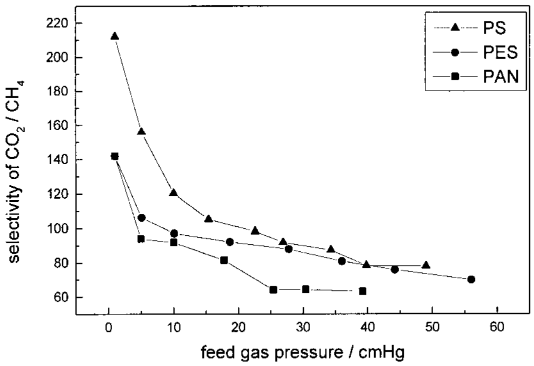

Figure 4 Effect of different support membranes on the selectivity of CO_2 over CH_4. The molecular weight cutoff : PS, 50,000; PES, 30,000; PAN, 50,000. Testing temparature: 300 K.

acrylonitrile (PAN) membrane (molecular weight cutoff, 50,000), as shown in Figures 4 and 5.

The gases tend to dissolve in polymeric media of similar chemical structure with them.[10] The structure of CO_2 is similar to that of sulfone groups. Apparently the sulfone groups favor the solubility of CO_2. Therefore, the solubilities of PS and PES support membranes for CO_2 are higher than that of PAN support membrane. Moreover, PAN has a very rigid backbone and high crystallinity, which leads to low diffusion coefficients. Consquently, both the selectivities and permeance of the composite membrane with the PAN support are not as good as that of the composite membranes with the PS and PES supports. Although PES is a totally amorphous material with a high density of sulfone groups, the average pore diameter of the PES membrane is smaller than that of the PS membrane, owing to its small molecular weight cutoff; thus, the CO_2 permeance of composite membrane with the PES support is lower than that of the composite membrane with PS support. As a result, the composite membrane with the PS support possesses the best performance.

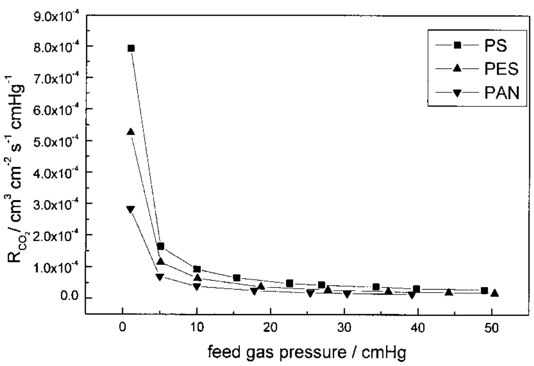

Figure 5 Effect of different support membranes on CO_2 permeance. The molecular weight cutoff : PS, 50,000; PES, 30,000; PAN, 50,000. Testing temparature: 300 K.

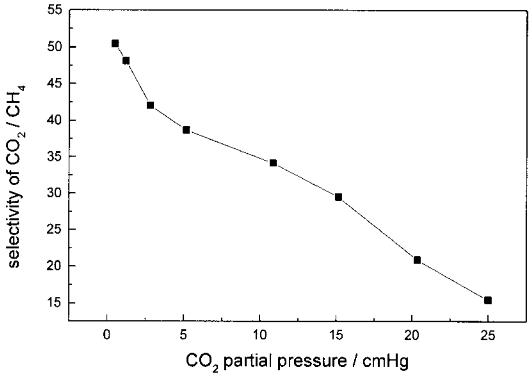

Figure 6 Effect of CO_2 partial pressure on the selectivity of CO_2 over CH_4 by using mixed gases. Testing temperature: 299 K, PS support membrane, feed gas: 50 vol % CO_2 + 50 vol % CH_4.

The composite membrane performance was also investigated by using mixed gases, as shown in Figures 6 and 7. From the figures, it can be seen that the selectivity of CO_2 over CH_4 and CO_2 permeance are not as good as that by using the pure gases. This is because of coupling effects between CO_2 and CH_4. It will be studied in detail in our later work.

From the above results, it can be seen that the composite membranes possess high CO_2 permeance and selectivity of CO_2 over CH_4. A permselectivity comparison of the membrane obtained in this work with other fixed carrier membranes is shown in Table I.

In the process to make membrane-casting solution, a very important step is to remove the low molecular weight impurities. Most of these impurites are sodium hydroxide left by the hydrolysis reaction. During the evaporation of the cast film, the low molecular weight impurities will crystallize. When the evaporation rate is fast, the crystal is small and the crystallinity is high; when the evaporation rate is slow, the crystal is large and complete. The effects of low molecular weight impurities on the membrane structure and perfor-

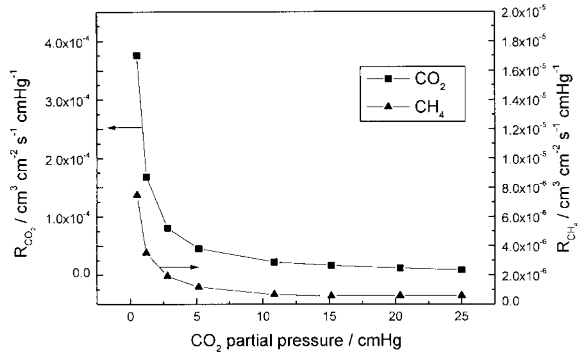

Figure 7 Effect of CO_2 partial pressure on the permeance of CO_2 (■) and CH_4 (▲) by using mixed gases. Testing temperature: 299 K, PS support membrane, feed gas: 50 vol % CO_2 + 50 vol % CH_4.

