Title: Oxidative Coupling of Methane Using Inorganic Membrane Reactor.

PI(Authors): Y.H.Ma,W.R.Moser, A.G.Dixon, A.M.Ramachandra,Y.Lu and C.Binkerd.

Institution: Worcester Polytechnic Institute, Worcester, MA.

Contract Number: DE-AC-92PC92113

Period of Performance: 1994-1995.

Objective:

The goal of this research is to improve the oxidative coupling of methane in 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 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 facility permits balancing the rate of oxidation and reduction of the catalyst. In addition, membrane reactors minimize the concentration of gas phase oxygen thus reducing non selective gas phase reactions, which are believed to be a main route for formation of CO_x products. Such gas phase reactions are a cause for decreased selectivity in oxidative coupling of methane in conventional flow reactors. 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.

Accomplishments and Conclusions:

Introduction

The aim of the experimental studies in this project was to investigate the effect of controlling the oxygen feed supplied for the methane coupling reaction. C_2 hydrocarbons, ethane and ethylene, which form as a result of methane coupling, have a higher affinity for gas phase oxygen than methane. Thus both the reactant CH_4 and the intermediate products (C_2 hydrocarbons) convert into the complete oxidation products CO and CO_2. Hence, it is advantageous to regulate the supply of one of the reactants along the length of the catalyst bed to maximize the yield of the intermediate products. Research efforts were aimed at porous Vycor membrane reactors that were used to study oxidative coupling of methane under a variety of experimental conditions. Using tubular porous Vycor membranes in a shell and tube type of reactor, gas flow was metered in from the high pressure shell side into the catalyst packed tube side of these membrane reactors.

A second avenue of research was the study of oxygen conducting perovskite materials, their synthesis and characterization. These materials are also intended to be used in shell-and-tube membrane reactors. A third research focus was the development of a novel radial flow catalytic membrane reactor. Methane coupling was also investigated in this reactor configuration. Modeling work which aimed at predicting the observed experimental trends in porous membrane reactors was also undertaken in this research program.

Reactor Performance Comparisons

Experimental studies were made with porous Vycor membrane reactors and conventional non-porous packed bed reactors operating under identical conditions. Figure 1(a) shows the C_2 selectivities in the porous Vycor membrane reactor and the quartz non-porous reactor operated at the same contact time (experimental parameters are listed in Table 1). C_2 selectivities were consistently higher in the Vycor membrane reactor over the temperature range 700°C-800°C, compared to the non-porous quartz tube reactor. With increasing temperature, the non-selective gas phase methane conversion to CO_x products increased. Hence the C_2 selectivity decreased as reaction temperature went up. The overall C_2 yields were about the same in both reactor configurations as shown in Figure 1(b). The membrane reactor has an overall C_2 yield of 11%, while the quartz tube fixed bed reactor has 10% C_2 yield at the same conditions. Due to the necessity of larger reactor volumes in porous membrane reactors, higher levels of methane conversions have not been achieved. A larger bed cross-section is not desired as that would increase methane loss to non-selective reactions on the shell side. Total methane conversions for the two reactor systems are shown in Figure 1(c) for the reactors. The higher conversions seen for the quartz tube fixed bed reactor however, are mainly caused by the deep oxidation to CO_x products as seen by the low values of C_2 selectivity at the corresponding temperatures for this reactor configuration. Figure 1(d) shows a conversion versus selectivity plot that compares the performance of the Vycor membrane reactor with the co-feed non-porous reactor. At the same level of conversion, membrane reactors yield higher C_2 selectivity. Conditions of equal methane conversions were obtained at different reaction temperatures for the two reactors. The higher C_2 selectivity in the membrane reactor shows that for the methane coupling reaction, regulating the supply of oxygen along the length of the packed bed is beneficial for C_2 product formation.

TABLE 1. Experimental Conditions for VYCOR membrane reactors

Experimental. Parameter	Set 1	Set 2
Helium Flow rate	200 ml/min	100 ml/min
Methane Flow Rate	40ml/min	20.3ml/min
Oxygen Permeate	20ml/min	10.2ml/min
Shell side Pressure	65 psi	30 psi
Reactor Bed Length	12 cms	6 cms
Catalyst loading	2.4 gms	1.2 gms
Temperature Deviation	10°C	5°C
Temperature range	650°C-850°C	650°C-800°C

