Improving selectivity during methane partial oxidation by use of a membrane reactor

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Received 31 October 1991; accepted 10 December 1991

A reactant-swept catalytic membrane reactor for partial oxidation of methane to formaldehyde has been modeled. Kinetic parameters were taken from the literature for a V_2O_5/SiO_2 methane partial oxidation catalyst, and membrane parameters characteristic of commercially available materials were used. The models show that the selectivity for formaldehyde can be significantly improved by using a membrane reactor.

Keywords: Methane partial oxidation; membrane reactor; modeling; selectivity

The partial oxidation of methane to formaldehyde and/or methanol using molecular oxygen is a challenging catalytic problem. Both formaldehyde and methanol are oxidized much more easily than is methane, and consequently it is very difficult to prevent the reaction from proceeding to total combustion. Currently the only way to achieve reasonable selectivities to the partial oxidation products is by operating the reactor at very low conversion. In fact, at present, the conversion must be kept so low that the direct partial oxidation of methane is not commercially viable [1,2]. Nonetheless, direct partial oxidation remains a very attractive possibility for the conversion of natural gas, if the conversion can be increased without a detrimental effect upon selectivity. This has motivated a number of investigations of the catalytic partial oxidation of methane (for reviews, see [3] and [4]), always with the hope that a catalyst will be discovered which allows simultaneously high conversion and high selectivity.

Methane partial oxidation can be viewed as a series of consecutive reactions wherein the intermediate products are the ones that are most desirable. To date, most effort has been directed at engineering the reactivity to favor partial oxidation. The goal then, is to change the reactivity so that partial oxidation products which are formed can survive long enough to flow through the remainder of the catalyst bed and ultimately be recovered upon exiting the reactor. The intent of this letter is to suggest a parallel avenue of investigation, namely the engineering of the reaction environment to remove the partial

oxidation products without forcing them to flow through the remainder of the catalyst bed.

A number of ways of removing the partial oxidation products from the reactor may be envisioned; the method to be discussed here is the use of a membrane reactor. The idea is to place the catalyst inside a tube which has walls that are permeable [5]. This permeable tube is then placed inside a second, concentric tube. In this way the partial oxidation products can permeate through the walls of the reactor (i.e. the inner tube) instead of flowing through the remainder of the catalyst bed. The annular space outside the reactor tube can then be swept by a gas to remove the partial oxidation products as they permeate through the tube. Recently this type of reactor has been analyzed for a generic series of consecutive catalytic reactions [6,7]. When an inert gas is used to sweep the zone outside the catalyst tube, the reactor may be called an inert-swept catalytic membrane reactor (ISCMR). The analysis of an ISCMR [6] indicates that if it is to function properly the membrane must be permselective for the partial oxidation products. That is, the partial oxidation products may pass through the membrane more easily than the reactants. If the membrane is not permselective, the reactants are preferentially lost into the annular space while the partial oxidation products remain behind (and consequently get converted into total combustion products).

Unfortunately, methane partial oxidation requires elevated temperatures where the choice of membrane materials is limited. Porous ceramics or porous Vycor® glass are two materials which are suitable. These high temperature membranes separate on the basis of molecular size, and since methane is smaller than methanol or formaldehyde, they do not possess the required permselectivity. Hence, the use of porous ceramics or porous Vycor® in an ISCMR will not improve selectivity for partial oxidation. Another membrane reactor geometry, the reactant-swept catalytic membrane reactor (RSCMR) described below, does not require a permselective membrane, and hence a porous ceramic or porous Vycor® membrane can be used effectively to increase selectivity in an RSCMR.

The requirement of a membrane which is permselective in an ISCMR arises due to the loss of reactant through the membrane. If the same concentric tube geometry as described above is used, the loss of reactant through the membrane can be reduced by replacing the inert sweep gas with reactant gas. This eliminates the driving force loss of reactant through the membrane and consequently eliminates the need for a permselective membrane. The resulting RSCMR has been evaluated recently for use with consecutive catalytic reactions [7].

