1.2.1.1.5 Development of Sulfur Poisoning Resistant Zeolite Membranes for Hydrogen Fuel Production by Membrane Reaction

Report Title

CO_2 Capture Project - An Integrated, Collaborative Technology Development Project for Next Generation CO_2 Separation, Capture and Geologic Sequestration

Development of Sulfur Poisoning Resistant Zeolite Membranes for Hydrogen Fuel Production by Membrane Reaction

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1.2.1.1.5.1 Abstract

This report summarizes preparation, characterization, permeation/separation properties involving H_2, H_2O, CO and CO_2 for silicalite membranes with minimized intercrystalline pores. The silicalite membranes were prepared by the template-free secondary growth method. XRD analysis indicates that silicalite can grow well without an organic template on the surface of the silicalite seeded α-Al_2O_3 supports. SEM shows a thickness of the silicalite membrane of about 5 μm. The membranes were further characterized by pervaporation experiments with 1,3,5-triisopropylbenzene and xylene and the results indicated good quality of the silicalite membranes prepared in this work. For the single gas mixture under dry conditions, the ideal separation factors of H_2/CO and H_2/CO_2 are as high as 6 at 500ºC with hydrogen permeance of 1.2×10^{-6} mol/m^2.s.Pa. However, at low temperature the separation factors of H_2/CO and H_2/CO_2 are not so high. The ideal separation factor of H_2/CO and H_2/CO_2 for the silicalite membranes under wet conditions are as high as 9.4 and 8.8, respectively, and the permeance of hydrogen is around 10^{-7}mol/m^2.s.Pa. With the protocol syngas as the feed in the separation experiments, separation factors for H_2/CO and H_2/CO_2 as high as 11.6 and 12, respectively, were obtained for the silicalite membrane. The separation factor decreases at the higher feed side pressure, especially for H_2/CO_2. The silicalite membranes are chemically very stable. Temperature dependency for the permeability for the linear flux equation was obtained for H_2, CO and CO_2 for the silicalite membrane prepared in this project.

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1.2.1.1.5.3 List(s) of Graphical Materials

1.2.1.1.5.4 Introduction

Gasification of heavy feedstock to produce hydrogen rich fuel gas using current technology includes partial oxidation to produce syngas, water-gas-shift reaction (WGS) to convert carbon monoxide with water to hydrogen, separation of hydrogen from the product steam, and removal of water vapor and other impurities (such as H_2S) from CO_2 containing stream. Recently, membrane technique has been considered to simplify the commercial WGS two or more reactor stages to a single membrane reactor. The membrane removes product hydrogen from the reactor, facilitating higher conversion at a given temperature. If sufficient conversion is achieved, a non-permeate stream comprising mainly CO_2 can be obtained.

The membrane WGS reactor technology depends largely on the availability of the inorganic membranes with desired properties. WGS reaction involves H_2, H_2O, CO and CO_2, and the membrane should be hydrogen permselective. The objective of this work is to synthesize high quality α-Al_2O_3-supported silicalite membrane by template-free secondary growth method and to study the permeation/separation properties for syngas condition of these zeolite membranes. XRD and SEM measurements were used to characterize the membranes structure and morphology. Pervaporation technique was used to determine the quality of membranes. Permeation/separation experiments were conducted with simple gas mixture and protocol syngas mixture under dry and wet conditions to evaluate the separation and permeation properties of the silicalite membranes.

1.2.1.1.5.5 Experimental

1.2.1.1.5.5.1 Template-Free Synthesis of silicalite membrane

1.2.1.1.5.5.1.1 Preparation of Silicalite Suspension

Silicalite suspension was prepared according to the following procedure. (1) NaOH-TPAOH solution was prepared by dissolving NaOH (Aldrich, 99.99%) pill in 1 M TPAOH solution in a capped Teflon flask (0.014 g NaOH per 1 ml TPAOH solution). (2) A given amount fumed silica was dissolved into this NaOH-TPAOH solution at around 80ºC with vigorous stirring. (3) After a clear solution was obtained, the solution was cooled down to the room temperature and aged for 3 hours and them hydrothermally treated in a Teflon lined stainless steel autoclave at 120ºC for 12 hours. The composition of the synthesis solution was 1 g SiO_2-5ml (1M) TPAOH-0.07 g NaOH. (4) The seeds were purified by repeated centrifugation washes with deionied water. The final silicalite slurry contains 0.12 g/ml silitcalite with pH = 10. (5) The suspension used for coating was prepared by adding 0.5 wt.% hydroxy propyl cellulose (HPC) solution and deionized water in the silicalite slurry in desired amounts with final composition of the suspension: 1 g silicalite-0.14 g HPC-94 ml H_2O.

1.2.1.1.5.5.1.2 Preparation of Silicalite Seed Layer on Porous α-Al_2O_3 Support

Homemade porous α-Al_2O_3 disks with thickness of 2 mm and diameter of 20 mm were used as the supports. The α-Al_2O_3 disks were prepared according to the following procedure: (1) 10 g α-Al_2O_3 powder (calcined, A15SG, Alcoa) and 0.8 g deionized water were fully mixed in a mortar; (2) 2.1 g mixture was filled in a stainless steel mould and pressed at force of 5,000 pound for 1 min first, then the stainless steel die was turned up-side-down and pressed at force of 20,000 pound for 1.5 min; (3) The raw disks were dried at 40ºC for two days; (4) The dried disks were sintered in a temperature programmable furnace to a maximum temperature of 1260ºC. The average pore diameter and porosity of the α-Al_2O_3 supports were about 0.2 μm and 45%, respectively.

Silicalite seed layer was dip-coated to the alumina support by the following procedure: 0.5g HPC powder was added into 100 ml de-ionized water contained in a 250 ml glass flask. It was stirred at room temperature for 45 min, then heated to 50ºC for 2 hrs. The α-Al_2O_3 disks was polished with SiC sand paper #500, then #800 by a polishing machine, and then dried at 40ºC for 2 days. 1 g silicalite suspension was mixed with 3 g HPC solution and 6 g de-ionized water, followed by addition of 2-3 drops of 1N HNO_3 into the mixture to adjust pH of the obtained dip-coating solution to about 3-4. The polished α-Al_2O_3 disks were brought in contact with the dip-coating solution, with contact time of 5 seconds. The coated alumina disks were dried in a preheated oven at 40ºC under 60% relative humidity for 2 days, followed by calcination in a temperature programmable furnace with the following temperature program: RT(20ºC/hr)$\rightarrow$450ºC(for 8hr)(20ºC/hr)$\rightarrow$650ºC(for 8hr)(30ºC/hr)$\rightarrow$RT.

1.2.1.1.5.5.1.3 Preparation of MFI Zeolite Membrane by Secondary Growth

Silica sol for secondary grown membrane was prepared by adding a given amount of fumed silica powder into NaOH solution (1.5 wt. %) at around 80ºC with vigorous stirring. The composition of the synthesis sol is 0.16 g NaOH-1 g SiO_2-10.5 g H_2O. After cooling down and aging for 1.5 h, a viscous silica sol was obtained. It was subsequently dispersed in an ultrasonic bath for 30 min. No template was used in the synthesis sol. The silica sol with silica concentration of 0.1 g/ml and pH of 12 was used for the secondary growth. The dip-coated alumina disks, with seeded silicalite layer, were put in the bottom of a Teflon lined stainless steel autoclave filled with the silica sol with the zeolite layer upwards. The autoclave was closed and placed in a preheated oven at 180ºC for a certain time. After cooling down to room temperature, the membrane samples were taken out of the autoclave, washed with water for 10 min, then dried in air at 40°C under 60% relative humidity for 2 days.

The samples prepared by the above procedure were denoted as SS1~SS8 and SG1~SG6. The different letters were used to indicate the samples prepared by two different persons.

1.2.1.1.5.5.2 Membrane Characterization

1.2.1.1.5.5.2.1 Surface Morphology

X-ray diffraction analysis (Siemens D-500) was used to determine phase structure of silicalite membrane samples. The thickness of silicalite membrane samples were determined by SEM.