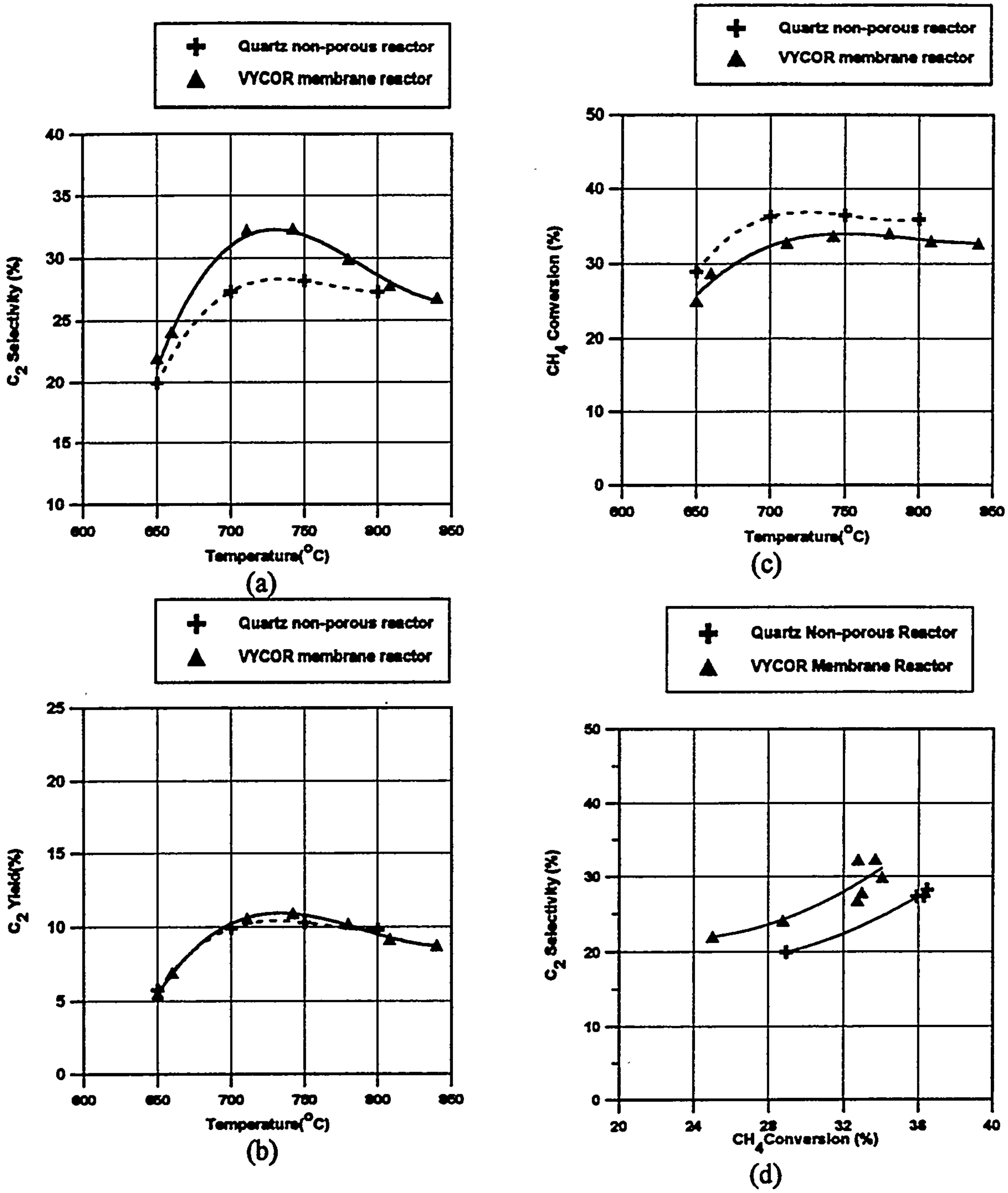


Figure 1. Comparison of (a) C_2 selectivities (b) C_2 yields, and (c) CH_4 conversions from porous Vycor membrane reactor and co-feed, non-porous quartz reactor. (d) conversion vs. selectivity plot. where the different conversions were obtained at different reaction temperatures.

Methane coupling under varying methane to oxygen feed ratios

The VYCOR membrane reactor was operated at various methane to oxygen feed ratios to study the effect of the variations in methane and oxygen concentrations on the methane coupling reaction. The catalyst (Sm_2O_3) was packed on the tube side of the membrane reactor and a constant flow of oxygen permeated from the shell to the tube side. The methane flow on the tube side was varied to change the methane to oxygen ratio. Figures 2 shows the effect of the changing methane to oxygen ratio at various reaction temperatures. It was seen that highest C_2 yields were obtained at a methane to oxygen ratio of 2.0, where both the CH_4 conversions and C_2 selectivities were optimal. Similar trend was observed at other temperatures. A majority of our studies on methane coupling were done at the methane to oxygen ratio of 2.0 and in the temperature range of 650°C to 850°C, thereby exploring the active thermal range of the coupling reaction.

Methane coupling under oxygen rich conditions

These studies were aimed at exploring the effects of conducting the methane coupling experiments under conditions where the oxygen conversion was far from complete. Since we were investigating a reactor system that operates on the principle of metering the oxygen supply, it was necessary to study the reaction under conditions where the oxygen was present in an excess.

Figure 3 shows a comparison of the methane conversion with reaction temperature from porous VYCOR membrane reactors under oxygen rich and oxygen lean environments, run at equivalent flow conditions and at a methane to oxygen ratio of 0.5. Oxygen lean conditions result in almost complete conversion of oxygen, limiting the amount of methane that can be converted to between 40% and 60%. Though this limitation on methane conversion was overcome under oxygen rich conditions, a decline in C_2 selectivity was observed as shown in Figure 3. These results indicate that metering the oxygen flow through porous membrane reactors is beneficial to the methane coupling reaction when most of the oxygen supplied to the catalyst bed is used up before exiting the reactor. This was ascertained by carrying out similar experiments at various methane to oxygen ratios as shown in Table 2.

Table 2. Performance of Vycor membrane reactor under O_2 rich conditions.

CH_4/O_2	Methane Conversion	Oxygen Conversion	C_2 Selectivity	C_2 Yield
2.0	20%-25%	40%-90%	30%-20%	5%-10%
1.0	10%-30%	30%-60%	20%-15%	2%-5%
0.5	90%-100%	40%-50%	10%-2%	2%-5%

Metering methane flow in membrane reactors

Since oxygen was the competing reactant for methane coupling as well as for methane deep oxidation, most of the experimental work done earlier in this project involved metering in oxygen flow through the porous membrane tube of the reactor. Due to the higher affinity of C_2 hydrocarbons over methane for oxygen, metering in oxygen flow was counter-productive in the lower part of the catalyst bed and detreimental to C_2 selectivity.

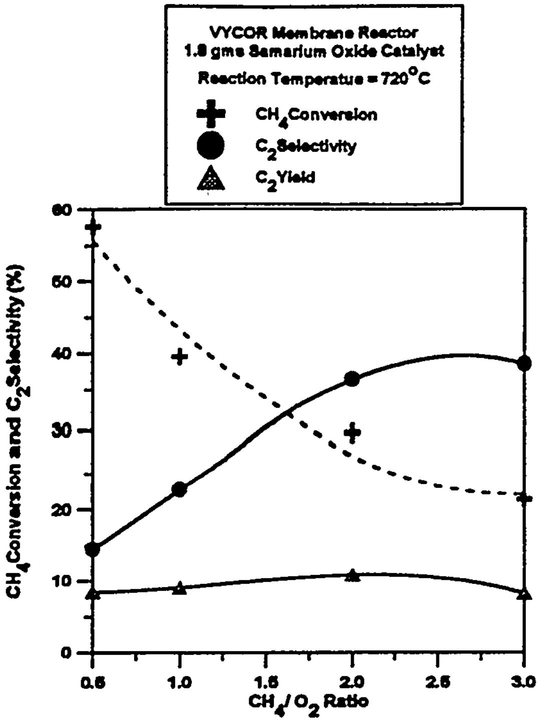


Figure 2. Effect of varying methane to oxygen ratio in Vycor membrane reactor.

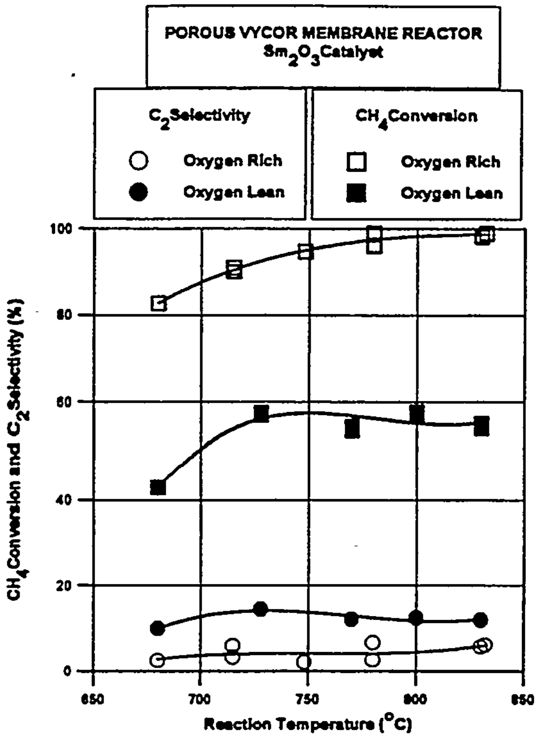


Figure 3. CH$_4$ conversion and C$_2$ selectivity in Vycor membrane reactors operated under O$_2$ rich and O$_2$ lean conditions.

