Direct Methane Conversion to Methanol

**Annual Report
October 1993 - September 1994**

Richard D. Noble
John L. Falconer

January 1995

Work Performed Under Contract No.: DE-FG21-90MC27115

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
University of Colorado
Boulder, Colorado

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January 1995

DIRECT CATALYTIC CONVERSION OF CH₄ TO CH₃OH IN A NON-ISOTHERMAL MEMBRANE REACTOR

TECHNICAL PROGRESS REPORT -- YEARLY

(10/01/93 -- 09/30/94)

PROJECT DESCRIPTION

We proposed 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 feedstock, 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. In the original proposal, the membrane was used to selectively remove methanol from the reaction zone before carbon oxides form, thus increasing the methanol yield. Methanol synthesis and separation in one step would also make methane more valuable for producing chemicals and fuels. However, all the membranes tested in this laboratory lost their selectivity under the reaction conditions. A modified non-isothermal, non-permselective membrane reactor then was built and satisfactory results were obtained. The conversion and selectivity data obtained in this laboratory were better than that of the most published studies.

SUMMARY OF PROGRESS

The cooling tube inserted inside the membrane reactor has created a low temperature zone that rapidly quenches the product stream. This system has proved effective for increasing CH₃OH

selectivity during CH_4 oxidation. Both ceramic and metal membranes were tested in this study and similar results were obtained. The ceramic membranes broke during experiments apparently because of the large radial thermal gradient and axial thermal expansion difference. A metal membrane was used to avoid the membrane breakage problem. A series of experiments were carried out in order to optimize the operation of the process. A methanol yield of 3.8% was obtained when 8% O_2 was fed in the reactant mixture. In order to separate CH_3OH from the condensed product mixture, a liquid phase separation system is built and pervaporation experiments are conducted.

One paper on CH_4 oxidation and two papers on zeolite membranes have been prepared and submitted for publication.

TECHNICAL PROGRESS

Methanol Formation

Since similar results were obtained by using both ceramic and metal membranes (please refer to last yearly report). Metal membranes were used to avoid the membrane breakage problem. In previous experiments, two ends of the metal membrane were glued into alumina support tubes. During experimentation, the alumina support tubes broke due to the different thermal expansion of the metal and ceramic tubes. Conversions of CH_4 and O_2 dropped significantly because the reactant mixture short-circuited through the cracks. To solve this problem, a metal membrane was welded to a stainless steel sealing tube and a supporting tube

(Figure 1). The sealing tube and the support tube were covered by an alumina tube and a quartz tube respectively in order to isolate the metal surface from the gas mixture.

Several process parameters were investigated in a series of experiments. Figure 2 shows the changes of the combined $\text{CH}_3\text{OH} + \text{CH}_2\text{O}$ selectivity and yield with a change in pressure under conditions of constant reactor wall temperature (800 K), constant flow rate (0.5 L/min) and constant O_2 concentration (8%). The combined selectivity decreased with an increase in pressure due to the increased residence time. The combined yield reached a maximum of 3.3% at a pressure of 3.5 MPa because of the increase in CH_4 conversion. Conversions of CH_4 and O_2 are plotted as functions of pressure in Figure 3. When the pressure changed from 1.5 to 4.5 MPa, O_2 conversion increased from 62 to about 98%. At high O_2 conversion, CH_4 conversion decreased with an increase of pressure. The increase of residence time allowed oxidation to go completely to $\text{CO}_2 + \text{H}_2\text{O}$, and this required more O_2 .

When the reaction pressure was changed, the residence time also changed, and thus conversion changed. Thus, experiments were carried out in which the pressure was changed and the temperature was adjusted to maintain 95% conversion for O_2 . The gas flow rate (0.5 L/min) and O_2 concentration (8%) remained constant. As showed in Figure 4, when the pressure changed from 2.5 to 3.5 MPa, the combined $\text{CH}_3\text{OH} + \text{CH}_2\text{O}$ selectivity increased from 33 to 45% and the combined yield increased from 2.3 to 3.4%. When the reaction pressure changed from 3.5 to 4.5 MPa, the combined yield only increased from 3.4 to 3.6%.

The effect of residence time was also investigated by changing the reactant flow rate. At a constant pressure of 3.5 MPa and a constant reactor wall temperature of 800 K (Figure 5), the

combined selectivity increased from 41% at a flow rate of 0.4 L/min (equivalent to a residence time of 25 sec) to 46% at a flow rate of 0.54 L/min (residence time of 19 sec) and the combined yield changed from 2.8 to 3.5%. The lower methane conversion at the longer residence time was caused by a lower selectivity.

