

Microporous inorganic membranes for CO₂ separation

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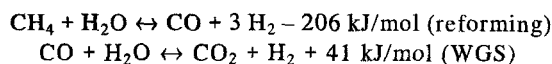
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A MFI zeolite membrane shows CO₂/H₂ separation factor 34 at room temperature. While the separation ability decreased with temperature, the membrane showed CO₂ separation ability up to 200°C. H⁺ type and NH₃-H⁺ type zeolite membrane showed almost the same permselectivity, suggesting the CO₂ adsorption occurs on to the zeolitic frame or surface silanol groups. The results suggest a possibility in separating CO₂ by enhancing the adsorption strength at high temperature.

Key words: CO₂ sequence, water gas shift, zeolite membrane, high temperature

1. INTRODUCTION

Hydrogen is a carbon free energy carrier and fuel for production of power by fuel cells and new gas turbines. Applying H₂ or CO₂ selective membranes in the water gas shift (WGS) reaction is a means to separate the products to H₂ and CO₂.



The major difference between H₂ and CO₂ selective extraction by membranes is the H₂ pressure after the membrane reactor. In case of applying H₂ selective membranes, the H₂ pressure is lowered by the permeation and a compressor may be required before the turbine. On the other hand, employing a CO₂ selective membrane instead, H₂ is kept in the high-pressure lead stream (see Figure 1). In addition, non-converted CH₄ and CO are in the same stream as H₂ to be fed to the turbine. Accordingly, energy loss is expected to be smaller in the latter case.

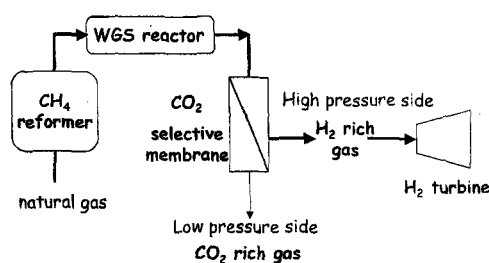


Figure 1 Schematic image of the process

The technical challenge of CO₂ extraction is the development of a membrane having sufficient CO₂ separation ability under low temperature WGS conditions (c.a. 200-300 °C) in H₂O vapor. Much study has been done on CO₂/N₂ separation targeting the CO₂ capture from waste gas. Various types of membranes, such as silica¹, zeolites², carbon or polymers³ have been examined. To enhance the selectivity, several modifications

are also have been investigated^{2,4,5}. This work shows that CO₂/N₂ separation ability is sensitive to temperature and separation ability significantly drops with temperature. This is because the separation is dominated by CO₂ adsorption strength to the membrane materials. The same mechanism can be expected for the CO₂/H₂ separation⁶. Moreover, this is more difficult than CO₂/N₂, as H₂ is a smaller molecule than N₂ and can permeate through pores that CO₂ cannot penetrate.

There are different approaches to reach CO₂ selective permeation. One is to use dense membranes having CO₂ selective transport ability (see left image of Figure 2). Nair *et al.* used molten carbonate as a CO₂ carrier⁷. They covered porous supports with molten Li₂ZrO₃, and obtained CO₂/N₂ separation factor about 5 at 600 °C. In principle, as the CO₂ permeation is based on a reaction, high CO₂ selectivity can be expected. Preferentially, lithium carbonate should be in a molten phase to obtain a faster reaction rate than what is possible in the solid phase^{8,9}. Accordingly, the operation temperature should be higher than 400 °C in order to have molten phase. It may be some difficulty in maintaining the molten carbonate on/in the support and thinner the molten layer thickness to obtain higher permeating flux.

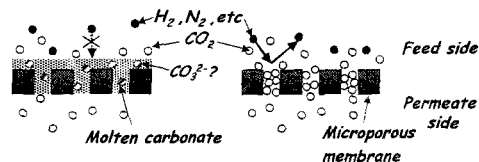


Figure 2 Schematic image of CO₂ extraction by membranes (left: dense membrane case, right: porous membrane case)

The other approach is to enhance the CO₂ adsorption strength of the membrane materials (see right image of Figure 2). While CO₂ adsorption ability of zeolites or carbon is rapidly lost with temperature, some microporous membranes show

CO₂ adsorption at high temperature. Table 1 showing some data. Alkaline metal or alkaline earth-metal oxides (c.a. Li₂O, K₂O, Na₂O, CaO, MgO), alkaline metal carbonate (c.a. Li₂CO₃, Na₂CO₃) or amine groups have basic properties, and show strong affinity to CO₂. Accordingly introducing such basic sites can enhance the CO₂ capture ability. By selecting polymers with amine groups, it is possible to have CO₂ separation ability with high capacity at higher temperature than zeolites. Temperature of c.a. 150–200 °C is, however a limitation due to the decomposition of polymer. On the contrary, inorganic materials have rather smaller CO₂ adsorption capacity, but the CO₂ adsorption can be achieved at higher temperature (c.a. 400°C). Some chemisorbents keep CO₂ adsorption ability even at low water vapor pressure^{13,14}.