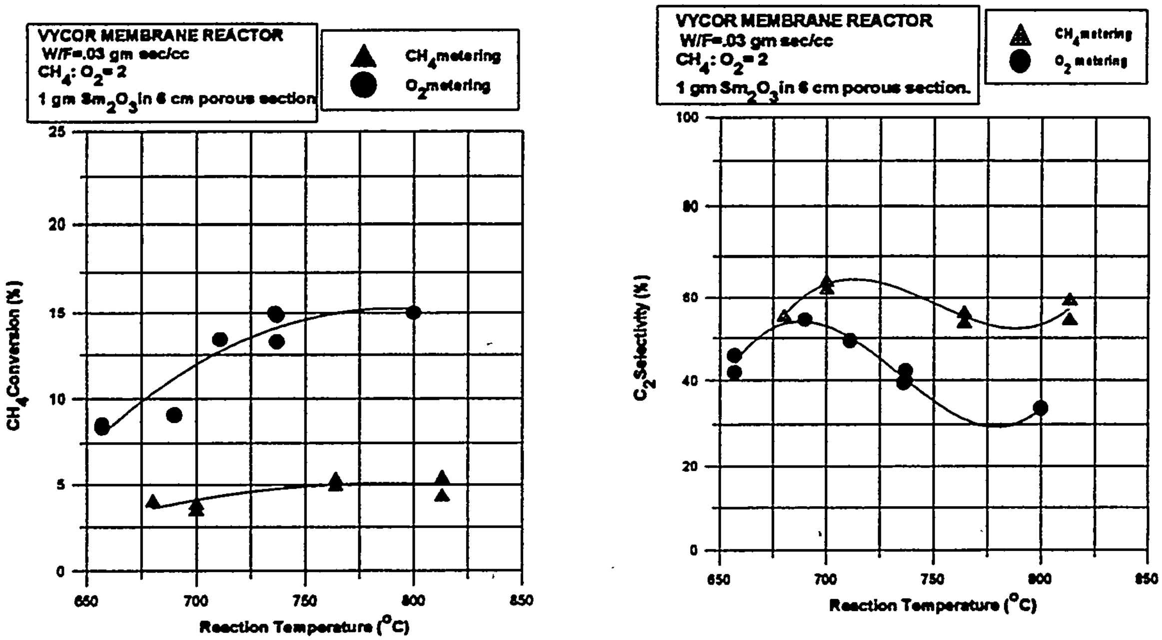


Figure 4. Comparison of (a) CH$_4$ conversions, and (b) C$_2$ selectivities in Vycor membrane reactors under O$_2$ and CH$_4$ metering.

The following experiments were performed to test the effect of metering methane flow into a flowing stream of oxygen. Since the C$_2$ products that were produced in the earlier sections of the reactor bed were susceptible to oxidation, these experiments of metered methane flow were aimed at improving the overall C_2 selectivity. The Vycor membrane reactor was run in a configuration where pure methane was fed to the shell side while oxygen mixed with helium diluent was fed in the tube side (catalyst packed inside the tube). Methane permeate flow for methane metering was equal to the oxygen permeate flow for the oxygen metering experiments and all these experiments were run at an overall methane to oxygen ratio of 2.0.

Figure 4(a) compares the methane conversions and Figure 4(b) compares the C_2 selectivities in these experiments with those of oxygen metering at equivalent flow conditions. An improvement in the overall C_2 selectivities was obtained as expected, as compared to the earlier studies which were run with oxygen on the shell side. Lower methane conversions, however, offset the higher selectivities, resulting in very low C_2 yields.

Modeling Studies

Oxidative coupling of methane involves a series-parallel reaction scheme where methane and oxygen are consumed in parallel reactions resulting in the formation of desired C_2 products and the undesired CO_x products. The C_2 products could further react with oxygen to form CO_x products through complete oxidation. The reaction scheme is as follows :

$$CH_4 + O_2 \xRightarrow{k1} C_2H_4$$

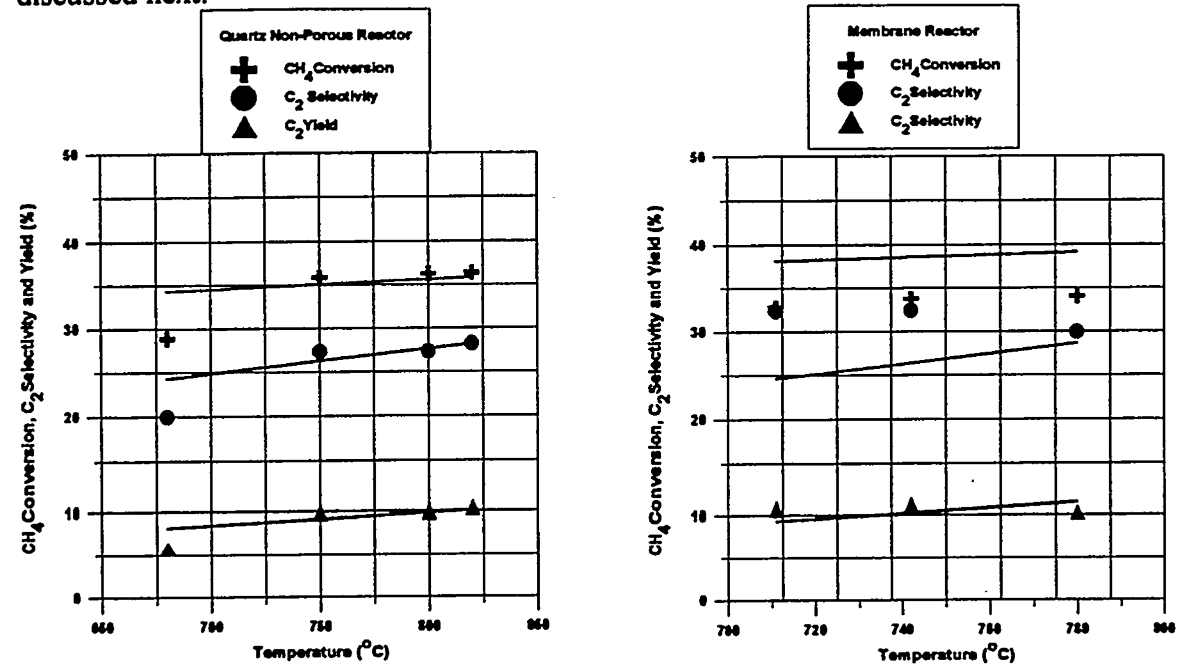
$$CH_4 + O_2 \xRightarrow{k2} CO_x$$

$$C_2H_4 + O_2 \xRightarrow{k3} CO_x$$

Modeling studies of the methane coupling reaction incorporated the above three reactions and the kinetics parameters from Tung and Lobban [1]. A theoretical fit was obtained for the methane coupling experimental data in the quartz non-porous fixed bed reactor as shown in Figure 5(a). The experimental data obtained at various reaction temperatures, at a constant methane to oxygen ratio of 2.0 were fitted with the kinetic model. Figure 5(a) shows that the theoretical fit is in good agreement with the experimental data. Using the parameters obtained from this fit of the model to the fixed bed reactor data, and the experimental conditions of the VYCOR membrane reactor experiments, the model predicted trends in methane conversion and hydrocarbon selectivity and yield in membrane reactors. A reasonably good agreement was obtained between the predicted model trends and experimental results with the VYCOR membrane reactors as shown in Figure 5(b). The model is being further refined by incorporating other kinetic schemes to predict the trends of the methane coupling reaction in VYCOR membrane reactors obtained under different sets of experimental conditions.

