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HYDROGEN PURIFICATION USING A MICROPOROUS HYDROTALCITE-SILICA COMPOSITE MEMBRANE

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ABSTRACT: - A novel thin microporous composite membrane of a dual-element hydrotalcite-silica was prepared on porous alumina support by sol-gel method. Strong CO_2 adsorption on hydrotalcite material inhibited the diffusion of H_2 through the membrane and decreased H_2 permeances significantly so that CO_2 preferentially permeated. The effects of pressure difference across the membrane, operating temperature and CO_2 feed concentration on the CO_2 separation performance of the membrane were investigated using synthetically mixed gas. The CO_2 permeance and CO_2/H_2 separation selectivity decreased with increasing the temperature due to the loss of the membrane ability for CO_2 adsorption with temperature. Further increase of the pressure difference across the membrane decreased both CO_2 permeance and CO_2/H_2 separation selectivity. The CO_2 feed concentration with 40% showed the best performance with a CO_2/H_2 separation selectivity of 10.59.

Keywords: Hydrogen Purification, Hydrotalcite Membrane, Surface Diffusion, Microporous Membrane.

1- INTRODUCTION

Hydrogen is a high-quality and an environmentally clean fuels [1-2]. Recently, hydrogen has an increasing attention as a way to reduce our reliance on fossil fuels and due to growing demand of hydrogen in petroleum refining and petrochemical production [1, 3]. Currently, hydrogen is mainly produced from the synthesis gas purification, primarily consisting of CO_2 and H_2, resulting from steam reforming of natural gas followed by water gas shift reaction [1]. Most hydrogen is separated from the synthesis gas by conventional separation processes such as aqueous amine absorption [4]. On the other hand, Membrane technology is an attractive alternative and a novel method to facilitate H_2 separation from a gas mixture. Membranes act as filters that enable continuous separation of one or more gases from a feed mixture based on the differences in physical properties of the gases and/or chemical interplays between the membrane material and the gas [5-6]. The separation of H_2 using membrane technologies provides many advantages over the other conventional separation technologies due to its low energy consumption, relatively easy to operate and control and also easy to scale-up [7]. The most reported membranes for CO_2/H_2 separation preferentially permeate H_2, which is obtained at low pressures from the permeate side, and it must then be recompressed at considerable energy cost .The CO_2-selective membranes that preferentially permeate CO_2 can minimize H_2 recompression [3].

Hydrotalcite (HT) has been intensively investigated in recent years as adsorbents for CO_2 at high temperature to reduce the greenhouse emission into atmosphere. HT has adequate mechanical strength when it is exposed to high pressure, it exhibits high capacity and selectivity to adsorb CO_2 at high temperature, adequate CO_2 adsorption/desorption kinetics for CO_2 at operating conditions, and stable adsorption capacity of CO_2 after repeated adsorption/desorption cycles [8-10]. In this research the fabrication of novel membrane from HT material modified microporous silica membranes to increase the separation selectivity of CO_2 from synthesis gas is a subject of this study. Modification of the internal pore surface of silica membrane with HT increases the amount of adsorbed CO_2 resulting in increase of the CO_2 diffusion and separation selectivity [11-12]. The composite membrane of HT-silica is expected to provide high CO_2 permeance due to the surface affinity of HT to CO_2 gas and adequate separation factor.

2- EXPERIMENTAL

2.1 Preparation of macropours α-alumina support

The home-made macroporous α-alumina discs of 25 mm in diameter and 2mm in thickness were prepared using high purity α-alumina powder (>99.99%) with particle size of 45 μm (Sumitomo Co, Japan, AA-04). The alumina powder of 32 g was thoroughly mixed with 2.6 g of de-ionized water prior to pressing. For each support, 3.5 g of the mixture was introduced in a stainless still mold and pressed at 600 kg/cm^2 for 1 min using hydraulic press pelletizer. The supports were then dried overnight at 80 ºC to remove the water binder, and then calcined at 1000 ºC for 30 h using a programmable furnace. After calcination, the discs were polished with 800 and 1000 grit sand paper, washed with deionized water and then dried overnight in oven at 80 ºC.

