1.0

2.8   2.5

3.2   2.2

3.6

1.1   4.0   2.0

1.8

1.25   1.4   1.6

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Direct Methane Conversion to Methanol

Annual Report
October 1, 1992 - September 30, 1993

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John L. Falconer

October 1993

By
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DISCLAIMER

Direct Methane Conversion to Methanol

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

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DIRECT CATALYTIC CONVERSION OF CH_4 TO CH_3OH IN A NON-ISOTHERMAL

MEMBRANE REACTOR

PROJECT STATUS REPORT -- Annually

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

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.

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 methanol selectivity during CH_4 oxidation. The membranes broke during experiments, however, apparently because of the large radial thermal gradient and axial thermal expansion difference. Our efforts concentrated on improving the membrane lifetime by modifying this non-isothermal

membrane reactor. A one-end-closed Al_2O_3 tube was installed instead of the normal Al_2O_3 tube to allow the membrane to freely expand. Since the dimension of cooling tube inside membrane affects the radial thermal gradient, a new cooling tube (3/16" of diameter) was installed instead of 1/4" cooling tube. The experimental results were as good as those from the experiments with 1/4" cooling tube. An alignment tube was used to line-up the cooling tube inside the membrane to eliminate the liquid condensation on the membrane. With all these modifications, as shown in Fig 1, the ceramic membrane did not break after three days of operation. Thus, operation in this new mode can allow us to obtain data more rapidly.

A Mott porous metal tube with 0.5 μm pore size was also used instead of the US Filters alumina membrane to try to solve the membrane breakage problem. The experimental results were similar to those from the experiments with ceramic membrane tubes. At a high temperature (820 K), however, the alumina support tubes at both sides of the metal membrane broke due to the different thermal expansion coefficient between the metal and the ceramic tube.

We also re-calibrated the GC for O_2, CH_4, CO, CO_2, and CH_3OH by mixing with CH_4, since the reactant and effluent contain mostly CH_4. The excellent overall and species mass balances were obtained by using the new calibration data.

A zeolite-A membrane was prepared using a technique similar to that for silicate membrane synthesis. Using a silica substrate membrane, a zeolite-A composite membrane was synthesized. Because the mixture of synthesizing zeolite-A is strongly basic, the alumina membrane was destroyed during the synthesis. Thus, we decided to synthesize ZK-5, which has the same pore diameter as zeolite-A, but requires low alkalinity for synthesis.

TECHNICAL PROGRESS

Modifications of Ceramic Membrane Reactor

In the previous experiments, the membranes were broken when removed from the system, apparently because of the large radial thermal gradient and axial thermal expansion difference. To allow the membrane expand freely, an Al_2O_3 tube with one end closed was installed instead of the normal Al_2O_3 tube (Fig. 1). The use of the Al_2O_3 tube with one end closed produced the same methanol selectivity and methane conversion during methane oxidation as did the previous tubes. For example, the methanol selectivity was around 45%, and the methane conversion was 5 to 8%. Unfortunately, even with this modification, the membrane broke after 24 h of operation.

Use of the original cooling tube (1/4 inch) caused the membranes to break, as reported previously. When membranes were broken inside the reactor, both lower selectivity for methanol and conversion of methane were obtained. An optimal cooling tube size should avoid this problem. Since the dimension of cooling tube inside membrane affects the radial thermal gradient, a new cooling tube (3/16" of diameter) was installed instead of 1/4" cooling tube. The experimental results were as good as those from the experiments with 1/4" cooling tube (Fig. 2), and the reactor wall temperature decreased 20 to 30 K for comparable methane conversion and CH_3OH selectivity. This comparable performance with reduced reactor wall temperature was caused by the change in the radial thermal gradient in the reactor. Experiments were also performed by using another cooling tube with a even smaller diameter (5/32"). When the smaller cooling tube was used, selectivity to methanol was not as high as for the 1/4 inch tube. The highest methanol selectivities obtained were around 35% with the smaller tube (Fig. 2). These results demonstrate that the change in the reactor radial temperature profile had an effect on

methanol selectivity. The smaller tube resulted in a number of changes in the reactor properties. The temperature gradient changed and the membrane temperature was thus different. The distance that molecules traveled before contacting the cooling surface increased and also the volume between the cooling tube and the membrane increased. This also affected the resident time in this region.

