Quarterly Technical Progress Report

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ABSTRACT

The temperature dependence of the oxygen flux across the BaCe$_{0.8}$Gd$_{0.2}$O$_3$ dense membrane (BCG membrane) tube was investigated. In the temperature range of 688°C to 955°C, the increase in the oxygen flux with temperature obeyed the Arrhenius law. An increase in the helium sweep flow rate in the tube side resulted in an increase in the oxygen flux through the membrane tube.

The oxygen fluxes through the BCG dense membrane tube were measured at different oxygen partial pressures in the shell side. The oxygen flux increased with the oxygen partial pressure in the shell side.

The BCG dense membrane was tested in a membrane reactor for the catalytic oxidative coupling of methane. The BCG membrane is not a complete combustion catalyst, and the catalytic activity of the BCG membrane was found to be much higher than the Argonne dense membrane. As the oxygen partial pressure in the shell side increased, the C$_2$ selectivity decreased while the C$_2$ yield remained unchanged, indicating that non-selective, gas phase reactions still played a significant role in the membrane reactor.
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 $C_2$ hydrocarbons at very high selectivity and relatively higher yields than in a fixed bed reactor 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 rates 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. Temperature dependence of the oxygen flux across the BCG dense membrane tube

The BaCe$_{0.8}$Gd$_{0.2}$O$_3$ powder was prepared by the Ethylene Glycol method, and the BCG dense membrane tube provided by the Argonne National Laboratory was made by extrusion. The membrane tube (length = 11 cm long, I.D. = 4.6 mm, and O.D. = 6 mm) was connected to a quartz tube on each end with a Vycor glass seal. Air was fed from the shell side of the quartz reactor module while helium was fed from the top of the reactor into the tube side. The mixture of oxygen and helium was withdrawn from the bottom of the membrane tube side and analyzed by an on-line gas chromatograph.

Figure 1 shows the oxygen fluxes at helium flow rates of 26 cc/min and 108 cc/min as functions of temperature. The air flow rate was kept at 86.5 cc/min during these measurements. Over a temperature range of about 300°C, the oxygen flux increased by a factor of 5. The oxygen flux is close to those obtained with the Argonne membrane tube. The semi-logarithm plot of oxygen flux versus the reciprocal of absolute temperature (1/T) fell closely on a straight line. Based on the Arrhenius plot, the activation energies for the oxygen permeation for the helium sweep flow rates of 26 cc/min and 108 cc/min were 57.9 and 65.2 kJ/mol, respectively. The small difference between these two values of activation energy may be the result of a minor mass transfer resistance at the surface.
2. Effect of oxygen partial pressure on the oxygen flux through the BCG dense membrane tube

The oxygen fluxes through the BaCe_{0.8}Gd_{0.2}O_3 (BCG) dense membrane tube were measured at different tube side oxygen partial pressures. A mixture of pure oxygen and helium was fed to the tube side of the membrane tube. The partial pressure of oxygen in the shell side was changed by varying the flow rates of oxygen and helium. The total flow rate in the shell side was kept at about 80 cc/min and the shell side outlet was open. Helium (26 cc/min) was fed from the top of the reactor into the tube side. The mixture of oxygen and helium was withdrawn from the bottom of the membrane tube side and analyzed by an on-line gas chromatograph.

Figure 2 shows the oxygen fluxes as a function of oxygen partial pressure in the shell side at 778°C. For the oxygen partial pressures higher than 0.1 atm on the semi-logarithm plot, the oxygen flux increased linearly with oxygen partial pressure.

3. Methane oxidative coupling using the BCG membrane reactor

Methane oxidative coupling reactions were carried out in the BCG dense membrane reactor with no catalyst packed in the tube side. A mixture of air and helium was fed from the shell side while the mixture of methane and helium was fed from the top of the reactor into the tube side. For comparison purposes, the reactor module was also run in a co-feed mode by feeding the mixture of methane, oxygen, and helium into the tube side. In both cases, the product stream was withdrawn from the bottom of the membrane tube side and analyzed by an on-line gas chromatograph.

C_2 yields up to 14% were obtained when the reactor was operated in the co-feed mode, indicating that the BCG membrane is not a total combustion catalyst. Since no detectable C_2 products were observed in the Argonne membrane tube without catalyst, the BCG membrane tube is much more active than the Argonne membrane tube for methane oxidative coupling.

Figure 3 shows the C_2 selectivity - methane conversion plots for both membrane and co-
feed reactors at 778°C. The methane flow rate was kept at 1.4 cc/min. For the membrane reactor, the methane conversion was changed by changing the oxygen to helium ratio in the shell side, while for the co-feed reactor, the methane conversion was changed by varying the oxygen flow rate in the tube side. For both membrane and co-feed reactor, the C₂ selectivity dropped rapidly as the methane conversion increased. The highest C₂ yield was about 16.5% (observed at a selectivity of 62.5%), which is higher than the highest yields obtained in the Argonne and Eltron dense membrane reactors. Although the membrane reactor showed slightly higher selectivity than the co-feed reactor at the same methane conversion level, the steep drop in C₂ selectivity as a result of the increase of oxygen partial pressure in the shell side indicated that the non-selective, gas phase reactions still played a significant role.

Figure 4 shows the BCG dense membrane reactor performance at different shell side oxygen partial pressures. As the oxygen partial pressure in the shell side increased, a decrease in C₂ selectivity and an increase in the methane conversion were observed. The C₂ yield remained unchanged in the entire oxygen partial pressure range used in the experiments.

**Future work**

More methane coupling experiments will be conducted with the BCG membrane reactor to investigate the effect of methane flow rates on the reactor performance and the effect of MOC reactions on the oxygen flux through the membrane. The final report of this project is in progress.
Figure 1. Arrhenius plot for the oxygen flux through the BCG membrane tube

Air = 80 cc/min (shell side)

- **He=108 cc/min**  \( E = 65.24 \text{ kJ/mol} \)
- **He=26 cc/min**  \( E = 57.86 \text{ kJ/mol} \)
Figure 2. Effect of oxygen partial pressure on the oxygen flux through the BCG dense membrane tube.
Figure 3. Comparison of $\text{C}_2$ selectivity between a co-feed and a membrane-feed reactor

T = 778°C

selectivity, %
methane conversion, %
Figure 4. Effect of oxygen partial pressure in the shell side on the dense membrane reactor performance.