2.2 Preparation of mesoopours γ-alumina intermediate layer

On the surface of the calcined α-alumina support, 2 layers of intermediate mesoporous γ-Al_2O_3 were prepared by sequential dip-coating technique with a boehmite coating sol. The boehmite sol was prepared by slowly addition of 12.8 ml aluminum tri-sec butoxide (ATB) (Merck, 97 %) to 90.3 ml deionized water at 90°C and stirred vigorously for 1 h to achieve completely hydrolysis of ATB. Afterward, 2.1 ml Polyvinyl alcohol (PVA) solution (4 g PVA/100 ml H_2O) was added to the mixture as a membrane binder. The resulting sol was then peptized by adding 7.5 ml of hydrochloric acid solution (1 M) drop-wise and kept under reflux conditions for 24 h at 90 °C. The molar ratios of ATB, HCl and water were 1:100:0.07. For supported γ-Al_2O_3 membrane, the calcined α- Al_2O_3 supports was dipped in the boehmite sol for 10 s and dried at ambient temperature for 24 h before it was calcined at 600 ºC for 3 h using a programmable furnace. In order to produce crack free γ-Al_2O_3 membrane, dipping, drying and calcination processes are repeated once [13].

2.3 Preparation of microporous HT-silica composite membrane

An HT sol was first prepared following a previously described sol-gel technique [14-15]. Briefly, 54 ml of absolute ethanol (EtOH) (Merck, 99.8 %) was refluxed at 70 ºC, and thereafter 3.92 g of aluminum tri-sec- butoxide (ATB) was added slowly into the ethanol at 70 ºC and refluxed under constant stirring for 1 h. For partial hydrolysis, 0.155 ml of nitric acid solution (3 M) (Merck, 65 %) was then added drop-wise to the solution under vigorous stirring for 1 h while keeping the solution heated at 70 ºC. The mixture was then subsequently cooled to room temperature. Afterward, 0.885 ml of acetic acid (AA) (Aldrich, 99.7 %) was added under vigorous stirring for 1 h as a complexing agent to hinder future hydrolysis reactions. After that the temperature of the mixture was lowered to 0 ºC and 40 ml of magnesium methoxide solution (MgM) (Aldrich, 6-10 wt. %) was added drop-wise to the mixture. The mixture was brought back to room temperature and stirred for 18 h. Finally, 0.155 ml of deionized water was added to achieve the desired molar ratio of H_2O to ATB. The molar ratios of ATB, EtOH, HNO_3, AA and H_2O used in the experiment to prepare the HT sol were 1:60:0.03:0.5:1

Polymeric silica sol was prepared by acid-catalyzed (HNO_3) hydrolysis and condensation of tetraethyl orthosilicate (TEOS) (Merck, 99 %) in ethanol as decried previously [16-17]. A mixture of 0.35 ml HNO_3 and 10.4 ml of de-ionized water was carefully dropwise to a mixture of 20 ml TEOS and 20 ml of EtOH at room temperature under vigorous stirring. During the addition of acid and water mixture, a mixture of ethanol and TEOS was placed in a water-bath to avoid partial hydrolysis. Afterward, the mixture solution was refluxed at 65 ºC for 3 h under constant stirring. The molar ratios of TEOS, EtOH, water and HNO_3 used in the experiment were 1:3.8:6.4:0.085.

Mixed HT-silica sols (the microporous membrane precursor) were prepared by slowly addition of 7.5 ml HT sol to 50 ml silica sol under vigorous stirring. The mixture was then stirred rigorously for 30 min at room temperature. The resulting mixed sol was diluted 10-times with ethanol to obtain the final dip solution. The supported microporous HT-silica composite membranes were prepared by dipping α-alumina pellet support coated with γ-alumina intermediate layer into freshly prepared ethanol diluted HT-silica mixed sol for 5 sec. After dipping, the supported membranes were calcined at 500 ºC for 3 h with a heating and cooling rate of 0.5 ºC /min. Second dipping procedure was applied after calcination to repair possible cracks or pinholes. The second dipped sol was prepared by diluting a standard sol 200 times, which is 20 times more diluted than for first dipped sol.

