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Direct Methane Conversion to Methanol

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ABSTRACT

One objective of this project was to demonstrate the effectiveness of a catalytic membrane reactor (a ceramic membrane combined with a catalyst) to selectively produce methanol by partial oxidation of methane. Methanol is used as a chemical feed stock, gasoline additive, and turbine fuel. Methane partial oxidation using a catalytic membrane reactor has been determined as one of the promising approaches for methanol synthesis from methane. Methanol synthesis and separation in one step would also make methane more valuable for producing chemicals and fuels.

Another valuable fuel product is H_2. Its separation from other gasification products would make it very valuable as a chemical feedstock and clean fuel for fuel cells. Gasification of coal or other organic fuels as a source of H_2 produces compounds (CO, CO_2, and H_2O that require high temperature (1000- 1500°F) and high pressure (600- 1000 psia) separations. A zeolite membrane layer on a mechanically stable ceramic or stainless steel support would have ideal applications for this type of separation. Separations using zeolite membrane was also evaluated for use in the production in the above fuels.

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EXECUTIVE SUMMARY

A high pressure, high temperature apparatus was constructed to perform the methane and methanol reaction/separation experiments. Many membranes were tested but none of them could selectively remove methanol at the pressure and temperature necessary for methanol formation. As an alternative approach, a cooling tube was inserted inside the membrane reactor to create a low temperature zone that rapidly quenched the product stream. This system has proven effective for increasing methanol selectivity during methane oxidation. Selectivity for CH_3OH formation is significantly higher with quenching than in the experiments without quenching. For CH_4 conversion of 4% to 7%, CH_3OH selectivity is 40% to 50% with quenching and 25% to 35% without quenching. In order to separate CH_3OH from the condensed product mixture, a liquid phase separation system was built and pervaporation experiments were conducted.

The temperature measured for the catalyst layer is about 470 K when the temperature of exiting water from the cooling tube was about 300 K This temperature is not high enough to catalyze the reaction. The catalyst layer may act as a high surface area material to inhibit free-radical, gas-phase reactions. The membranes, both ceramic and metal membranes, do not effect any separations. Thus the roles of catalyst and membrane in this process will be investigated. Systematic experiments will be performed to better understand the mechanisms inside the reactor, and suitable conditions will be determined to obtain optimal CH_3OH yield.

Low oxygen concentration was used to stay below the explosion limit. This means the yield of methanol is small. One possibility to increase CH_4 conversion is to use an air-like mixture instead of pure O_2. A reactant mixture above the upper explosion limit of methane may be used. Under our experimental conditions, this limit is about 25% methane in air.

For the H_2 separation phase of the research, we successfully fabricated a silicalite zeolite - alumina composite membrane with a γ-alumina layer (5 nm pore diameter) as the substrate. Single gas permeances of H_2, Ar, n-C_4H_{10}, and SF_6 were measured and mixtures of H_2/i-C_4H_{10} and H_2/SF_6 were separated to characterize the silicalite membrane. The silicalite membrane demonstrated behavior that was dramatically different from an alumina membrane without the silicalite layer. Permeances for the alumina membrane decreased with increasing temperature, and separation selectivities were lower than values expected for Knudsen diffusion. The silicalite membrane showed activated permeance behavior. The ratio of single gas permeances was as high as 136 for H_2 to SF_6 and 1100 for H_2 to i-C_4H_{10} at 298 K. Separation selectivities at elevated temperatures were significantly above Knudsen diffusion selectivity for the silicalite membrane and were larger than ratios of pure gas permeances at the same temperature. Single gas permeation experiments were performed on CH_4, CO_2, N_2, and H_2 using a silicalite-1 membrane with an ideal N_2/SF_6 selectivity of 234. Additionally, this membrane was used for gas separation experiments involving the binary mixture of H_2 and CO_2.

For the zeolite membrane separations, the separations of interest (CO_2/H_2, CO/H_2, H_2O/H_2, etc.) require zeolite membranes with even smaller pore sizes. Efforts were made to produce other zeolite membranes on alumina or stainless steel supports that have the potential for better H_2 selectivity. Attempts to synthesize zeolite NaA membranes did not result in membranes with promising gas separation capabilities. Zeolite ZSM-5 membranes have been prepared with ideal N_2/SF_6 selectivities of 50. These membranes have pore sizes identical to that of silicalite- I but also have the potential for ion exchange processes that can reduce the effective pore size. In addition, the technique of chemical vapor deposition can be used to improve the gas separation performance of silicalite-1 membranes.

INTRODUCTION

Thermodynamically, the partial oxidation reaction of CH_4,

$$CH_4 + 1/2\ O_2 \rightarrow CH_3OH$$
$$\Delta G_{700\ K} = -22\ kcal/mol$$

is feasible, but the reactions

$$CH_4 + 3/2\ O_2 \rightarrow CO + 2\ H_2O$$
$$\Delta G_{700\ K} = -136\ kcal/mol$$

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$$
$$\Delta G_{700\ K} = -189\ kcal/mol$$

are more favored (1). This means that CH_3OH, an intermediate product, would not be present if the process went to completion. Thus, most published studies of partial oxidation of CH_4 by O_2 report significant selectivity for CH_3OH only at very low CH_4 conversions.

Both homogeneous and heterogeneous oxidation processes have been studied. Helton (2) found that with 6.5% O_2 in the feed gas, selectivities to CH_3OH were 30% to 35% with 99% O_2 consumption at 5 MPa and 675 K. Foulds et al. (3, 4) and Foral (5) reported that, for an O_2 concentration of 8%, the selectivities to CH_3OH were 30% and lower. Recently, Chun and Anthony (6, 7) reported CH_3OH selectivities between 30% to 40% at an O_2 concentration of 4.35%. All of these studies reported that CH_3OH selectivities decreased with increased temperature and O_2 concentration. For example, when the O_2 concentration in the feed gas increased to 9.5%, Helton (2) observed that selectivities to CH_3OH decreased to 25% or 30%. Foulds et al. (4) observed the selectivity to CH_3OH decreased from 38% at an O_2 concentration of 5% to 28% at an O_2 concentration of 7.5%.

Hunter et al. (8), and Yarlagadda et al. (9), using pressures from 2 to 12.5 MPa and temperatures from 625 to 755 K, observed CH_3OH selectivities over 80% at CH_4 conversion levels up to 10%. Hunter et al. (8) also observed that the addition of sensitizers (e. g., higher hydrocarbons) to the system reduced the reaction temperature and increased the selectivity to CH_3OH. This indicated that natural gas was a better feed than pure methane. However, their results have been difficult to reproduce in other laboratories (10, 11).

METHODOLOGY USED

Selective and continuous removal of CH_3OH from the reaction zone would increase CH_3OH selectivity, but no process has been successfully demonstrated. Another way to increase CH_3OH selectivity is to inhibit further oxidation of CH_3OH. A modified membrane reactor design was used in an attempt to remove CH_3OH from the reaction region before further oxidation. A cooling tube was inserted inside the membrane reactor so that the system operated non-isothermally. A low temperature region was created within the reactor by the cooling tube, and the product stream reaching this region was quenched. Further oxidation of CH_3OH was effectively inhibited and the selectivity to CH_3OH was increased.

High Pressure System

A high pressure membrane reactor system (designed for a pressure of 10 MPa) was built for this study (Figure 1). Brooks mass flow controllers were used to meter the reactant gases into the system. A 1-m long, 6.35-mm OD stainless steel tube was used to mix CH_4 and O_2 before they enter the reactor. A stainless steel reactor was designed to allow leak-free connection of the ceramic and metallic parts. A quartz tube was inserted into the reactor to isolate the hot stainless steel surface from the reactant mixture. The reactor was externally heated by a Mellen cylindrical furnace. The pressure of the system was controlled by TESCOM back-pressure regulators installed downstream of the reactor. On-line analysis was done by an HP 5890 gas chromatograph equipped with a thermal conductivity detector.

