Synthesis and Characteristics of Novel Fixed Carrier Membrane for CO_2 Separation

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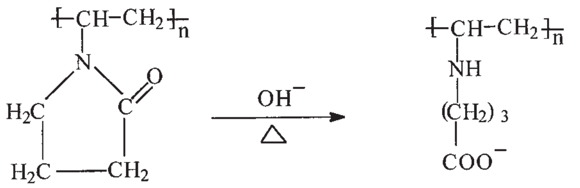
Permeation of CO_2 was investigated by using synthetic polymeric membranes having secondary amine and carboxyl groups which can act as carriers for CO_2. Selectivity of CO_2 over CH_4 was measured. The membranes possessed better CO_2 permeance than that of other fixed carrier membranes reported in literature.

Separation and removal of CO_2 using membrane has an advantage over the conventional separation methods because of low cost and high-energy efficiency. The commercially available polymeric membranes often have either high permeability or high selectivity, but not both.[1] Facilitated transport membranes selectively permeate CO_2 due to the reversible reaction between CO_2 and the carriers, and they possess high permeability as well as high selectivity. The fixed carrier membranes are generally favorable compared with supported liquid membranes (SLMs) and ion-exchange membranes because of their superior durability. In recent years, the fixed carrier membranes, especially the membranes having amine moiety[2–6] have been investigated extensively. In this paper, the carriers, secondary amine and carboxyl groups, were introduced into the membranes by the hydrolysis of polylvinylpyrrolidone, which are easily polymerized by radical polymerization. The selective permeation of CO_2 bases on the reversible reaction between CO_2 and the active groups.

Membrane material was prepared by the hydrolysis of polylvinylpyrrolidone (PVP) in an alkali solution at boiling temperature for a period of time.



PVP was obtained through radical polymerization in 20% N-vinylpyrrolidone (NVP) aqueous solution by using azobisisobutyronitrile (AIBN) as the initiator at 60 °C in the inert atmosphere of nitrogen gas.[7] The resulting polymer was purified by precipitating from acetone. The content of active carriers of amine and carboxyl groups was measured by titration method. The molecular weight of the resulting polymer was obtained from that of PVP and the conversion of the hydrolysis reaction. The viscosity molecular weight of PVP (M) was calculated from intrinsic viscosity (η) according to the equation[8]: $[\eta] = 1.4 \times 10^{-2} \times M^{0.7}$.

The aqueous solution of the resulting polymer was cast on a substrate by an applicator to form a film, then the cast film was dried at room temperature. The gas permeation experiments were carried out by using a set of apparatus. The effective area of the 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 swelling degree of the membrane is about 60%. The downstream pressure is one atmosphere.

Figure 1 and 2 show the effects of pressure difference on the performance of the membrane by using pure CO_2 and CH_4. The membrane possesses higher CO_2 permeance and selectivity of CO_2 over CH_4 which are comparable with the data in literature. A comparison of these values with those of other fixed carrier membranes is shown in Table 1. Both the permeance of CO_2 and selectivities of CO_2/CH_4 decrease with the increasing pressure difference. This is the characteristics of the facilitated transport mechanism.[4] With increasing pressure difference, CO_2 flux increases greatly in the lower pressure region and the extent of increment become gentle in the higher pressure region because of the saturation of the limited carrier. Therefore, the permeance, which is the function of the flux and pressure difference decreases

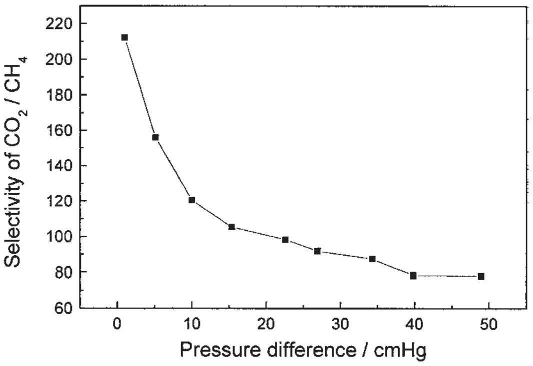


Figure 1. Effect of pressure difference on the selectivity of CO_2 over CH_4 by using pure gases. Testing temperature: 299 K, PS substrate, $M = 6.4 \times 10^5$, content of amine salt: 26.8%.

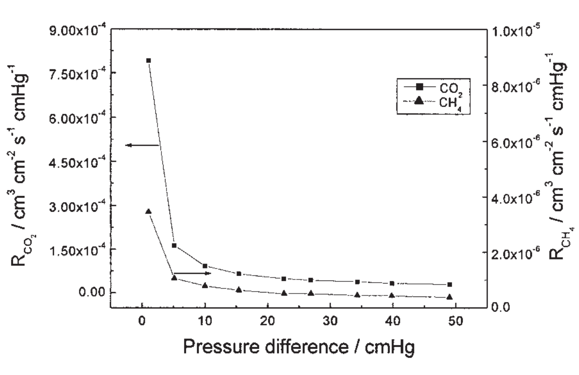


Figure 2. Effect of pressure difference on the permeance of CO_2(■) and CH_4(▲) by using pure gases. Testing temperature: 299 K, PS substrate, $M = 6.4 \times 10^5$, content of amine salt: 26.8%.