1.2.1.1.5.5.2.2 Pervaporation Setup and Procedure

The quality of silicalite membranes was tested by pervaporation with 1,3,5-triisopropylbenzene and p-xylene and o-xylene. The silicalite membranes with p- to o-xylene separation factor of above 10 should be considered as good quality silicalite membranes with minimized intercrystalline micropores.

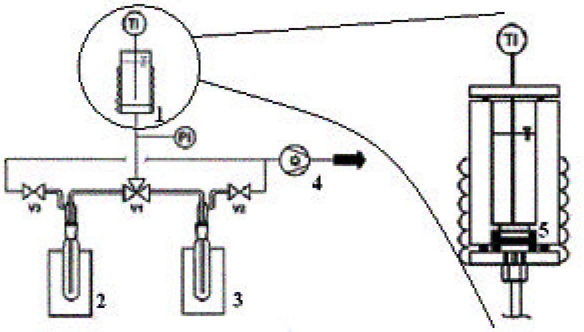

Figure 1 Schematic pervaporation steup, (1) Heated membrane cell with feed tank; (2), (3) Liquid nitrogen cold trap; (4) Vacuum pump; (5) membrane position

The experimental set-up used for the pervaporation experiments is shown in Fig. 1. The membrane was placed in the pervaporation cell with the zeolite layer facing upward and sealed with xylene-resistant fluorocarbon O-rings (Parker Seals V884, Parker Hannifin, Cleveland, OH). The liquid feed was stored in a tank (43 ml) at atmospheric pressure above the membrane. An externally installed heating tape was used to heat the feed tank and membrane cell unit. The temperature of the feed was measured by a thermocouple placed right above the membrane surface. The downstream side of the pervaporation unit was evacuated by a vacuum pump (1.7 mm Hg during pervaporation operation). Heating tape was used to keep the downstream tubes at a temperature of about 50ºC in order to prevent the condensation of permeate. Two liquid nitrogen cold traps were used alternately to freeze the permeate vapors. After the sampling period, valves V1 and V2 (V3) were closed and the cold trap was warmed up to room temperature. Finally, the vacuum in the trap was released by introducing the ambient air. The amount of permeate was measured by weighing the cold trap before and after the pervaporation experiment.

1.2.1.1.5.5.3 Gas Permeation/Separation Experiments

Single gas permeation experiments were conducted on an unsteady state gas permeation setup with pure gas as the feed. The setup measured trans-membrane pressure drop and the permeation flow rate. Three sets of multi-component gas permeation/separation experiments were conducted as described next.

Simple gas mixture permeation/separation experiments under dry conditions were conducted with the setup shown in Fig.2. In experiments, a silicalite membrane was mounted in a specially designed membrane cell with the membrane surface on the feed side, and sealed by a graphite gasket. He gas was used as the sweep gas. The sweep gas and feed gas flow rates were maintained at 10.1 and 11.1 ml/min, respectively. Retentate and permeate were analyzed by GC. Both effluent flow rates were also measured by bubble flow meters. Pressures of the feed side and sweep side were maintained at atmospheric pressure this time. Temperatures were controlled by electrical furnace from 25 to 500°C with ramping rate of 2°C/min. At each temperature, GC analysis was performed after 15-20 min when the temperature reached to the desired temperature. The feed composition: H_2:33.3%, CO: 33.3%, CO_2:33.3%.

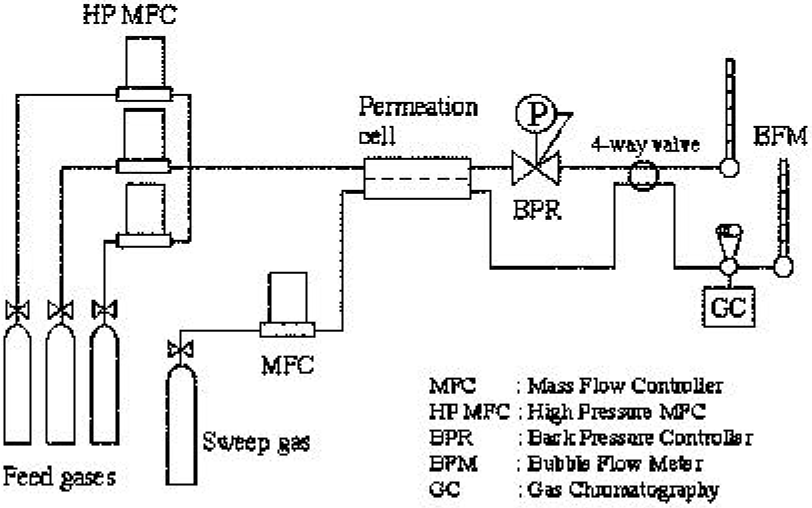

Figure 2. Experimental set up for simple gas mixture permeation/separation experiments under dry conditions

Simple gas mixture permeation/separation experiments under wet conditions were conducted with the setup modified from the one shown in Fig.2. The modified setup is shown in Fig.3. As shown in Fig. 3, water was introduced to the system by a bubble column which was put in a water bath. The percentage of water vapor in the feed gas was controlled by the temperature of the water bath. In this experiment, the temperature of water bath was set at 80ºC to get about 50% water in volume in the feed gas. The feed (upstream, at flow rate of 10 cc/min) was this gas mixture at a total pressure of 2 atm or 3 atm. Helium was used as the purge (at flow rate of 10 cc/min) in the downstream side at the total pressure of 1 atm. H_2, CO and CO_2 in the retentate and permeate were analyzed by GC. Water vapor content in the permeate and retantate was measured by a humidity sensor. Both effluent flow rates were controlled by the mass flow meters and also measured by a bubble flow meter. Temperatures were controlled by an electrical furnace from 100 to 500°C with ramping rate of 2°C/min. The feed composition was: H_2: 16.7%, CO: 16.7%, CO_2: 16.7%, H_2O: 50%.

The third set of permeation/separation experiments was conducted with simulated syngas (protocol syngas) as the feed. Fig.4 shows the setup for this set of experiments. A stainless steel water vapor generator with two coupling containers was used to introduce water vapor to the system based on the desired water percentage (43.5%). The two coupling containers were especially designed to ensure that water vapor at the saturated water vapor pressure was obtained. The water vapor generator was put in an insulated bath wrapped with cotton to keep the temperature stable. The connection between the water vapor generator and permeate cell were wrapped with heating tape to prevent water condensation inside tubings. The composition of the feed is:

H_2	66.93%,
N_2	0.19%,
CO	3.72%,
CO_2	29.15%,
H_2S	625ppm
H_2O	43.5%

According to the different feed total pressure, the relative temperature to obtain the saturated water vapor pressure is shown in Table 1. The high temperature/pressure multi-component gas permeation/separation experiments with syngas were carried out under the following conditions:

Temperatures: 350, 400, and 450ºC
Feed Pressure: 5, 10, and 15 bar
Permeate side pressure: 1 atm (He used as sweep gas).