Fig. 1 shows a schematic diagram of a RSCMR for partial oxidation of methane. As the figure shows, the reactants are fed to the annular space. As the reactants flow through this annular space, they sweep out the partial oxidation

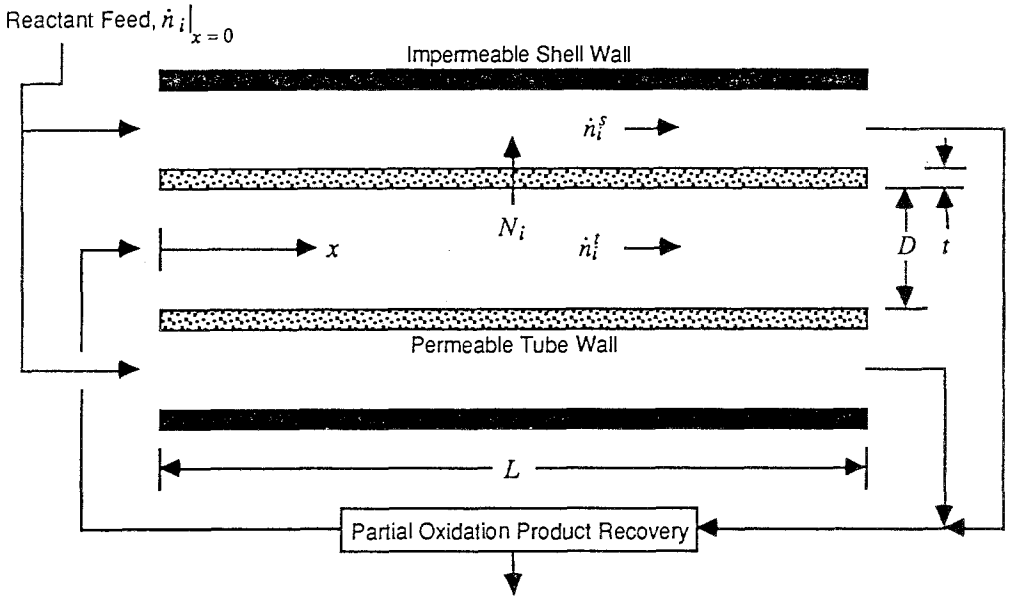

Fig. 1. Schematic diagram of a co-current reactant-swept catalytic membrane reactor.

products which permeate through the wall from the inner (reactor) tube. The sweep gas exits the annular space and the partial oxidation products are recovered. After removal of the partial oxidation products, the remaining gas becomes the feed to inner tube. The inner tube is packed with the catalyst and is where the reaction takes place. The reactant gas in the inner tube does not permeate through the tube wall because there is no driving force to do so. Additional partial oxidation products can be recovered from the stream leaving the central tube. The present letter reports the initial results of mathematical modeling of such a RSCMR for methane partial oxidation. The modeling uses kinetic data and membrane parameters taken from the literature.

Spencer [8,9] has studied the partial oxidation of CH_4 with O_2 using MoO_3 on SiO_2 and V_2O_5 on SiO_2 as catalysts. Spencer and Pereira [10] have analyzed the data and found that for V_2O_5/SiO_2 catalysts the reaction kinetics and selectivity can be captured quite well using three reactions:

$$CH_4 + O_2 \rightarrow HCHO + H_2O \quad (1)$$

$$HCHO + 0.5\ O_2 \rightarrow CO + H_2O \quad (2)$$

$$CO + 0.5\ O_2 \rightarrow CO_2. \quad (3)$$

Furthermore, for the reaction conditions studied (which includes a fixed CH_4/O_2 feed ratio) these three reactions are first-order in methane, formaldehyde, and carbon monoxide, respectively. Pre-exponential factors and activation energies are reported for these three reactions, and these can be used to calculate the conversion and selectivity at a pressure of 1 atm and temperature between

773 and 873 K. These rate expressions have been used in the present modeling study.

The co-current geometry shown in fig. 1 has been used in the modeling since the earlier analysis [7] indicated that it is preferred over counter-current flow. The figure defines a coordinate system (one-dimensional) as well as molar flow rates of species i on the shell (annular) side, $\dot{n}_i^s$; molar flow rates of species i on the tube (reactor) side, $\dot{n}_i^t$; membrane thickness, t; inner tube diameter, D; and reactor length, L. It is assumed that the reactor is at a uniform pressure, P, everywhere, and that it is isothermal at temperature T. The diffusion coefficient of species i within the membrane, $\mathscr{D}_i$, is assumed to equal the Knudsen diffusivity, and the rate constants for reactions (1) through (3) are represented by k_1 through k_3, respectively. It is further assumed that plug flow exists on both sides of the membrane, that there are no homogeneous reactions [8–10], and that all partial oxidation products are recovered from both the gas leaving the annular space and from the gas leaving the central tube.

