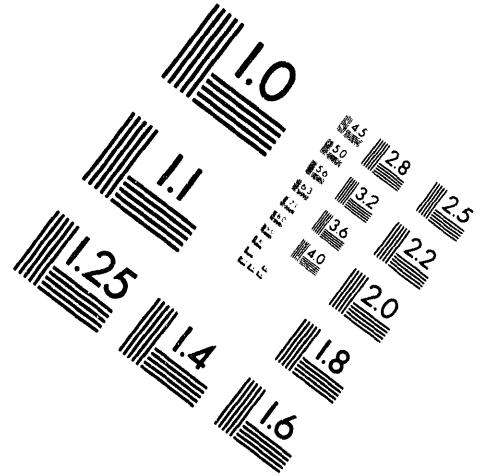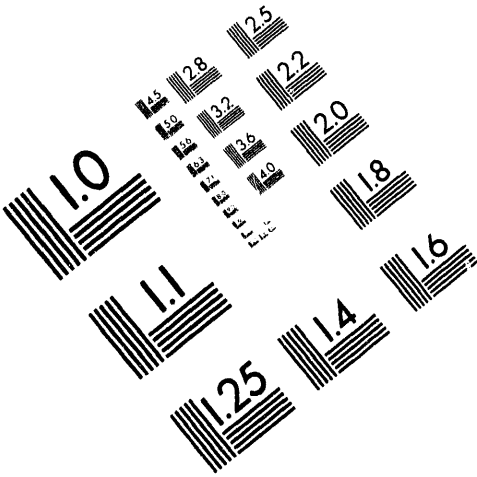# AIIM

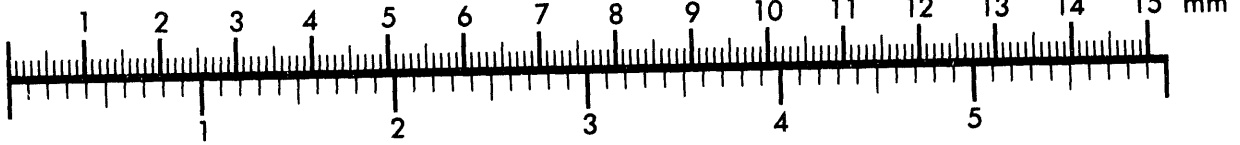**Association for Information and Image Management**
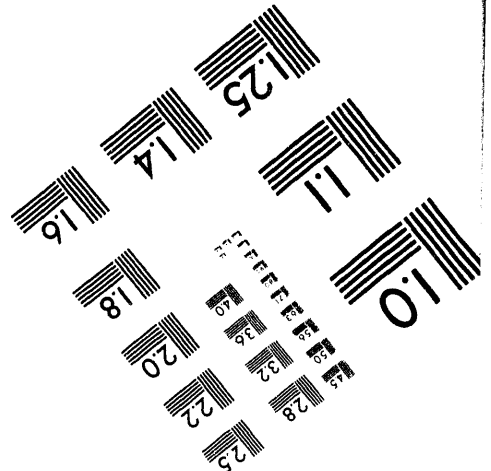
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Centimeter

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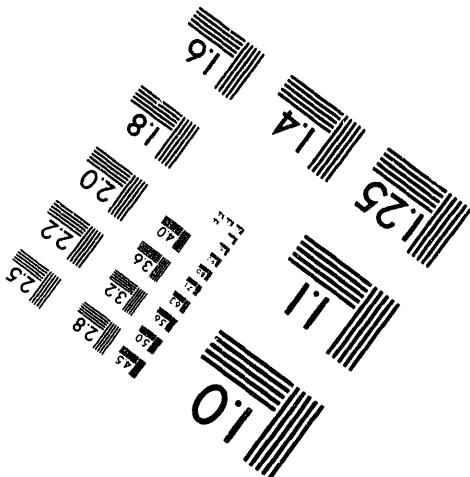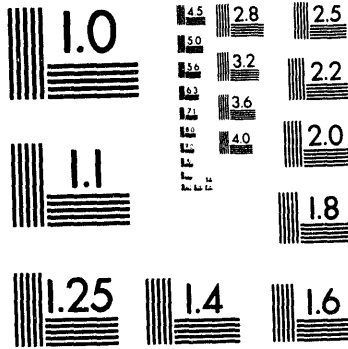
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1 of 1