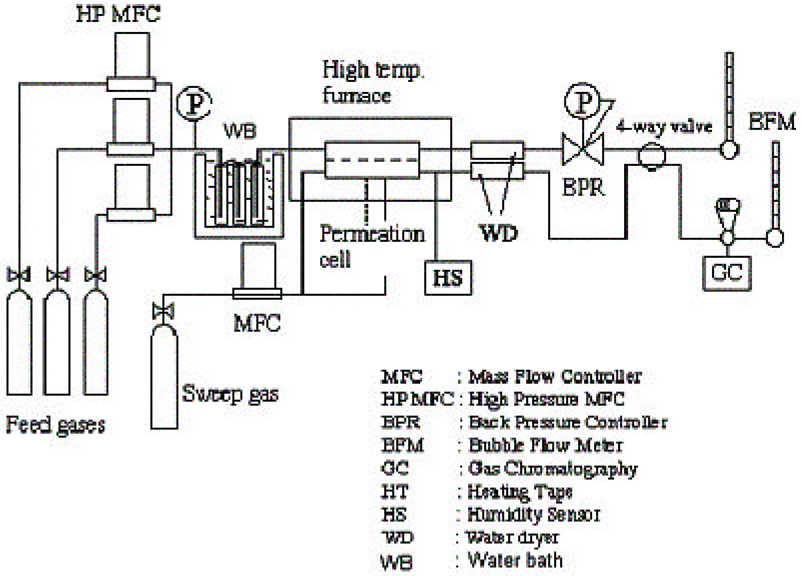

Figure 3. Experimental set up for simple gas mixture permeation/separation experiments under wet conditions

Table 1. The relationship between saturated water vapor pressure and temperature

Total Pressure (bar)	Water Vapor Pressure (bar)	Temperature (ºC)
1	0.435	78
5	2.175	123
10	4.35	146
15	6.525	161

The measurement started at membrane temperature of 350ºC and total feed pressure of 5 bar. The membrane was heated to desired temperature at ramping rate of 2ºC/min. The water vapor generator was heated to a desired temperature listed in Table 1 after the pressure for the system and temperature for permeation cell reached their desired values. When the system was stable for one hour, GC analysis was performed. The flow rates of both feed gas and sweep gas were measured by a bubble flow meter, and the water content in the permeate was measured by a humidity sensor.

The stability test was conducted by measuring gas permeance through a silicalite membrane with the protocol syngas as the feed under the conditions of 400ºC and 10 bar feed pressure and 1 atm permeate pressure. The total time of the whole test was about 7 days.

1.2.1.1.6 Results and Discussion

1.2.1.1.6.1 Phase structure and thickness of silicalite membranes

Typical XRD patterns of dip-coated seed layer, the zeolite membrane (SG1) after secondary growth, pure silicalite zeolite, and α-Al_2O_3 are shown in Fig.5. All silicalite membrane samples exhibit similar XRD patterns. The main peaks found at 8.3º, 9.2º, 23.5º, 24.3º, and 24.8º are attributed to the MFI type zeolite structure, the same structure as that of ZSM-5 zeolite. The relative intensity of peaks at 23.5º, 24.3º, and 24.8º is higher for samples after secondary growth as compared with dip-coated silicalite membrane.

Fig. 6 shows the SEM image of cross-sectional view of silicalite membrane obtained after dip-coating and secondary growth. The thickness of silicalite after dip-coating (upper image) is about 4 μm, while the thickness of secondary growth silicalite membrane (SG2) (lower image) is about 5 μm. These results indicate that the secondary growth somehow increases the thickness of the silicalite layer on the α-Al_2O_3 support.

1.2.1.1.6.2 Pervaporation Experiments with 1,3,5-triisopropylbenzene and Xylenes

Pervaporation experiments were first carried out with 1,3,5-triisopropylbenzene (TIPB) (97%, Aldrich) to examine the quality of different alumina-supported zeolite membranes after calcination. Every run was performed at 26ºC for 6 hrs; 1 h was taken for system equilibration and 5 hrs for the sampling of the permeate. After the pervaporation experiments all membranes were heated in air at 350ºC (heating and cooling rate of 0.58C/min) to remove the adsorbed TIPB molecules before performing the pervaporation experiments with xylenes on the membrane sample. No TIPB sample was obtained in the liquid sample collection container. This indicates that the samples don't have cracks or defects with size larger than 0.8 nm (molecular size of 1,3,5-triisopropylbenzene). Samples SS1~SS6 were characterized by xylene pervaporation experiments to verify the extent of the intracrystalline pores. P-xylene molecule (~0.58 nm) is smaller than the silicaltie crystalline pores (~ 0.6 nm) while m- and o-xylene molecules are larger than the later. A good selectivity of p-xylene to m- or o-xylene indicates good quality of a silicalite membrane without intercrystalline pores.

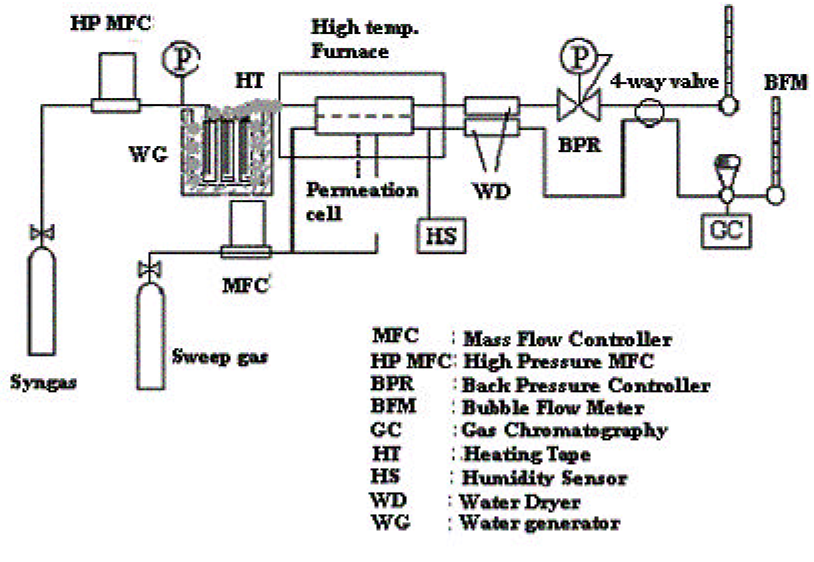

Figure 4. Experimental set up for protocol syngas permeation/separation

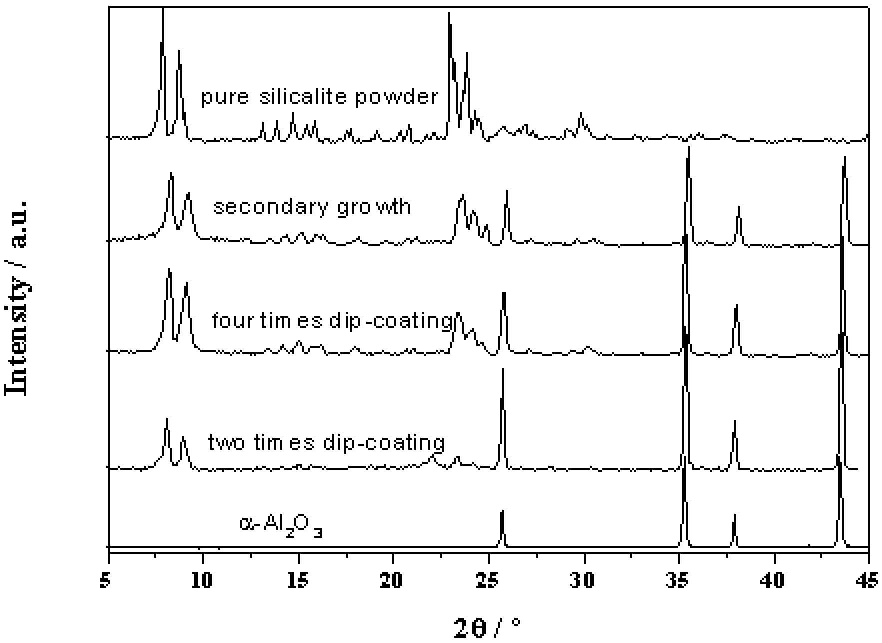

Figure 5 XRD patterns of silicalite membrane, a -Al_2O_3 support, and pure silicalite powder.