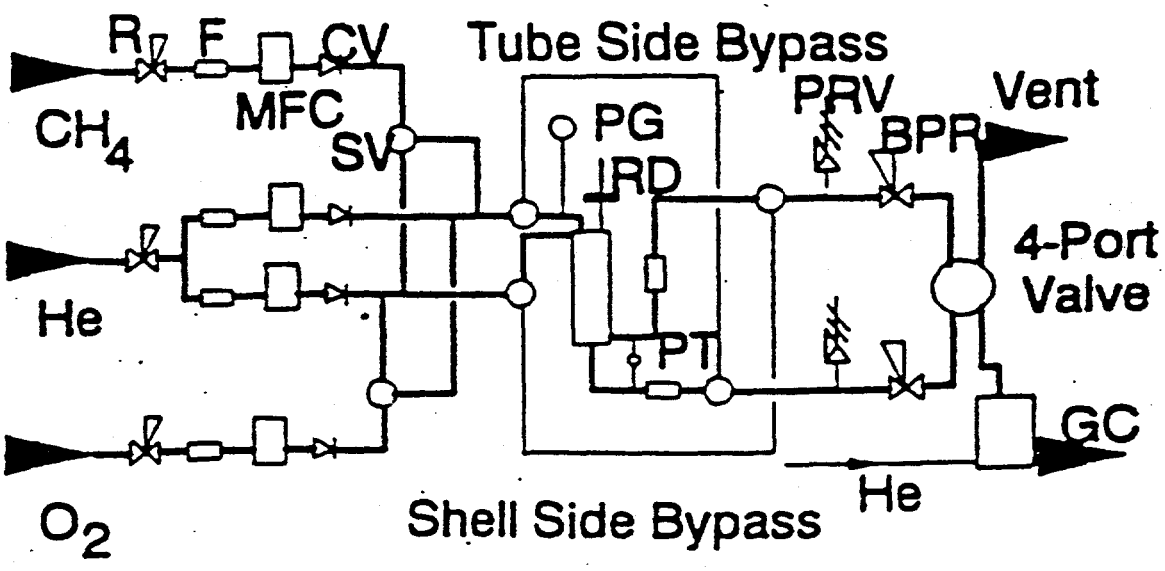


Figure 1. System Diagram

Catalyst

A 6.35 mm OD stainless steel tube was used as a model plug flow reactor to carry out catalysts studies. A CuO/SiO_2 catalyst, T - 1506, from United Catalysts Inc. formed only a trace amount of CH_3OH. Several molybdena based catalysts prepared in this laboratory were used and the best was 1.5% MoO_3/SiO_2, which yielded 25% selectivity to CH_3OH in the model reactor. A V_2O_5/SiO_2 catalyst was a good catalyst for CH_2O formation. Neither $FeO_3/MoO_3/SiO_2$, nor MoO_3/Al_2O_3 catalysts produced CH_3OH under our experimental conditions. Thus, MoO_3/SiO_2 was used in the membrane reactor.

Quenching Method

A tube with cooling water inside was inserted into the center of the membrane tube (Figure 2) to create a low temperature zone in the reactor. The product stream was collected from the tube side of the membrane. The flow of the gas stream through the membrane was perpendicular to the cold front, and when the gas reached the cool region, its temperature decreased rapidly. Experiments run without quenching indicated that quenching inhibited further gas phase reactions. Without quenching, the temperature of the region inside the reactor was more uniform, but it was probably not isothermal.

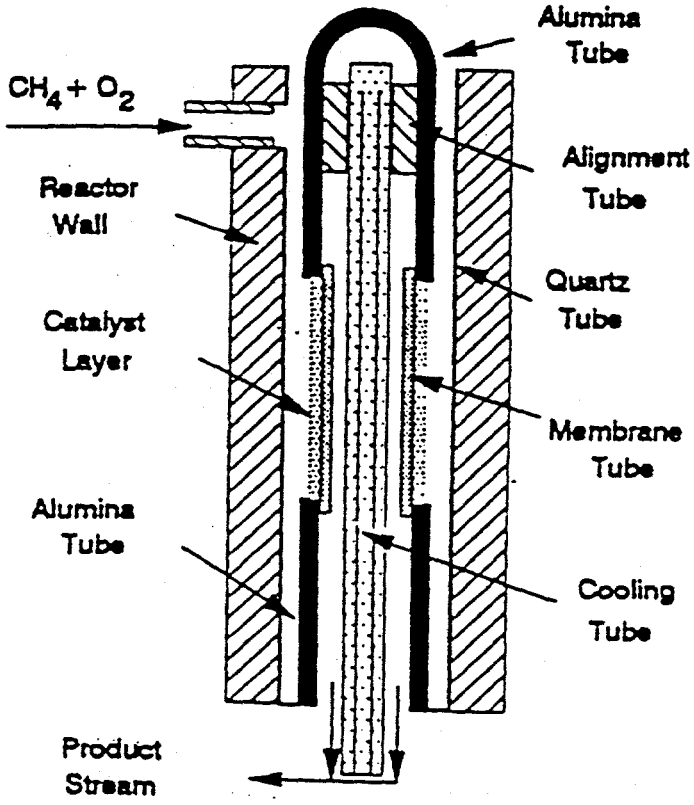


Figure 2. Reactor Diagram

Experimental Operation

Ceramic membranes with an average pore diameter of 5 nm and an outer diameter of 10 mm were used. The 15 cm-long membrane tube was glued to two supporting, nonporous α-alumina tubes. The catalyst layer (average thickness was approximately 1 mm) was wrapped on the outside of the membrane by an aluminum foil with small holes. With quenching, the temperatures of outer wall of the reactor were 770 to 830 K. Lower temperatures were used (690 to 710 K) in the absence of quenching because of the smaller radial temperature gradient inside the reactor. Chromel-alumel thermocouples with 304 stainless steel sheaths were inserted to measure the temperatures of the catalyst bed and the exit cooling water. A reactant mixture (8% O_2 in CH_4) was fed into the shell side of the membrane reactor with a flow rate of 0.2 to 0.5 L/min. The residence time in the shell side was about 10 to 20 s, including the time for preheating. The stream permeated radially through the catalyst layer and the membrane and was then quenched. This low temperature stream then left the reactor for GC analysis.

Molecular Sieve Membrane Preparation

Two important types of zeolites that have the potential to preferentially separate H_2 from other molecules are ZSM-5 and zeolite A. ZSM-5 zeolites have the same crystallographic structure but vary in their silicon to aluminum ratios. The Si/Al ratio can vary between 15 and infinity (silicalite-1) and imparts some difference in behavior to the different zeolites. All ZSM-5 zeolites have pore channels of two different sizes, 0.54 x 0.56 nm and 0.51 x 0.55 nm. Zeolite A is a strongly hydrophilic zeolite that has a narrowly distributed pore size. The most common of these, zeolite NaA, has a pore diameter of approximately 0.4 nm. This pore diameter is smaller than many hydrocarbons, and makes zeolite A promising for H2/hydrocarbon separations and gas drying.

ZSM-5 membranes were attempted via an in-situ synthesis on both γ-alumina and stainless steel supports with gels consisting of Si/Al ratios of 60 and 80. Gels with the latter Si/Al ratio proved to be too caustic and SEM analysis showed that the γ-alumina layer on the support was destroyed. Membranes made from the other gels were synthesized on alumina supports and stainless steel supports with a silicalite-1 intermediate. Single gas permeation experiments were performed on these membranes. Results for some of these membranes are as follows:

Membrane M7 - alumina support

Gas	Permeance 10^{-8} mol/(m^2 s Pa)	Selectivities
N_2	142	$N_2/SF_6 = 25$
SF_6	5.67	H_2/iBut = 170
H_2	170	nBut/iBut = 7
i-Butane	0.947	
n-Butane	6.59	

Membrane M8 - alumina support

Gas	Permeance 10^{-8} mol(m^{2}s Pa)	Selectivities
N_2	30.4	$N_2/SF_6 = 18$
SF_6	1.7	H_2/iBut = 53
H_2	35.4	nBut/iBut = 3
i-Butane	0.67	
n-Butane	2.02	

Membrane M9 - stainless steel with silicalite-1 intermediate

	Silicalite Membrane Only		ZSM-5 With Silicalite Layer	
Gas	Permeance 10^{-8} molol/m^2 s Pa)	Selectivity	Permeance 10^{-8} mol/m^2 s Pa)	Selectivity
N_2	38.6	44	35.4	50
SF_6	0.87		0.72	

Membrane M10 - stainless steel with silicalite-1 intermediate

	Silicalite Membrane Only.		ZSM-5 With Silicalite Layer	
Gas	Permeance 10^{-8} mol/m^2 s Pa)	Selectivity	Permeance 10^{-8} mol/m^2 s Pa)	Selectivity
N_2	70.8	41	53.1	50
SF6	1.73		1.47	

Similar preparation techniques were used to create zeolite NaA gels and their subsequent membranes. Zeolite NaA crystallizes within a narrow composition range, without the organic templates that were successfully applied to the ZSM-5 and silicalite-1 syntheses. The membranes were attempted on γ-supports which showed very little evidence of crystal growth. X-ray diffraction analysis confirmed that the crystals were in fact zeolite NaA, but a continuous layer did not form. SEM experiments also showed that the support was partially damaged by the caustic nature of the zeolite NaA gel.

Numerous attempts were made to synthesize a continuos layer of zeolite NaA on an cc-alumina support using the same basic in situ technique that works well for silicalite. All of these syntheses were performed without the use of a structure directing organic template, as in ZSM-5 and silicalite preparation. Because of this fact, high calcination temperatures were not needed. Two different synthesis gels were used for a hydrothermal preparation. The first used standard zeolite NaA molar reactant ratios of 2:1:2:120 for SiO_2:Al_2O_3:Na_2O:H_2O respectively. An autoclave was used with synthesis times from 3.5 to 6 hours and a temperature of 373 K. The second primary gel had vastly different reactant ratios of 5:1:50:1000. Preparation using this gel required milder conditions (333 K) and longer synthesis times (24 hours). Slight variations were made in these reactant ratios and synthesis conditions, but the resulting membranes all possessed N_2/SF_6 ratios of 1.3-1.6.

