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QUARTERLY REPORT

Report for the Period : June 25, 1993 to September 24, 1993

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Abstract

Several membranes have been investigated for use in a membrane reactor. Porous VYCOR has been tested for permeability changes with temperature. Three-sectional VYCOR membranes, with a porous central section, have been fabricated and tested in the experimental setup. Catalysts for methane coupling have been reviewed in the literature and five catalysts have been selected. Modeling studies of the methane oxidative coupling reaction in different reactor configurations shows higher C₂ selectivity and yield with membrane reactors as compared to conventional packed bed reactors.

Project Objective

The goal of this research is to develop and study an inorganic catalytic membrane reactor which will allow the oxidative coupling of methane to C₂ hydrocarbons at near 100% selectivity and relatively higher conversion, by control of 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. Such gas phase reactions are the main cause of decreased selectivity in oxidative coupling of methane in conventional flow reactors. Membrane reactor also provides better contacting of the reactant gases and the catalyst than conventional flow reactors.

1. Experimental Study

In choosing a membrane, several options are being investigated. Alumina membranes have the high temperature stability and alumina is inert to the methane coupling reaction. Gamma alumina membranes are commercially available with a pore size of about 40 Angstroms. These γ -alumina membranes have been cycled at high temperatures and have been found to be stable at temperatures up to 600°C. A thermal treatment at 875°C showed a doubling of the permeance, which was probably due to a structural change, since γ -alumina is known to

undergo phase changes at these higher temperatures. Since the temperature required for methane coupling reactions is in excess of 750°C, γ -alumina may not be the best choice for the membrane reactor. Alpha alumina membranes have very good high temperature stability up to 1000°C, but these α -alumina membranes are not available commercially in pore sizes less than 200 Angstroms. The permeance of a 200 Angstrom pore size α -alumina membrane is on the order of 10^{-6} mol./sec.m².Pa. and this is too high to control metered flow across the membrane. A possible alternative is a porous VYCOR glass membrane. VYCOR has a pore size of about 40 Angstroms and is commercially available in the form of tubes from Corning Inc.

Because of the collapse of successively larger pores with increasing temperature, porous VYCOR exhibits an increase in gas permeance as temperature increases. This change in permeance has been monitored by treating the 'as purchased' glass at higher temperatures. Since the real test for the VYCOR membrane is the longevity of porosity at the reaction temperature over time, gas permeance through VYCOR has been tested after thermal treatments at 750°C over prolonged time periods. Figure 1 shows the room temperature permeance measurements on an untreated porous VYCOR membrane, after 24 hours, 48 hours, 72 hours and 96 hours thermal treatments at 750°C. The permeance of porous VYCOR glass (to nitrogen gas) was found to stay steady after increasing by a factor of three (from 4.5×10^{-9} mol/sec.m².Pa. to 1.4×10^{-8} mol/sec.m².Pa) over long thermal treatments. Since a typical experimental run could last up to 48 hours, all the VYCOR membranes will be pre-treated at 750°C for 48 hours before use in an experimental study. The permeance values in porous VYCOR are considerably lower than those obtained with ceramic membranes. In industrial applications, this lower permeance might be a problem in terms of productivity. However, in our lab-scale experimental setup where the flow rates are comparatively small, a low permeance through the membrane in conjunction with lower flow rates might allow conditions where transfer of reaction gases through the membrane from shell to tube side can be metered.

Though VYCOR has stood up to the test of higher temperatures, there are other material problems to be overcome. In building a membrane tube, it is necessary to localize the porous region to the central part of the membrane, and have non-porous end regions. Because of the trapped air in the porous VYCOR, it is difficult to attach non-porous end sections to the central porous section. One technique employed to obtain non porous end sections on a long porous VYCOR tube is raising the temperature of the end sections gradually to 1200°C so as to collapse the pore structure. This achieves the task of forming a porous central region, but the uneven heating along the tube length causes warping of the tube. Also, porous VYCOR shrinks by about

15% when the pore structure collapses. Problems posed by this linear and radial shrinkage which hinder sealing the membrane in the stainless steel reactor body are currently being addressed. Also other techniques of joining porous and non-porous glass tubes are being tried.