A shorter membrane (2" of length) was also used instead of the original membrane (6" of length) in the system, for both 1/4" and 5/32" cooling tubes. The highest selectivity for methanol was about 40% at a CH_4 conversion of 6%. This is slightly lower than in our previous experiments. A higher temperature was needed for a given CH_4 conversion (for 5/32" cooling tube) compared to the previous experiments, apparently because of the shorter contact time with the catalyst.

Additional modification to the reactor also allowed the temperature of the catalyst bed and the exiting cooling water to be measured. The temperature of the catalyst bed is sensitive to the cooling tube temperature, and the catalyst bed is in a low temperature zone. While the temperature of exiting water of the cooling tube is about 289 K, the highest temperature measured for catalyst bed is about 473 K. This temperature does not seem to be high enough to catalyze the reaction.

Since the temperature of the catalyst bed is sensitive to the cooling tube temperature, a metering valve was also installed on cooling water line to adjust the flow rate of cooling water and thus to adjust the catalyst temperature and radial thermal gradient. The outlet water temperature can change from ambient temperature to above 373 K. Experiments showed that the flow rate of cooling water slightly affected methanol selectivity during methane oxidation. With

an increase in the flow rate of cooling water, the temperature of outlet water was lower, and the slightly higher methanol selectivity was obtained. However, at the higher flow rate of cooling water, the radial thermal gradient is greater and the membrane is easier to break.

In the previous experiments, the liquid, which formed during the reaction and condensed on the cooling tube, attacked the ceramic membrane. The liquid spot on the membrane could cause membrane breakage because of the localized steep thermal gradient in the membrane. To eliminate the liquid condensation on the membrane, an alignment tube was used to line-up the cooling tube inside the membrane (Fig. 1). Three sets of experiments were carried out in this new mode. The membranes did not break after three days of operation. Thus, operation in this new mode can allow us to change experimental conditions and obtain several sets of data without membrane failure.

In the previous experiments, a MoO_x/SiO_2 catalyst was wrapped outside of the ceramic membrane by Al foil. The temperature of the catalyst bed was at 520 K when the outlet water temperature was 305 K. To determine if the catalyst plays a role during methane oxidation, we performed experiments without the catalyst and the Al foil wrapping outside of the ceramic membrane (just bare membrane). The results were the same as those from the test with the catalyst and the Al foil. For example, CH_4 conversion is 6 to 8%, and CH_3OH selectivity is around 45%. Another experiment was carried out without the catalyst but with the Al foil wrapping outside of the ceramic membrane. A gas gap was left between the membrane and the foil to keep the same volume of space as the volume of the catalyst. The same results were obtained for CH_4 conversion and CH_3OH selectivity as previous experiments with both the catalyst and the foil. Further experiments are still needed to clarify the role of the catalyst

Sintered Metal Membrane Reactor

A Mott porous metal tube with 0.5 μm pore size was used instead of the US Filters alumina membrane to try to solve the membrane breakage problem. Two ends of the metal tube were glued into alumina support tube by Epibond 500. The reactor wall temperature was varied during the experiments. The results were similar to those from the experiments with ceramic membrane tubes. As the reactor wall temperature raised from 773 to 810 K, as shown in Fig. 3, CH_3OH selectivity decreased from 46 to 42%, and CO selectivity increased from 42 to 45%. The selectivity for CO_2 also increased slightly. Conversions of CH_4 and O_2 also increased with the reactor wall temperature (Fig 4). At a high temperature (820 K), however, the alumina support tubes at both sides of metal membrane broke due to the different thermal expansion coefficient between the metal and the ceramic tube. Conversions of CH_4 and O_2 dropped sharply, and CH_4 selectivity also decreased. We also noticed that the glue (Epibond 500), which was used to glue the alumina support tubes and membrane together, was burnt to form carbon after the experiments.