Table 1 CO₂ adsorption properties onto various materials

Adsorbents	P(CO ₂) (bar)	Adsorption amount (mmol/g-adsorbent)		
		Low temp.	75 °C	400 °C
Zeolite (H-MFI) ₁₀	0.5	1.7 (30°C)	0.04 (103°C)	<<
Amine sites (PEI on mesoporous silica) ¹¹	1	-	3	-
MgO ¹²	1			0.36
Hydrotalcite-like ¹³	1	0.23 (20°C)	0.15 (200 °C)	0.5 (300°C)
Li ₂ CO ₃ on alumina ¹⁴	0.67	-	-	2*
Na ₂ CO ₃ on alumina ¹⁴	0.67	-	-	1.4–4.7*

*calculated assuming no adsorption to alumina

When applying these basic chemisorbents as membrane material, a microporous structure is required to reject other molecules. As these sorbents hardly form microporous structure by themselves, some standard microporous membranes (c.a. silica, carbon and zeolite membranes) should be used as backbones and chemisorbents can be introduced by surface modification. Accordingly, a membrane preparation procedure can be 1) selection of proper candidate materials with enough CO₂ affinity at high temperature, 2) preparation of homogeneous sol, 3) preparation of microporous supports with well controlled pore size, 4) surface modification with control of chemisorbents layer thickness.

In this study, CO₂/H₂ separation has

been studied with zeolite membranes as a model system for CO₂/H₂ by adsorption selective separation.

2. EXPERIMENTS

Zeolite membranes

H-MFI zeolite crystals (Si/Al ratio of 10¹⁶, pore size 5.1x5.4 Å) are synthesized hydrothermally to plug the pores of supporting materials (α -alumina, 0.2 μ m pore size). Detailed procedure is described elsewhere¹⁵. The membrane was of 150 mm length, formed in the inside top layer of the interior surface of a cylindrical support with effective membrane area of about 28 cm².

The zeolite crystals have H⁺ form as prepared. Ammonia gas was introduced to the membrane to cover the acidic site.

The property of the prepared membrane was characterized by single gas permeation tests using H₂, CO₂, N₂ and CO₂/H₂ and CO₂/N₂ separation tests at room temperature to 400°C. The pressure difference was changed from 0.5 bar to 3.5 bar. All the measurements were performed by pressure drop method and no sweep gas was used. Before the permeation and separation tests, the membrane was heat treated to remove any adsorbed molecules. The pretreatment conditions are at 400°C under dry nitrogen flow for both sides of the membrane for more than 1 day. The heating rate was kept smaller than 2°C/min. The separation factor is calculated by equation below.

$$S_f(A/B) = (x_{A_{perm}}/x_{B_{perm}})/(x_{A_{feed}}/x_{B_{feed}})$$

where x_A, x_B represents the molar ratio of component A and B, respectively.

3. RESULTS and DISCUSSION

CO₂/H₂ separation with zeolite membranes at room temperature

Figure 3 shows the CO₂/H₂ separation property of a H-MFI membrane at room temperature. Separation factor (S_f) increased with CO₂ pressure in feed, and showed more than 30 at room temperature. Open keys show the flux obtained in single gas permeation, and closed keys show the flux in separation. CO₂ flux is almost the same in pure gas permeation and in separation with gas mixture. H₂ flux in separation is however, significantly smaller in separation compare to the single gas permeation flux. Apparently, H₂ permeation is hindered by co-existing CO₂. This suggests that pores of c.a. 5 Å diameter can be plugged by CO₂ molecules (3.3 Å) if the surface has a sufficient adsorption strength, and that H₂ (2.89 Å) can not pass in the pores.

