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Enclosed please find reports identified below as required in connection with referenced contract.

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1. Report/ Plan
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ABSTRACT

The experimental study was continued on methane oxidative coupling using an oxygen-permeable dense membrane reactor. The oxygen permeance through the dense membrane was measured and preliminary experiments were conducted with the catalytic membrane reactor. The oxygen permeance was found to be similar to that obtained earlier without catalyst packing. No C₂ hydrocarbons were observed in the catalytic membrane reactor for methane coupling. In order to reduce the non-selective, total oxidation activity of the dense membrane material, the inner surface of the dense membrane tube was deposited by the sol-gel technique with BaCe₀.₅Sm₀.₅O₃, which is a catalytic, oxygen-conductive material without total oxidation catalytic activity. The dense membrane tube was examined by XRD before and after the deposition. Catalytic experiments with the coated dense membrane reactor were carried out and higher C₂ selectivity was observed than with the co-feed reactor.
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. Oxygen Permeance Through Dense Membrane Tube

The oxygen-permeable dense membrane tube provided by Argonne National Laboratory was housed in a quartz tube as the shell of the membrane reactor. A quartz thermowell with 1 mm ID was inserted into the tube side and, in the annular space between the thermowell and the membrane tube, 1.6 g La/MgO catalyst was loosely packed to avoid breaking due to the thermal expansion of the catalyst during heating. Before methane was fed into the tube side, the permeance of oxygen through the dense membrane tube was measured with air fed on the shell side of the reactor module and helium in the membrane tube. Figure 1 shows the oxygen permeance at 910 °C and 1 atm and compared with those obtained earlier without catalyst packing at 950 °C. The oxygen permeance observed was consistent with the earlier data. Again, the permeance was only about 20 % of the reported value of 0.3 cc/min/cm² by Balachandran et al. (1995) under non-reaction conditions, and it reached a stable level within a relatively short period of time on stream. The oxygen permeance increases with an increase in either helium sweep flow rate or the air flowrate.

2. Experimental Results with the Catalytic Dense Membrane Reactor

After the oxygen permeance measurement, methane was fed into the tube side and air into the shell side. No detectable C₂ hydrocarbons were observed in these experiments at temperatures of 770 to 910 °C. This suggested that the total oxidation of methane by the dense membrane material dominated the catalytic reaction in this configuration. Once CO₂ is formed, it cannot be reduced to C₂ hydrocarbons, in contrast to methane partial oxidation to syngas, where the CO₂ formation is the first step in producing CO and H₂. In another experiment with the same reactor, instead of feeding air to the shell side as in the previous runs, air was co-fed with methane to the tube side and nothing
was fed to the shell side of the membrane reactor. Since the methane coupling reaction took place in the catalyst bed before the reactant mixture contacted the total oxidation dense membrane material, 7% C₂ yield was observed during these runs. These results indicated that different contact modes of reactants with the catalyst resulted in different reactor performances.

3. Deposition of BaCe₀.₆Sm₀.₄O₃ on the Dense Membrane Tube

As mentioned earlier, the dense membrane material is a total oxidation catalyst, and carbon dioxide was formed when the dense membrane interacted with the mixture of methane and oxygen. As a result, no C₂ hydrocarbons were observed in the product stream in a reaction run with a packed-bed dense membrane reactor. In order to prevent the contact of the reaction mixture with the dense membrane, the inner surface of the membrane tube was deposited with BaCe₀.₆Sm₀.₄O₃ by the sol-gel technique. Appropriate amounts of Ba(C₂H₅O₂)₃, Ce(C₂H₅O₂)₃, 1.5H₂O, Sm(NO₃)₃ 6H₂O, and citric acid were dissolved in ethylene glycol and hydrochloric acid was added into the solution until all the salts were dissolved. Then the solution was heated for about 5 hours to form the gel. The inner wall of the dense membrane tube was coated with the gel and treated at 350 °C overnight, followed by calcination at 1020 °C for 5 hours. This procedure was repeated once and the tube was installed in to a membrane reactor set up for the catalytic experiments. The membrane tube before and after the deposition were studied by X-ray diffraction. Figure 2 shows the XRD patterns of the membrane tube before and after the sol-gel deposition of BaCe₀.₆Sm₀.₄O₃.

4. Catalytic Study of the Dense Membrane Reactor after the Coating of BaCe₀.₆Sm₀.₄O₃

After the deposition, the tube was installed into a membrane reactor set up with the La/MgO catalyst packed inside the membrane tube. Figure 3 shows the C₂ selectivity vs methane conversion plot at 810 °C and 1 atm. Comparing to the same plot for the co-feed reactor configuration, the membrane reactor gives higher C₂ selectivity for the same methane conversion level. However, the C₂ yield is still less than 10%. This may have resulted from the non-complete coverage of the inner wall of the membrane tube by the deposited BaCe₀.₆Sm₀.₄O₃ material.
FUTURE WORK

SEM and EDX studies of the deposited membrane tube will be conducted to study the morphology and quality of the deposited layer. Efforts will be made to improve the quality of the coated film by means of surface pretreatment. Catalytic experiments will be carried out using the dense membrane tube with a better quality of coated film.

Other methane coupling catalysts with better catalytic performance will be tested with the BaCe₀.₆Sm₀.₄O₃-coated membrane reactor to achieve higher C₂ selectivity and C₂ yield.

REFERENCE

Figure 1. Oxygen permeance through dense membrane. (air fed in the shell side and helium in the tube side)
Figure 2. XRD patterns of dense membrane tube before and after deposition of $\text{BaCe}_0.6\text{Sm}_{0.4}\text{O}_{3-x}$ by sol-gel technique

after 1180 °C calcination

before

after 1020 °C calcination
Figure 3. $C_2$ selectivity vs methane conversion of the dense membrane reactor and co-feed reactor