GC Calibration

The GC re-calibration was done for CH_4, O_2, CO, CO_2, and CH_3OH, because the previous calibration was about two years old. One interesting point is that CH_4 gas can enhance the GC peak areas of other gases. For example, the mixture of O_2/CH_4 gives a higher GC area for O_2 than the mixture of O_2/He. This may be one reason for poor mass balances for many published studies. Since the reaction gas (8% O_2/92% CH_4) and products contains mostly CH_4, we did calibrations by mixing CH_4 with other gases. The previously experimental results were recalculated by using new calibration data. For both new and old experimental data, the overall and species mass

balances are excellent ($100 \pm 5\%$). If the old calibration data is used to calculate mass balance, the oxygen balance is about 80% (see last year annual technical report).

Zeolite Membrane Synthesis

In previous studies, zeolite silicalite-1 composite membrane was prepared and tested for CH_3OH separation from CH_3OH/H_2 and CH_3OH/CH_4 mixtures. During this period of study, a zeolite-A membrane was prepared using a similar technique as for silicalite membrane synthesis. Using a silica substrate membrane, a zeolite-A composite membrane was synthesized. The zeolite-A membrane showed a N_2 permeance 20 times lower than the substrate and a permeance ratio P_{N_2}/P_{CO_2} of 4. These initial results indicate that the *in-situ* synthesis technique can be applied to other types of zeolite membranes.

Since the mixture for synthesizing zeolite-A is strongly basic, an alumina membrane used as the substrate is destroyed during the synthesis. We studied the synthesis of ZK-5, which has the same pore diameter as zeolite-A, but requires low alkalinity for synthesis. Through optimization experiments, ZK-5 crystals can be synthesized at 423 K in 22 hours. ZK-5 crystals, however, do not grow into a dense layer on the substrate.

FUTURE WORK

1. Clarify the role of the catalyst bed in this process. The catalyst will be replaced with SiO_2, which is inactive for methane oxidation, to examine if the catalyst plays a role at the current condition we used. The temperature profile of the reactor will be adjusted to make the reactions occur in the center zone of the reactor. Thus, we can examine if methane oxidation occurs on the catalyst surface and try to find a more active catalyst for this reaction by using different catalysts.

2. Clarify the role of the membrane in this process. The US Filters alumina membrane will be replaced with other membranes (different material, different pore size). The reactor will further be modified so that the membrane will not be broken inside the reactor.

3 Systematic studies to determine optimal operating conditions. Experiments will be carried out to determine the appropriate temperature, pressure, resident time, and oxygen concentration.