Oxygen Conducting Materials : Perovskites

One of the proposed avenues of research was the synthesis of dense membrane reactors, where the dense membranes are made of materials that allow only the permeation of oxygen across the membrane. Perovskites of rare earths like Sr, La, Ce and Yb in combination with group VIII elements like Fe and Co are known to permit oxygen conduction through their bulk. Litereature reports also suggest that the oxygen that is conducted through these materials is not molecular oxygen, but rather an oxygen anion. This research thus aims at not only looking for materials that would conduct oxyge and are catalytically active for methane coupling, but also aims at changing the chemistry of the methane coupling reaction by bringing in oxygen in a form that is not molecular oxygen. Research efforts on the synthesis and characterization of these perovskites are discussed next.



(a) Quartz Non-Porous Co-Feed Reactor (b) Porous Vycor Membrane Reactor

Figure 5. Comparison of model predictions for CH_4 conversions and C_2 selectivities in porous VYCOR membrane reactors with experimental data. (Solid line shows the predicted trend).

Perovskite Synthesis

The oxygen conducting perovskite, $Sr_{0.8}La_{0.2}FeO_3$, was synthesized by both the conventional solution precipitation technique as well as by the cavitation technique. Synthesis by cavitation was accomplished in the Microfluidizer which produces nanometer size particles of the perovskite. KOH and NH_4OH were used as precipitating agents in the Microfluidizer and the perovskite was precipitated from a mixture of the corresponding metal nitrates, while being subjected to cavitational forces. Water and 2-Propanol were used as solvents in both the conventional and the Microfluidizer synthesis techniques. The perovskites were characterized using XRD, DSC and TGA.

The synthesized perovskite was subjected to high temperature calcinations at progressively higher temperatures. XRD analysis of the calcined materials showed that the Microfluidizer-synthesized $Sr_{0.8}La_{0.2}FeO_3$ showed the characteristic perovskite peaks at a calcination temperature of 590°C when KOH was used as the precipitating agent, in both water and 2-Propanol media. Figure 6 shows the XRD spectra from $Sr_{0.8}La_{0.2}FeO_3$ samples that were prepared using the different methods, precipitating agents and solvents, and calcined at 590°C. The materials prepared by using NH_4OH did not show the perovskite structure under XRD for the calcination temperature of 590°C. This was probably due to phase separation of strontium oxide during synthesis, since strontium oxide does not easily precipitate from NH_4OH.

Characterization of Perovskites

$Sr_{0.8}La_{0.2}FeO_3$ prepared both by the conventional and the cavitation techniques showed reversible exotherms on the DSC spectrum at 150°C and 350°C only when KOH was used as the precipitating agent in 2-Propanol medium. Using KOH in water resulted in the perovskite structure as evidenced by XRD, but this material did not show the reversible DSC exotherms. Since such reversible exotherms occur when a material undergoes structural or polymorphic changes, it is likely that the material prepared in 2-Propanol resulted in perovskites with a defect structure in which there was a measurable energy difference between the two polymorphic forms as evidenced by the reversible exotherms at 150°C and 350°C as shown in Figure 7.

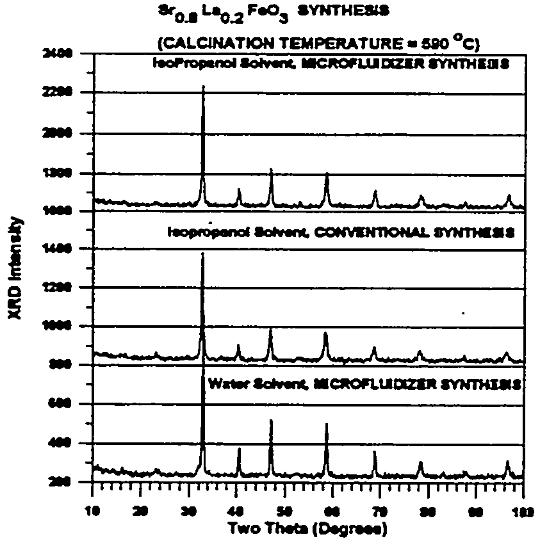


Figure 6. XRD Spectra from samples of the $Sr_{0.8}La_{0.2}FeO_3$ prepared by the conventional and the cavitation techniques.

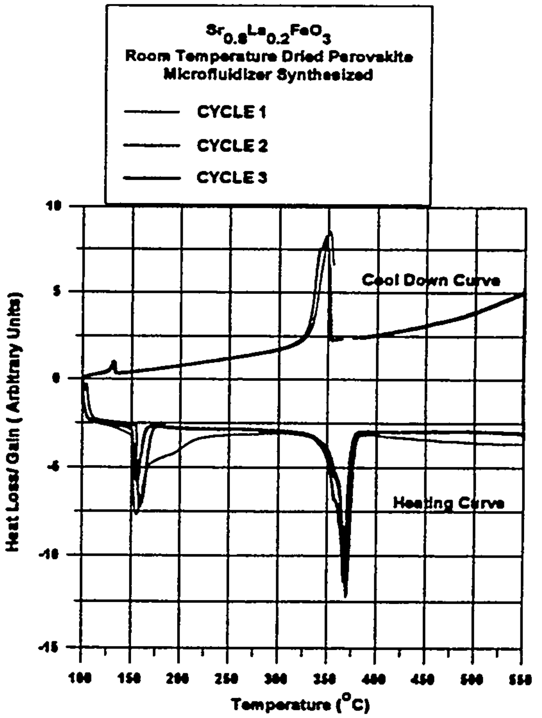


Figure 7. DSC spectra from a sample of $Sr_{0.8}La_{0.2}FeO_3$ showing the reversible exotherms and endotherms.

Comparison of catalytic activity of the perovskites

Methane coupling activity of the synthesized perovskite materials was tested by using these materials as catalysts in a quartz tube fixed bed reactor. Blank reactor experiments were performed in the non-porous quartz tube reactor at standard flow conditions typically used for the methane coupling experiments. Methane to oxygen ratio was maintained at 2.0, with a 10% oxygen dilution in helium. Methane conversions were found to be less than 5% over the temperature range 650°C to 850°C, indicating that the contribution from the quartz chips and the reactor tube walls was minimal.