Two other techniques were combined with these preparations, but they had similar results. First, an preliminary NaA layer was attempted at atmospheric pressure to replicate the "seeding" that is often used for NaA synthesis. This technique produced the most crystals on the support surface but did not affect the N_2/SF_6 ratios on the subsequent membranes. Second, a silicalite membrane (N_2/SF_6 selectivity = 32) was prepared on an α-alumina support to provide an intermediate layer for NaA membrane production. The addition of the caustic NaA gel destroyed the silicalite layer and reduced the selectivity back to a Knudsen type value.

Promising results have been obtained in the area of ZSM-5 synthesis. Again, the synthesis technique was similar to that of silicalite membranes with different conditions and gel compositions. Zeolite ZSM-5 membrane preparation was carried out at 448 K for 24 hours using a gel with a composition of 1 TPAOH: 6 TEOS: 583 H_2O: 4 NaOH: 0.04 Al. A membrane synthesized in this manner was found to have an ideal N_2/SF_6 selectivity of 52 and an H_2/SF_6 selectivity of 163. The aluminum content of this membrane makes ion exchange possible, which in turn can decrease the effective pore size and improve gas separation performance.

The technique of chemical vapor deposition (CVD) has been favorably used to improve existing silicalite membranes. This process may be used to improve the performance of ZSM-5 and NaA membranes as well. In CVD silicon methoxide is deposited in the surface layer. Silicalite-1 membranes with N_2/SF_6 ideal selectivities of approximately 150 have been improved substantially with this modification. The N_2/SF_6 ratio changed to 560 and the ideal H_2/SF_6 selectivity became 2400. It is not known at present whether the process decreases the effective pore size or closes up the intercrystalline "cracks" in the membrane layer. More characterization of this technique needs to be performed.

X-ray diffraction analysis was performed on crystals grown under reaction conditions similar to the zeolite A membranes. These results indicate that the actual crystal growth is zeolite X, another zeolite with high aluminum content but much larger pores (0.7-0.8 nm). Zeolite X has the ability to preferentially adsorb CO_2, so these membranes may be valuable for H_2/CO_2 separation, especially after they are treated via chemical vapor deposition.

RESULTS AND DISCUSSION

Methanol Production

The selectivity to CH_3OH was 40 to 50% with quenching at a CH_4 conversion level of 4 to 7%. Without quenching, this selectivity decreased to 25 to 35% at similar CH_4 conversion levels. Methanol selectivity is plotted in Figure 3 as a function of CH_4 conversion at a constant flow rate of 0.5 L/min and a constant pressure of 3.5 MPa. The CH_3OH selectivities decreased with increased CH_4 conversion. With quenching, CH_3OH selectivity was about 50% at 4% CH_4 conversion and about 40% at 7% CH_4 conversion. Without quenching, CH_3OH selectivity varied from 35% at 3% CH_4 conversion to 25% at 7% CH_4 conversion. Quenching significantly improved CH_3OH selectivity in this process.

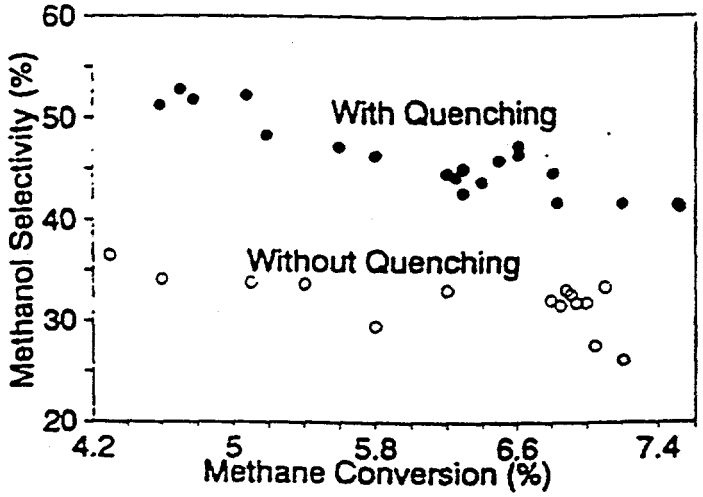


Figure 3. CH_3OH Selectivity vs CH_4 Conversion

Although the cooling tube improved CH_3OH selectivity, it also caused the membrane to break, due to the large radial thermal gradient and the different axial thermal expansion between the hot stainless steel reactor wall and the cooler ceramic tubes. To solve this problem, a porous metal tube with 0.5 µm pore size was used instead of ceramic membrane. Results from both ceramic membranes and porous metal tubes are included in Figure 4. Although CH_3OH selectivities were almost the same for both ceramic membranes and porous metal tubes, the methane conversions were slightly higher when ceramic membranes were used.

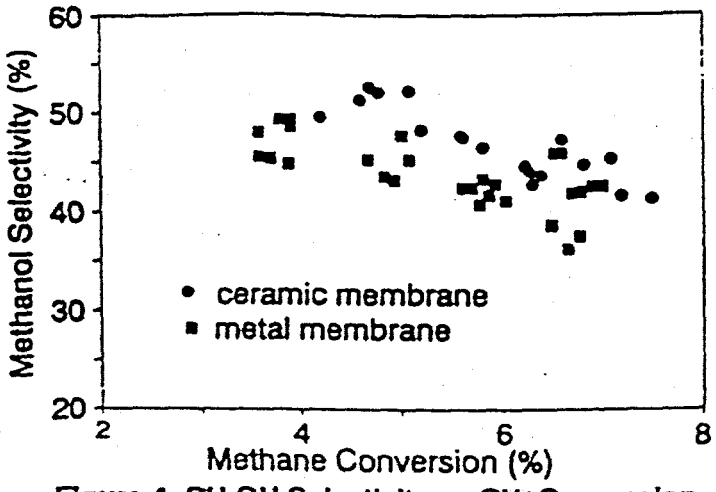


Figure 4. CH_3OH Selectivity vs CH_4 Conversion

Figure 5 shows that the combined selectivities of CH_3OH and CO were almost constant at 85 to 90%, with the rest being CO_2, both with and without quenching. Helton (2) made the same observation. Carbon dioxide was detected at low CH_4 conversions in this study, but CO was detected only when CH_3OH or CH_2O were detected. These results indicated that CO was formed from direct oxidation of CH_4, but CO may have formed from oxidation of CH_3OH and CH_2O. This is in agreement with the observations by Spencer et al. (12, 13). Thus, when quenching was used, the CO selectivity decreased as CH_3OH selectivity increased.

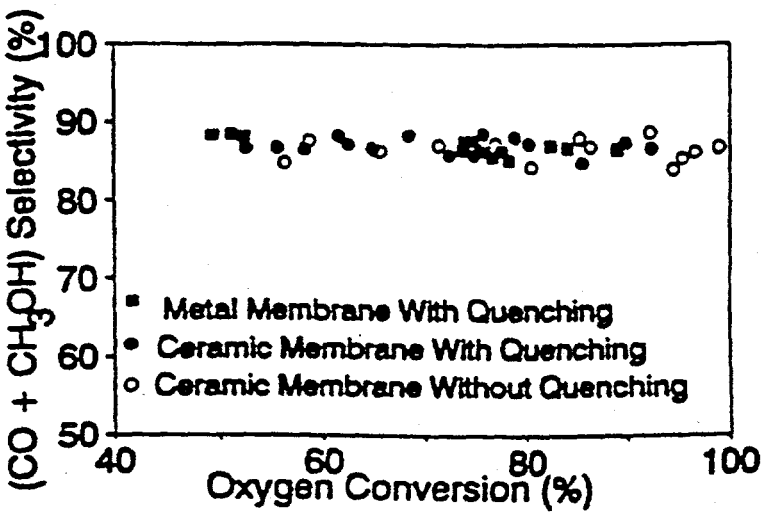


Figure 5.
Combined Selectivity vs O_2Conversion

Our selectivities to CH_3OH without quenching were almost the same as those recently published. With quenching, CH_3OH selectivities were higher, even though we used pure CH_4. Higher selectivities to CH_3OH might be expected for natural gas. Formaldehyde selectivities were 1 to 3% at low CH_4 conversion (about 4%), and it was detected only in trace amounts at higher CH_4 conversion. Carbon, hydrogen and oxygen mass balances were all in the range of 100±5%.