Using the three section VYCOR membrane, packed bed experiments have been performed. The membrane tube was filled with a mixture of the pelletized catalyst and pelletized quartz in the porous region and just the pelletized quartz in the non-porous regions. The three sectional VYCOR membrane developed cracks along the interfaces between the porous and non-porous sections due to the thermal stresses in the VYCOR membrane. Hence, the feasibility of using VYCOR membranes depends on the ability to make robust bonding between the porous and non porous sections and efforts are underway to try other techniques such as indirect bonding to achieve this goal.

2. Analytical Characterization (SEM)

Porous inorganic membranes have been investigated using Scanning Electron Microscopy to study the pore structure of alumina membranes. Sample preparation techniques have been modified to include coating the membrane samples with a gold-palladium alloy deposit to enable better electrical grounding of the sample. High magnification images show the porous nature of the fine membrane. Similar studies will be attempted on porous VYCOR membranes. The EDX facilities available on the SEM also allow elemental mapping across the specimen and this feature will be utilized to study the extent of catalyst penetration during membrane doping for preparing catalytic membranes.

3. Literature Study (Choice of Catalyst)

Each of the three different configurations of the membrane reactors that are proposed to be studied in the course of this research impose physical constraints on the choice of catalyst. In addition to the three membrane reactors, a conventional packed bed reactor will also be studied with the same catalyst to obtain a comparison of the membrane reactor's performance. This packed bed reactor and the porous membrane packed bed reactor need catalyst in pelletized form, with the pellet size determined by the surface area available and the pressure drop permissible in the packed bed. The porous catalytic membrane reactor, where the catalyst would be in the pores of the membrane, requires a catalyst synthesis technique that would involve precipitation of the solid catalyst from a solution, so that the membrane pores can be infiltrated with the catalyst solution. In the case of a dense membrane reactor, the catalyst will be deposited

on the dense membrane itself and hence the catalyst material should bind to the oxygen transferring material that constitutes the dense membrane. Hence, these additional factors have to be considered in selecting a catalyst for membrane reactor studies. We have first reviewed the literature to select good methane coupling catalysts in general. Depending on what reactor configuration would be studied, synthesis of one of the selected catalysts would be undertaken.

Methane coupling catalysts can be classified under five broad categories. The first is (promoted) Group IIA Metal-Oxide catalysts. The most commonly used catalyst in this class is the Li/MgO catalyst which is an active catalyst but the C_2 yields are generally low [5,8]. La/MgO catalysts seem to exhibit higher yields and relatively higher selectivity for C_2 production. They are also superior to Li/MgO catalysts in that Lithium tends to evaporate and the catalyst loses its activity fairly rapidly at high temperatures of operation needed for methane coupling reaction. The second class of catalysts is the Lanthanide Metal-Oxide catalysts [6]. Oxides of La, Sm, Ce, promoted sometimes with alkali metals are the chief members of this class. The third category is the Transition Metal-Oxide Catalysts. Chlorides and oxides of alkali earth metals, which when used to promote members of this class, i.e., oxides of transition metals like Ti, Zn, Co, and Ni provide high C_2 yields in methane coupling reactions [2]. Significant literature is also present on the fourth class of catalysts namely the Group IIIA, IVA, and VA Metal-Oxide catalysts, though relatively low conversions and C_2 yields are obtained [7]. The last class of methane coupling catalyst are the Complex Oxide Catalysts, and the Perovskites (La-Sr-Fe-Oxides) come under this class [1,3,4].

A criterion that is normally employed to choose a catalyst is the yield of the favorable product that is produced by that catalyst. In this study, the reported literature C_2 yields were ratioed to a "theoretical maximum C_2 yield" to give a number that would be used as an index of the efficiency of the catalyst. This additional criterion, the 'theoretical maximum', is obtained by imposing limitations on the operating conditions and on what products are allowed to be formed. Thus for each of the reported catalysts, this criterion was employed to assess what would be the maximum theoretical C_2 yield of that catalyst.