2.4 Gas permeation and separation measurement

The membrane performance was determined based on the mixed gases permeation and separation results. Prior to the permeation test, the membrane was heated to 100 ºC for 1h and hydrogen gas was fed into the module at 20 ml/min. The permeate side was evacuated by a vacuum pump to remove adsorbed gases from the pores. The membrane performance was determined in terms of gas permeance, selectivity and separation selectivity. The permeance of gas species *i* in the binary gas mixture, K_i^{mix}, was defined as:

$$K_i^{mix} = \frac{N_i^{mix}}{\Delta p_{ln,i}} \tag{1}$$

Where: N_i^{mix} is the mole flux of gas species *i* in the gas mixture permeate through the membrane and $\Delta p_{ln,i}$ is the log-mean pressure difference (Pa) across the membrane was used to determine the driving force from the partial pressures as below:

$$\Delta p_{ln,i} = \frac{(p_{F,i} - p_{P,i}) - (p_{R,i} - p_{P,i})}{\ln[(p_{F,i} - p_{P,i})/(p_{R,i} - p_{P,i})]} \tag{2}$$

Where: $p_{F,i}$, $p_{P,i}$ and $p_{R,i}$ are the partial pressures for gas species *i* (Pa) in feed, permeate and retentate, respectively.

The selectivity and the separation selectivity were used to measure the mixed gases separation performance across the membrane. The selectivity in the mixed gases, $\alpha_{i/j}^{com}$, was calculated from the mole fractions of gas species *i* at permeate and retentate streams as shown below:

$$\alpha_{i/j}^{com} = \frac{y_i/y_j}{x_i/x_j} \tag{3}$$

Where: y is the mole fraction of gas species in the permeate stream, and *x*, the mole fraction of gas species in the retentate stream.

The separation selectivity in the mixed gases, $\alpha_{i/j}^{sep}$, was calculated from the ratio of the gas permeances for mixtures as shown below:

$$\alpha_{i/j}^{sep} = \frac{K_i^{mix}}{K_j^{mix}} \tag{4}$$

3-RESULTS AND DISCUSSION

3.1 Effect of pressure difference

Figure 1 shows the effect of pressure difference on CO_2 and H_2 gas permeances through HT-silica micropores membrane for equimolar CO_2/H_2 binary gas mixture at 30 ºC. Both CO_2 and H_2 permeances decreased with increase in pressure difference from 100 to 500 kPa. The decreasing CO_2 permeance was due to low CO_2 adsorbed concentration gradient relative to the increase in CO_2 partial pressure difference (CO_2 log-mean partial pressure difference). Whereas, the decreasing H_2 permeance was due to the blocking effect by the CO_2 adsorption layer that resulted in the decrease of the H_2 permeance [18-19]. The highest value of CO_2 permeance obtained at 30 ºC and 100 kPa was (4.2×10^{-7} $mol.m^{-2}.s^{-1}.$ Pa^{-1}).

Figure 2 presents the effect of pressure difference on CO_2/H_2 selectivity and separation selectivity for equimolar CO_2/H_2 binary gas mixture at 30 ºC. It can be observed that the CO_2/H_2 selectivity increased as the pressure difference was increased from 100 to 500 kPa and reached the highest value of 4.32 at 500 kPa pressure difference. On the contrary, the increasing pressure difference decreases CO_2/H_2 separation selectivity from 9.28 to 4.8. The highest value of CO_2/H_2 separation selectivity was 9.28 obtained at 30 ºC and 100 kPa pressure difference. This is due to the competitive adsorption between CO_2 and H_2 and also to the CO_2 pore blocking effect. The movement of the gases molecules through membrane pores was affected by the intermolecular collision, the interaction between gas molecules and membrane pore wall, and the interplay between the movements of different gas molecules and its relation with the kinetic diameter of the gas molecule [3, 19-20].

3.2 Effect of temperature

The effect of temperature on the CO_2 and H_2 permeances through HT-silica micropores membrane for the equimolar CO_2/H_2 mixture at 100 kPa pressure difference is shown in Figure 3. It can be noted that the increasing operating temperature from 30 to 190 ºC results in the decrease of the CO_2 permeance from 4.2×10^{-7} to 2.1×10^{-7} $mol/m^2.s.Pa.$ and increase in the H_2 permeance from 0.453×10^{-7} to 1.03×10^{-7} $mol/m^2.s.Pa.$ The decreasing CO_2 permeance was due to the decrease the adsorption ability of the HT-silica membrane with the increase in the operating temperature [10]. Whereas, the small kinetic diameter of the unadsorb H_2 resulted in increase in the H_2 permeance with the increase in the operating temperature due to the micropore diffusion effect [21]. The effect of operating temperature on CO_2 and H_2 permeances through HT-silica membrane is similar to that observed previously, consistent with previous work using SAPO-34 zeolite membrane [22].