Other quenching methods have been reported (2, 15, 16). Dowden and Walker (15) injected liquid water directly into their product stream, and this cooled the stream below 473 K within 30 ms. No comparison data were presented without quenching. Wilms (16) also described a rapid quenching method. At pressures of 4 to 6 MPa and temperatures between 743 and 793 K, CH_4 and air were mixed in a small stainless steel reactor. After a residence time of 0.3 to 1.2 min. the mixture was quenched by expansion through a Delaval nozzle. A maximum CH_3OH selectivity of 85% was reached, but the CH_4 conversion was low, only 0.01 to 0.1%. Although these studies concluded quenching was useful, a comparison study by Helton (2) found that quenching had no influence on product selectivities. He cooled the product stream below 535 K at the exit of the reaction zone by cryogenic quench. Selectivities for products were the same as those without quenching.

The quenching method we used has several advantages over previous approaches (2, 15, 16). No extra water is added into the product stream and thus the downstream separation is simplified. The small gas-stream pressure drop makes recycling of unconverted CH_4 easy. A significant difference from previous approaches is that this method quenches the product stream within the reactor instead of at the reactor exit. Quenching improved the process by inhibiting further reactions of CH_3OH. The cooling tube also removed the reaction heat and thus the reaction temperature could be better controlled. In other reactor configurations, reaction heat can raise the reaction temperature, which can accelerate CH_3OH oxidation.

Large discrepancies in CH_3OH selectivities and CH_4 conversions have been reported, with CH_3OH selectivities ranging from less than 10% (17) to over 80% (8, 9, 14). Brown and Parkyns (18), and Burch et al. (11) suggested that CH_3OH selectivity is sensitive to temperature distribution, flow configuration, and detailed reactor design.

Single Gas Permeation Experiments with Zeolite Membranes

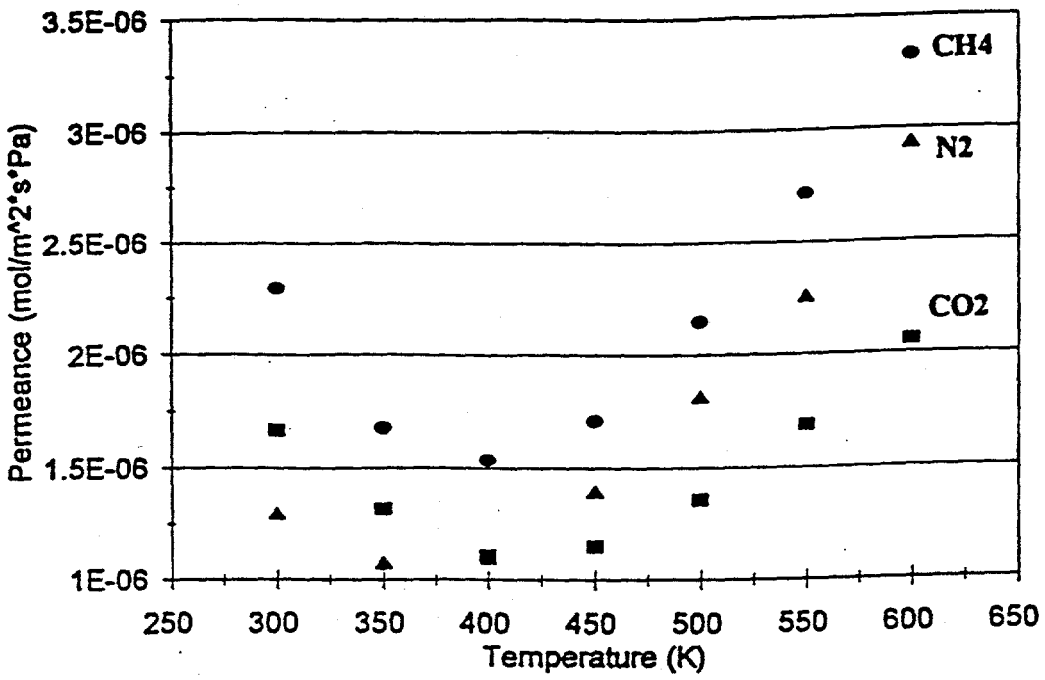
Single gas permeation experiments for N_2, CO_2, and CH_4 were carried out through a silicalite-1 membrane at 1.3 bar from 300 to 600 K. The membrane was mounted in a brass module with three ports: feed inlet, feed outlet, and permeate outlet. Silicone o-rings were used to seal the feed inlet and outlet ports, and pipe threads with Teflon tape were used to seal the permeate outlet. Permeate and feed fluxes were measured at each temperature setting using bubble flow meters. The readings were taken at intervals of 15 minutes until consecutive measurements were within 2% precision, indicating steady state. A thermocouple attached to steel tubing that flowed into the bubble meters was used to confirm that the gases were at room temperature.

Figure 6 shows a plot of single gas permeances versus temperature. The permeance values for each component go through a minimum (400 K for CH_4 and CO_2, 350 K for N_2). Experiments performed on a different silicalite membrane also showed the same sort of minima, although the values were shifted approximately 50 degrees higher. Activation energies (Ea) for permeation were calculated for each gas from the portions of the plots where the permeances increased with temperature. These values and some ideal selectivities can be found below:

Gas	**Kinetic Diameter (A)**	**Ea (Kj/mol)**
N_2	3.64	10.6
CO_2	3.3	8.5
CH_4	3.8	9.7

	Ideal Selectivity		
Gases	@ 300 K	@ 500 K	**@ 600 K**
CH_4/N_2	1.8	1.2	1.1
CH_4/CO_2	1.4	1.6	1.6

Figure 6
Single Gas Permeances (Silicalite -1)

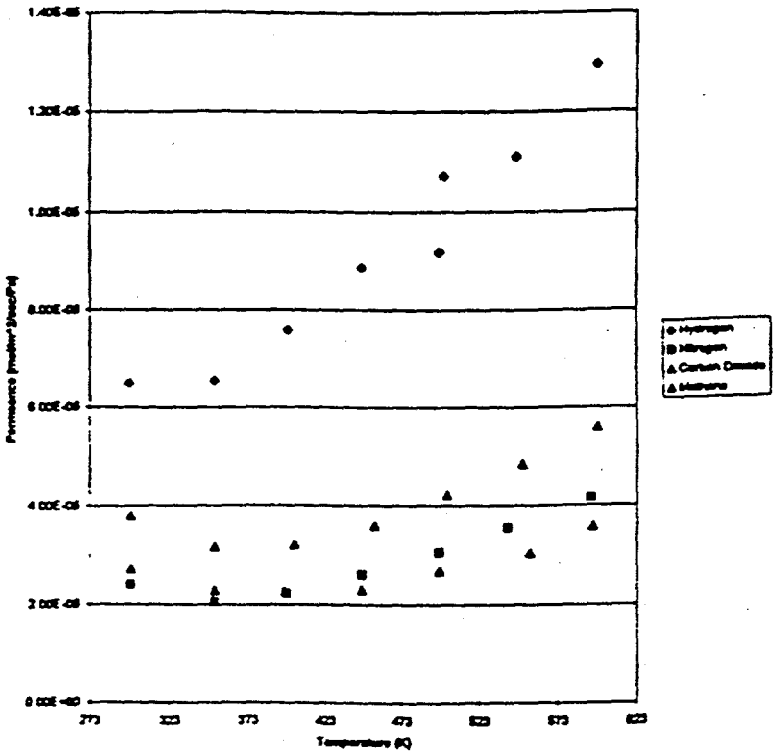


Single gas permeation experiments for H_2, N_2, CO_2, and CH_4 were carried out through a very high quality (N_2/SF_6 = 234) silicalite-1 membrane at 1.3 bar from 300 to 600 K. Figure 7 shows a plot of single gas permeances versus temperature. The results are similar to previous experiments using a silicalite-1 with a lower ideal selectivity (N_2/SF_6 = 80). The permeance values for components other than H_2 again go through a minimum (375 K for CH_4 and CO_2, 350 K for N_2) in the temperature range studied. The values for H_2 appear to level off at room temperature but do not go through an apparent minimum in the experimental temperature range. Activation energies (Ea) for permeation were calculated for each gas from the portions of the plots where the permeances increased with temperature. These values and some ideal selectivities can be found below:

Gas	Kinetic Diameter (A)	Ea (Kj/mol)
H_2	2.89	3.5
N_2	3.64	*5.1*
CO_2	3.3	4.5
	3.8	.1

	Ideal Selectivity		
Gases	@ 300 K	@ 500 K	@ 600 K
H_2/N_2	2.7	3.3	3.1
H_2/CO_2	2.4	3.7	3.6
H_2/CH_4	1.7	2.4	2.3

Figure 7
Single Gas Permeances on Silicalite-1



Single gas permeation experiments were also performed on H_2, CH_4, CO_2, and CH_4 at temperatures that were below ambient. The experimental setup was very similar to the one described above. The membrane module was suspended in a bath of dry ice and allowed to equilibrate at 253 K. The ideal selectivities at this temperature were the following: H_2/N_2 = 1.9, H_2/CO_2 = 2. 1, and H_2/CH_4 = 1.4. Permeance values of all components increased at the decreased temperature, continuing the trend exhibited by previous experiments.