With these assumptions a set of mole balance equations can be written for each species on both the tube and shell sides of the reactor. It is convenient to rearrange these equations in dimensionless form as given in table 1. The dimensionless parameters appearing in the equations are defined in table 2. As has been discussed previously [7], the assumptions used to arrive at the equations in table 1 have been used in other studies of membrane reactors, and it has been shown that the resulting models agree quite well with experiment. Finally, the boundary conditions needed to solve these coupled ordinary differential equations are listed in table 3 along with definitions of the conversion of methane and the selectivity to formaldehyde. The boundary conditions are that only methane and oxygen are fed to the shell side of the reactor in a 9 to 1 ratio (which is what Spencer and Pereira used in all their studies), that all formaldehyde is removed from the stream leaving the shell side, and that everything else in this stream is then fed to the reaction side of the reactor. Conversion is defined in terms of the total methane fed to the reactor, and selectivity is defined in terms of all formaldehyde being recovered from both the shell and tube side effluent streams.

Before the mole balance equations can be solved the parameters must be assigned values. To do so, the kinetic parameters of Spencer and Pereira were used, as was their reactor diameter of 0.375 in and their methane to oxygen feed ratio of 9.0. The temperatures considered, 773, 798, 823, 848, and 873 K are the same temperatures for which the kinetic parameters were determined as was the total pressure of 1 atm. The Damköhler number can then be varied by changing the ratio of reactor length to molar methane feed rate. In the present study this parameter was varied over the range needed to produce conversions in the range from 0 to 7%, which once again is the range in which the kinetic parameters were determined. The only remaining parameters are associated with the membrane material.

Table 1
Mole balance equations used to model methane partial oxidation in a reactant-swept catalytic membrane reactor

$$\frac{dF^t_{CH_4}}{dz} = Da[-\frac{F^t_{CH_4}}{F^t_{total}} + \frac{1}{DaPe}(\frac{F^t_{CH_4}}{F^t_{total}} - \frac{F^s_{CH_4}}{F^s_{total}})]$$

$$\frac{dF^t_{O_2}}{dz} = Da[-\frac{F^t_{CH_4}}{F^t_{total}} + \frac{\mathscr{R}_2 F^t_{HCHO}}{2F^t_{total}} - \frac{\mathscr{R}_3 F^t_{CO}}{2F^t_{total}} + \frac{1}{S_{O_2} DaPe}(\frac{F^t_{O_2}}{F^t_{total}} - \frac{F^s_{O_2}}{F^s_{total}})]$$

$$\frac{dF^t_{HCHO}}{dz} = Da[\frac{F^t_{CH_4}}{F^t_{total}} - \frac{\mathscr{R}_2 F^t_{HCHO}}{F^t_{total}} + \frac{1}{S_{HCHO} DaPe}(\frac{F^t_{HCHO}}{F^t_{total}} - \frac{F^s_{HCHO}}{F^s_{total}})]$$

$$\frac{dF^t_{H_2O}}{dz} = Da[\frac{F^t_{CH_4}}{F^t_{total}} + \frac{\mathscr{R}_2 F^t_{HCHO}}{F^t_{total}} + \frac{1}{S_{H_2O} DaPe}(\frac{F^t_{H_2O}}{F^t_{total}} - \frac{F^s_{H_2O}}{F^s_{total}})]$$

$$\frac{dF^t_{CO}}{dz} = Da[\frac{\mathscr{R}_2 F^t_{HCHO}}{F^t_{total}} - \frac{\mathscr{R}_3 F^t_{CO}}{F^t_{total}} + \frac{1}{S_{CO} DaPe}(\frac{F^t_{CO}}{F^t_{total}} - \frac{F^s_{CO}}{F^s_{total}})]$$

$$\frac{dF^t_{CO_2}}{dz} = Da[\frac{\mathscr{R}_3 F^t_{CO}}{F^t_{total}} + \frac{1}{S_{CO_2} DaPe}(\frac{F^t_{CO_2}}{F^t_{total}} - \frac{F^s_{CO_2}}{F^s_{total}})]$$

$$\frac{dF^s_{CH_4}}{dz} = -\frac{Da}{DaPe}(\frac{F^t_{CH_4}}{F^t_{total}} - \frac{F^s_{CH_4}}{F^s_{total}})$$

$$\frac{dF^s_{O_2}}{dz} = -\frac{Da}{S_{O_2} DaPe}(\frac{F^t_{O_2}}{F^t_{total}} - \frac{F^s_{O_2}}{F^s_{total}})$$

$$\frac{dF^s_{HCHO}}{dz} = -\frac{Da}{S_{HCHO} DaPe}(\frac{F^t_{HCHO}}{F^t_{total}} - \frac{F^s_{HCHO}}{F^s_{total}})$$