4. Continue the synthesis of ZK-5 composite membranes using the alumina membrane as a substrate.

5. Conduct permeance measurements from room temperature to 523 K to understand the transport mechanism of gases through ZK-5 and ZSM-5 composite membranes of various Si/Al ratios.
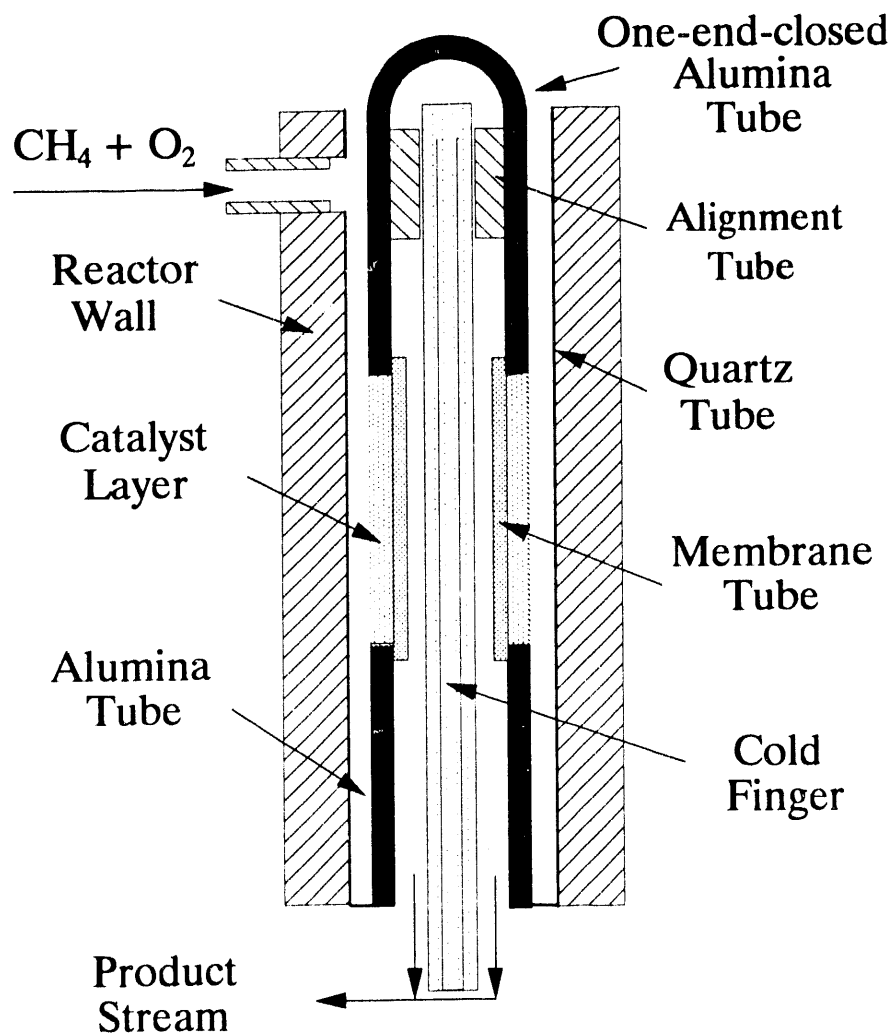
Figure 1. Scheme of the ceramic membrane reactor with one-end closed alumina support tube, 3/16" diameter of cooling tube, and an alignment tube.
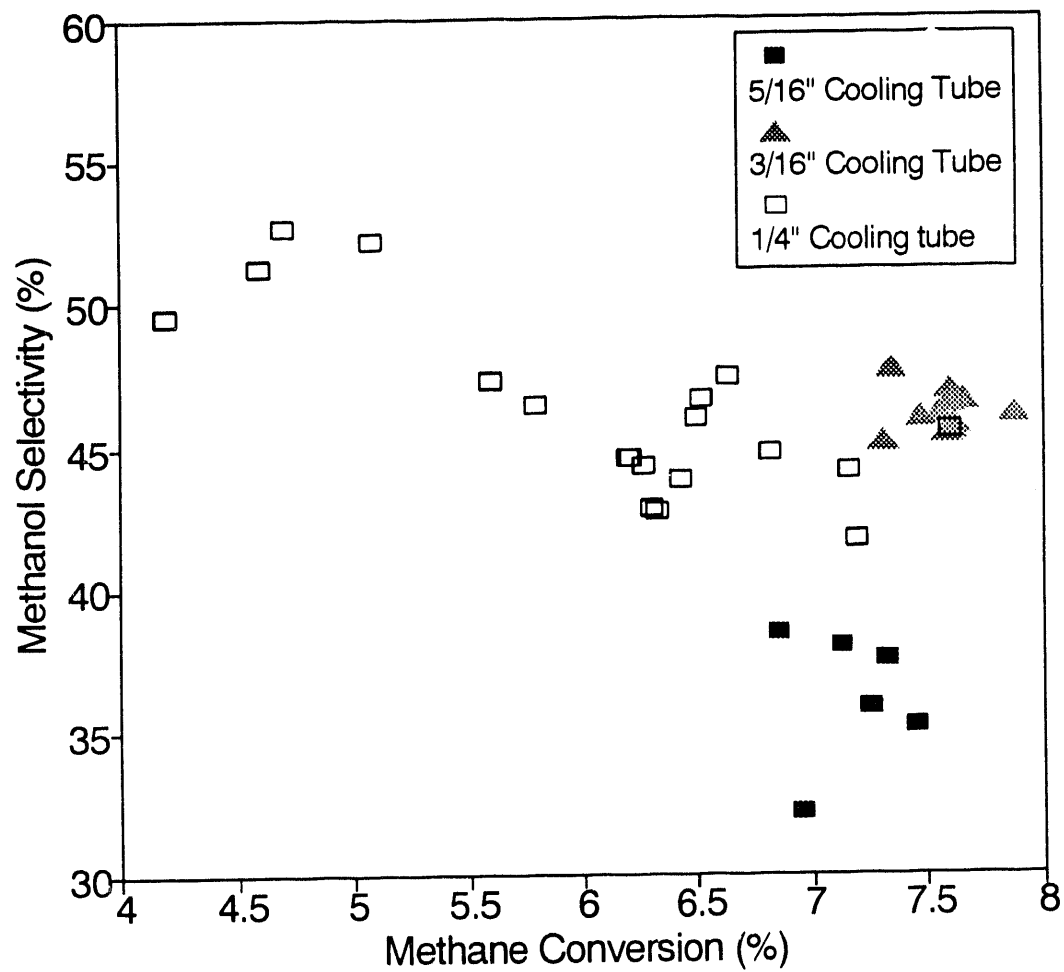