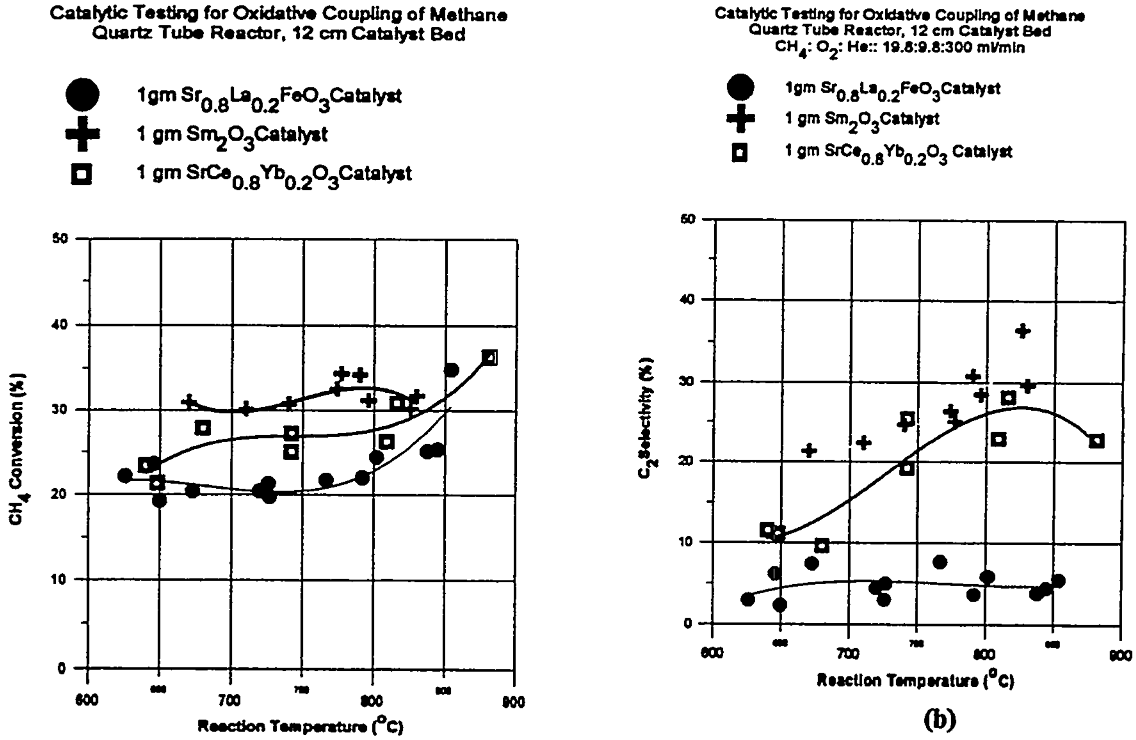
Two perovskites, $Sr_{0.8}La_{0.2}FeO_3$ and $SrCe_{0.8}Yb_{0.2}O_3$ were tested for their catalytic activity towards methane coupling by packing the materials in fixed bed non-porous reactor. The performance of both perovskites was compared with that of Sm_2O_3 over the temperature range of study. Figure 8(a) compares the methane conversions by all three materials, $Sr_{0.8}La_{0.2}FeO_3$, $SrCe_{0.8}Yb_{0.2}O_3$, and Sm_2O_3 operating under identical flow conditions. Catalyst loading of about 1gm was used for all these experiments. The catalyst was mixed with quartz chips and packed in the quartz tube, making up a 10 cm reaction zone. Over the entire temperature range of study, both the perovskite materials showed constant activity and stability over several hours on-line. Methane conversions were significantly higher than the blank reactor conversion of 5%. Over the entire temperature range studied, samarium oxide had 5-10% higher methane conversions than both the perovskites. $SrCe_{0.8}Yb_{0.2}O_3$exhibited higher conversions than the $Sr_{0.8}La_{0.2}FeO_3$.

Figure 8(b) compares the C_2 selectivities of the three materials. Of the two perovskites, $Sr_{0.8}La_{0.2}FeO_3$ acts as a deep oxidation catalyst with very low C_2 selectivities, and no significant hydrocarbon yields. C_2 selectivity of $SrCe_{0.8}Yb_{0.2}O_3$ lies midway between that of samarium oxide and $Sr_{0.8}La_{0.2}FeO_3$.

Although these studies were done using the perovskite materials in packed beds and not as membranes, the catalytic results suggest that the use of $Sr_{0.8}La_{0.2}FeO_3$ as a dense membrane material would be disadvantageous. We would like to synthesize dense membranes from materials that exhibit oxygen conductivity at elevated temperatures, while, at the same time, are good methane coupling catalysts, so that they would not lower the overall C_2 selectivity of the reactor. $SrCe_{0.8}Yb_{0.2}O_3$ is a more promising candidate since it has both methane coupling activity as well as oxygen conducting ability. Though literature reports do not indicate very high oxygen conductivity of this material, changes in relative compositions of cerium and yitribium are postulated to enhance the oxygen flux transported through the material. Hence, other compositions of this family of perovskites could serve as a potential candidate for dense membrane synthesis. Further work involving synthesis and catalytic testing of different compositions as well as other prospective materials is underway.

Fabrication of supported thin films of perovskite

In parallel with the research on dense membrane materials, work was also oriented toward finding a robust way of making thin films of the perovskite materials. Thus, while on one hand, we are looking for a good catalyst/oxygen conductor, on the other hand, we are working on supports and structural stability. A spray technique was developed to synthesize a perovskite dense membrane supported on porous alumina substrates. A 2000 Angstrom pore size α-alumina was used as the support material. Nitrates of metals constituting the perovskite which serve as precursors for perovskite formation were deposited on top of the support using the spray technique. The perovskite precursors deposited as a thick layer on top of the support. The perovskite structure evolved after the 1200°C treatment, but the film developed cracks. To achieve crack-free films and improve adhesion with the support, modifications of porous alpha alumina supports as well as microporous gamma alumina membranes were done as described below.



(a)

(b)

Figure 8. Comparison of (a) CH_4 conversions and (b) C_2 selectivities of the perovskites and Sm_2O_3 under identical operating conditions.

Modification of porous gamma alumina membranes

Experiments were performed to stabilize the gamma alumina top layer of the 40 Angstrom pore size alumina membranes since commercially available gamma alumina membranes were unstable at temperatures above 700°C. The stabilization process involved treating gamma alumina membranes with lanthanum nitrate solution, followed by repeated calcinations, to form lanthanum aluminate on the gamma alumina. The unmodified gamma alumina had higher permeance after calcination at 900°C, due to pore opening and loss of stability. The modified gamma alumina membrane showed lowered permeance and good thermal stability. Permeance increased only slightly after 50 hours at 900°C, indicating good stability of the modified membrane. The lower permeance of the lanthanum modified alumina, as compared to the unmodified alumina, indicated that either a partial pore blockage or a change in morphology had occurred in the alumina substrate. An oxygen conducting perovskite ($Sr_{0.8}La_{0.2}FeO_3$) was deposited on the modified gamma alumina membrane by solution deposition technique. The perovskite caused a lowering of permeance to gas flow at room temperature indicating that partial pore filling had occurred. XRD analysis of the deposit showed it to have the perovskite structure. Experiments are underway to achieve complete pore closure and to make high temperature oxygen conduction measurements through these dense membranes.

Pore filling of porous alpha alumina membranes.