Figure 4 shows the effect of operating temperature on CO_2/H_2 selectivity and separation selectivity for equimolar CO_2/H_2 mixture at 100 kPa pressure difference. It is observed that both CO_2/H_2 selectivity and separation selectivity decreased with increase in operating temperature from 30 to 190 ºC at fixed pressure difference. The decreasing CO_2 permeance and the increasing H_2 permeance with increase in the operating temperature was due to reduction of the CO_2 adsorption ability for HT-silica membrane and increase in the activation energy of H_2 that resulted in decrease of both CO_2/H_2 selectivity and separation selectivity [22-23]. The HT-silica micropores membranes could selectively separate CO_2 from CO_2/H_2 mixture at high temperature as can be seen from Figure 4, since both CO_2/H_2 selectivity and separation selectivity was higher than 1. This selectivity can be improved further at higher pressure so that the adsorption capacity of HT can be increased [24].

3.3 Effect of CO_2 feed concentration

Figure 5 shows the effect of CO_2 feed concentration on CO_2 and H_2 gas permeances through HT-silica membrane for CO_2/H_2 gas mixture at 30 ºC and 100 kPa pressure difference. When the CO_2 feed concentration increased from 10 to 50% at fixed operating temperature and pressure difference, both CO_2 and H_2 permeances decreased. The decreasing

CO_2 permeance was due to the increasing adsorbed concentration gradient of CO_2 that is less than the CO_2 partial pressure difference. While the decreasing in H_2 permeance was due to the competitive adsorption and the hindrance effect which increased with increase in CO_2 feed concentration [3, 19, 25].

The CO_2 feed concentration dependency of the CO_2/H_2 selectivity and separation selectivity through HT-silica membrane for the equimolar CO_2/H_2 mixture at 30 ºC and 100 kPa pressure difference is shown in Figure 6. The CO_2/H_2 selectivity increased with increase in CO_2 feed concentration from 10 to 50% to reach a highest value of 3.1 at 50% of CO_2 feed concentration. This tendency is due to faster diffusion of CO_2 molecules when fewer H_2 molecules were present in the pores which resulted in increase in the CO_2 permeate concentration with increase in CO_2 feed concentration [19]. Moreover, the CO_2/H_2 separation selectivity reached maximum value of 10.59 at 40% of CO_2 feed concentration.

4-CONCLUSION

Hydrotalcite compound for use in developing a microporous silica membranes for CO_2 separation from synthesis gas was successfully prepared using sol-gel method. The microporous HT-silica membrane was found to enhance the CO_2 permeance and selectivity from CO_2/H_2 gas mixture. The membrane removed CO_2 from CO_2/H_2 binary gas mixture because CO_2 adsorbed more strongly on the membrane pore wall than H_2. The CO_2/H_2 selectivity had a maximum as a function of CO_2 feed concentration, and the selectivity decreased as the temperature increased. At low temperatures and high pressures, the CO_2/H_2 selectivity was greater than 10, and thus a HT-silica membrane will have potential for applications.

