Development of novel facilitated transport membrane for selective separation of CO_2 from H_2 and N_2

R. Yegani(1),(2),(3), M. Teramoto(1),(2), H. Hiorozawa(1), H. Himei(2), O. Okada(2), N. Ohmura(1) and H. Matuyama(1)
(1) Department of Chemical Science and Engineering, Kobe University, Rokkodai, Nada-ku, Kobe, 657-8501, Japan
(2) Renaissance Energy Research Co. 3-2-23, Kitahama, Chuo-ku, Osaka, 541-0041, Japan
Faculty of Chemical Engineering, Sahand University of Technology, SahandNew Town, Tabriz, Iran, Post Box: 51335-

***Abstract*— A novel facilitated transport membrane consisting of 2,3-diaminopropionic acid (DAPA) as a selective carrier of CO_2 and PVA/PAA gel as support was developed for the removal of CO_2 from the water gas shift reactor in the hydrogen production plants. The membrane performance was tested by the experiments on the selective separation of CO_2 at the temperature from 125°C to 160°C and the feed gas pressure from 100 kPa to 700 kPa. High CO_2 permeance and CO_2/H_2 selectivity were obtained at higher temperatures. Obtained results showed that the water content in the membrane is one of the key factors, which determines the CO_2 permeance and CO_2/H_2 selectivity. It was also found that increasing the carrier concentration could significantly enhance the membrane performance, especially at elevated temperatures.**

١ Introduction

A water-gas-shift (WGS) reactor for the conversion of carbon monoxide (CO) and water to hydrogen (H_2) and carbon dioxide (CO_2) is widely used in chemical and petroleum industries [1]. In water gas shift (WGS) reaction, CO in the synthesis gas from the reformer reacts with H_2O to form H_2 and CO_2.

$$CO\ (g) + H_2O\ (g) \leftrightarrow CO_2\ (g) + H_2\ (g) \qquad (1)$$

This reaction can be enhanced significantly through a CO_2-selective membrane, which removes the reaction product, CO_2, to overcome the reaction equilibrium and shift the reaction towards the product side. The CO_2-selective WGS membrane reactor has advantages including (1) a high-purity H_2 product is recovered at the high pressure (feed gas pressure) and (2) air can be used as the sweep gas to remove CO_2, on the low-pressure side of the membrane to have a high driving force for the separation, which eliminates an unwanted compressor, lowers CO concentration and increases H_2 purity and recovery.

As the membrane is used at high temperatures, nonvolatile carriers such as amino acids are preferable [2]. 2, 3 –Diaminopropionic acid (DAPA) has been reported as an efficient CO_2 carrier at 160 °C for selective separation of CO_2 from N_2 [3], [4]. In our previous work, we have developed a novel facilitated transport system, which consisted of PVA/PAA gel and DAPA, and the membrane performance was tested by the experiments on the selective separation of CO_2 from a mixture of CO_2, N_2 and H_2O. In order to increase the water content, as an important parameter in membrane performance, at such high temperatures, we pressurized the feed gas so that the water content in the membrane can be maintained as high as possible. Here, we report the effect of various conditions such as temperature and carrier concentration on the CO_2 permeance and CO_2/H_2 selectivity.

II MATERIAL AND METHODS

1-1. Materials and membrane preparation method

Poly(vinyl alcohol)-Poly(acrylic acid) copolymer(PVA/PAA copolymer), L-5HP type, DL-2,3-diaminopropionic acid hydrochloride (DAPA-HCl), a mobile CO_2 selective carrier and cesium hydroxide as a neutralizing agent for DAPA-HCl were dissolved in deionized water by stirring the solution for 24hr at 25 °C in a screw-capped vessel. The prepared solution was centrifuged at 5,000 rpm at room temperature for 30 min to remove small bubbles, which might cause membrane instability. Then the solution was cast onto hydrophobic or hydrophilized microporous PTFE membranes, which were used as supports for coated gel membrane, using an applicator with a gap setting of 254 or 500 µm.

1-2. Gas permeation

A model feed gas consisting of 3.65 mol % CO_2, 32.9 mol% H_2 and 63.5 mol% H_2O was used unless otherwise described. The feed gas was pre-heated by a coiled heat exchanger and introduced into the cell at the flow rate of 2.24×10^{-2} mol wet gas/min (200ml dry gas/min at 25°C, 1atm). The feed side pressure was controlled by a back-pressure regulator in the range from 1 to 7 bars.

Argon was supplied to the permeate side of the cell as a sweep gas through a coiled heat exchanger at the flow rate of 20 ml (STP)/min and carried the penetrated gas to a gas chromatograph to determine the composition of the permeate. The pressure in the sweep side was kept constant at almost atmospheric pressure.