The primary products observed in the high temperature oxidative coupling of methane are CO_2 , H_2 , C_2H_4 , C_2H_6 , CO , and H_2O . If we assume that there are no CO_x products formed, then we can define a "maximum theoretical C_2 yield". Also, since most methane coupling reactions are carried out at low oxygen concentrations, we assume that there is no oxygen left in the end products to simplify the calculations. By incorporating the Gibbs Free Energy of formation of each species and its dependence on temperature, the conversion of the

reactant species is computed to obtain yields of C_2 products, C_2H_4 and C_2H_6 . By summing the yields of both these C_2 products, a value for theoretical maximum C_2 yield is obtained. The catalysts listed in the table below are chosen based on this criterion. In addition to this criterion, traditional requirements on activity, selectivity, operating temperature, and longevity of the catalyst, and the particular reaction configuration etc., have to be all considered in selecting a catalyst.

Table 1. Catalysts selected from literature based on theoretical maximum yield.

Catalysts	Authors	Temperature	CH ₄ /O ₂ Ratio	Selectivity	C ₂ Yield (Y)	Y/Y* (%)
SrCe _{0.9} Yb _{0.7} O _{2.95}	Machida [1](1987)	750°C	2	60.1%	31.6%	31.6%
MnO/NaCl/TiO ₂	Feng- Chang [2](1989)	750°C	2.75	61%	26%	35.3%
Pb ₂ Mn ₂ Si ₂ O ₉ /SiO ₂	Thomas [3] (1988)	800°C	7.7	67.5%	20.3%	67.2%
Li NiO ₂	Kikhtyanin [4] (1987)	697°C	6	46.7%	12.1%	68.3%
Li/MgO	Lunsford [8] (1985)	720°C	2	50.3%	19.0%	19%

4. Modeling Study

To model the specific membrane reactor configurations and the kinetics of oxidative coupling of methane in these membrane reactors, certain simplifying assumptions were made in developing the computer model. Methane gas (diluted 50% in a helium stream) flows on the tube side and oxygen (or air), diluted with helium (1:4), flows on the shell side (tube and shell side total flow rates are set at 1ml/min). The catalyst is present only on the tube side (tube I.D. = 6.7 mm and O.D. = 10.24 mm.) and chemical reactions occur only on the tube side.

Isothermal operation is assumed and calculations are carried out at a constant temperature of 800°C. Steady state operation is assumed, at isobaric conditions (i.e., no pressure gradient between shell and tube side). Depending on the pore size, Knudsen (pore size in the range of 50 Angstroms) or molecular diffusion is the transport mechanism considered. For porous catalytic membrane reactors, all the catalyst is assumed to be inside the pore structure and the flow rates on tube and shell sides are balanced so that there is no free oxygen seeping into the tube side. For dense membrane reactors, only oxygen gas is assumed to transfer from shell to tube side, and the value of permeability of the dense membrane to oxygen gas was adjusted to control a steady, low, flux of oxygen into the tube side. The kinetic rate expressions for the oxidative coupling reaction have been taken from Tung and Lobban [9], making adjustments for different reactor configurations as discussed below.

To compare the membrane reactors with conventional packed bed reactor, the geometry of the reactor was modified so that the well-mixed reactant gases (methane and oxygen) flow only in the tube side which holds the packed bed. Since there is oxygen present in large quantities in a conventional packed bed reactor, gas phase kinetics have to be considered in modeling such a reactor. We have included this effect by modifying the kinetic rate expression (setting the coefficient of the CO_x production reaction to 1.35 in this and other configurations, as suggested by Tung and Lobban [9]). Though this does not present a completely realistic picture of gas phase reactions in a packed bed reactor, it will serve to present the differences in reactor performance between conventional and porous membrane reactors.

Figure 2 shows the modeling results of a packed bed reactor. The catalyst is packed in the tube and the tube side flow consists of a mixture of methane and oxygen in the ratio 3:1. The maximum C_2 yield is about 20% and is obtained at a reactor length of 0.1 m. All the oxygen is exhausted within this reactor length. The excess of oxygen availability at the reactor entrance allows CO_x formation reactions to occur at a competitive rate and C_2 selectivity is low at the reactor entrance. As more and more oxygen is consumed, the CO_x reactions are inhibited and selectivity increases. Because of availability of oxygen, methane conversion rises steeply and saturates at a value of 40%, and a C_2 yield of 18%, when there is no more oxygen for the reaction to proceed.