H_2/CO_2 Binary Gas Experiments

Binary experiments on silicalite-1 were carried out from 300 to 585 K using a gas feed mixture of 55.7% H_2 and 44.3% CO_2 on a molar basis. The experimental setup was identical to that for the single gas experiments with the exception of gas composition determinations. The retentate and permeate compositions were directly sampled using a gas chromatograph (HP Series III 3396). The feed gas pressure was 25.7 psia for all temperatures and the total differential pressure across the membrane was maintained at 0.9 psi. Permeate gas flows were below 20% of the total to minimize any gradients in driving force along the membrane.

Figure 8 shows a plot of the total gas permeance versus temperature. The total permeance undergoes the same sort of minimum at approximately 400 K that had previously been observed for CO_2 single gas permeation through a silicalite membrane. The total permeance ranges from this minimum of about 2.2 x 10^{-6} to about 3.4 x 10^{-6} mol/(m^2s Pa). The gas permeances were calculated both using a log mean pressure gradient and the normal pressure gradient across the membrane. Individual gas permeances using the normal gradient are shown in Figure 9 and those calculated with a log mean are found in Figure 10. The primary difference in the two results is the more pronounced minimum that occurs for CO_2 permeances in the log mean calculations.

Figure 8
Total Permeance for H2/CO2 Mixture

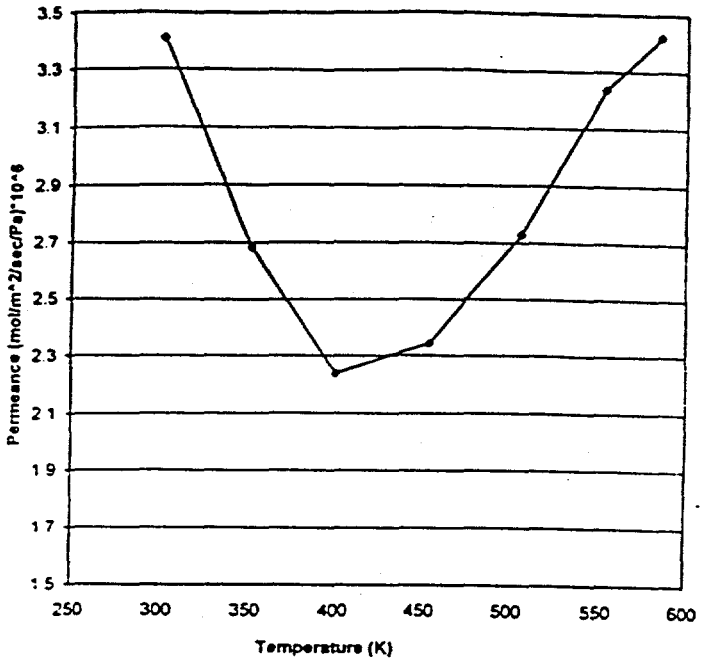


Figure 9
Permeances (using regular pressure values)

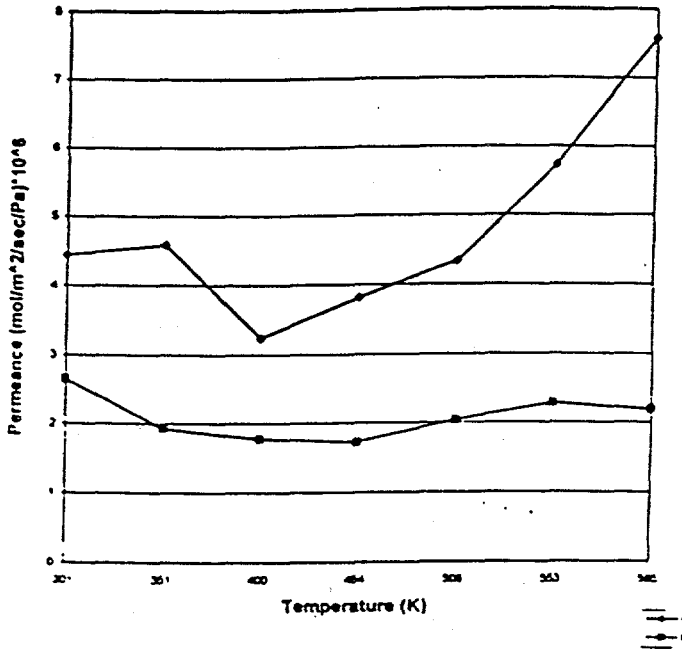
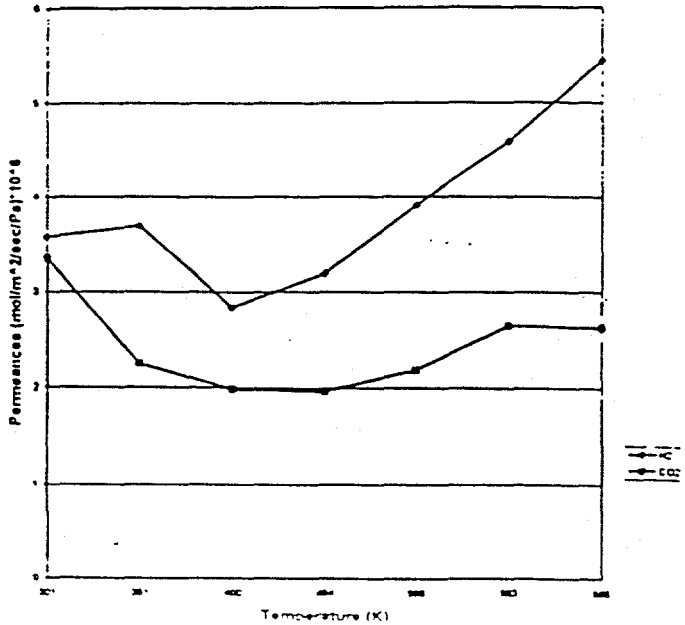
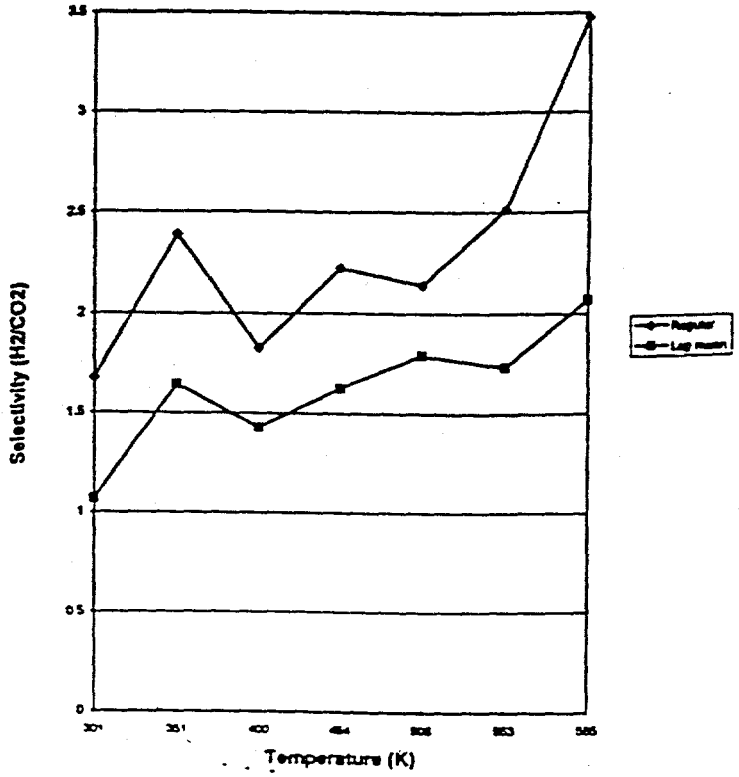


Figure 10
Permeances (using log mean pressure)



The binary results do not differ dramatically from the ideal, single gas results for the same membrane (Figure 7). The actual selectivities are graphed as a function of temperature in Figure 11. The values range from 1.7 to 3.5 (for the calculations with a regular driving force) and 1.1 to 2.1 (for the log mean driving force). The ideal selectivities that are shown above are slightly higher than these values. Both the ideal and actual selectivities appear to increase in the higher temperature range.