DIRECT METHANE CONVERSION TO METHANOL

Project Status Report - Quarterly

(1/1/94 -- 3/31/94)

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Morgantown Energy Technology Center

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DISCLAIMER

DIRECT CATALYTIC CONVERSION OF CH_4 TO CH_3OH IN A

NON-ISOTHERMAL MEMBRANE REACTOR

PROJECT STATUS REPORT -- QUARTERLY

(01/01/94 -- 3/31/94)

PROJECT DESCRIPTION

We prcposed 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.

CURRENT SITUATION

The cooling tube inserted inside the membrane reactor has created a low temperature zone that rapidly quenches the product stream. Both ceramic and metal membranes were tested in this study and similar results were obtained. This membrane reactor system has proved effective for increasing methanol selectivity during CH_4 oxidation. We are currently using this non-isothermal, non-permselective membrane reactor, and evaluating modifications to further improve performance. 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. The catalyst, MoO_3/SiO_2, was found not good for this methane partial oxidation process.

PROGRESS

Methane Oxidation

In order to increase CH_3OH yield, high O_2 concentration in feed was tested. A gas mixture of 300 CH_4 + 100 O_2 + 100 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 analysis. 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 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, MoO_3/SiO_2 was ground to powder and then coated on the treated glass surface with an average thickness of about 0.1 mm (Figure 1). The temperature of the inner wall of the liner tube is the highest in the non-isothermal reactor. However, with a catalyst coating, 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, MoO_3/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.

A manuscript describing these results has been prepared and is included with this report.

Molecular Sieve Ni-SAPO Membrane Preparation

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 was as high as 9.5 was observed.

The SAPO-34 membranes grown on γ-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 H_2O 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-Al_2O_3 layer of a membrane tube. The largest ratio of single gas permeances for CO_2 to N_2 was 9.5, whereas the largest separation selectivity obtained was 4.8. The ability to separate CO_2 and N_2, 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 CO_2 permeance increased from 18×10^{-7} to 37×10^{-7} mol/s/m^2/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 N_2 permeance decreased with time from 5.1 to 3.9 $\times 10^{-7}$ mol/s/m^2/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 CO_2 and the N_2 were passed through $CaSO_4$ (Drierite) to remove water, stable values of CO_2 and N_2 permeance were obtained after 10 min. The ratio of CO_2 to N_2 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 CO_2 adsorption on the Ni-SAPO-34.

A 50/50 mixture of CO_2 and N_2 was used to measure the ability of the Ni-SAPO-34 membrane to separate these gasses. At 300 K, the permeance ratios of CO_2 to N_2 were 3.8 when the gases were dried by $CaSO_4$. The permeances, calculated from the concentrations and flow rates, were 14×10^{-8} mol/s/m^2/pa for N_2 and 53×10^{-8} mol/s/m^2/Pa fro CO_2. 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 N_2 decreased to 12×10^{-8}, but permeance of CO_2 increased to 55×10^{-8} mol/s/m²/Pa and the selectivity ratio was 4.6.

Two manuscripts on this aspect of the research are included with this report.