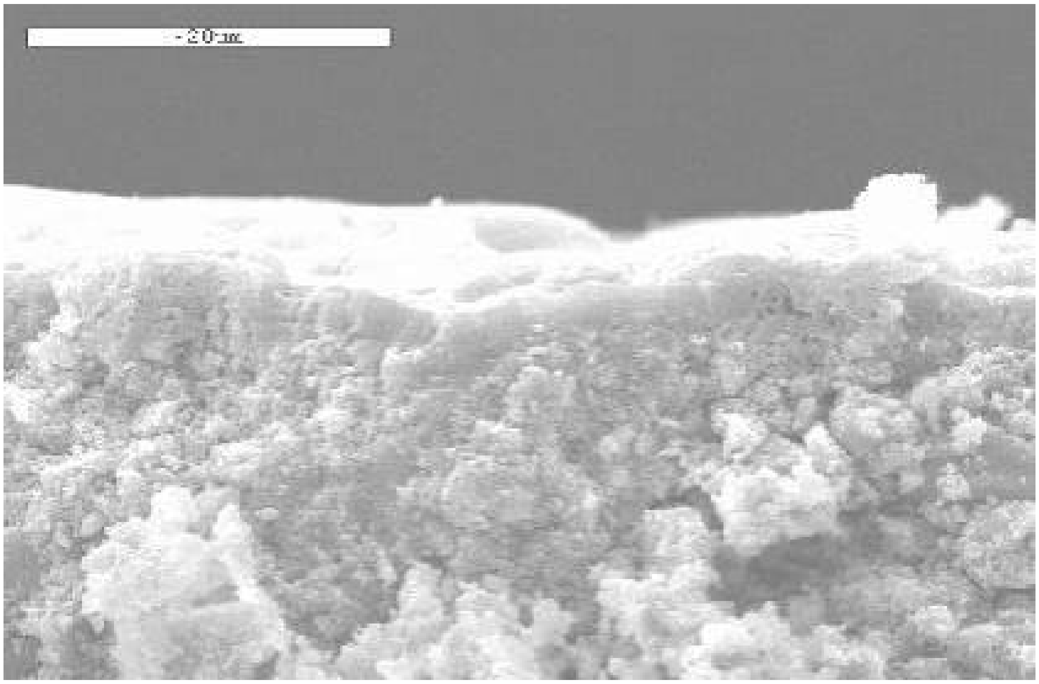

Figure 6a SEM photographs of cross-sectional view of silicalite membrane obtained after dip-coating (upper) and secondary growth treatment (bottom)

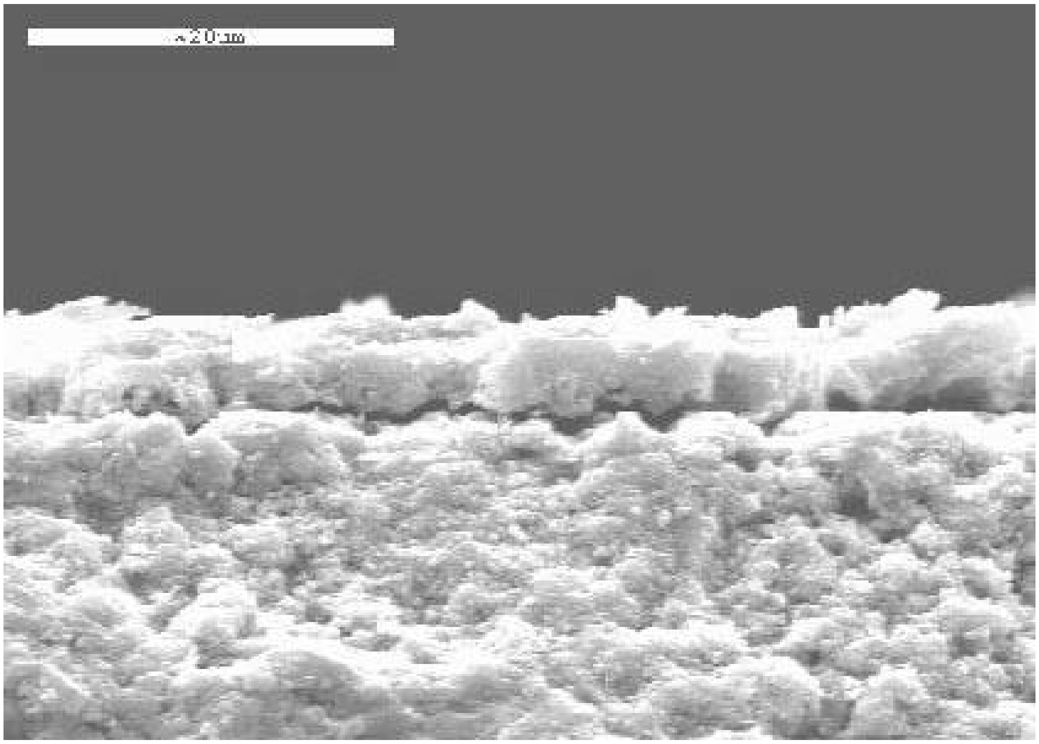

Figure 6b SEM photographs of cross-sectional view of silicalite membrane obtained after dip-coating (upper) and secondary growth treatment (bottom)

Table 2. Pervaporation fluxes of single xylene isomers -Effects of dip-coating time

Sample	Flux (10^{-4} mol m^{-2} s^{-1})			Separation factor	
	p-xylene	o-xylene	m-xylene	p/m	p/o
SS1	6.78	0.28	0.32	24	21
SS2	6.25	0.33	0.39	19	16
SS3	6.62	1.47	1.35	4.5	4.9
SS4	6.95	3.23	4.11	2.1	1.7

Silicalite membrane SS1-SS4 samples were prepared by secondary growth in the same batch. Prior to the secondary growth in a template-free synthesis solution, SS1 and SS2 samples were dip-coated with silicalite suspension twice, and SS3 and SS4 were dip-coated once. Therefore, the SS1 and SS2 samples had a thicker silicalite layer. Single component xylene pervaporation fluxes on these four silicalite membranes are shown in Table 2. Obviously, the membranes with twice-coated silicalite layer exhibit much higher p-/m- or p-/o-xylene separation factor.

Four more silicalite membranes were prepared in another batch by the template-free secondary growth method. All membranes were coated with the silicalite layer twice by the dip-coating method prior to secondary growth. Single and binary xylene pervaporation were performed for the two of the four silicalite membranes prepared in the secondary growth batch. For binary pervaporation, data were measured with equal molar of p-/ o-xylene mixture as the feed. Table 3 is a summary of the results of single and binary xylene pervaporation experiments. These two membranes exhibit even better p- to o-xylene separation factor than the two samples listed in Table 2. The fluxes and p-/o-xylene selectivity of binary xylene pervaporation are slightly lower than those of the single xylene pervaporation. This indicates that the presence of a xylene molecule in the silicalite membrane pore hinders permeation of the other xylene molecules. The silicalite membranes prepared in this work have p-xylene selectivity similar to, and p-xylene flux two orders of magnitude larger than the best silicalite membranes reported in the literature. These results indicate the good quality of the silicalite membrane with minimized microporous intercrystalline pores.

Table 3 Pervaporation fluxes of single and binary xylene isomers (at 50°C)*

Sample	Flux (10^{-4} mol m^{-2} s^{-1})		Separation factor
	p-xylene	o-xylene	p/m
SS5	7.36 (3.58)	0.13 (0.086)	56 (41)
SS6	7.41 (3.02)	0.11 (0.077)	67 (39)

* Binary data are in parenthesis

1.2.1.1.6.3 Gas Permeation/Separation

1.2.1.1.6.3.1 Simple gas permeation

Single gas permeation experiments were performed on sample SS7. Experiments were carried out for four gases (H_2, He, CO_2, CO) at 350-450°C using the unsteady-state gas permeation apparatus available in our lab. The results of the single gas permeation are shown in Fig.7. Gas permeance increases with increasing temperature, characteristic of single gas permeation through microporous zeolite membrane in the high temperature range. The separation factors for H_2/CO_2 and H_2/CO are about 4 and 3, respectively, and do not change in 350-450°C.