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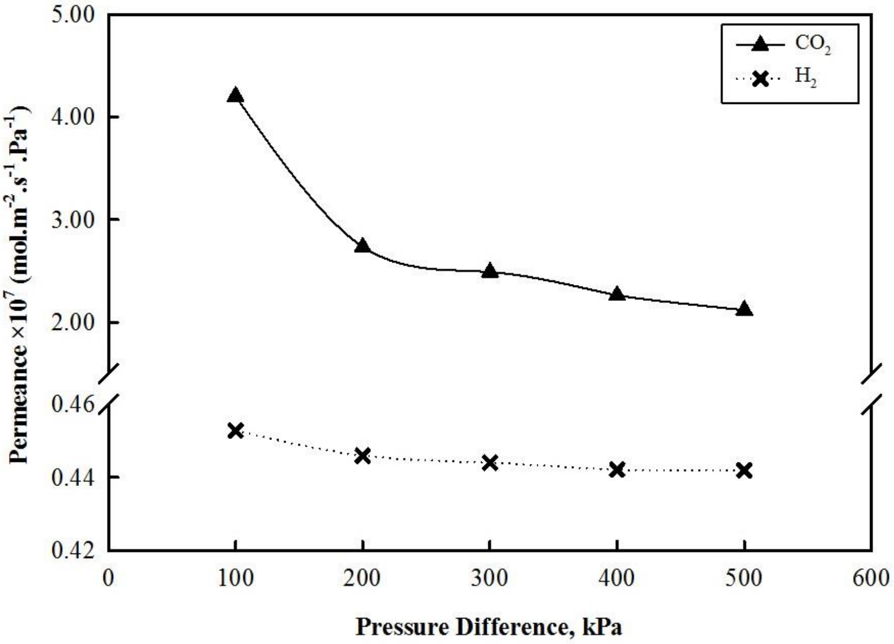

Figure (1): CO_2 and H_2 permeances through HT-silica micropores membrane for a CO_2/H_2 mixture (50/50 feed) at 30 ºC as a function of pressure difference across the membrane

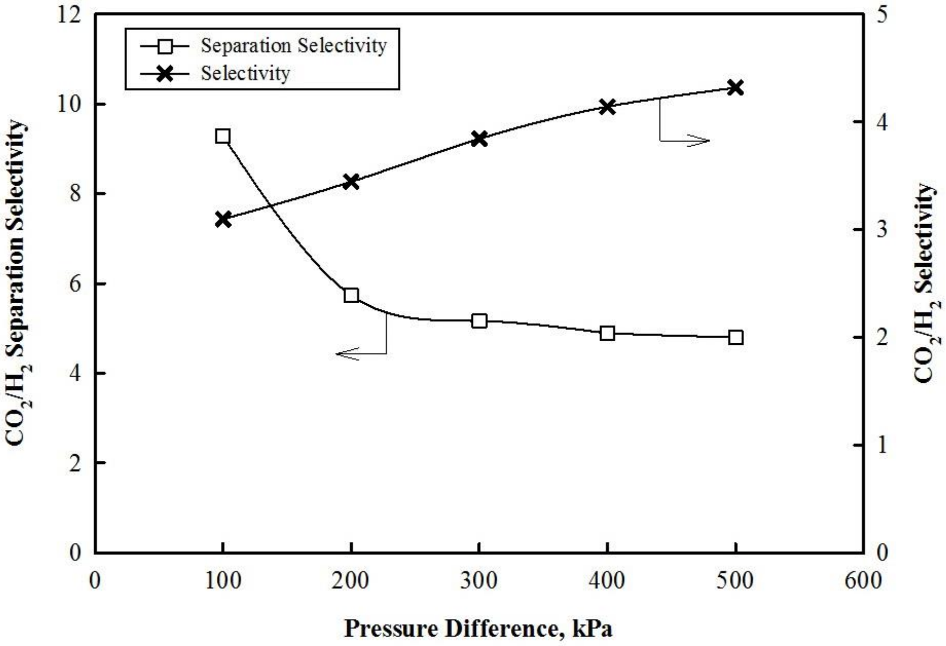

Figure (2): Separation selectivity and selectivity through HT-silica micropores membrane for a CO_2/H_2 mixture (50/50 feed) at 30 ºC as a function of pressure difference across the membrane