Another approach taken to develop perovskite thin films was by filling up the pores in large pore diameer support material. By progressively narrowing the pore size with a different material, it was hoped that a more robust thin film membrane could be synthesized. Alpha alumina membranes with large pores (1.2 micron pore diameter) were used as the starting material. A high pressure technique based on *cavitation* effects in fluids was used to synthesize nanometer size particles. The nitrates of lanthanum and aluminum are subjected to high pressure (20,000 psig) in the presence of ammonium hydroxide in a specialized apparatus called the *Microfluidizer* to produce nanometer sized grains of $LaAlO_3$ with a particle size of 0.5 microns. $LaAlO_3$ synthesized in the Microfluidizer has been studied by XRD to determine phase purity with increasing temperature of calcination as shown in Figure 9. A comparison with the JCPDS line spectra of $LaAlO_3$ showed that the perovskite structure formed after the 900°C calcination. On the basis of these results, the porous alpha alumina discs containing the $LaAlO_3$ gel produced in the Microfluidizer were calcined at 900°C.

Lanthanum aluminate nanoparticles produced in the Microfluidizer were deposited inside the 1.2 micron pores of the alpha alumina substrate, partially filling the pores of the membrane. $LaAlO_3$ showed better adhesion to the alpha alumina support at high temperature, probably due to the fact that they have similar thermal expansivity. Figure 10 shows the change in gas permeance in the pore-filled alumina as a function of increasing number of pore fillings. The figure compares the gas permeance achieved in the pore blocked alumina with that of 40 Angstrom pore diameter gamma alumina and the 40 Angstrom pore diameter Vycor.

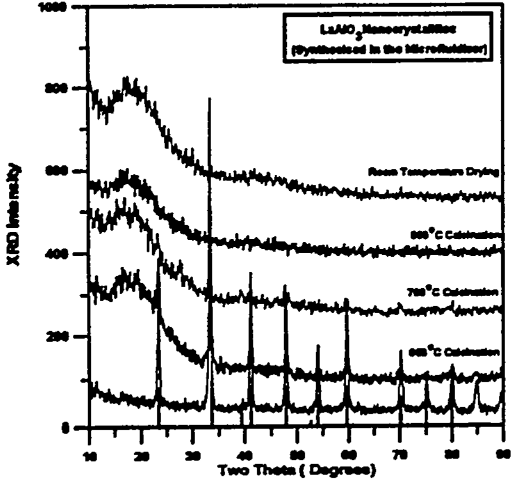


Figure 9. XRD patterns of $LaAlO_3$ synthesized in the Microfluidizer showing evolution of crystallinity with increasing temperature of calcination.

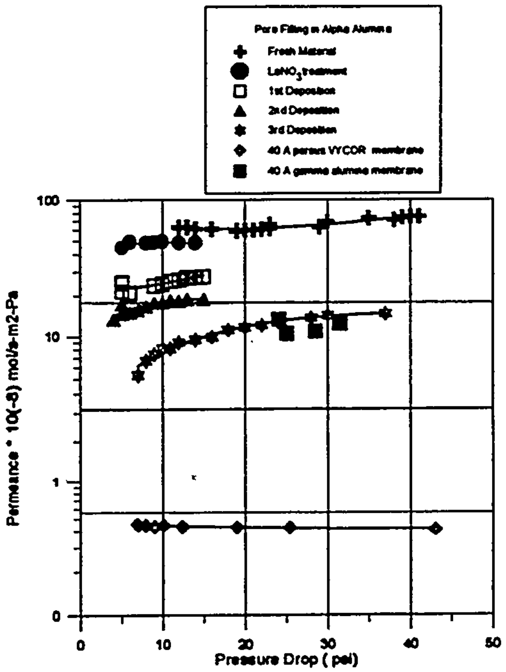
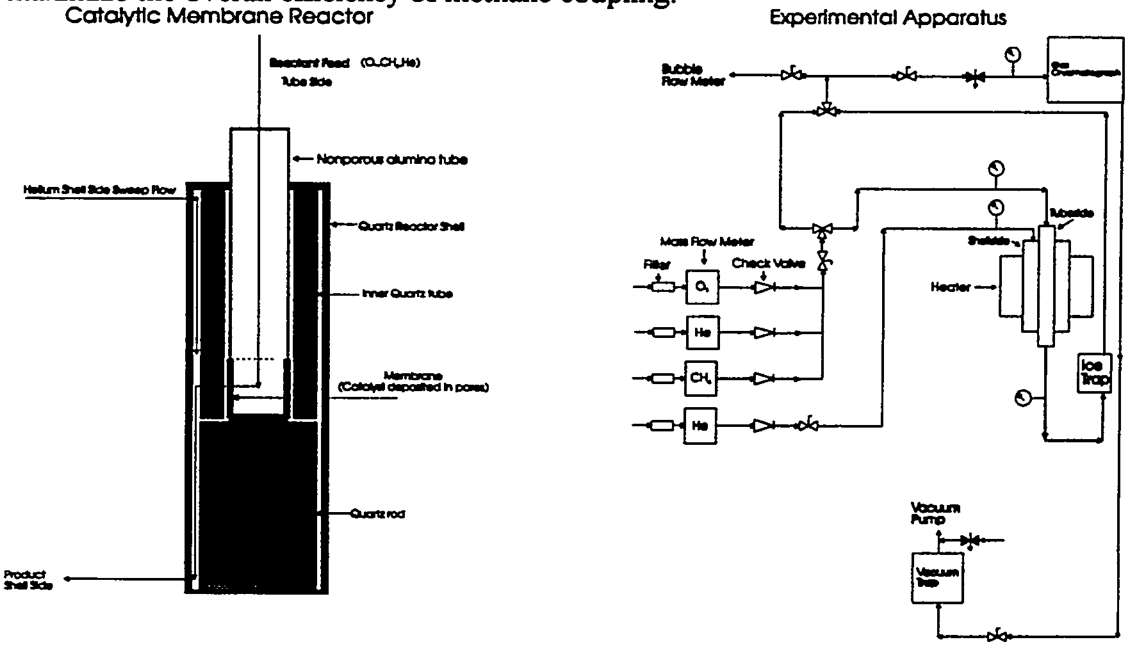


Figure 10. Comparison of gas permeance in pore-filled alumina with increasing number of fillings.

Methane Coupling in Radial Flow Catalytic Membrane Reactor.

The third proposed avenue of membrane reactor research was the study of porous catalytic membrane reactors. The following work aims at using a porous membrane that is also catalytically active for methane coupling. Reactant gases flowing through the membrane pores are brought in contact with the methane coupling catalyst deposited inside the membrane pores in this catalytic membrane reactor.

Recent literature reports indicate that external mass transfer limitations present during highly reactive methane coupling catalytic reactions detrimentally affect methane conversion and total C_2 production rates. External mass transfer limitations can be reduced by increasing the linear velocity of reactant gases over the catalyst. By using porous catalytic membranes of different pore diameters and by varying the flow rates of reactant gases passing through the catalytic membrane, one can regulate the contact time of the reactant gases with the active catalyst in the membrane pores. The combined effect of membranes coated with the active catalyst and the reactor flow configuration was postulated to minimize external mass transfer limitations. The result was expected to maximize the overall efficiency of methane coupling.


Catalytic Membrane Reactor

Experimental Apparatus

Figure 5. (a). Cross section view of the catalytic membrane reactor and (b). Schematic of the experimental setup of a catalytic membrane reactor.