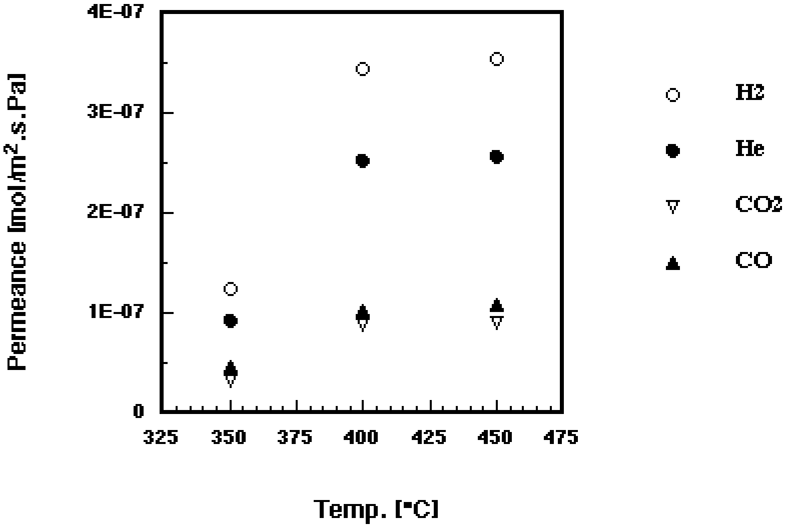

Figure 7. Single gas permeation results on the obtained zeolite membrane

1.2.1.1.6.3.2 Simple gas mixture permeation/separation under dry conditions

Figure 8 shows simple gas mixture permeation/separation data without water on the silicalite membrane SS8 at various temperatures. The hydrogen to CO and CO_2 separation factor as high as about 6 is achieved at 500°C. Furthermore, hydrogen permeance is very high (1.2×10^{-6} mol/m^2.s.Pa at 500°C). This is the best result for H_2-CO_2 separation on zeolite membranes at high temperatures as compared to the literature data.

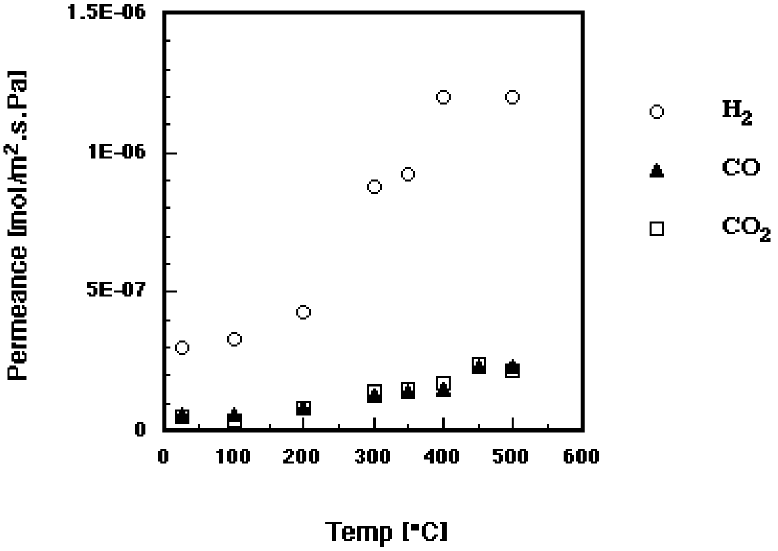

Figure 8 Permeance data at various temperatures on silicalite membrane

1.2.1.1.6.3.3 Simple gas mixture permeation/separation under wet conditions

Simple gas mixture permeation/separation experiments under wet conditions (with water) were performed on silicalite membrane sample SG3. Experimental results show that water permeance is negligible through this silicalite membrane. This probably is due to the hydrophobic nature of the silicalite or relatively large size of water molecule as compared to the other permeants. Permeance of H_2, CO and CO_2 for the silicalite membrane at various temperatures under two feed total pressures (2 atm and 3 atm) (permeate side total pressure is 1 atm) are shown in Figs. 9 and 10, respectively.

Figure 11 shows the separation factor of H_2/CO and H_2/CO_2 versus temperature. At the 2 atm feed pressure at 200ºC, the separation factor of H_2/CO is 9.4 and increases slightly with temperature, while the separation factor of H_2/CO_2 is 8.8 and decreases with temperature. At 3 atm feed pressure, the separation factor of H_2/CO is slightly higher than that at lower pressure, while separation factor of H_2/CO_2 is lower. Note that the permeance of H_2O can be considered zero in the pressure and temperature range studied.

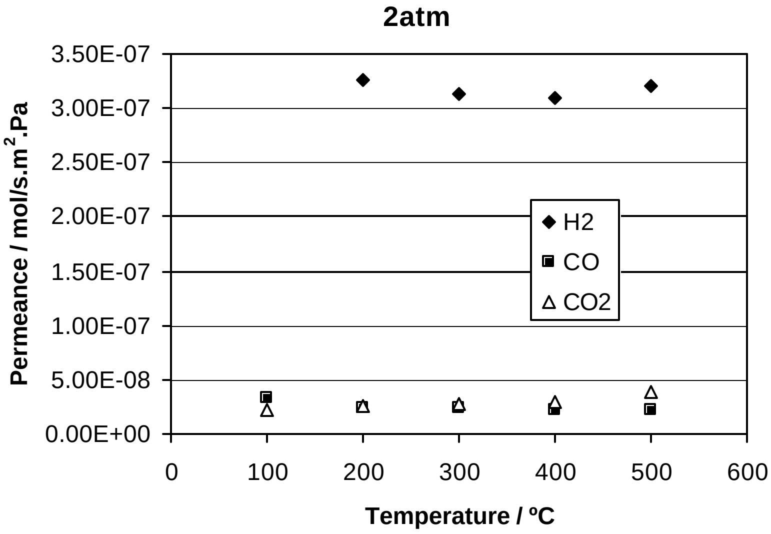

Figure 9. Permeance versus temperature at the feed total pressure of 2 atm

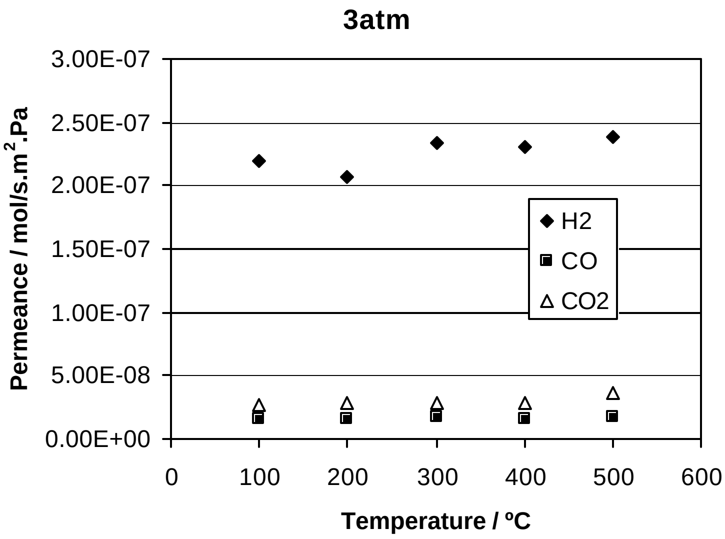

Figure 10. Permeance versus temperature at feed total pressure of 3 atm

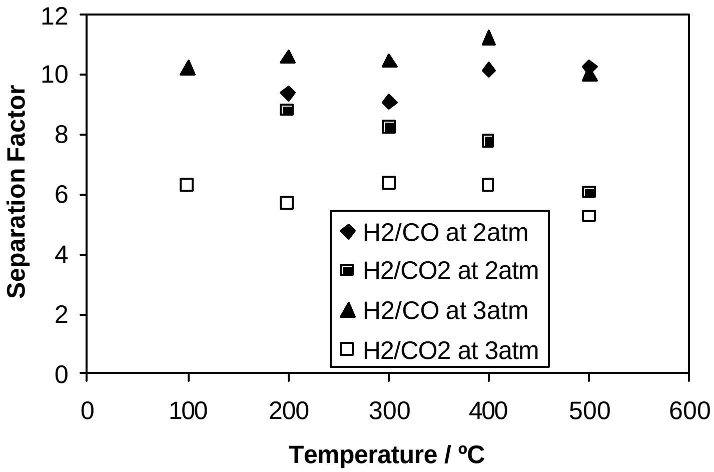

Figure 11. Separation factor versus temperature for silicalite membrane SG3 sample

1.2.1.1.6.4 Flux Equations

1.2.1.1.6.4.1 Linear (ECN) Model

The ECN team suggested to use the following linear flux equation to describe the gas permeation through silicalite membrane:

$$J_i = Q_i(P_{f,i} - P_{p,i}) \tag{1}$$

where J_i is flux of component gas i, mol/s.m^2; $P_{f,i}$ and $P_{p,i}$ are the partial pressures of component gas i at the feed and permeate sides, respectively (unit Pa). Q_i is the permeation constant (or permeance). As shown in Figures 9 and 10, the permeance is not the same at two pressures, indicating that eq.(1) does not describe well the permeation through the silicalite membrane. Nevertheless, we still used Eq.(1) to fit the permeation data at two different feed total pressures (corresponding to two different feed partial and permeate partial pressures) by the least squared regression. The constant Q_i obtained are listed in Table 4.