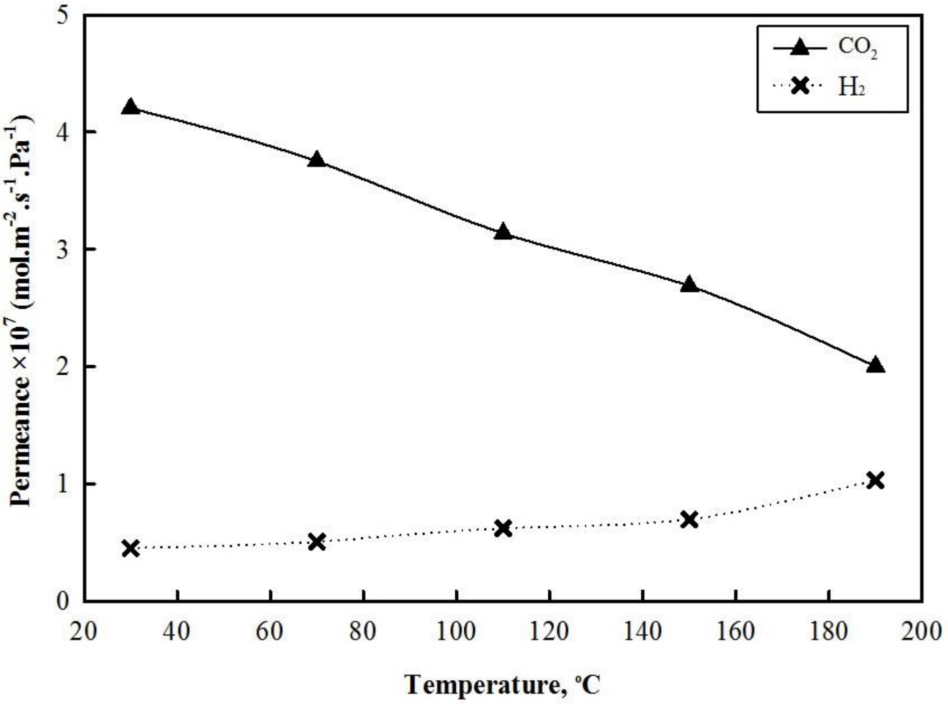

Figure (3): CO_2 and H_2 permeances through HT-silica micropores membrane for a CO_2/H_2 mixture (50/50 feed) at 100 kPa pressure difference across the membrane as a function of temperature.

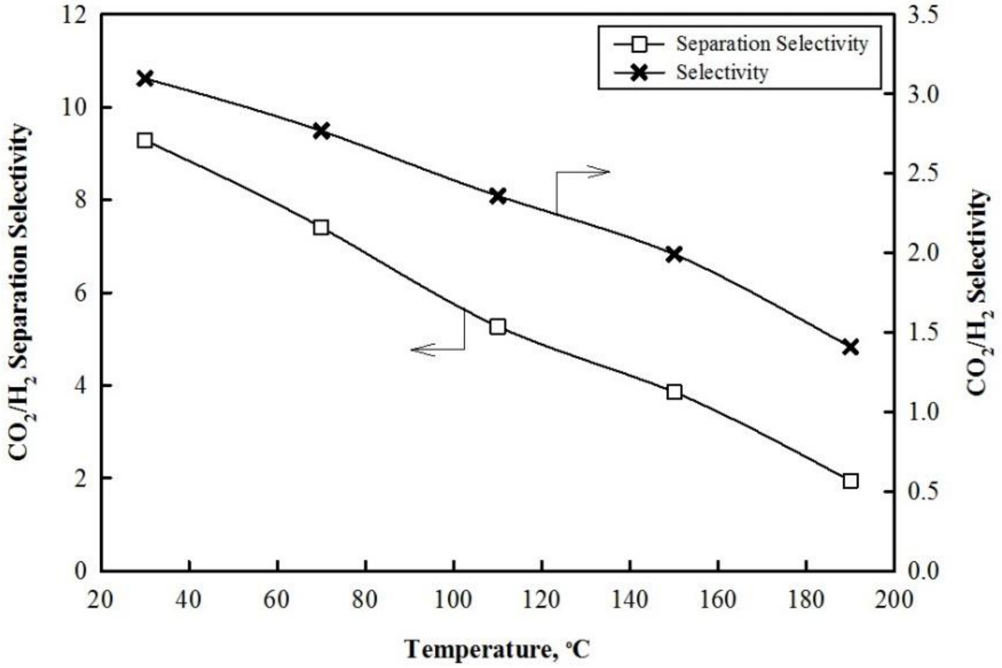

Figure (4): Separation selectivity and selectivity through HT-silica micropores membrane for a CO_2/H_2 mixture (50/50 feed) at 100 kPa pressure difference across the membrane as a function of temperature.

