OXIDATIVE COUPLING OF METHANE USING MEMBRANE REACTORS

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Introduction

The aim of the experimental studies in this project is to investigate the effect of controlling the oxygen feed for the methane oxidative coupling reaction. The desired C_2 hydrocarbon products (mainly ethane and ethylene) can be further oxidized to CO_x (CO and CO_2) at a much faster rate than that of the oxidation of methane. Examination of the reaction order in oxygen of the kinetic expressions indicated that, for almost all of the methane coupling catalysts, the apparent reaction order in oxygen for the methane coupling is lower than that for deep oxidation. Therefore, modes of contact which maintain a low oxygen concentration throughout the reactor should favor the desired methane coupling reaction. This can be realized by using a membrane reactor with the membrane as an oxygen distributor to control the supply of oxygen along the reactor length, such that the intermediate C_2 hydrocarbon yield can be maximized.

The first reactor configuration used was a porous Vycor glass membrane reactor. A porous Vycor glass membrane has a uniform pore size of 40 Å across the entire thickness of the membrane tube wall, and there will be sufficient pressure drop across the membrane so that the oxygen flux can be easily controlled by adjusting the pressure on the feed side of the membrane. The second configuration tested was a radial-flow reactor, in which the catalyst was deposited inside the wall of an alumina membrane tube, and methane and oxygen were co-fed from one side of the membrane. By increasing the linear velocity of reactant gases over the catalyst, mass transfer limitation would be reduced so that the methane conversion and total C_2 production rates would be improved. In the third configuration studied, oxygen-conducting dense membranes would allow selective passage of oxygen to the reaction zone, thus eliminating the methane and C_2 loss through the pores encountered in the porous membrane reactors and, in addition, less expensive oxygen sources such as air can be used without contaminating the products.

In order to elucidate the effects of operating/kinetic parameters on the reactor performance, a general model was proposed for the simulation of cross-flow reactors with six types of feed policies. All of the six types of cross-flow reactors were analyzed for series-parallel reaction systems and their optimal feed distributions were determined by maximizing the desired product yield at the outlet of the reactor. The general model was applied to methane oxidative coupling with kinetics reported in the literature and compared with a co-feed reactor in terms of reactor configuration, contact time, temperature, pressure, and dilution ratio.

Experimental Study of Vycor Glass Membrane Reactors for Methane Coupling

Experimental studies were carried out with porous Vycor membrane reactors[1] with oxygen fed to the shell side and methane diluted with helium fed into the tube side. Figure 1(a) shows the C_2 selectivities of the porous Vycor membrane reactor and the co-feed, non-porous quartz tube reactor operated at methane inlet flow rate of 40 cc/min, methane to oxygen ratio of 2, and helium dilution rate of 10 with 2.4 g of Sm_2O_3 catalyst. It can be seen that Vycor membrane reactor gave a higher C_2 selectivity than the co-feed reactor. With increasing temperature, the non-selective gas phase reactions to CO_x products increased and the C_2 selectivity decreased as reaction temperature went up. A C_2 yield-methane conversion plot is given in Figure 1(b). Under the same methane conversion level, the membrane reactor always showed higher C_2 yield than the conventional co-feed reactor, indicating that

regulating the supply of oxygen along the length of the packed bed is beneficial for C_2 product formation.

Methane Coupling in Radial Flow Catalytic Membrane Reactor

Recent literature reports[2,3] indicated 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, the objective was to regulate the contact time of the reactant gases with the active catalyst in the membrane pores so that the overall efficiency of methane coupling can be maximized.

Alpha alumina membranes with pore sizes from 0.02 to 5 μm were used to form these catalytic membranes[4]. The reactant gas mixture of oxygen, methane and helium diluent was fed in the tube side of the catalytic membrane reactor, flowing through the membrane pores and brought in contact with the methane coupling catalyst deposited inside the membrane pores. All the gas was forced out of the membrane pores into the shell side of the membrane reactor. Oxidative coupling of methane was carried out in the radial flow membrane reactor in the temperature range of 750°C-900°C. Samarium nitrate was impregnated into the membrane top layer as the catalyst using a vacuum solution deposition technique. X-ray digital mapping of the porous membrane cross-section revealed high intensity of samarium in the active catalyst within the top-layer. Even though different flow regimes existed over the range of pore diameter reactors used in the experiments, the methane conversion rates and total C_2 selectivity were essentially the same. Catalytic experiments and X-ray digital mapping of the 0.02 μm pore diameter membrane tubes showed that more evenly distributed catalyst within the top-layer of the membrane gave higher C_2 yield. It appears that the location of the catalyst within the reactors had an effect on the reactor performances of the radial flow reactors.