As detailed in the cross section of the catalytic membrane shown in Figure 11(a), the catalytic membrane reactor provides the experimental capability to research the effects of high reactant linear velocities. Figure 11(b) shows a schematic of the experimental setup. Large pore size (0.02 µm to 2 µm pore size) alpha alumina membranes were used to form these catalytic membranes. The reactant gas mixture of oxygen, methane and helium diluent was fed in the tube side of the catalytic membrane reactor. All the gas was forced out of the membrane pores into the shell side of the membrane reactor. The free volume on both the tube side and the shell side of the membrane reactor was filled with quartz rods and quartz chips to minimize the gas phase reaction contribution. A small helium sweep flow was maintained on the shell side to prevent back mixing on the shell side. Methane coupling occurs inside the membrane pores as the reactant gases pass from the tube side to the shell side of the membrane reactor. The product gases mixed with the helium sweep gas and exited on the shell side of the catalytic membrane reactor. The exit stream was then sent through a water trap and then through the sample loop for GC analysis.

The catalytic membrane which acts as the tube of the shell-and-tube membrane reactor was constructed by welding together a porous membrane tube and a non-porous alumina tube with a high temperature ceramic glaze. The end of the membrane tube not welded to the non-porous segment was blocked off and sealed with a high temperature glaze. This welding procedure minimized the length of the porous alpha alumina membrane to be used in the reactor setup. Porous membrane tubes with a standard length of 2.6 cm and of different pore diameters, (0.02 µm, 0.1 µm, 0.2 µm, 0.5 µm, 2.0 µm), made of both alpha alumina and zirconia have been used for these studies. In all cases, blank reactions have been run in each reactor to establish the base-line conversions of the empty reactor. As shown in Figure 12, the conversion of methane was negligible over the range of flow rates used for the experimental study. Methane conversion was less than two percent for total feed flow rates greater than 150 ml/min at reaction temperatures of 750°C to 850°C. The reactivity of the blank porous membrane tubes for all pore sizes was minor.

Oxidative coupling of methane was carried out in the radial flow membrane reactor in the temperature range of 750°C- 900°C. The membrane reactors chosen for the catalytic studies were of pore diameters of 2.0 µm, 0.2 µm, and 0.02 µm. By covering the range of two orders of magnitude, these experiments were designed to study the effect of membrane pore size on the reactor performance for oxidative coupling of methane.

The catalyst was impregnated as samarium nitrate into the membrane top layer using a vacuum solution deposition technique. High temperature calcination converted the nitrate into samarium oxide and rendered it active for methane coupling. X-ray digital mapping of the porous membrane cross-section revealed high intensity of samarium in the active catalyst within the toplayer. This is advantageous, since the reactant gas mixture would be expected to pass through most of the membrane support without contacting the catalyst on the walls of the support, until it entered the top layer, in which the pore diameter is accurately known. A summary of the reaction conditions is given in Table 3.

The stability of both the reactor and the catalyst was investigated by keeping the membrane reactor on-stream in excess of 100 hours. Results indicated only relatively minor catalyst deactivation over a six day period as shown in Figure 13. Methane conversions and C_2 selectivities were relatively unchanged even after 125 hours on-line. This indicates that there was no loss in catalytic activity either due to catalyst poisoning or from loss in catalyst surface area due to sintering.

Figure 14 shows the experimental results for the 2.0 µm, 0.2 µm, and 0.02 µm pore diameter reactors. The 2.0 µm and 0.2 µm pore diameter tubes show similar results with a trend showing higher CH_4 conversions, and lower total C_2 selectivities with decreasing flowrates (WHSV). Lower contact times result in lower CH_4 conversions and higher total C_2 selectivities. The 0.02µm pore diameter tube shows constant and lower total C_2 selectivities in comparison to the larger pore diameter tubes over the entire flow range.

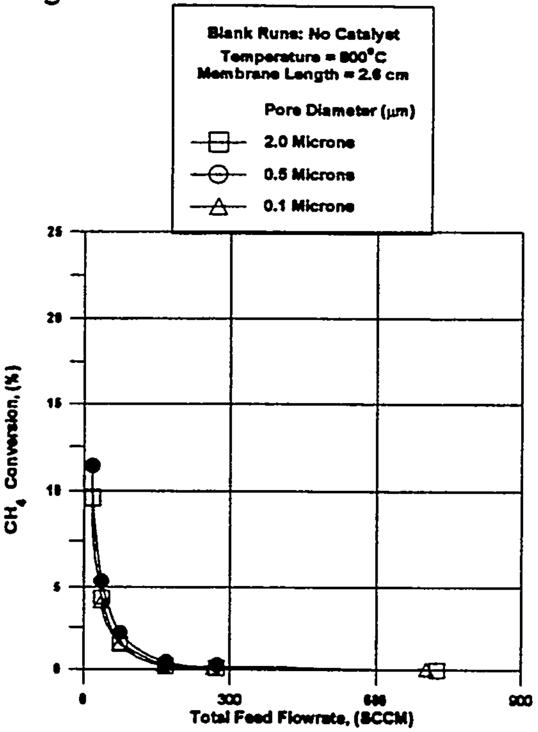


Figure 6. Blank Reactor Conversion Data at 800°C.

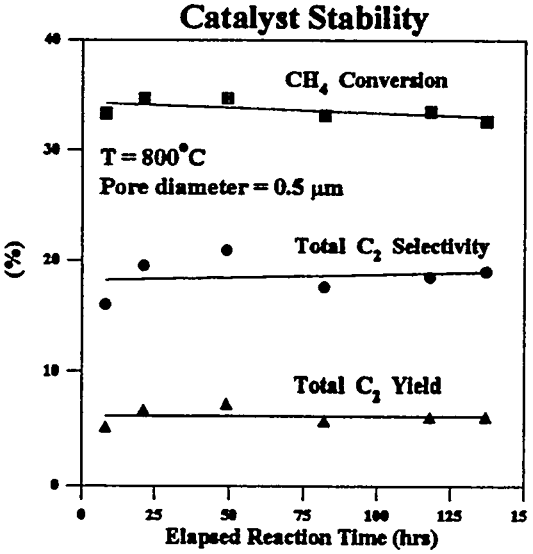


Figure 7. Stability test for the Sm_2O_3 catalyst in the radial flow membrane reactor.

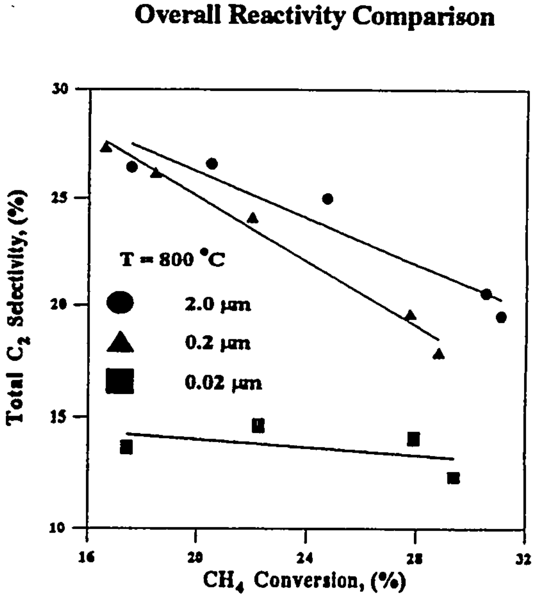


Figure 8. Reactor performance of different pore diameter membranes used in radial flow reactor.