III RESULTS AND DISCUSSION

A. Effect of mobile carrier concentration and feed side pressure on membrane performance

The effect of carrier concentration on the membrane performance was investigated using membranes containing 0-65 wt% DAPA at 125°C. As shown in Fig. 1, the CO_2 permeance as well as CO_2/H_2 selectivity increased with increasing the DAPA concentration. However, little effect on H_2 permeance was observed. It is known that with increasing the feed side pressure, the water content of membrane, an essential parameter in membrane performance, is increased,

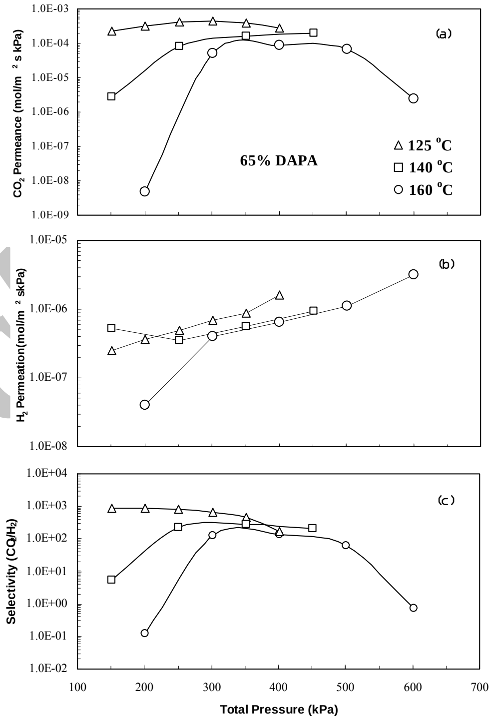

Fig.1. Effect of carrier concentration on (a) CO_2 permeance, (b) H_2 permeance and (c) CO_2/H_2 selectivity at 125 °C.

which would result in higher CO_2 permeance [4]. H_2 permeance is continuously increased with increasing the feed side pressure, which result that the selectivity is gradually decreased. It is considered that with increasing feed side pressure, the partial pressure of water in feed side and the water content in the gel layer increase, which increases the CO_2 permeance. As shown in Fig.2, the membrane becomes unstable in higher DAPA concentration, at higher temperatures e.g. 65% at 160 ^{o}C. This is because the higher the DAPA concentration, the lower the copolymer concentration and also lower the efficiency of cross-linking.

B. Effect of temperature on membrane performance

Fig. 2 also shows the effect of temperature on the membrane performance. The CO_2 permeance as well as CO_2/H_2 selectivity decreased with increasing temperature. As temperature increases, the rate of reaction between CO_2 and the carrier increases, which would results in a high CO_2 permeance. However, with increasing temperature, the chemical equilibrium constant becomes small, which decreases the absorption of CO_2 in the membrane at the feed side and lowers the CO_2 permeance. A low water content of the gel membrane at high temperatures also decreases the rate of reaction between CO_2 and DAPA. The combined effects may be the reason for lower CO_2 permeance at high temperatures.

IV conclusion

The prepared gel membrane consisting of DAPA and PVA/PAA gel exhibited high CO_2 permeance and CO_2/H_2 selectivity at relatively high temperatures (125 –160°C), and can be a candidate of the CO_2 selective membrane used in the water gas shift catalytic membrane reactor. Increasing the carrier concentration considerably enhanced the CO_2 permeance and CO_2/H_2 selectivity. The membrane performance decreased with increasing temperature.

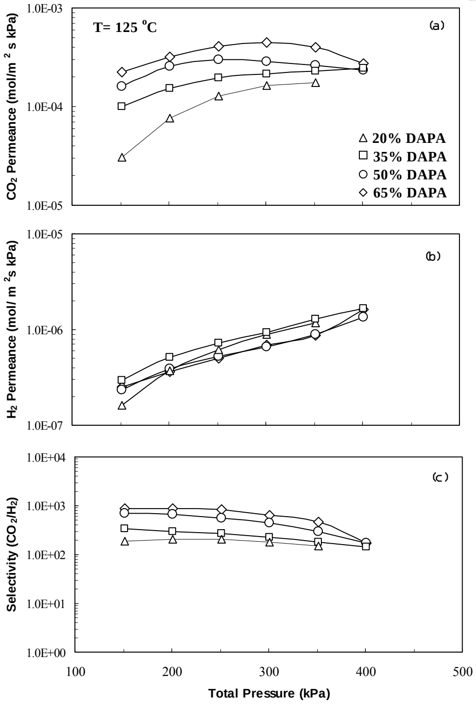

Fig.2. Effect of temperature on (a) CO_2 permeance, (b) H_2 permeance and (c) CO_2/H_2 selectivity of membrane consisiting 65% DAPA

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