Table 4 Permeation constant Q_i (mol/ s.m^2.Pa) at different temperatures

T(^oC)	H_2	CO	CO_2
100	1.74E-07	2.13E-08	2.13E-08
200	2.37E-07	1.80E-08	2.80E-08
300	2.55E-07	1.93E-08	2.82E-08
400	2.51E-07	1.75E-08	2.87E-08
500	2.61E-07	1.93E-08	3.66E-08

The permeation constant Q_i can be correlated to temperature by:

$$Q_i = Q_o EXP(-E_k/RT) \qquad (2)$$

with **Q_i is in mol/m^2.s.Pa** and **T in Kelvin**. The above equation can be used in the temperature range of 100-500^{o}C. A logarithm plot of Q_i vs 1/T is given in Figure 12. The regression gives the following equations for Q_i for the four species (see Table 5).

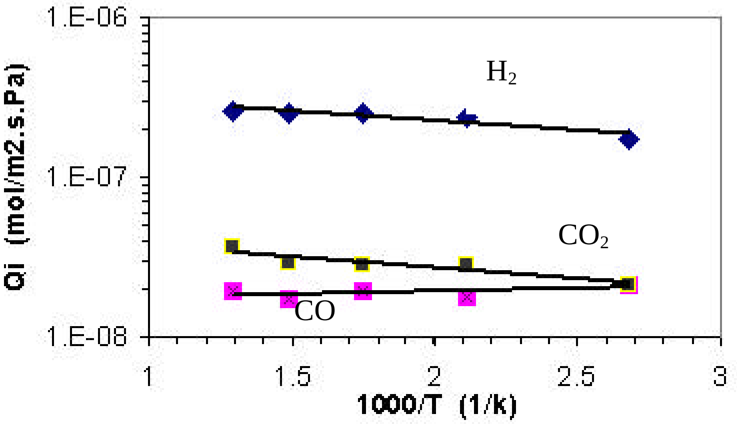

Figure 12 Permeation constant versus temperature

Table 5 Temperature dependency of permeation constant (Q_i is in mol/m^2.s.Pa and T in Kelvin)

H_2	$Q_i = 3.9\times10^{-7}\exp(-276/T)$
CO	$Q_i = 1.6\times10^{-8}\exp(-84/T)$
CO_2	$Q_i = 4.1\times10^{-8}\exp(185/T)$
H_2O	$Q_i = 0$

1.2.1.1.6.4.2 Non-linear Flux Equation Model

The gas permeation flux for component i in this multi-component permeation through the silicalite microporous membrane can be more accurately described expressed by the following 2 parameter equation according to the literature [*Y.S. Lin, I. Kumakiri, B.N. Nair, H. Alsyouri, "Microporous Inorganic Membranes", Separation and Purification Methods, 32(2), 229-379 (2002)]:*

$$J_i = a_i \frac{(1+K_i P_{f,i})}{(1+K_i P_{p,i})} \qquad (3)$$

and a_i and K_i are constant of component gas i, dependent on temperature.

Again, at a given temperature, we have permeation flux data at two feed partial pressures (corresponding to 2 and 3 atm total feed pressures, with known partial pressures at the permeate side measured by GC). Thus, values for a_i and K_i at the temperature for a given component can be found using these two sets of the data at that temperature. Table 6 lists the values of these two constants for the three permeants.

Table 6. The values of a_i and K_i constant in different temperature.

Temperature (°C)	a_i (mol/s.m^2)			K_i (Pa^{-1})		
	H_2	CO	CO_2	H_2	CO	CO_2
300	4.35×10^{-3}	7.14×10^{-4}	-1.51×10^{-4}	4.17×10^{-5}	3.67×10^{-6}	-2.02×10^{-4}
400	4.39×10^{-3}	5.82×10^{-4}	-1.90×10^{-5}	3.86×10^{-5}	6.80×10^{-6}	-1.47×10^{-3}
500	4.45×10^{-3}	3.76×10^{-4}	2.30×10^{-4}	4.16×10^{-5}	2.88×10^{-5}	1.28×10^{-4}

To estimate the flux at any temperature in the range of 300-500°C, these two constants should be correlated to temperature by a certain equation. For **hydrogen (H_2)**, the a_i and K_i are independent on temperature, as shown in Table 6. So, the average of the constants at the three temperatures can be used for a_i and K_i in equation (1):

$a_a=4.40\times10^{-3}$ mol/s.m^2,

$K_a=4.06\times10^{-5}$ Pa^{-1}.

For **carbon monoxide (CO)**, the following equation is used for the temperature dependence of a_i and K_i:

$$a_i = a_o \mathrm{EXP}(-E_a/RT) \qquad (4)$$

$$K_i = K_o \mathrm{EXP}(-E_k/RT) \qquad (5)$$

Values of a_o, E_a, K_o, and E_k were obtained by plotting $\ln(a_i)$ to 1/T and $\ln(K_i)$ to 1/T. The result is shown in Table 7 for CO.

Table 7. Temperature dependency constants for CO gas

Gas	a_o (mol/s.m^2)	E_a (kJ/mol)	K_o (mol/s.m^2)	E_k (kJ/mol)
CO	6.68×10^{-5}	-11.5	7.26×10^{-3}	36.91

For **carbon dioxide (CO_2)**, the relationship between a, K and temperature can be simulated by the following polynomial equations,

$$a\ (\mathrm{mol/s.m^2}) = 1\times10^{-9}T^2 + 5\times10^{-7}T - 8.0\times10^{-4} \qquad (6)$$

$K\ (Pa^{-1}) = 5\times10^{-9}T^2 - 5\times10^{-6}T + 1.2\times10^{-3}$ (7)

where **T is in Kelvin**.

Note the above temperature dependency constants are valid only in 300-500^{o}C. The permeation flux for H_2O is approximately zero.

1.2.1.1.6.5 Protocol Syngas Permeation/Separation

1.2.1.1.6.5.1 Permeation and Separation Data

Fig. 13 shows the permeance of H_2, CO and CO_2 versus temperature for the silicalite membrane SG4 with the protocol syngas as the feed at the feed pressure of 5 bar. By comparing with the permeance/separation result of membrane sample SG3, the use of the protocol syngas resulted in an increase in the permeance of all gases but a slight decrease in separation factor of H_2/CO and H_2/CO_2. Note that these two membranes have similar structure properties as they were prepared in the same batch under identical conditions.

The separation factors of H_2/CO and H_2/CO_2 on sample SG4 with protocol syngas are around 4.2 and 3.2. respectively at measured temperatures. The permeance/separation experiments over sample SG3 were conducted under the conditions of lower pressure and equal feed gas composition. It seems that H_2 permeation with the protocol syngas feed is not as good as that with the simple mixture gas feed. In both cases, water permeance is very low. With the protocol syngas as the feed, the separation factor of H_2/H_2O with syngas is above 10.