Figure 11
H2/CO2 Selectivity



High Temperature H_2/CO_2 Binary Gas Experiments

Previous experiments were carried out from 300 to 585 K using a gas feed mixture of 55.7% H_2 and 44.3% CO_2 on a molar basis. Data was obtained for the same mixture over a temperature range of 590 to 700 K for the same membrane. Figure 12 shows a plot of the total gas permeance versus temperature. The total permeance undergoes the same sort of minimum at approximately 400 K that had previously been observed for CO_2 single gas permeation through a silicalite membrane. The total permeance ranges from this minimum of about 2.2×10^{-6} to about 4.3×10^{-6} mol/(m^2 s Pa), which occurs at 632 K. The higher temperature data indicate that a plateau occurs after this point, and that the total permeance does not increase. Figure 13 shows the change of the permeance of each component (H_2 and CO_2) with temperature. The initial data (for temperatures up to 585 K) indicated that better H_2/CO_2 selectivity could be obtained at higher temperatures. However, the H_2 gas permeance reaches a maximum at 660 K and the CO_2 gas permeance does not change significantly with temperature. The net result is that the highest H_2 selectivity of 3.6 is obtained at 660 K. The H_2 selectivity is simply the ratio of the H_2 permeance to the CO_2 permeance and is shown as a function of temperature in Figure 14.

Figure 12

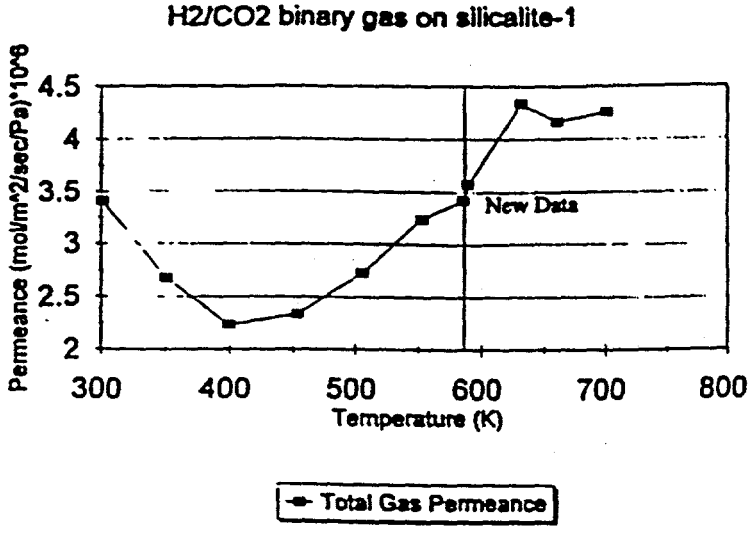


Figure 13

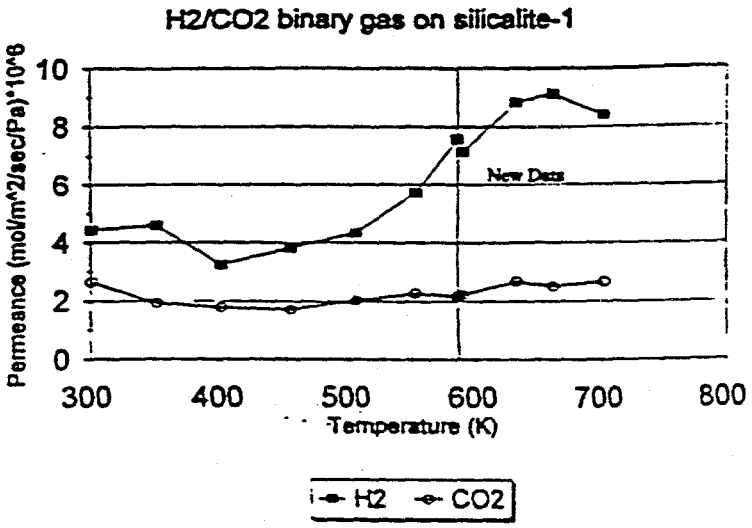
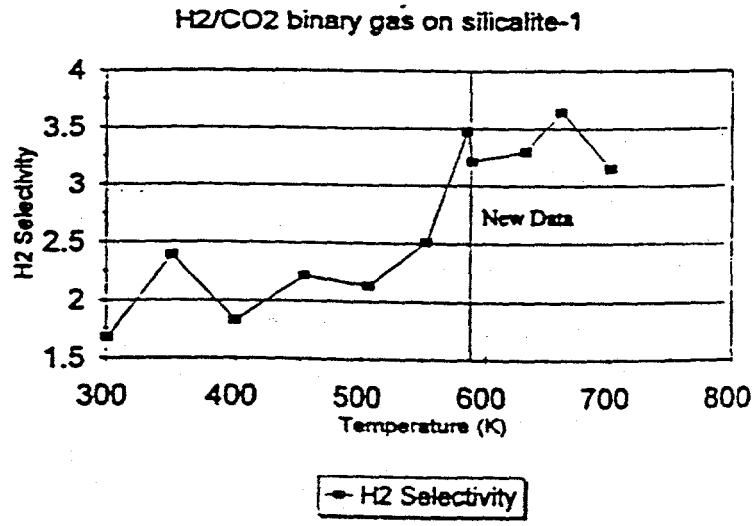


Figure 14



NaX Membrane Preparation and TIPB Treatment

Zeolite NaX membranes (where Na is the cation in the zeolite X matrix) have been prepared with N_2/SF_6 ideal selectivities of 1.9, which is less than the value for Knudsen diffusion (2.28). However, SF_6 is too small to be a good indicator of the quality of a zeolite X membrane. However, ideal H_2/CO_2 selectivities of 3.6 to 3.8 for these same membranes were obtained, which are higher than the value of 2.4 which was obtained for the best silicalite membrane (N_2/SF_6 = 234). Because of this behavior, a representative zeolite X membrane was used for a binary H_2/CO_2 experiment. In addition, treatment with triisopropylbenzene improved the ideal H_2/CO_2 selectivity of a zeolite X membrane (96ZX05) from 3.8 to a value of 5.7 (see Table 1).

A variety of zeolite membranes were treated with 1,3,5 - triisopropylbenzene (Aldrich, 97%) by soaking in the liquid, followed by heating at high temperature. The theory behind this process is that the triisopropylbenzene is too large (diameter > 0.8 nm) to infiltrate the zeolite pores, but is small enough to permeate into the mesopores, or membrane defects. The dense membrane layer could then be improved by forming carbon deposits in the mesopores during heating. The soaking and heating conditions varied a little for each membrane. All membranes were pre-treated by calcination at 480°C for 8 hours. The experimental conditions were as follows:

1. Membrane = 96Z512, a ZSM-5 membrane on (γ-alumina; soaked for 24 hours, heated at 0.01 °C/sec to 480°C, temperature held for 8 hours, then cooled at 0.05 °C/sec.
2. Membrane = Sil #13, a silicalite on γ-alumina; soaked for 25 hours, heated at 0.017 °C/sec to 480 °C, temperature held for 2 hours, then cooled at 0.017 °C/sec.
3. Membrane = 96ZX05, a NaX membrane on (γ-alumina; soaked for 25 hours, heated at 0.017 °C/sec to 480 °C, temperature held for 2 hours, then cooled at 0.017 °C/sec.
4. Membrane = 96Z512 (second treatment), a ZSM-5 membrane on (α-alumina; soaked for 24 hours, heated at 0.017 °C/sec to 500 °C with a slow N_2 purge, temperature held for 2 hours, then cooled at 0.017 °C/sec
5. Membrane = 96ZX05 (second treatment), a NaX membrane on (α-alumina; soaked for 24 hours, heated at 0.017 °C/sec to 500 °C with a slow N_2 purge, temperature held for 2 hours, then cooled at 0.017 °C/sec.
6. Membrane = 96SI26, a silicalite on stainless steel; soaked for 24 hours, heated at 0.017 °C/sec to 500 °C with a slow N_2 purge, temperature held for 30 hours, then cooled at 0.017 °C/sec
7. Membrane=95SI32,a silicaliteon(α–alumina; soaked for 24hours, heated at 0.017 °C/sec to 500 °C with a slow N_2 purge, temperature held for 30 hours, then cooled at 0.017 °C/sec

The membranes were immersed in a glass vial full of triisopropylbenzene during the soaking phase, and the heating occurred with the membranes open to the atmosphere. A nitrogen gas purge was used during the heating stage for a few of the experiments indicated above. There was never any significant change in membrane weight after the treatment with triisoproplybenzene. The gas permeation results were erratic and can be found in the table below:

Table I

Membrane	Condition	H_2 Perm.	N_2 Perm.	CO_2 Perm.	SF_6 Perm.	N_2/SF_6 Ideal
96Z512	before TIPB	32	9.40	8.4	0.21	44
	after I layer		7.1		0.22	32
	after 2 layers		9.0		1.2	7.6
Sil #13	before TIPB		6.8		0.071	96
	after I layer		3.9		0.49	8
96ZXO5	before TIPB		0.95		0.49	1.9
	after I layer	12	3.2	2.1	1.7	2.3
	after 2 layers	18	4.6	3.7	2.2	2.1
96SI26	before TIPB		1.6		0.36	4.4
	after I layer		0.84		0.3	2.8
95SI32	before -IPB		0.0056		0.000086	66
	after I layer		*0.015*		0.014	1.1

* note - Permeance units are mol/(m^2*sec*Pa) *10^{-7}

H_2/CO_2 Binary Gas Experiments on NaX Membrane

Experiments were carried out from 300 to 540 K using a gas feed mixture of 55.3% H_2 and 44.7% CO_2 on a molar basis. The experimental setup was identical to that for the silicalite-1 binary gas experiments discussed previously. Figure 15 shows the total gas permeance through the zeolite X membrane. The permeance steadily decreases with temperature, which is indicative of Knudsen type diffusion and is not promising for potential gas separations at the high temperatures of interest. The component gas permeances can be found as a function of temperature in Figure 16. Both H_2 and CO_2 gas permeances decrease with temperature, with H_2 decreasing the most in magnitude, although it appears to reach a plateau at 500 K. The H_2 selectivity (Figure 17) stays fairly constant between 4 and 4.5. These results are not promising for high temperature H_2/CO_2 separation, although the possibility exists that the adsorption characteristics will permit improved separation at higher feed pressures.