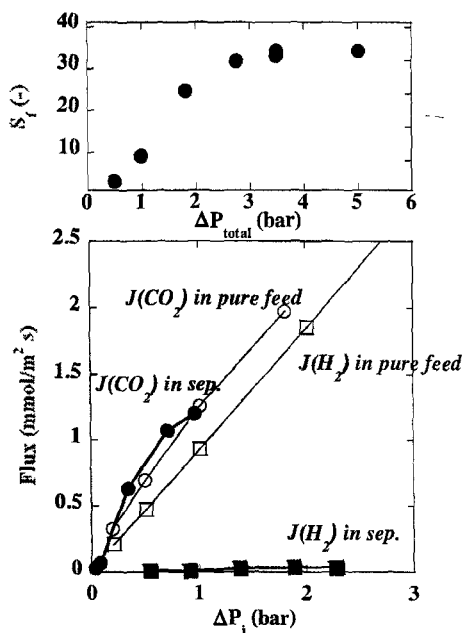


Figure 3 CO₂ and H₂ permeation fluxes in single gas feed and in separation as a function of pressure difference at room temperature (open keys: pure gas feed, closed keys: 1:1 mixture as feed)

Influence of cation type of zeolite membranes

Ammonia molecules have basic property and adsorbs strongly on to the acidic H⁺ site. H₂, N₂ and CO₂ permeation are almost the same with ammonia molecules, while CH₄ permeation flux became smaller with ammonia. This suggests that H⁺ site has strong influence on CH₄ adsorption, while the major CO₂ adsorption site is not the H⁺ site.

Table 2 summarizes the CO₂ separation performance at room temperature. Separation factors show order of CO₂/H₂ > CO₂/N₂ > CO₂/CH₄. The CO₂ selectivity is lowered as the adsorption strength of counter molecule increases. On the contrary, the separation ability is not changed with ammonia.

The three major different adsorption sites are cation sites, silanol on the outer surface (1-2 silanol groups/unit cell¹⁷) and bridged oxygen in the zeolitic framework. Based on the little influence of cation type on permeation and separation properties, CO₂ adsorption on to the latter two sites are contributing the CO₂ plugging the zeolitic pores.

Table 2 CO₂ separation ability at room temperature with 1 bar pressure difference

	CO ₂ /H ₂	CO ₂ /N ₂	CO ₂ /CH ₄
H-MFI	9.3* (1.9)**	4.9 (2.4)	-
NH ₄ -MFI	9.5 (1.9)	4.2 (2.4)	3.4 (4.3)

* Separation factor, ** Total flux (mmol/ m² s)

Effect of temperature

Figure 4 shows the influence of temperature on CO₂/H₂ and CO₂/N₂ separation properties. The H₂ and N₂ fluxes increased significantly in the low temperature range (from room temperature to 150°C), and finally reached the same value as single gas permeation flux at 400 °C. Accordingly, the highest separation factor was achieved at the lowest temperature for both systems. The membrane showed CO₂/H₂ selectivity up to 200 °C, and CO₂/N₂ selectivity up to 400 °C. As the CO₂ adsorption to zeolites become decrease with temperature¹⁰, the pore

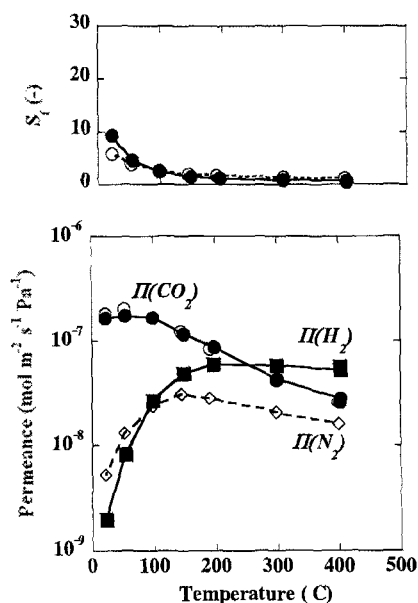


Figure 4 Effect of temperature on CO₂/H₂ separation (closed keys) and CO₂/N₂ separation (open keys) (1:1 mixture as feed, ΔP_{total}=1 bar)

4. CONCLUSIONS and PROSPECTS

The model case with H-MFI zeolite membrane showed CO₂/H₂ separation ability; S_f above 30 at R.T.. The separation factor increased with pressure, while decreased with temperature. The membrane showed and CO₂/H₂ selective up to 200°C, and CO₂/N₂ up to 400°C.

The results show co-existing CO₂ hinder the H₂ permeation. Applying stronger CO₂ adsorbents on the microporous membrane surface, CO₂/H₂ separation ability will possibly be obtain at higher temperature.

Acknowledgement

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