Table 8 Summary of Q_0 and E_k under different feed total pressure for silicalite membrane SG5 (Q_0 is in mol/m^2.s.Pa and E_k/R is in Kelvin)

Pressure (Bar)	H_2		CO		CO_2	
	Q_0	E_k/R	Q_0	E_k/R	Q_0	E_k/R
5	3.93×10^{-8}	-152.53	4.00×10^{-9}	-672.71	1.12×10^{-9}	-1597.1
10	2.60×10^{-9}	-1600.7	5.44×10^{-9}	-215.5	8.44×10^{-11}	-3100
15	9.08×10^{-9}	-1209.7	1.44×10^{-8}	-62.224	1.32×10^{-8}	-283.51

Fig. 14 shows the permeance of H_2, CO and CO_2 for membrane sample SG5 versus temperatures under different feed total pressures with the protocol syngas. The permeance data for three gases are smaller than those for sample SG4. The reason is that the silicalite layer of the membrane sample SG5 is thicker than membrane sample SG4 because these two membranes were taken from different batches. However, the separation factor of H_2/CO and H_2/CO_2 for membrane SG5 is similar to those with membrane SG4. The permeate data of sample SG5 was fitted by the linear flux equation, Eq. (1). Table 8 lists the Q_0 and E_k in equation (2) under different pressure

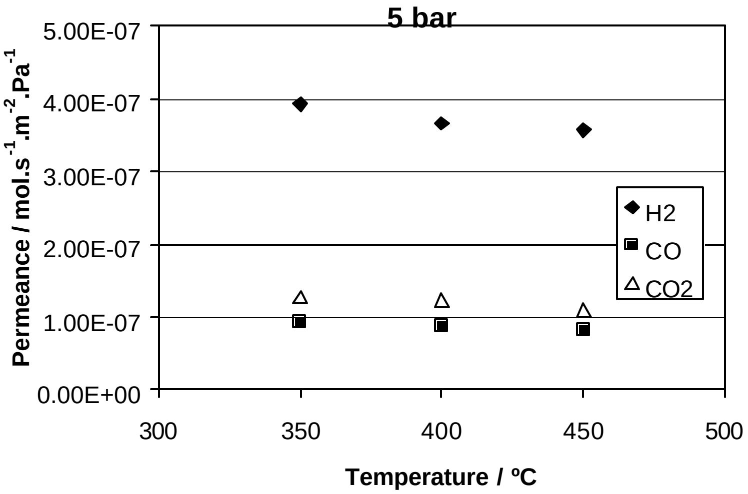

Figure 13. Permeance versus temperature at the feed total pressure of 5 bar for silicalite membrane sample SG4 with protocol syngas as the feed

Table 9 Summary of Separation Factors

Pressure (Bar)	H_2/CO			H_2/CO_2		
	350ºC	400ºC	450ºC	350ºC	400ºC	450ºC
1	11.2	11.6	10.5	9.3	12.0	10.9
5	7.0	6.8	6.4	4.5	4.4	4.5
10	4.2	5.0	4.3	2.6	2.9	2.8

Table 10 Summary of Q_0 and E_k under different feed total pressure (Q_0 is in mol/m^2.s.Pa and E_k/R is in Kelvin)

Pressure (Bar)	H_2		CO		CO_2	
	Q_0	E_k/R	Q_0	E_k/R	Q_0	E_k/R
1	5.12×10^{-7}	-87	4.47×10^{-8}	-1333	1.81×10^{-8}	-743
5	2.09×10^{-8}	-2052	5.30×10^{-9}	-1695	4.75×10^{-9}	-2042
10	1.46×10^{-7}	-474	2.67×10^{-8}	-605	3.46×10^{-8}	-755

Fig. 14 shows the permeance of H_2, CO and CO_2 versus temperature for the silicalite membrane SG6 with the protocol syngas as the feed. Table 9 lists the separation factor of H_2/CO and H_2/CO_2 under various feed side pressures at different permeation temperatures. The permeance of H_2 is about 6×10^{-7} mol/m^2.s.Pa and decreases with increasing feed side pressure. The separation factors under 1 bar pressure are up to about 11.6 and 12.0 for H_2/CO and H_2/CO_2, respectively. However, the separation factors decreases with increasing feed pressure. The permeate data of sample SG6 was also fitted by the linear flux equation, Eq.(1). The permeation constant Q_i correlated to temperature was will be determined by Eq. (2). Table 10 lists the Q_0 and E_k under different feed pressures.

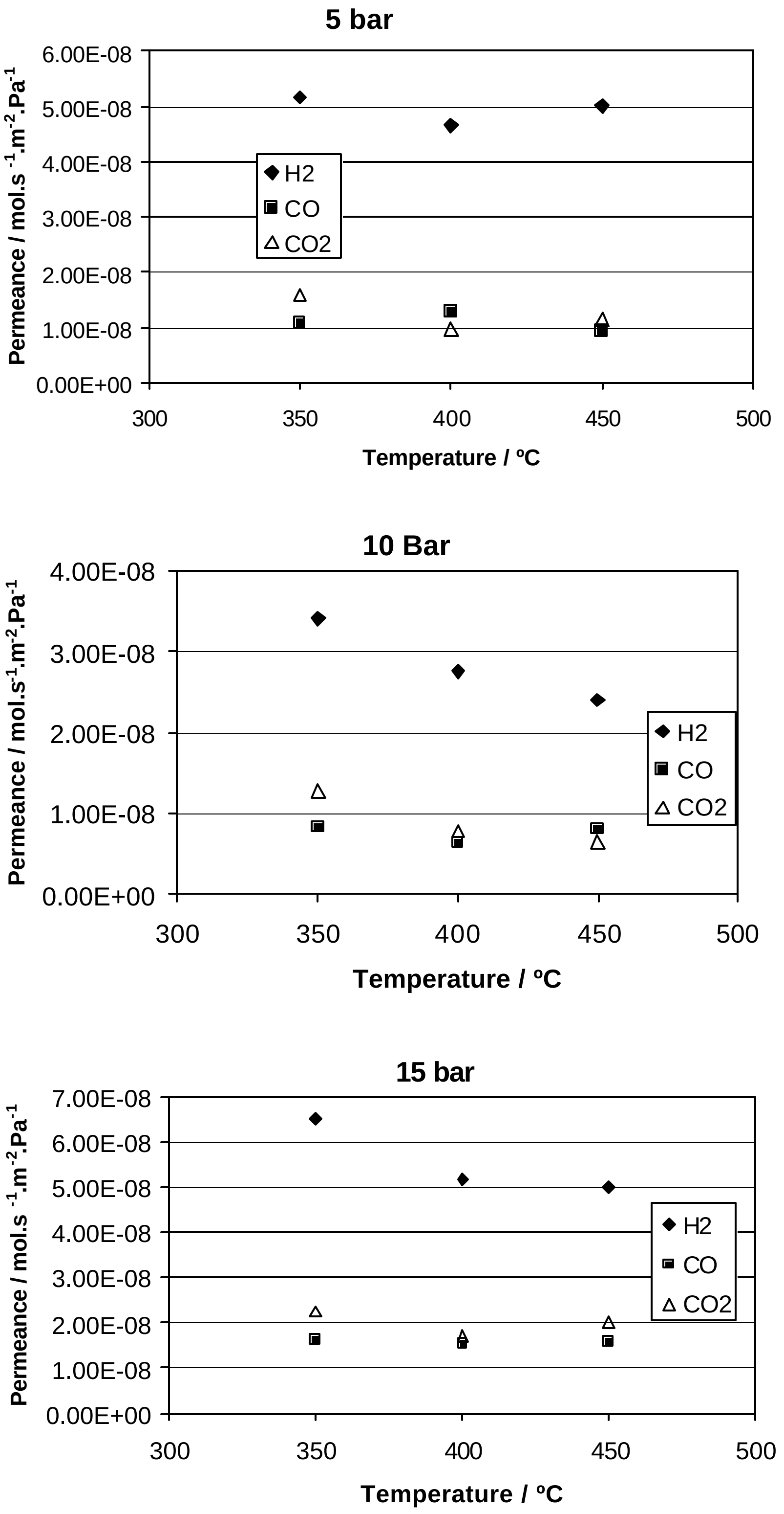

Figure 14. Permeance versus temperature at various feed site pressures for silicalite membrane sample SG5 with protocol syngas as the feed