Figure 2. Effect of CH_3OH selectivity on CH_4 conversion during CH_4 oxidation in the ceramic membrane reactor with different diameters of cooling tubes. The reaction condition is as follow: total gas flow rate: 500 sccm; reactant composition: 8% O_2/92% CH_4; and system pressure: 500 psig.
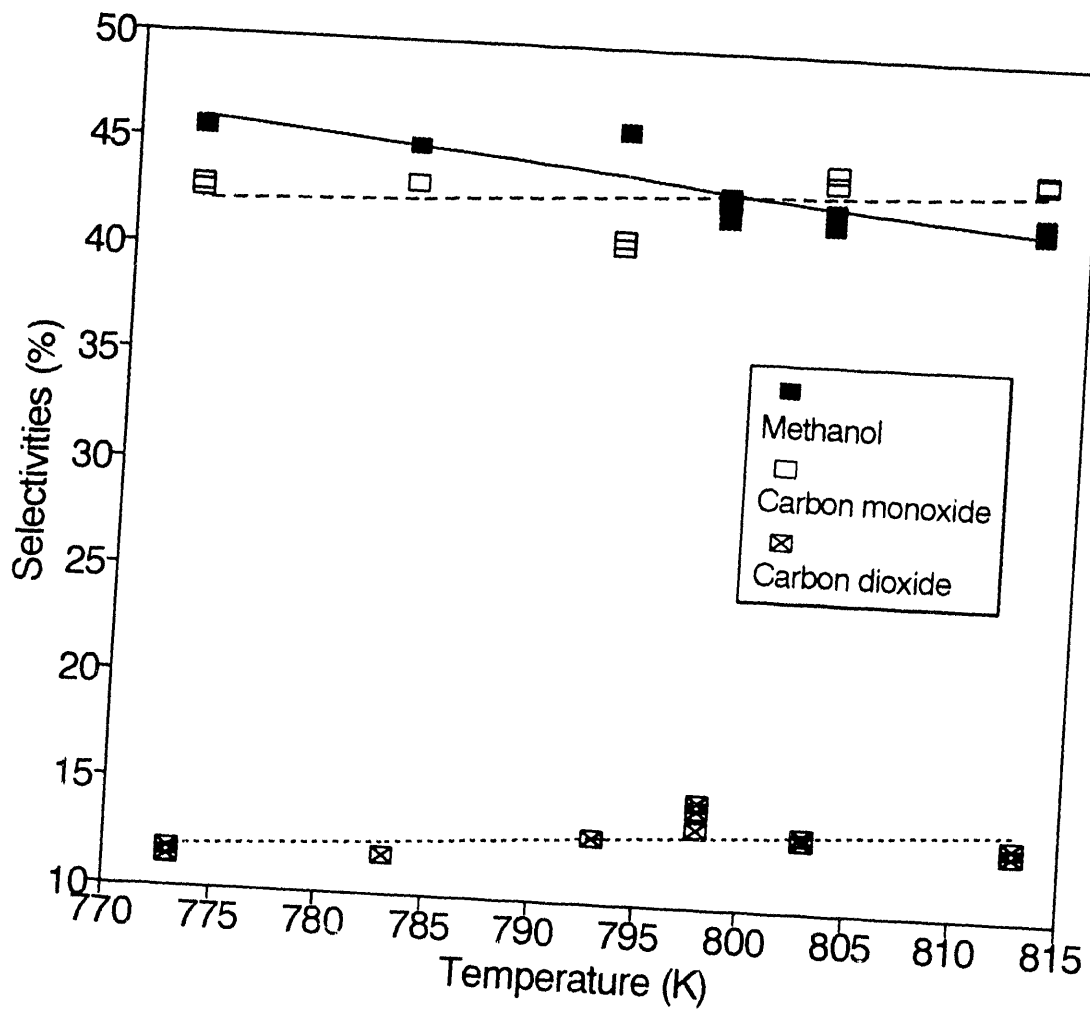
Figure 3. Dependence of the selectivities of CH_3OH, CO, and CO_2 on the reactor wall temperature during CH_4 oxidation in the metal membrane reactor. The reaction