WORK PLANNED FOR CURRENT QUARTER

1.   Continue membrane reactor experimental studies.

2.   Synthesize Ni-SAPO-34 on a silicalite layer.

3.   Permeation study of synthesized Ni-SAPO-34 membrane for CO_2 and N_2 with and without the presence of H_2O.
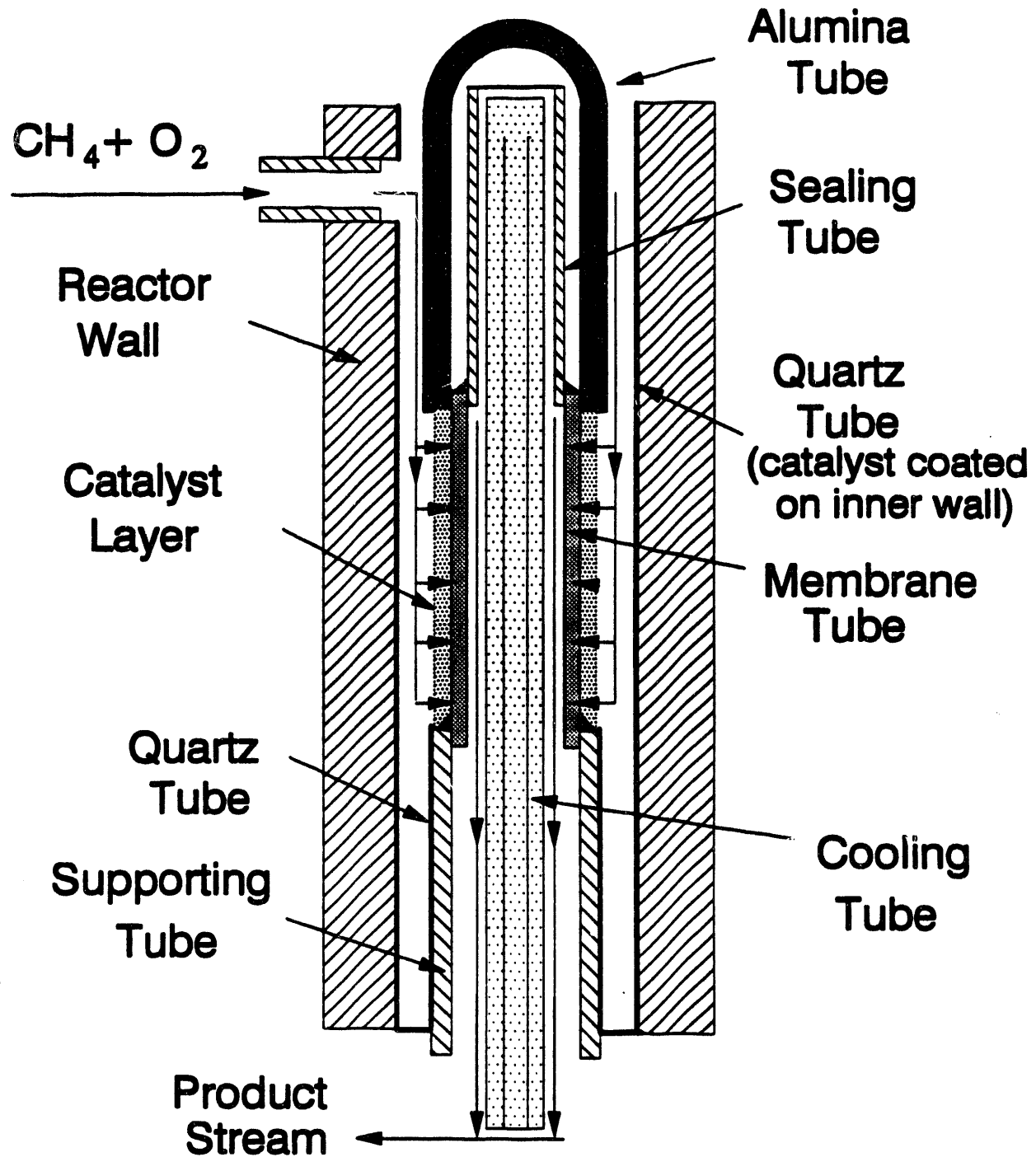
Figure 1. Reactor Diagram

Table1: Comparison of Conversions and Selectivities, W/ vs. W/O Catalyst Coated
(P: 3.5 MPa, F: 500 sccm, C_{O2}: 8%)

03/31/94	T (K)	775	785	795	805
With Catalyst Coating	CH_4 Conv.	< 1%	1%	6.5-7%	6.5-7%
	O_2 Conv.			>95%	98%
	CO Sel.			30-35%	30-35%
	CO_2 Sel	100%	100%	35-40%	35-40%
	CH_3OH 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_3OH Sel.	50-55%	50-55%	45-50%	40-45%

DATE
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10/12/94

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