Figure 15

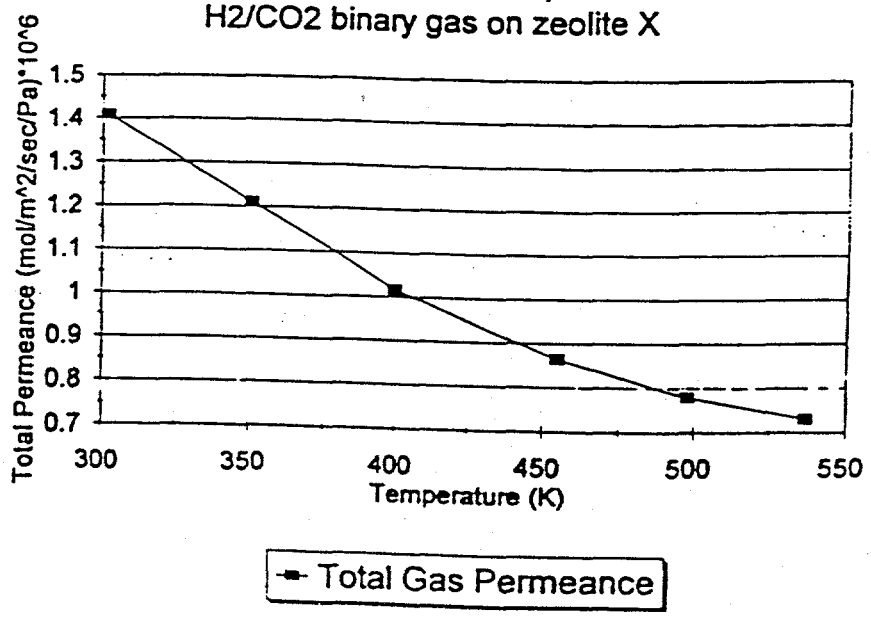


Figure 16
H2/CO2 binary gas on zeolite X

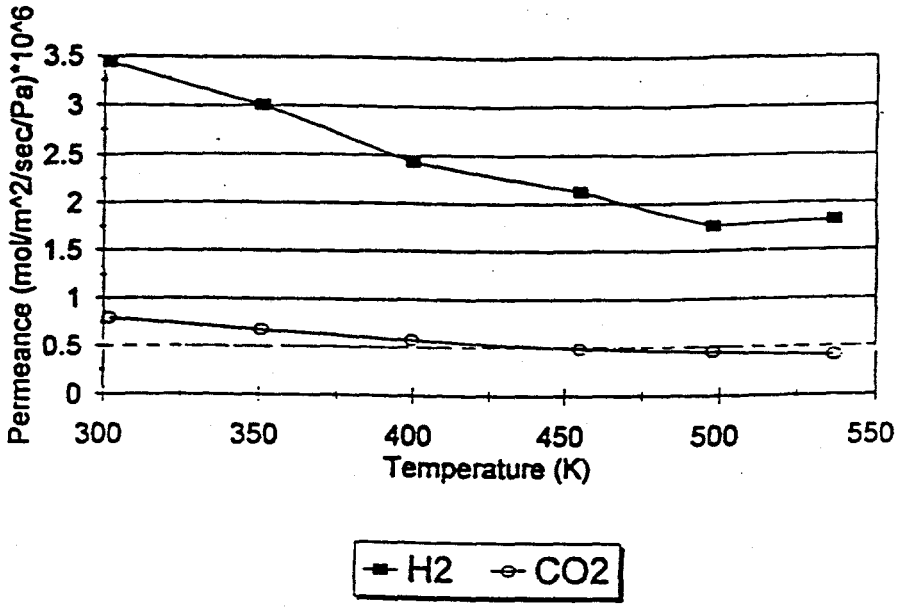
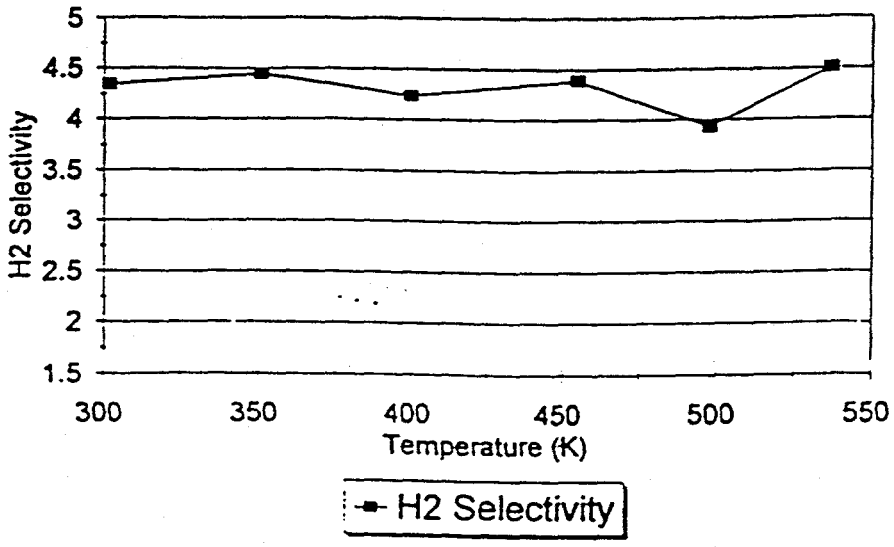


Figure 17
H2/CO2 binary gas on zeolite X



Methanol Separation

Condensable product mixture of partial oxidation of CH_4 process contains mainly H_2O and CH_3OH. Since membranes in our non-isothermal membrane reactor are not selective under the reaction conditions, the required product, CH_3OH, has to be separated by using other separating techniques. A liquid separation (pervaporation through a zeolite membrane) system was designed and built for separating CH_3OH from its water solution (Figure 18). This separation can be used in conjunction with the methanol formation in the membrane reactor to obtain a high purity methanol product.

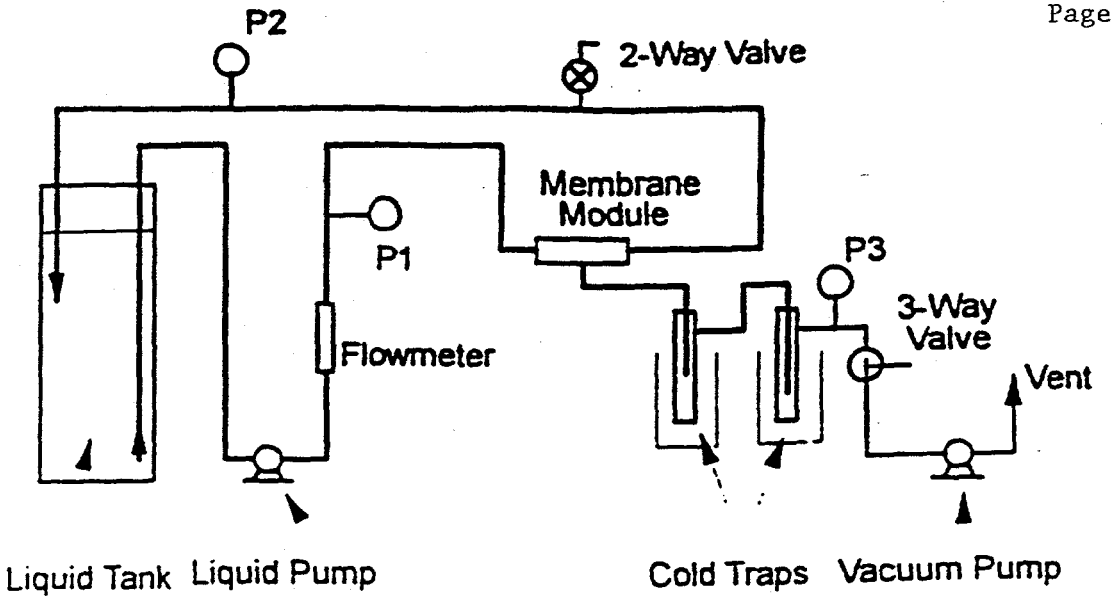


FIGURE 18

Pervaporation experiments were conducted by using the above mentioned liquid separation system (Figure 18). The membrane used for pervaporation was a stainless steel supported silicalite-1 membrane prepared in this laboratory. Before use in pervaporation, the membrane was checked by performing single gas permeation to make sure that no major defects exist on the membrane layer. The membrane tube was sealed in a brass module. Liquid mixture was pumped into the tube side and the shell side was evacuated at the beginning of the experiment. Liquid N_2 was used as cooling agent for cold traps to condense the permeants and to keep the shell side evacuated. The condensed permeates were analyzed by GC and optical method (refractive index). At ambient temperature, CH_3OH concentration (in H_2O) was varied and satisfactory separation results were obtained.