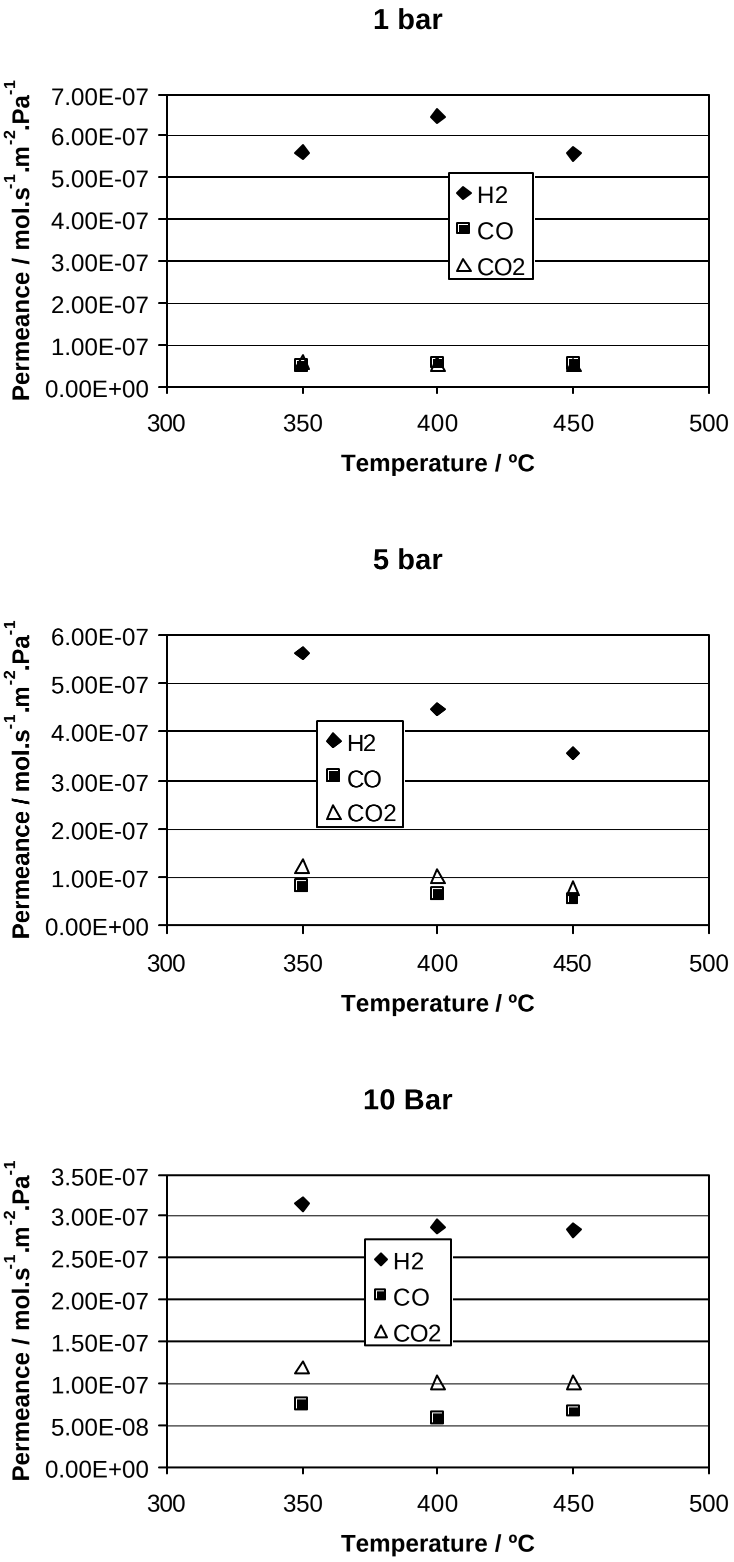

Figure 15 Permeance versus temperature at various feed side pressures for silicalite membrane sample SG6 with protocol syngas as the feed

1.2.1.1.6.5 Membrane Stability

Fig. 15 shows the permeance of H_2, CO and CO_2 for membrane sample SG5 versus time with the protocol syngas as the feed under various conditions (in most time the feed was at 10 bar pressure and the membrane was at 400ºC). As shown, the hydrogen permeance remains constant (in fact increased slightly) after 7 days. The separation factors of H_2/CO and H_2/CO_2 remain constant at about 4 and 3, respectively. The membrane is stable for the permeate/separation test.

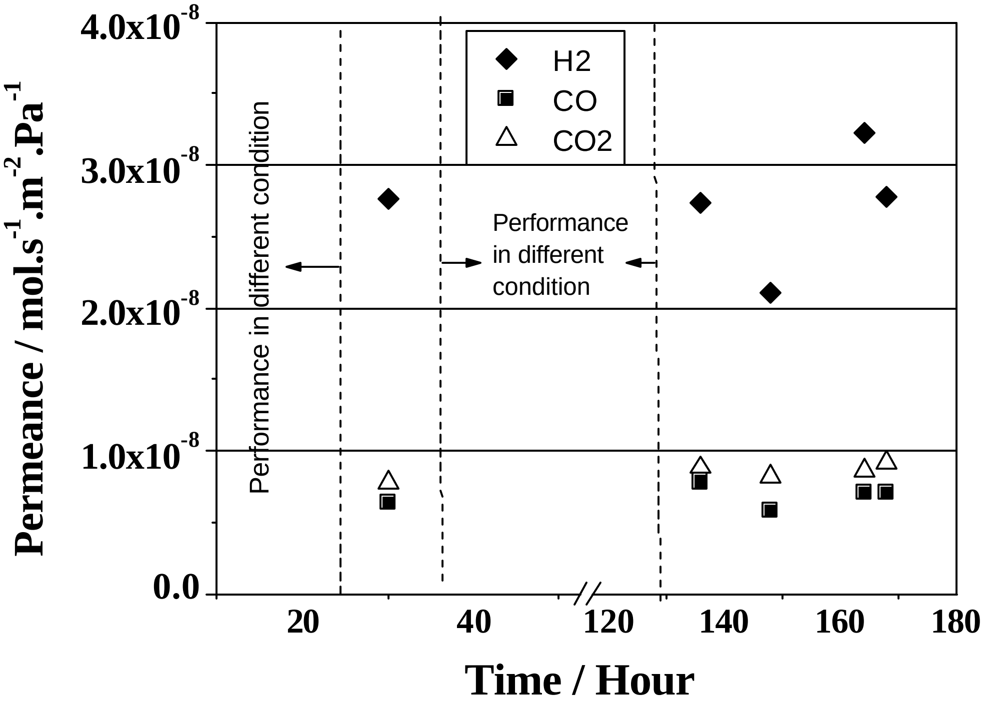

Figure 15. Permeance versus time at 400ºC and 10 bar feed total pressure for silicalite membrane sample SG5

2.1.1.5.7 Conclusion

Good quality silicalite membranes could be prepared by the template-free secondary growth method. The membranes exhibit good p-xylene/o-xylene separation factor (as high as 40), indicating that intercrystalline pores of the silicalite membranes have been minimized.

The ideal separation factors of H_2/CO and H_2/CO_2 are as high as 6 at 500ºC with hydrogen permeance of 1.2×10^{-6} mol/m^2.s.Pa. The ideal separation factors of H_2/CO and H_2/CO_2 are lower at low temperatures. The permeation/separation studies with multi-componet feed gas show that the separation factors of H_2/CO and H_2/CO_2 on silicalite membranes are as high as 9.4 and 8.8, respectively, with a wet gas mixture as the feed. The permeance of hydrogen is around 10^{-7}mol/m^2.s.Pa.

The highest separation factors of H_2/CO and H_2/CO_2 are 11.6 and 12, respectively, on silicalite membranes with the protocol syngas feed at 1 bar feed side pressure. Increasing the feed pressure decreases the separation factors, especially for H_2/CO_2. Flux equations with linear model of permeance were given.

Silicalite membranes are stable under the permeation/separation experiments with the protocol syngas as the feed.

1.2.1.1.5.8 References

No references are applicable.

1.2.1.1.6 Design, Scale Up and Cost Assessment of Membrane Shift Reactor for Use in Gasification Process for Decarbonizing Fossil Fuel