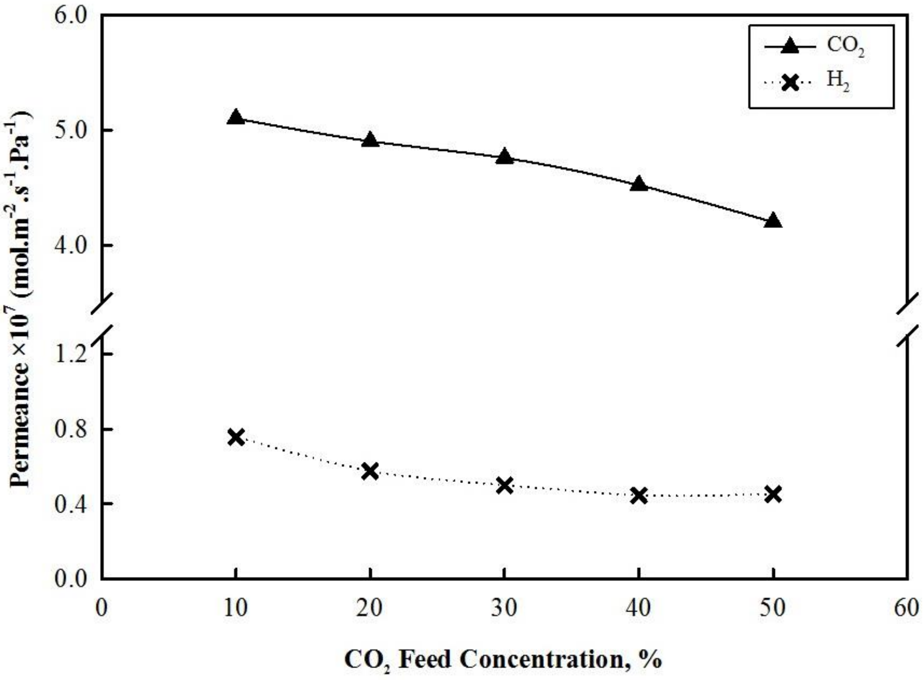

Figure 5: CO_2 and H_2 permeances through HT-silica micropores membrane for a CO_2/H_2 mixture as a function of CO_2 feed concentration at 100 kPa pressure difference across the membrane and 30 °C temperature

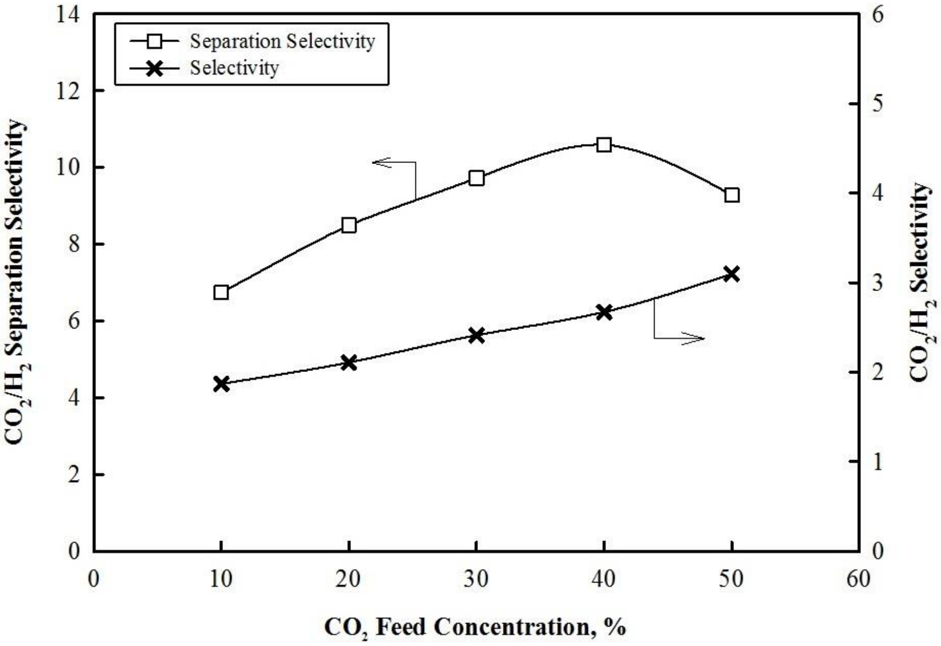

Figure 6: Separation selectivity and selectivity through HT-silica micropores membrane for a CO_2/H_2 mixture as a function of CO_2 feed concentration at 100 kPa pressure difference across the membrane and 30 °C