Figure 3 shows the simulation results for two porous membrane reactors with average pore sizes of 40 Angstroms and 4 Angstroms respectively. At the entrance of the reactor, in the tube side (where the catalyst is present), selectivity is high at first, as there is initially a high methane-to-oxygen ratio. As the oxygen permeates into the tube, selectivity drops. As oxygen

gets depleted, methane conversion also decreases and both selectivity and conversion (and hence the yield) remain constant when all the oxygen is exhausted. Since the reaction scheme used for modeling does not involve any reactions accounting for disappearance of C_2 products once formed, the C_2 yield curves stay horizontal. In the case of the 4 Angstroms porous membrane, the trough (minimum) in selectivity is spread out further down the reactor length and the values of selectivity are higher, since now the oxygen transfer is slower than in the 40 Angstrom membrane. This slower oxygen transfer also causes a more gradual rise in the methane conversion curve and the maximum C_2 yield is about 35%, obtained at a reactor length of 0.15 m.

Figure 4 shows the results for a dense membrane reactor. The C_2 yields are highest in this reactor configuration. Here, oxygen permeability is varied to assess the reactor performance. For a value of 1.0×10^{-9} for oxygen permeability, a C_2 yield of 35% is obtained at a reactor length of 0.1 m (which is comparable with the 4 Angstrom porous membrane reactor configuration). When the permeability value is dropped to 1.0×10^{-10} mol/s.m².Pa., higher yields are obtainable because of the high values of selectivity in this reactor configuration. However, since supply of oxygen is slow, methane conversion rises slowly and a longer reactor length (0.5 m) is needed.

5. Conclusions

Several membrane materials have been investigated for use in a membrane reactor for carrying out the methane coupling reaction. Gamma alumina membranes undergo structural changes and do not exhibit steady permeation rate for gas flows at temperatures above 600°C. Porous VYCOR shows stability of permeance to gas flows across the membrane at 750°C up to 96 hours and has been tried as a membrane in the membrane reactor. A three-region VYCOR membrane has been fabricated, with porous central region and non-porous end regions. Problems caused due to shrinkage and mechanical strength of VYCOR are currently being addressed.

Catalyst selection is based on comparison of C_2 yields reported in the literature with theoretical maximum yields and also on special requirements specific to the reactor configuration. Preliminary results from kinetic modeling of membrane reactors show better C_2 yields with membrane reactors when compared to conventional packed bed reactors operating under approximately same conditions.

6. Future Work

New methods will be attempted to achieve complete pore blockage of porous membranes to develop a dense membrane reactor that would allow metering of oxygen gas flow. Incomplete pore blockage in alumina membranes will be investigated through SEM studies of membranes subjected to several depositions of the perovskite. Alternative techniques of developing dense membranes will be tried.

Problems posed by this linear and radial shrinkage of porous VYCOR membranes which hinder sealing the membrane in the stainless steel reactor body will be investigated. Also, other techniques of joining porous and non-porous glass tubes will be tried. Analytical characterization of the porous VYCOR membranes using SEM will also be undertaken.

When the composite porous VYCOR membranes are fabricated, kinetic experiments will be attempted. The first membrane reactor configuration that will be studied is the fixed bed porous membrane reactor. A suitable catalyst would also be chosen from the list of selected catalysts so that the porous membrane can be doped by depositing the catalyst or its pre-cursor from a solution of the catalyst and synthesize a catalytic porous membrane. A conventional packed bed reactor will also be studied using a perovskite type catalyst. Comparison of C_2 yields and selectivities will then be made between a conventional packed bed reactor, a porous membrane packed bed reactor and a catalytic membrane reactor.

The modeling program will be modified to reflect a porous VYCOR membrane and reactions and transport inside the membrane pores. Comparison will be made between model predictions and experimental results from the catalytic membrane reactor. Experimental results from packed bed studies will also be compared with packed bed reactor model predictions, which will be improved to include gas phase reaction kinetics.

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Figure 1. Permeance stabiliziation in porous VYCOR at 750°C over long times.

Figure 2. Modeling results for a conventional packed bed reactor.

Figure 3. Modeling results for 40 Angstrom and 4 Angstrom pore size packed bed membrane reactor.

Figure 4. Model predictions for a dense membrane reactor.

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