When the catalyst ($\text{MoO}_3/\text{SiO}_2$) bed was replaced by a layer of silica particles, the same results were obtained. The catalyst was not active because of the low temperature. When the silica layer was removed and the membrane was not shielded, the combined $\text{CH}_3\text{OH} + \text{CH}_2\text{O} + \text{CO}$ selectivity was not as constant as in previous experiments. This selectivity changed from 80 to 90% when the residence time changed from 20 sec to 12 sec. One possible explanation for this observation is that SiO_2 , a high surface material, quenched the free radical gas phase reactions. The selectivity change may also be caused by a change in the thermal gradient in the reactor since any physical change inside the reactor will change the reactor temperature profile.

In order to increase CH_3OH yield, high O_2 concentration in feed was tested. A gas mixture of $300 \text{ CH}_4 + 100 \text{ O}_2 + 100 \text{ He}$ was used. This composition was well above the upper explosion limit for CH_4 in O_2 enriched air. Helium instead of nitrogen was used to make up an O_2 enriched air-like mixture for the purpose of simplicity in GC analyses. A constant pressure of 3.5 MPa was used for this study. Higher reactor wall temperature (825 K to 835 K) was used to get a similar O_2 conversion with that in previous experiments. A methane conversion of 18% was obtained at an O_2 conversion of 85%. However, CH_3OH selectivity was only 15%. Thus, the overall CH_3OH yield was only 2.7%, even lower than that when 8% O_2 was used.

The catalyst was tested again in the high temperature region to see if it can improve the methane partial oxidation process. The liner glass tube (Pyrex) was treated by HF to get a rough

inner surface. The catalyst, $\text{MoO}_3/\text{SiO}_2$ was ground to powder and then coated on the treated glass surface with an average thickness of about 0.1 mm. The temperature of the inner wall of the liner tube is the highest in the non-isothermal reactor. With a catalyst coating, however, CH_4 and O_2 conversions were lower at low temperatures (775 to 785 K) than that without a catalyst coating at same temperatures. At high temperatures (795 to 805 K), O_2 conversions were higher than that without catalyst at same temperatures. For both temperature ranges, the methanol selectivities were lower than that without catalyst coating. The comparisons of conversions and selectivities are shown in Table 1. The catalyst, $\text{MoO}_3/\text{SiO}_2$, did not catalyze CH_3OH formation, but catalyzed instead CH_3OH and CO oxidation. Apparently, the high surface area silica gel quenched the gas-phase radical reactions at low temperature since O_2 conversion was lower with the catalyst at 775 and 785 K. At higher temperature, 795 to 805 K, the silica gel became active for complete oxidation and high O_2 conversion was obtained.

Formaldehyde Formation

Formaldehyde is less stable than methanol at high temperature in the presence of oxygen. Thus, it is expected that quenching would benefit the CH_2O formation. An experiment was carried out at low pressure (0.1~0.3 MPa). Water, mentioned by other researchers as a formaldehyde stabilizer, was added to the reaction system by a syringe pump with a flow in the range from 0 to 10% (mol%) of the gas flow rate. We found that CH_4 conversion was very sensitive to the cooling water flow rate (or the temperature of the cooling water). However, at all conditions, no significant amount of CH_2O was formed. A catalyst was not used since previous researchers have reported that CH_2O can be formed by homogeneous reaction under these conditions. We do not plan to pursue CH_2O formation any further due to these results.

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 6). This separation can be used in conjunction with the methanol formation in the membrane reactor to obtain a high purity methanol product.

Pervaporation experiments were conducted by using the above mentioned liquid separation system (Figure 6). 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 7 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.

The total flux ($\text{CH}_3\text{OH} + \text{H}_2\text{O}$) and separation factor were plotted as functions of the feed concentration in Figure 8. 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.

Alumina supported silicalite membrane was also tested in pervaporation study. The separation factor obtained for $\text{C}_2\text{H}_5\text{OH}$ and H_2O 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 , was difficult to be separated from their aqueous solutions.

Zeolite Membranes

Silicalite-alumina composite membranes were prepared by an in-situ zeolite synthesis method using an alumina membrane tube as a substrate. Both single gas permeations and mixture gas separations were carried out to characterize the silicalite membrane properties. For comparison, an alumina membrane without a silicalite layer was also studied.

Table 2 shows permeation results for several gases at room temperature. The permanence ratios of H_2/Ar and SF_6/Ar were close to the ratios expected for Knudsen diffusion of 4.5 and 0.52. The permeances of $i-C_4H_{10}$, $n-C_4H_{10}$, and $i-C_4H_8$ were approximately twice the Ar permeance. The higher flows of $i-C_4H_{10}$ and $i-C_4H_8$ are attributed to surface flow. Both $i-C_4H_{10}$ and $i-C_4H_8$ can adsorb on alumina surface and diffuse along the surface concentration gradient.