condition is as follow: total gas flow rate: 500 sccm; reactant composition: 8% O_2/92% CH_4; and system pressure: 500 psig.
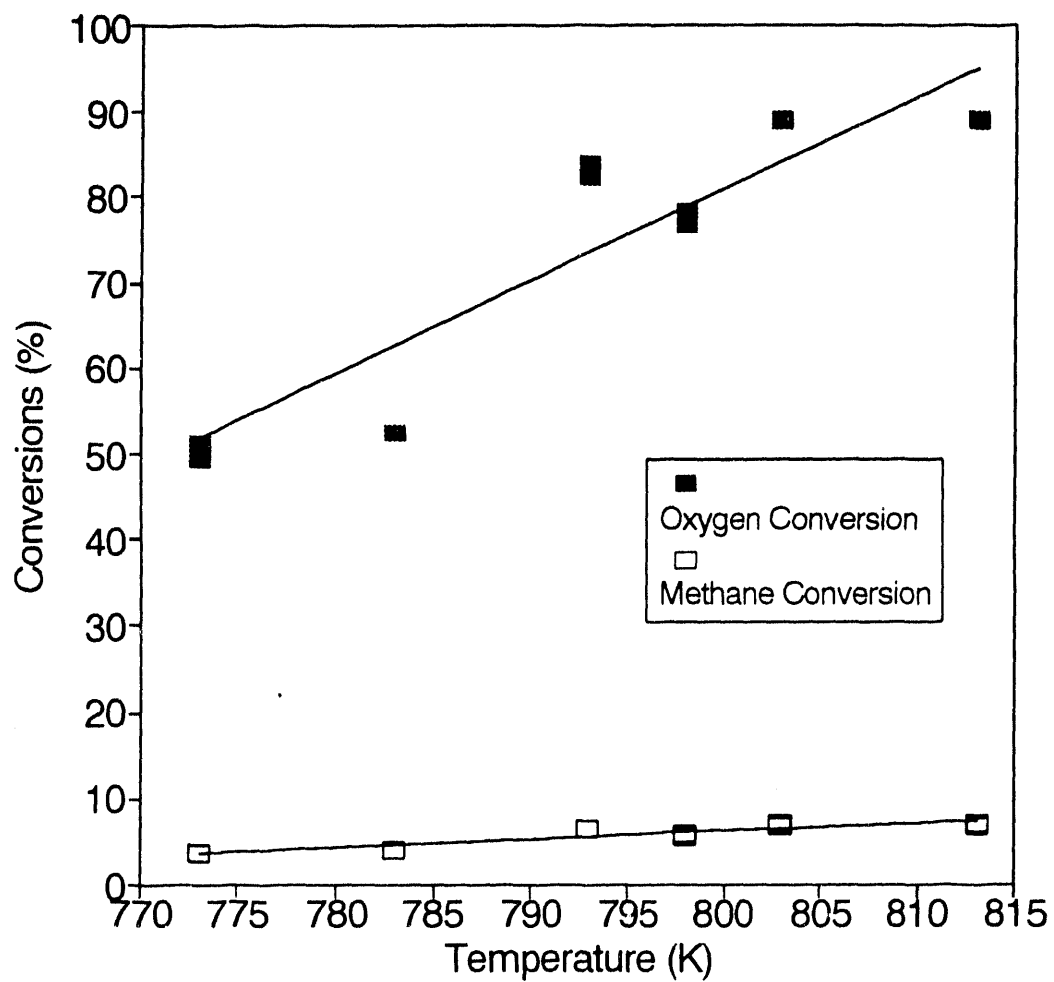
Figure 4. Dependence of the conversions of CH_4 and O_2 on the reactor wall temperature during CH_4 oxidation in the metal membrane reactor. The reaction condition is as follow: total gas flow rate: 500 sccm; reactant composition: 8% O_2/92% CH_4; and system pressure: 500 psig.

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