Quarterly Technical Progress Report

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Methane oxidative coupling experiments were conducted in a porous gamma alumina membrane reactor using Mn-W-Na/SiO₂ catalyst, and its performance was compared with a packed reactor. By varying the helium flow rate and keeping the temperature, methane flow rate, and oxygen flow rate constant, the membrane reactor gave 10% higher C₂ yield and 30% higher C₂ selectivity than the co-feed reactor operated at the same methane conversion. At similar C₂ yield and C₂ selectivity, the methane conversion of the membrane reactor was 15% lower than that of a co-feed reactor. By varying the oxygen flow rate and keeping the temperature, methane flow rate, and helium flow rate constant, at the same methane conversion, the membrane reactor gave about 3% higher C₂ yield and C₂ selectivity than the co-feed reactor. Higher helium flow rate gave higher C₂ selectivity and yield, whereas changing methane flow rate did not significantly affect the reactor performance.

The powder of an oxygen conducting material (BaCe₀.₈Gd₀.₂O₃₋ₓ) has been synthesized by the ethylene glycol method. 500 grams of such material has been sent to Argonne National Laboratory to make the dense membrane tube.
PROJECT OBJECTIVE

The goal of this research is to improve the hydrocarbon yield from oxidative coupling of methane by using a catalytic inorganic membrane reactor. A specific target is to achieve conversion of methane to C₂ hydrocarbons at very high selectivity and relatively higher yields than in a fixed bed reactors by controlling the oxygen supply through the membrane. A membrane reactor has the advantage of precisely controlling the rate of delivery of oxygen to the catalyst. This property permits balancing the rate of oxidation and reduction of the catalyst. Membrane reactors could also produce higher product yields by providing better distribution of the reactant gases over the catalyst than the conventional plug flow reactors.
1. Effect of helium flow rate on the oxidative coupling of methane in a porous membrane reactor

Methane coupling experiments were conducted in a porous gamma alumina membrane reactor. The reactor tube was prepared by treating a 14.2 cm long 40 Angstrom gamma-alumina tube with La(NO$_3$)$_3$ aqueous solution and calcining at 900°C. Then each end of the membrane tube was welded to a 19 cm long non-porous alumina tube with a high temperature glaze. The curing process of the glaze was started at room temperature overnight, followed by treating at 60, 90, and 120°C for 2-3 hours at each stage. Then the membrane tube was installed into the membrane reactor setup. 2.1 gram Mn-W-Na/SiO$_2$ catalyst was packed in the annular space between the gamma-alumina membrane (I.D.=7 mm) and the thermowell (I.D.=3 mm) placed concentrically inside the reactor tube. The height of the packed-bed was about 14 cm. Methane was fed to the tube side and a mixture of oxygen and helium was fed to the shell side. In order to reduce the amount of hydrocarbon loss from the tube to the shell side, the outlet of the shell side was blocked. For comparison purposes, the membrane reactor was also operated in the co-feed mode by feeding the mixture of methane and oxygen to the tube side and helium to the shell side with the shell side outlet blocked.

Figure 1 and Figure 2 show the C$_2$ selectivities and yields as functions of methane conversion of the membrane and co-feed reactors at 805°C and methane and oxygen flow rates of 6.5 cc/min and 3.7 cc/min respectively. The helium flow rates were changed over a range of 0-212 cc/min, while the temperature, methane flow rate, and oxygen flow rate were kept the same. It can be seen that the membrane reactor gave lower methane conversions than the co-feed reactor, which is due to the lower average partial pressure of
oxygen, and thus the lower average reaction rate, in the membrane reactor. If the two reactors are compared at similar methane conversions (i.e. 46%), the membrane reactor has 30% higher C₂ selectivity and 10% higher yield than the co-feed reactor. If the two reactors are compared at same C₂ selectivity and C₂ yield, the methane conversion of the membrane reactor was 15% lower than that of the co-feed reactor. This means that, for the same amount of C₂ hydrocarbons produced, less methane was consumed by using a membrane reactor.

The reactor performance as a function of helium flow rate is shown in Figure 3. Higher C₂ selectivity was observed in a membrane reactor at helium flow rates higher than 40 cc/min. It can be seen from Figure 3 that higher C₂ selectivity in a membrane reactor mainly resulted from the higher ethane selectivity and lower CO selectivity than the co-feed reactor.