The separation selectivity for $H_2/i-C_4H_{10}$ using the alumina membrane at room temperature was 4.2 when Ar was used as a sweep gas, and 4.3 for SF_6 as a sweep gas. The permeance of pure H_2 was about 10 times and pure $i-C_4H_{10}$ was 30 times higher than the corresponding values of the mixture. This phenomenon can not be explained by Knudsen diffusion, where there are no significant interactions between gases. The momentum exchange between gases moving in opposite directions decreased the gas flows across the asymmetric alumina membrane.

The formation of the silicalite layer on the alumina membrane substrate decreased the permeances of all gases studied. For the H_2 and Ar, the permeances were 7~8 times smaller than those on the alumina membrane. The permeance of SF_6 which is a much bigger molecule, decreased a factor of 170. The permeance of $i-C_4H_{10}$, however, was a factor of about 6000 lower through the silicalite layer, and the $n-C_4H_{10}/i-C_4H_{10}$ permeance ratio was 22. which were

far above the Knudsen diffusion limitation. The permeances of all components studied were activated, and activation energies ranged from 8.5 to 16.2 kJ/mol.

When Ar was used as a sweep gas, the separation selectivities for $H_2/i-C_4H_{10}$ were 6.2 ~ 6.4, which were slightly higher than the Knudsen diffusion value of 5.4. However, selectivities calculated from single gas permeances were a factor of 6 larger at the same conditions. When SF_6 was employed as a sweep gas instead, permeances of both H_2 and $i-C_4H_{10}$ decreased.

Table 3 showed the separation results for $H_2/i-C_4H_{10}$ and H_2/SF_6 using a pressure drop. The separation selectivity was 12.8 for $H_2/i-C_4H_{10}$ and 11.9 for H_2/SF_6 . The separation selectivities increased slightly as the temperature increased from 361 K to 583 K. The separation results for $H_2/i-C_4H_{10}$ and H_2/SF_6 were quite similar. The molecular sizes of SF_6 and $i-C_4H_{10}$ are close (SF_6 : 0.55 nm, $i-C_4H_{10}$: 0.52 nm) although their molecular weights are quite different (SF_6 : 156, $i-C_4H_{10}$: 58).

A composite membrane was prepared that consisted of silicalite and SAPO-34 layers on a composite alumina membrane tube. Single gas permeance measurements showed that the SAPO-34 membrane with Ni had a much higher single gas permeance to CO_2 than for N_2 and the permeance ratio was increased by H_2O vapor. A ratio of CO_2/N_2 permeance as high as 9.5 was observed.

The SAPO-34 membranes grown on $\gamma-Al_2O_3$ appeared to show interesting differences in permeances for CO_2 and N_2 , with CO_2 moving through the membrane faster. That is, the ability of CO_2 to adsorb on the molecular sieve, rather than its size, appeared to govern the permeance. The problem with these membranes was that the permeances of CO_2 and N_2 were not reproducible and vary over a wide range from one measurement to the next. The stability of SAPO-34 membranes

has been reported to be affected significantly by H₂O vapor, even at room temperature, and this probably contributed to our difficulty in obtaining a stable membrane. We obtained a more stable membrane by a multilayer procedure in which a silicate layer, a SAPO-34 layer, and finally a Ni-SAPO-34 layer were grown onto a γ -Al₂O₃ layer of a membrane tube. The largest ratio of single gas permeances for CO₂ to N₂ was 9.5, whereas the largest separation selectivity obtained was 4.8. The ability to separate CO₂ and N₂, however, indicates the potential of these membranes.

Initial effects to measure gas permeances resulted in significant changes in the gas permeances as a function of time. The CO₂ permeance increased from 18×10^{-7} to 37×10^{-7} mol/s/m²/Pa over a period of 225 min, and the permeance still had not stabilized. This was not a continuous increase with stages but appeared to exhibit periods of slow increases and then large jumps in the permeance. Similarly, the N₂ permeance decreased with time from 5.1 to 3.9×10^{-7} mol/s/m²/Pa.

The difficulty of obtaining reproducible permeance values, which we did not observe for silicalite membranes in previous studies, was attributed to water vapor. When the CO₂ and the N₂ were passed through CaSO₄ (Drierite) to remove water, stable values of CO₂ and N₂ permeance were obtained after 10 min. The ratio of CO₂ to N₂ single gas permeance was 4.3. When the gases were not dried, ratios as high as 9.5 were obtained. In either case, the permeances are significantly higher than expected from Knudsen's diffusion (0.8), most likely due to CO₂ adsorption on the Ni-SAPO-34.