Table 3. Experimental conditions for the catalytic membrane reactor.

Temperature	700°C - 850°C
Feed	$CH_4 : O_2 : He = 2 : 1 : 10$
Flowrate	200 - 2000 cc/min
Catalyst Weight	Sm_2O_3, 100 mg
Support materials	α - Al_2O_3, ZrO_2
Membrane Dimensions	Tubular membrane, 7 mm ID, 10 mm OD Length = 26 mm
Toplayer	Thickness = 30 µm
Toplayer Pore Diameters	α - $Al_2O_3 \Rightarrow d_p = 2.0$, 0.5, 0.2 µm $ZrO_2 \Rightarrow d_p = 0.02$ µm

The observed results are believed to be the result of the characteristic flow regime for each membrane pore size. Table 4 shows the results of calculations at reaction conditions for the relationship between the molecular mean free path and pore radius. The results reveal that the smallest pore size tube (0.02 µm pore diameter) is clearly in the Knudsen flow regime where molecule-wall collisions are predominant. As the pore size increases the flow behavior changes to viscous flow where the benefits of higher total C_2

selectivities are observed. Evidence in the literature [2] shows C_2 products to have approximately 5-10 times greater affinity for the catalyst active sites than CH_4. It is believed that the lower C_2 selectivity for the smallest pore size is due to the more intimate contact of the C_2 products with the active sites on the pore walls, with the result being further oxidation. These initial reactor investigations show a trend of increasing methane coupling performance with larger pore sizes.

These results provide insight into the general understanding of the oxidative coupling of methane. The fact that coupling in the Knudsen flow regime resulted in lower C_2 selectivities at the same degree of conversion, when compared to the viscous flow experiments, suggests that at the conditions of the experimental study, it is not advantageous to have a porous catalyst of high surface area. The flow regime in high surface area catalysts is predominantly Knudsen inside the catalyst pores and would therefore be disadvantageous for methane coupling.

Table 4. Flow regimes [l = molecular mean free path, r = pore radius]
Temperature = 800°C ; Pressure = 1 atm

Pore Diameter (μm)	Knudsen Number (Kn) = λ/r	Flow Regime
2.0	0.2	Viscous
0.2	2.0	Transition
0.02	20	Knudsen

Conclusions

Methane coupling experiments showed that under equivalent conidtions, C_2 selectivities were 10% higher in the membrane reactors as compared to the conventional co-feed non-porous reactors in the temperature range 650°C to 850°C. Studies involving variation of methane to oxygen ratios showed that both the methane conversions and C_2 selectivities were high at a methane to oxygen ratio of 2.0. Experiments run at conditions where the oxygen conversion was less than 100% resulted in lowered C_2 selectivity and higher methane conversions because of oxygen availability. Experiments involving metering of methane flow from the high pressure shell side into a mixture of oxygen and helium on the catalyst packed tube side showed that improved hydrocarbon selectivity is overshadowed by a lowered methane conversion. These results indicate that metering the oxygen flow through porous membrane reactors is beneficial to the methane coupling reaction when most of the oxygen supplied to the catalyst bed is used up before exiting the reactor. Modeling studies focused on fitting the experimental results obtained in VYCOR membrane reactors with a simplified kinetic model. The parameters for the fit were obtained by using the experimentally obtained values of methane conversions and C_2 selectivities and yields from fixed bed reactor experiments. The trends in experimental data on methane conversions, and C_2 selectivities and yields agreed reasonably well with the predicted trends of the model.

Oxygen conducting perovskites have been synthesized using conventional as well as cavitation techniques and characterized by XRD, TGA and DSC. $Sr_{0.8}La_{0.2}FeO_3$, an oxygen conducting perovskite that was synthesized in the Microfluidizer showed interesting DSC and TGA spectra that indicated a change in the crystal structure at relatively moderate temperatures of 150°C and 350°C. Perovskites of lanthanum, strontium and iron oxides which form good oxygen conductors showed very poor methane coupling activity in comparison to the commonly used methane coupling catalyst, samarium oxide. Hence, a dense membrane reactor that employs this material for metering oxygen flow for methane coupling might inherently cause very low hydrocarbon selectivities. On the other hand, perovskites of the strontium-cerium-yitribium series showed moderate activity for methane coupling, which lay between that of samarium oxide and the La-Sr-Fe oxides. Since these Sr-Ce-Yb-oxides also show moderate oxygen conduction properties, they might be better choices as potential candidates for dense membranes in membrane reactors.

Experiments aimed at modifying the porous alumina included stabilization of gamma alumina and pore filling of alpha alumina supports. The lanthanum modified alumina exhibited lower permeance as compared to the unmodified alumina, indicating that either a partial pore blockage or a change in morphology had occurred in the alumina substrate. A high pressure technique based on *cavitation* effects in fluid was used to synthesize nanometer size $LaAlO_3$ particles which were deposited inside the 1.2 micron pores of the alpha alumina substrate. A lowering of gas permeance was achieved, wherein gas permeance decreased with increasing number of pore fillings.

Catalytic results of the high temperature oxidative coupling of methane in radial flow membrane reactors indicate an interesting observation in regard to oxidative coupling of methane. By exploring the reactor performance in membranes of pore diameters of 2.0 μm, 0.2 μm, and 0.02 μm, the effect of the flow regime on the methane coupling activity can be postulated. The lower pore (0.02 μm) diameter membrane reactor showed much lower hydrocarbon selectivity than the other two membrane reactors. Theoretical calculations indicate the flow regime in this 0.02 μm membrane reactor to be in the Knudsen region, in contrast to the higher pore diameter membrane reactors where the flow is predominantly viscous flow. This suggests that high surface area catalysts, where the flow inside the catalyst pores is in the Knudsen regime, do not offer big advantages for oxidative coupling of methane.

References

1. Web-Yuan Tung and Lance L. Lobban, *Ind. Eng. Chem. Res.*, **31**, 1621-1625 (1992).
2. Cherrak, A., Hubaut, R., Barbaux, Y., *J. Chem. Soc. Faraday Trans.*, **88**, (21), 3241-3244, (1992).

Plans:

Radial flow catalytic reactors will be used for studying methane coupling under varying experimental conditions and the reactor performance will be compared with a conventional non-porous fixed bed reactor operating under the same experimental conditions. In addition, comparison studies of CH_4 conversion rates and C_2 selectivites in the radial flow catalytic membrane reactor and the conventional co-feed packed bed reactor, will be investigated.

Methane coupling activity of materials that are oxygen conducting will be expanded to identify candidates for dense membrane synthesis. Dense membrane reactors will be used for methane coupling studies.

The modeling work will be continued to predict the trends of various process parameters and the predicted trends will be compared to our experimental data on the oxidative coupling of methane in the porous VYCOR packed bed membrane reactors. The kinetic scheme used in the modeling studies will be improved to include kinetics specific to samarium oxide catalyst.