$$\frac{dF^s_{H_2O}}{dz} = -\frac{Da}{S_{H_2O} DaPe}(\frac{F^t_{H_2O}}{F^t_{total}} - \frac{F^s_{H_2O}}{F^s_{total}})$$

$$\frac{dF^s_{CO}}{dz} = -\frac{Da}{S_{CO} DaPe}(\frac{F^t_{CO}}{F^t_{total}} - \frac{F^s_{CO}}{F^s_{total}})$$

$$\frac{dF^s_{CO_2}}{dz} = -\frac{Da}{S_{CO_2} DaPe}(\frac{F^t_{CO_2}}{F^t_{total}} - \frac{F^s_{CO_2}}{F^s_{total}})$$

Models like the one used here have been shown to predict the behavior of membrane reactors with very good accuracy, e.g. [11,12]. If the membrane is a porous glass or ceramic, then the permeation will be in the Knudsen regime [13,14]. In the present modeling Knudsen diffusivities have been used assuming a porosity of 0.43, a tortuosity of 1.0, and a pore diameter of 5 nm. Commercial membranes are available with pore diameters at least as small as 3 nm [14], so that latter estimate is conservative. Finally, the membrane thickness has been assumed to be 100 μm. Again this is a conservative value, commercial membranes can be as thin as 5 μm with the average being 10 to 20 μm [14,15]. (The thickness here is not the total thickness, only that of the layer which determines permeability [14].)

The equations in table 1 were solved using the finite element method. The mathematical procedure has been described elsewhere [7]; here 250 linear elements were used in most cases. In addition, for each temperature examined, plug flow reactor (PFR) behavior was also calculated, using the same parameters. Temperatures of 773, 798, 823, 848, and 873 K were used. Fig. 2 compares the selectivity to formaldehyde obtained in a RSCMR as a function of methane

Table 2
Dimensionless variables and parameters appearing in the mole balance equations

Variable or Parameter	Significance	Definition
F_i^t	Flow of i on the tube side	$\dfrac{\dot{n}_i^t}{\dot{n}_{CH_4}^s\big\|_{x=0}}$
F_{total}^t	Total flow on tube side	$F_{total}^t = \sum_{all\ i} F_i^t$
F_i^s	Flow of i on shell side	$\dfrac{\dot{n}_i^s}{\dot{n}_{CH_4}^s\big\|_{x=0}}$
F_{total}^s	Total flow on shell side	$F_{total}^s = \sum_{all\ i} F_i^s$
z	Axial position	$\dfrac{x}{L}$
$\mathscr{R}_j$	Relative rate of reaction j	$\dfrac{k_j}{k_1}$
S_i	Permeability of CH_4 relative to species i	$\dfrac{\mathscr{D}_{CH_4}}{\mathscr{D}_i}$
Da	Damköhler number	$\dfrac{\pi k_1 LPD^2}{4RT\dot{n}_{CH_4}^s\big\|_{x=0}}$
Pe	Peclet number (membrane)	$\dfrac{RT\dot{n}_{CH_4}^s\big\|_{x=0}}{2\pi\mathscr{D}_{CH_4}LP}\ln\left(\dfrac{D}{D+2t}\right)$

$i = CH_4$, O_2, HCHO, H_2O, CO, or CO_2; $j = 2$ or 3.
(Most dimensional variables are defined in fig. 1, $\dot{n}_i$ is the molar flow rate of species i (superscript t denotes tube side and superscript s denoted shell side), k_j is the rate constant of reaction j, $\mathscr{D}_i$ is the diffusion coefficient of species i in the membrane, P is the total pressure, R is the ideal gas constant, and T is the temperature.)

Table 3
Boundary conditions used to solve the mole balance equations, and definitions of conversion and selectivity for the RSCMR

Variable	Boundary	Value
$F_{CH_4}^s$	$z = 0$	1
$F_{O_2}^s$	$z = 0$	1/9
F_i^s (i = HCHO, H_2O, CO and CO_2)	$z = 0$	0
F_i^t ($i = CH_4$, O_2, H_2O, CO and CO_2)	$z = 0$	$F_i^s\big\|_{z=1}$
F_{HCHO}^t	$z = 0$	0
Variable	**Symbol**	**Definition**
Conversion of CH_4	f_{CH_4}	$1 - F_{CH_4}^t\big\|_{z=1}$
Selectivity to HCHO	η	$\dfrac{F_{HCHO}^s\big\|_{z=1} + F_{HCHO}^t\big\|_{z=1}}{1 - F_{CH_4}^t\big\|_{z=1}}$