Figure 19 showed that CH_3OH concentration in permeate increases with the feed concentration. At a feed concentration of 46 vol% (as obtained from our CH_4 partial oxidation study), a permeate concentration of about 92 vol% was obtained. This indicated that the pervaporation can be effective separation process in conjunction with the CH_3OH formation in the non-isothermal membrane reactor to obtain a high purity CH_3OH product.

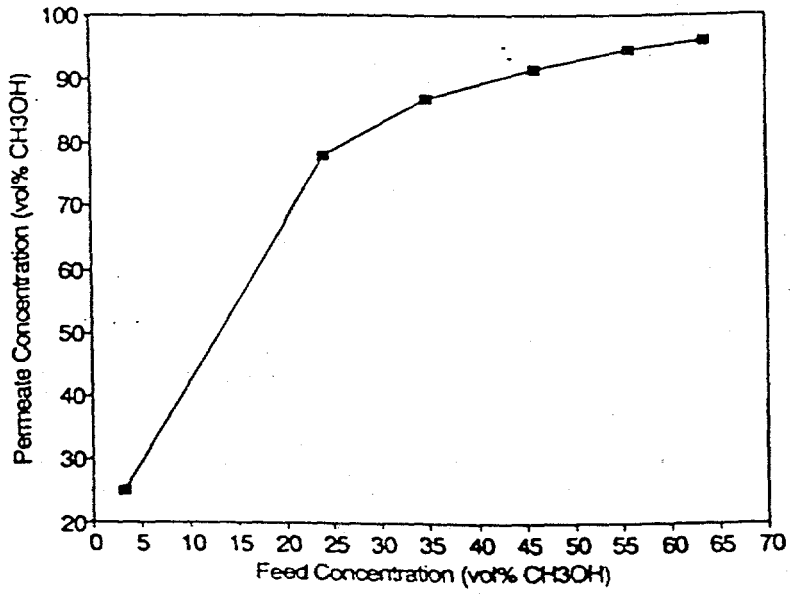


Figure 19 - Permeate Concentration vs. Feed Concentration

The total flux ($CH_3OH + H_2O$) and separation factor were plotted as functions of the feed concentration in Figure 20. The total flux increased with increasing feed concentration while the separation factor did not change much. Silicalite is a hydrophobic zeolite and CH_3OH has a higher flux through the membrane than that of H_2O. Thus, the total flux increased with increasing feed concentration of CH_3OH. The fairly constant separation factor may be explained by the following assumption. Methanol and H_2O may permeate through the membrane from different channels. For example, CH_3OH was transported mainly from normal silicalite pores since silicalite is highly organo-philic, while H_2O was transported mainly from small cracks of the membrane layer or from some hydrophilic impurity sites. This assumption can be better understood by viewing Figure 9. The partial flux of a component increased with its feed concentration, but the permeance of the component was almost constant except the low concentration point. This indicated that the transportation of CH_3OH and H_2O through the membrane was independent to each other except for the cases of very high (or very low) concentrations.

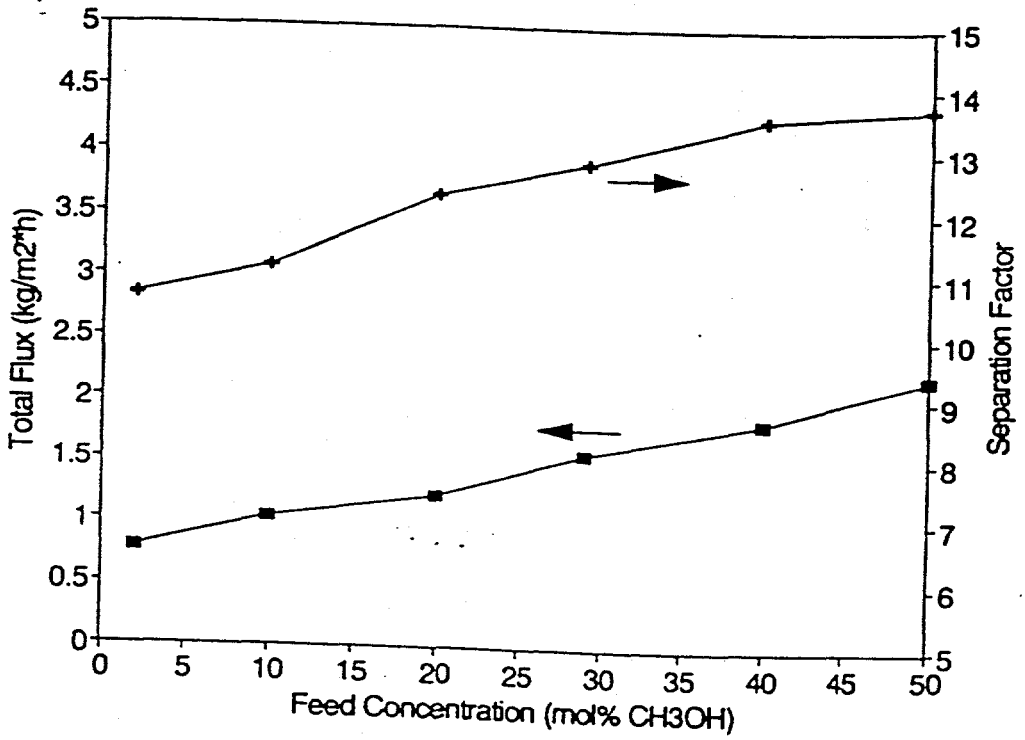


Figure 20 - Flux and Separation Factor vs. Feed Concentration

An alumina supported silicalite membrane was also tested in the pervaporation study. The separation factor obtained for C_2H_5OH and H_20 mixture was about 15, but never higher than 2 for CH_3OH and H_2O mixtures. The reason for this result was that alumina can be dissolved during the synthesis of the silicalite membrane, and the change of Al/Si ratio in the membrane layer would greatly affect the hydrophobicity of the membrane. Thus, molecules with weak organic properties, such as CH_3OH, were difficult to separate from their aqueous solutions.

CONCLUSIONS

A high pressure, high temperature apparatus was constructed to perform the methane and methanol reaction/separation experiments. Many membranes were tested but none of them could selectively remove methanol at the pressure and temperature necessary for methanol formation. As an alternative approach, a cooling tube was inserted inside the membrane reactor to create a low temperature zone that rapidly quenched the product stream. This system has proven effective for increasing methanol selectivity during methane oxidation. Selectivity for CH_3OH formation is significantly higher with quenching than in the experiments without quenching. For CH_4 conversion of 4% to 7%, CH_3OH selectivity is 40% to 50% with quenching and 25% to 35% without quenching. In order to separate CH_3OH from the condensed product mixture, a liquid phase separation system was built and pervaporation experiments were conducted.

For the H_2 separation phase of the research, we successfully fabricated a silicalite zeolite - alumina composite membrane with a γ-alumina layer (5 nm pore diameter) as the substrate. Single gas permeances of H_2, Ar, n-C_4H_{10}, and SF_6 were measured and mixtures of H_2/i-C_4H_{10} and H_2/SF_6 were separated to characterize the silicalite membrane. The silicalite membrane demonstrated behavior that was dramatically different from an alumina membrane without the silicalite layer. Permeances for the alumina membrane decreased with increasing temperature, and separation selectivities were lower than values expected for Knudsen diffusion. The silicalite membrane showed activated permeance behavior. The ratio of single gas permeances was as high as 136 for H_2 to SF_6 and 1100 for H_2 to i-C_4H_{10} at 298 K. Separation selectivities at elevated temperatures were significantly above Knudsen diffusion selectivity for the silicalite membrane and were larger than ratios of pure gas permeances at the same temperature. Single gas permeation experiments were performed on CH_4, CO_2, N_2, and H_2 using a silicalite-1 membrane with an ideal N_2/SF_6 selectivity of 234. Additionally, this membrane was used for gas separation experiments involving the binary mixture of H_2 and CO_2.

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APPENDIX

A copy of manuscripts published under this contract is attached.