In order to compare the performances of radial-flow reactors with the packed-bed reactors, a conventional packed-bed reactor was built. Crushed porous membrane doped with catalyst was used as the packing material. For both radial-flow reactors and the packed-bed reactors, higher space velocity resulted in higher methane conversion rate and, for the same space velocity, radial-flow reactor gave higher methane conversion rate. Figure 2 shows the C_2 selectivities of the two types of reactors, compared as functions of methane conversion. It is clear that higher C_2 selectivities were obtained by using a radial-flow reactor than by using the conventional packed-bed reactor.

Experimental Study of Methane Coupling Using a Dense Membrane Reactor

The current research effort has been focused on the experimental study of methane oxidative coupling using an oxygen-permeable dense membrane reactor. Before running the catalytic membrane reactor, the oxygen permeability through the membrane was measured. Also, a catalytic experiment with a conventional packed-bed reactor and a blank run in the membrane reactor without catalyst were conducted as a basis of comparison for the catalytic membrane reactor. The dense membrane reactor module was a shell-and-tube type reactor with a quartz tube as the shell side and the oxygen-conducting dense membrane as the tube side.

A La/MgO catalyst was prepared as the coupling catalyst and X-ray diffraction analysis showed that the major component was cubic magnesium oxide. It was reported[5] that this catalyst showed a significant improvement in C_2 yield by using a distributed oxygen feed reactor over that of a conventional co-feed reactor. The activity of **La/MgO catalyst was tested in a co-feed packed bed reactor as a comparison basis for the dense membrane reactor. C_2 yields up to 14.2% were observed at an initial CH_4 to O_2 ratio of 1.8 and a temperature of 790°C. The experimental results obtained are in agreement with those reported in the literature[5].**

The permeability of oxygen through the dense membrane tube was measured with air fed in the

shell side of the reactor module and helium in the membrane tube. As shown in Figure 3, the oxygen permeability observed was about 20% of the reported value[6] of 0.3 cc/min/cm^2 and the permeability reached a stable level within a relatively short period of time on stream. The oxygen permeability increases and then levels off with the increase in either helium sweep flow rate and the air flowrate. After the oxygen permeability measurement, methane was fed to the tube side with helium and air to the shell side in a membrane reactor containing no catalyst. The product was mainly carbon dioxide with little C_2 hydrocarbon, indicating that the membrane material is a total oxidation catalyst. Since the oxygen partial pressure is lower in the tube side during reaction, the oxygen permeability was found to be about four times higher than that observed in the non-reaction conditions.

The experiments conducted in a dense membrane reactor with catalyst packed in the tube side showed no detectable C_2 hydrocarbons. This suggested that the total oxidation of methane by the dense membrane material dominated the catalytic reaction in this configuration also. Once CO_2 is formed, it cannot be reduced to C_2 hydrocarbons, which is different from methane partial oxidation to syngas, where the CO_2 formation is the first step to produce CO and H_2. However, in another experiment with the same reactor except that air was co-fed with methane to the tube side of the membrane reactor (instead of feeding air to the shell side and methane to the tube side as in the original dense membrane reactor), 7% C_2 yield was observed due to the fact that the methane coupling reaction took place in the catalyst packed-bed before the reactant mixture contacted the dense membrane material.

General Model of Cross-flow Reactors and Its Application to Methane Oxidative Coupling

A general cross-flow reactor model with distributed reactant feed and product removal was developed[7], and the oxidative coupling of methane was studied based on the general model. The kinetic equations developed by Hinsen et al.[8] were used in this study. These kinetics are simple but include the further oxidation of C_2 to CO_x. The reactor configuration simulated in this study was a tubular reactor, in which methane, diluted with inert gas, is fed at the inlet of the reactor and oxygen is introduced into the reactor at different feed points along the reactor length. Any species may be removed from the reactor through the reactor wall, according to its permeability. Comparison studies were carried out to analyze the different performance of reactors with different configurations in terms of contact time, temperature, pressure, dilution ratio, and permeability. For each of the reactor configurations considered, the overall methane to oxygen feed ratio was optimized such that the C_2 yield at the reactor outlet was maximized.