Table 1. Comparison of membrane properties obtained in this work with those of other fixed carrier membranes

system	R_{CO2} $cm^3\,cm^{-2}\,s^{-1}\,cmHg^{-1}$	selectivity	P_{CO2} atm	ref
$CO_2/CH_4$3.5 vol%CO_2	4.5×10^{-4}	17	—	3
$CO_2/N_2$5.8–34.4 vol%CO_2	10^{-6}	230	0.065	4
$CO_2/N_2$2.7–58 vol%CO_2	10^{-6}–10^{-5}	130	0.047	5
pure CO_2 and N_2	10^{-9}–10^{-8}	60–90	0.03–0.06	6
pure CO_2 and CH_4	1.64×10^{-4}	155.9	0.067	this work
$CO_2/CH_4$50 vol%CO_2	4.59×10^{-5}	39.3	0.068	this work

with increasing pressure difference. The carriers are the secondary amine and carboxyl groups. The facilitated transport mechanism is as follow[5,9]

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

CO_2 was transformed into small and easy to move ion HCO_3^-, the CO_2 transport was enhanced by the carriers. This idea was characterized by FTIR using attenuated total reflectance techniques, as in Figure 3. Compared with the blank membrane, the humidified membrane absorbing CO_2 results in the appearance of several new bands, 1922 cm^{-1}, 1400 cm^{-1} and 997 cm^{-1}. The band at 1922 cm^{-1} should attribute to the complex of CO_2 and active groups. The band at 1420 cm^{-1} and 997 cm^{-1} should attribute to the HCO_3^-. Therefore, CO_2 can react reversible with the membrane. While the spectrum of the humidified membrane absorbing CH_4 does not display any new band or any shift of wavenumbers.

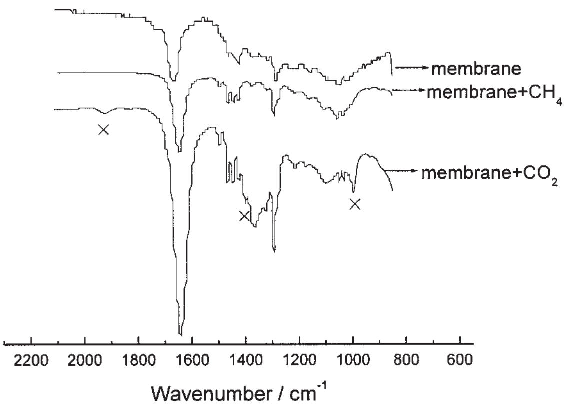


Figure 3. FTIR spectra of membrane absorbing CO_2 and membrane absorbing CH_4.

From the standpoint of the membrane structure, the high polarity in the membrane diminishes the solubility of non-polar component (CH_4), which is helpful to increase the CO_2 permeation and the selectivity of CO_2 over CH_4. Furthermore, the membrane is swollen by water and forms gel. Therefore, the diffusion coefficient was enhanced due to the decrement of movement resistance.

The performance of composite membrane was also investigated by using mixed gases, as Figure 4 and Figure 5. The results show the selectivity of CO_2 over CH_4 and CO_2 permeance were not as good as the data by using pure gases because of coupling effects between CO_2 and CH_4. It will be studied in detail in our later work.

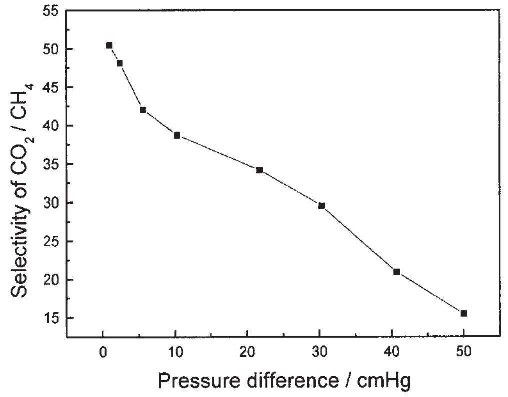


Figure 4. Effect of pressure difference on the selectivity of CO_2 over CH_4 by using mixed gas. Testing temperature: 299 K, PS substrate, feed gas: 50 vol% CO_2 + 50 vol% CH_4, $M = 6.4 \times 10^5$, content of amine salt: 25.9%.

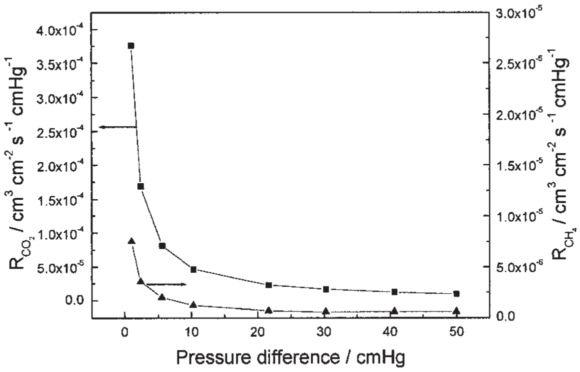


Figure 5. Effect of pressure difference on the permeance of CO_2(■) and CH_4(▲) by using mixed gas. Testing temperature: 299 K, PS substrate, feed gas: 50 vol% CO_2 + 50 vol% CH_4, $M = 6.4 \times 10^5$, content of amine salt: 25.9%.

References and Notes

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