2. Effect of oxygen flow rate on the oxidative coupling of methane in a porous membrane reactor

With the same porous membrane reactor setup as described above, methane coupling experiments were conducted with 2.6 gram Mn-W-Na/\text{SiO}_2 catalyst. Figure 4 and Figure 5 show the C₂ selectivities and yields as functions of methane conversion of the membrane and co-feed reactors at 805°C and methane and helium flow rates of 5.0 and 120 cc/min respectively. The methane conversions of both membrane and co-feed reactors were varied by changing the oxygen flow rates, while the temperature, methane flow rate, and helium flow rate were kept the same. If the two reactors are compared at similar membrane conversions, the membrane has about 3% higher C₂ selectivity and C₂ yield than the co-feed reactor.

Compared to the results obtained under different helium flowrates and fixed methane and oxygen flow rates, there was less improvement of C₂ selectivity and yield at the same methane conversion when a membrane reactor was used. In a membrane
reactor, the reaction rate is slower than that in a co-feed reactor due to the segregation of the reactants (methane and oxygen). Therefore, to reach the same methane conversion, a membrane reactor has to be operated at higher oxygen partial pressure, which will result in lower C₂ selectivity. If the comparisons were to be made at the same methane to oxygen ratio, the differences in C₂ selectivity between the membrane reactor and the co-feed reactor would be greater than those shown in these figures.

The product distributions of the two reactors as functions of methane conversion are shown in Figure 6. In the whole range of methane conversion shown in Figure 6, the membrane reactor showed higher ethylene selectivity than that of the co-feed reactor, while the ethane selectivities were about the same. In the low methane conversions, the CO₂ selectivities in the membrane reactor was higher whereas in the high methane conversions, the CO selectivities in the membrane reactor was higher than those observed in the co-feed reactor.

Figure 7 and Figure 8 show the C₂ selectivities and yields as functions of methane conversion in the membrane reactor at 810°C. The methane conversion was changed by changing the oxygen flow rate. Increasing the helium flow rate from 60 cc/min (open diamonds) to 120 cc/min (solid circles) resulted in a 2-3% increase in both C₂ selectivity and C₂ yield. However, when the methane flow rate was changed from 5.0 cc/min (solid circles) to 3.9 cc/min (crosses), no significant changes in the reactor performance were observed.

3. Preparation of the materials for making the oxygen conducting dense membranes

The oxygen-conducting dense membrane material that has been used in this project previously before was a total oxidation catalyst. Although the reactor performance was improved by coating BaCe₀.₆Sm₀.₄O₃ perovskite (which is a oxygen conducting and methane coupling catalyst), the C₂ yield obtained was still less than that obtained by the conventional packed-bed reactor due to the fact that the surface was not
completely covered by the coating material. Therefore, a dense membrane tube will be made from $\text{BaCe}_0.8\text{Gd}_0.2\text{O}_3$.x.

The powder of this material ($\text{BaCe}_0.8\text{Gd}_0.2\text{O}_3$.x) has been synthesized by the ethylene glycol method by dissolving the corresponding metal acetates in a solution of ethylene glycol and nitric acid, followed by drying and calcination. Figure 9 shows the X-ray diffraction patterns of the material after 1150°C calcination in air for 8 hrs. 500 grams of such material has been sent to Argonne National Laboratory to make the dense membrane tube.

**FUTURE WORK**

The dense membrane tubes obtained from Eltron Research Inc. and those made by $\text{BaCe}_0.8\text{Gd}_0.2\text{O}_3$.x material will be used to study methane coupling in a dense membrane reactor.
Figure 1. Comparison of C$_2$ selectivities in a membrane and co-feed reactor as functions of methane conversion
Figure 2. Comparison of C$_2$ yields in a membrane and co-feed reactor as functions of methane conversion.
Figure 3. Comparison of $C_2$ selectivities in a membrane and co-feed reactor as functions of helium flow rate.
Figure 4. Comparison of $C_2$ selectivities in a membrane and co-feed reactor as functions of methane conversion.
Figure 5. Comparison of C$_2$ yields in a membrane and co-feed reactor as functions of methane conversion.
810°C, CH₄:He = 5:120 cc/min with Mn-W/SiO₂
solid symbols: membrane reactor
open symbols: co-feed reactor

Figure 6. Comparison of product selectivities in a membrane and a co-feed reactor as functions of methane conversion
Figure 7. C<sub>2</sub> selectivities in a membrane reactor as functions of methane conversion.
Figure 8. C\textsubscript{2} yields in a membrane reactor as functions of methane conversion.
Figure 9. XRD pattern of BaCe$_{0.8}$Gd$_{0.2}$O$_3$ calcined at 1150 °C