Figure 4 shows the maximum C_2 yield at the reactor outlet as a function of contact time (defined by the ratio of catalyst weight to the initial methane flow rate) for co-feed reactor, membrane-feed reactor, and multiple stage-feed reactor with the numbers of feed points N=2, 3, 5, 10, 20, 50, 100, and 200 at 750 ^{o}C, and 1 atm. Three situations were considered here: a) no dilution gas addition and no product removal; b) dilution rate (initial molar ratio of methane to dilution gas) of 10 without product removal; and c) ethane and ethylene removed through the reactor wall and no dilution gas. Since the reaction orders in oxygen for C_2 formation are lower than those for CO_2 formation, the distributed feed of oxygen causes a relatively low oxygen concentration in the reactor and an increase in the number of feed points will help to decrease the oxygen concentration. So, both C_2 selectivity and yield increase with the number of feed points and the membrane reactor, in which the number of feed points is infinite, gives the highest selectivity and yield for the same contact time. For contact times longer than a certain value (which is ca. 400 g sec/mol in this case), the maximum C_2 yield of membrane-feed reactor is higher than that of a co-feed reactor operated at the same contact time, temperature and pressure. The improvement of C_2 yield by using reactors with a distributed feed of oxygen becomes greater as the contact time and/or the number of feed points increase. However in the low contact time region distributed feed reactors give slightly lower C_2 yields than the co-feed reactor. These results are consistent with the general analysis results[7]. It can be concluded that the contact time needs to be high enough for the distributed reactors to make a significant improvement in the C_2 yield obtained by the

co-feed reactor. In principle, 100 % C_2 yield could be realized when both the stage number and contact time approach infinity. Another advantage of using a distributed oxygen feed reactor is that it leads to a higher ethylene to ethane ratio.

From Figure 4 we see that dilution gas addition leads to higher C_2 yields, but longer contact time is required to achieve the same C_2 yield for any type of reactor considered here. For a reactor with a dilution ratio of 10 (initial feed ratio of dilution gas to methane), about 20-50 times longer contact time is required to achieve a similar level of C_2 yield to a reactor without dilution gas. Since a membrane reactor needs a longer contact time to show its advantage over a co-feed reactor, this means that much longer contact times would be required by a membrane reactor with dilution gas addition, compared to the contact times at which most of the co-feed packed-bed reactors have been operated. The C_2 yield can be greatly improved if the wall of the reactor is selectively permeable to C_2 products. Modeling results showed that an increase in C_2 product permeability results in higher maximum C_2 yield, and that selectively removing ethylene is more effective than removing ethane. As can be seen from Figure 5, using C_2 product-removal membrane reactors will greatly reduce the contact time that would be required by reactors without C_2 removal. In practice, though, it is difficult to make a reactor wall that is only permeable to C_2 hydrocarbons. Figure 5 shows the effect of methane permeability on the maximum C_2 yield at a separation factor of C_2 to CO_2 and H_2O of 5 and compared with the non-permeable wall situation, at 750°C, 1 atm, and 10 g sec/mmol. For C_2 to CH_4 separation factors below 200 (corresponding to dimensionless permeability of methane equal to 5, in Figure 5) , the yield of the permeable wall reactor gives a lower yield than the non-permeable one due to the loss of methane to the permeation side, and the membrane-feed reactor is worse than a co-feed reactor. This suggests that a low methane permeability is critical for product-removal reactors to be effective.

Conclusions

Experimental results with the Vycor glass membrane reactor showed that under equivalent conditions, a membrane reactor give higher C_2 selectivities and yield as compared to the conventional co-feed non-porous reactors. It can be concluded that metering the oxygen flow through porous membrane reactors is beneficial to the methane coupling reaction. Compared to the conventional packed-bed reactors, radial-flow membrane reactors give both higher methane conversion rate and C_2 selectivity.