TABLE I
Comparison of Membrane Properties Obtained in This Work with Those of Other Fixed Carrier Membranes

Membrane	Selectivity	R_{co2} (cm^3/cm^2s cmHg)	System	P_{co2} (atm)	Ref
Polymerized membrane from diisopropylamine	17	4.5×10^{-4}	CO_2/CH_4 3.5 vol % CO_2	—	11
Polyethylenimine/poly(vinyl-alcohol)	230	10^{-6}	CO_2/N_2 5.8–34.4vol % CO_2	0.065	4
Poly{2-(*N*,*N*-dimethyl) aminoethyl methacrylate}	130	10^{-6}–10^{-5}	CO_2/N_2 2.7–58 vol % CO_2	0.047	8
Poly{2-(*N*,*N*-dimethyl)aminoethyl methacrylate-co-acrylonitrile}	60-90	10^{-9}–10^{-8}	pure CO_2 and N_2	0.03-0.06	3
Membrane from polyvinyl-pyrrolidone by hydrolysis	212.1	7.93×10^{-4}	pure CO_2 and CH_4	0.013	this work
	155.9	1.64×10^{-4}		0.067	
Membrane from polyvinyl-pyrrolidone by hydrolysis	48.1	1.69×10^{-4}	CO_2/CH_4 50 vol % CO_2	0.016	this work
	39.3	4.59×10^{-5}		0.068	

mance are as follows. First, sodium hydroxide left in the membrane will react with CO_2 to form sodium carbonate, which further reacts with CO_2 to form sodium bicarbonate. This is helpful to improve the selectivity; second, the low molecular weight impurities will be induced by CO_2 to the membrane surface; as a result, the membrane effective area will be lessened; third, the crystal of impurities will be dissolved gradually by the water brought in by the sweep gas and feed gas, which leads to the formation of a void and the membrane will loss its selectivity. In addition, the existence of low molecular weight impurities affects the crystallization of the polymer. Figure 8 shows the appearances of the membrane surfaces. The membrane whose casting solution was purified is dense and smooth, while the membrane whose casting solution was not purified contains grainy substance. Figure 9 compares the selectivity of the two kinds of membrane. Apparently, the selectivity of the membrane without impurities is much more than that of the membrane containing impurities.

CONCLUSIONS

1. The composite membranes developed in this work can effciently separate CO_2 from CH_4 because the mass transport of CO_2 is enhanced by the fixed carriers in the membranes.
2. Among PS, PES, and PAN support membranes, the PS support membrane is the best for CO_2 permeance.

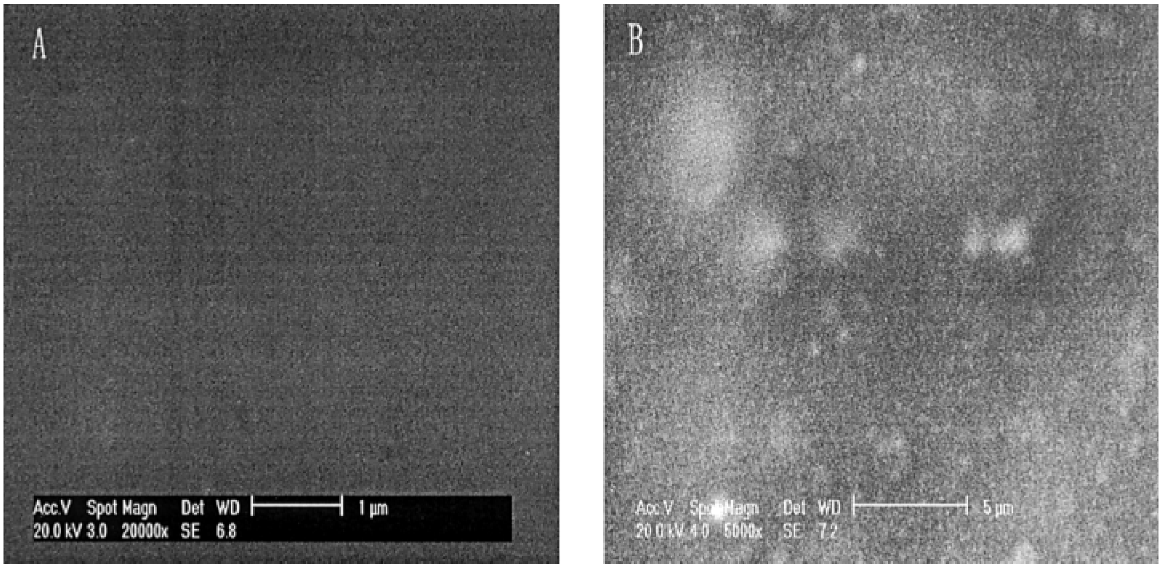

Figure 8 ESEM (environmental scanning electron micrograph) of membrane surface. PS support membrane. (A) Without impurities; (B) containing impurities.

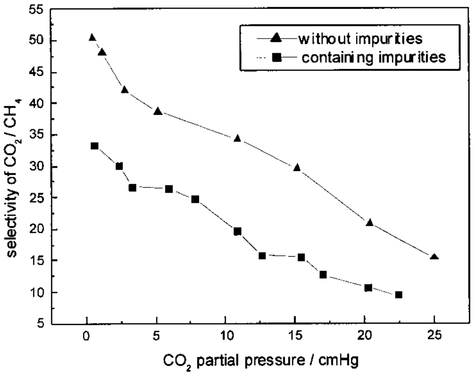

Figure 9 Effect of impurities on the selectivity of CO_2 over CH_4. PS support membrane. Testing temperature: 299 K, feed gas: 50 vol % CO_2 + 50 vol % CH_4.

3. To remove low molecular weight impurities in the membrane-casting solution is very important. The membrane without impurities possesses better surface structure and higher selectivity than the membrane containing impurities.

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