A 50/50 mixture of CO₂ and N₂ was used to measure the ability of the Ni-SAPO-34 membrane to separate these gasses. At 300 K, the permeance ratios of CO₂ to N₂ were 3.8 when the gases were dried by CaSO₄. The permeances, calculated from the concentrations and flow

rates, were 14×10^{-8} mol/s/m²/pa for N₂ and 53×10^{-8} mol/s/m²/Pa for CO₂. These are close to the single gas permeances, indicating that the molecules did not interfere with each other. When the separation was run with the membrane at 278 K, then the permeance of N₂ decreased to 12×10^{-8} , but the permeance of CO₂ increased to 55×10^{-8} mol/s/m²/Pa and the selectivity ratio was 4.6.

Permeation experiments for CO₂/H₂ with a Ni-SAPO-34 / sicalite-1 composite zeolite membrane on a porous alumina support were also performed. No significant single gas selectivity between CO₂ and H₂ could be observed. Compared to prior reported promising selectivities for N₂ / CO₂ with similarly prepared membranes, this lack of selectivity wasn't expected. This lack of selectivity can be attributed to technical problems during the preparation of the membranes investigated. The problems, which included temperature fluctuations in the synthesis oven have now been solved. The membrane formation apparently is very sensitive to variations in temperature which could lead to imperfections in the separation layer.

Further membrane synthesis using stable temperature conditions have been conducted. The permeation experiments with these membranes are in progress and results will be reported in the next report.

FUTURE WORK PLANNED

1. Try to separate some organic mixtures by using the current pervaporation system.
2. Continue to prepare Ni-SAPO-34 membranes using different gel compositions as well as other supports such as SAPO-membranes, stainless steel or silica.
3. Perform permeation studies for the prepared membranes.

Figure 1. Reactor Diagram

Figure 2. Effect of Pressure on Product Yield

Figure 3. Effect of Pressure on Reactants Conversion

Figure 4. Effect of Pressure at a Constant O₂ Conversion

Figure 5. Effect of Flow Rate on the Process

Figure 6. Pervaporation System

Figure 7. Permeate Concentration vs. Feed Concentration

Figure 8. Flux and Separation Factor vs. Feed Concentration

Figure 9. Flux and Permeance vs. Feed Concentration

Table 1: Comparison of Conversions and Selectivities, W/ vs.W/O Catalyst Coating
(Pressure 3.5 MPa, Flow rate: 0.5 L/min, O₂ concentration: 8%)

	T (K)	775	785	795	805
With Catalyst Coating	CH ₄ Conv.	< 1%	1%	6.5-7%	6.5-7%
	O ₂ Conv.	< 10%	~ 15%	>95%	98%
	CO Sel.	0	0	30-35%	30-35%
	CO ₂ Sel.	100%	100%	35-40%	35-40%
	CH ₃ OH Sel.	0	trace	25-30%	25-30%
Without Catalyst Coating	CH ₄ Conv.	3%	3.5%	5-6%	6-7%
	O ₂ Conv.	40%	40-50%	70-75%	75-85%
	CO Sel.	30-35%	35%	35-40%	40-45%
	CO ₂ Sel.	15%	15%	15%	15%
	CH ₃ OH Sel.	50-55%	50-55%	45-50%	40-45%

Table 2. Permeances of Single Gases at 298 K

<u>Membrane</u>	<u>Gas</u>					
	Ar	H ₂	SF ₆	i-C ₄ H ₈	n-C ₄ H ₁₀	i-C ₄ H ₁₀
<u>Alumina</u>						
Permeance (mol/s/m ² /Pa)10 ⁷	71	284	42	165	160	167
Permeance Ratio P _i /P _{Ar}	1	4	0.59	2.3	2.3	2.4
<u>Silicalite</u>						
Permeance (mol/s/m ² /Pa)10 ⁷	9.3	34	0.25	—	0.59	0.03
Permeance Ratio P _i /P _{Ar}	1	3.7	0.03	—	0.06	0.003

Table 3. Separation of H₂/i-C₄H₁₀ and H₂/SF₆ with Silicalite Membrane

Pressure Drop (kPa)	Temperature (K)	Permeance (mol/m ² /s/Pa)10 ⁷			Separation Selectivity (P _{H2} /P _i)
		H ₂	i-C ₄ H ₁₀	SF ₆	
69.1	361	36	3.3	/	10.9
58.7	443	41	3.8	/	10.8
69.1	583	50	4.2	/	11.9
69.1	583	51	/	4	12.8