Using a distributed oxygen-feed reactor, a reactor that selectively removes C_2 products, or a two-membrane reactor with both oxygen feed and product removal could greatly improve the reactor performance compared to the conventional co-feed reactor. However, much higher contact time (or catalyst weight to initial methane flow ratio) is required by the membrane reactor than that by a conventional co-feed reactor. Keeping a high separation factor of C_2 to methane is crucial to the product-removal membrane reactor to achieve higher C_2 yield.
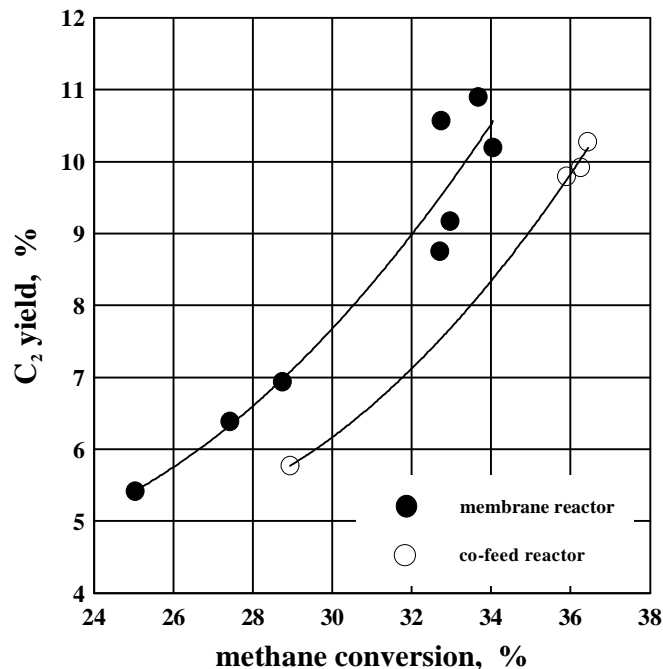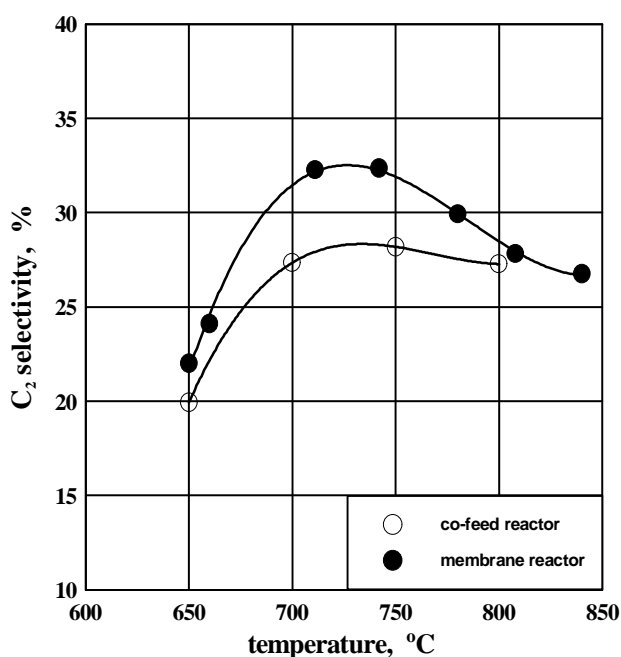
Future Work

In order to prevent the contact of oxygen with the dense membrane material, the inner wall of the dense membrane tube will be coated with a thin layer of a material which is both a oxygen conductor and a non-total oxidation/methane coupling catalyst. The tube side of the reactor may also be packed with coupling catalyst to expedite the coupling reaction and reduce the non-selective gas phase reactions.

The kinetic parameters in power-law type methane oxidative coupling kinetics for the catalyst used in this study will be evaluated from the packed-bed reactor experimental results. The kinetic parameters thus obtained will be used in the modeling of membrane reactors.

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(a)   (b)

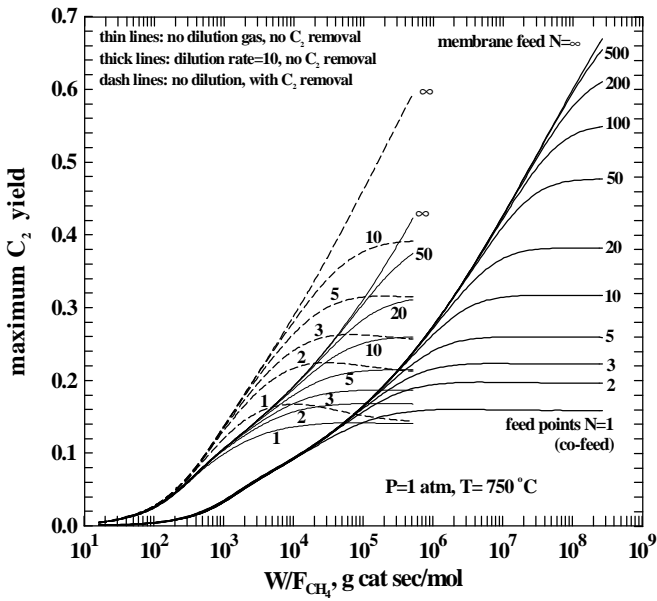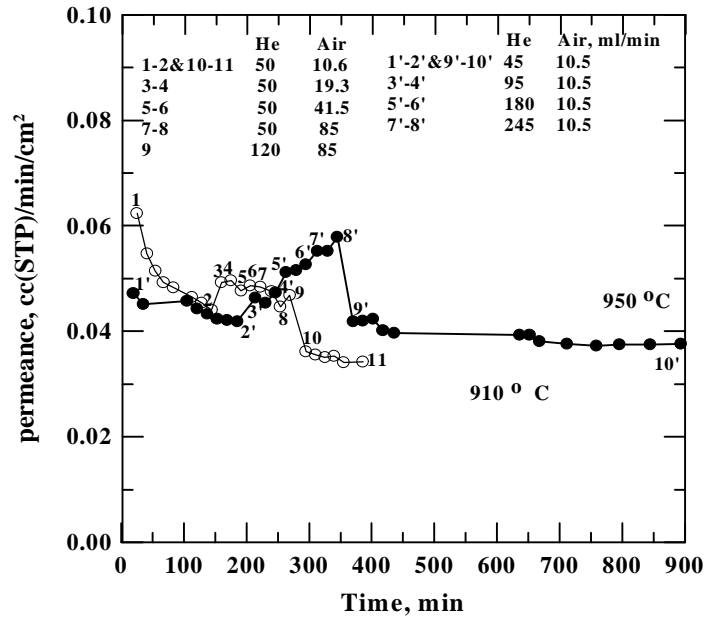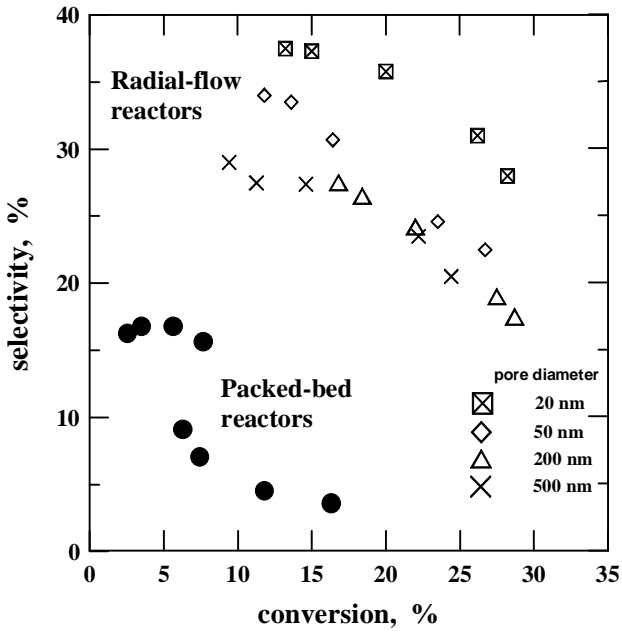Figure 1. Comparison of reactor performance of a Vycor membrane reactor and a co-feed reactor

Figure 2. C_2 selectivity - CH_4 plots for radial-flow

Figure 3. Oxygen permeance through dense membrane

reactors and packed-bed reactors

(air fed in the shell side and helium in the tube side)

Figure 4. Effect of contact time on the performance yield   of different types of reactors

Figure 5. Effect of CH_4 permeability on C_2 in O_2-feed reactors with product removal