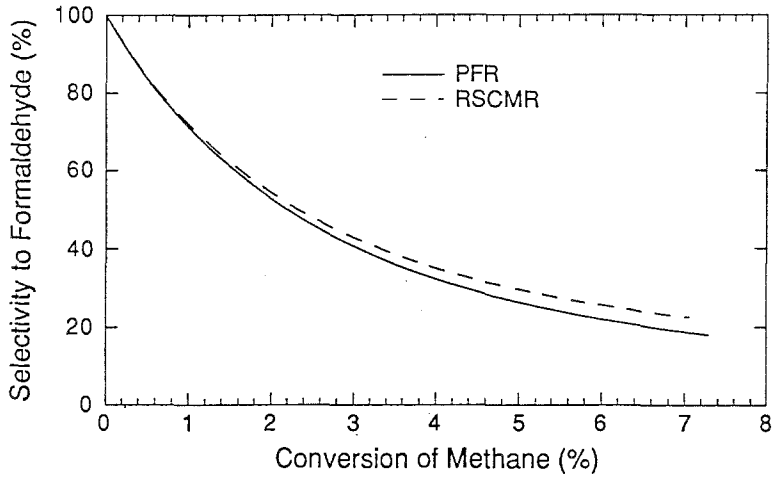

Fig. 2. A comparison of the performance of a RSCMR and PFR for V_2O_5/SiO_2 catalyzed partial oxidation of methane at 873 K.

conversion to that of a PFR, both reactors operating at 873 K. Fig. 3 makes the same comparison at a reactor temperature of 773 K.

The RSCMR gives a higher selectivity to formaldehyde at all temperatures and conversions studied. At 773 K the selectivity is as much as four times that of a PFR. This is a very encouraging result, especially as no attempt has been made to optimize the system parameters yet. A comparison between figs. 2 and 3 might give the impression that membrane reactor performance depends upon temperature, but this is not quite accurate. A more detailed analysis of the

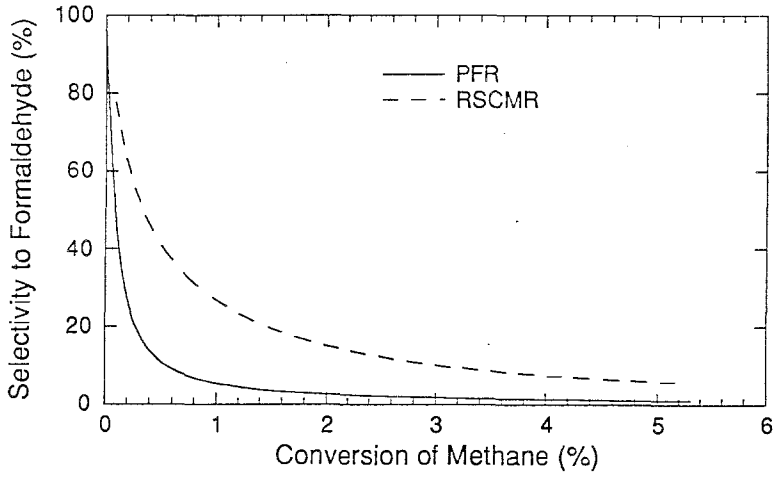

Fig. 3. A comparison of the performance of a RSCMR and a PFR for V_2O_5/SiO_2 catalyzed partial oxidation of methane at 773 K.

RSCMR [7] has shown that for any given set of rate parameters there is an optimum membrane thickness (or pore size). That is, there is a value of the dimensionless group *DaPe* which will maximize the improvement in selectivity. At both very high and very low values of this dimensionless group, the reactor will behave just like a plug flow reactor. This means that the RSCMR can always be expected to perform as well or better than a plug flow reactor. In the modeling presented here, the value of *DaPe* has been fixed at a single value for all temperatures studied.

There is little doubt that the RSCMR performance can be improved from that shown in fig. 2 by variation of the parameters contained within the group *DaPe*. Studies to optimize the performance at each temperature (still keeping within the limits of membrane parameters which are commercially available) is presently underway. Staged operation also offers improvement possibilities [7]. Of course, before too much time is spent optimizing performance using the model, it is important that the model be experimentally verified. For this reason both simulation and experimentation using RSCMRs for methane partial oxidation are being pursued in our laboratory. However, as already noted, the assumptions used in generating the model have been used with other reaction systems in membrane reactors, and the computed and experimental results show excellent agreement.

The main point here is that significant improvements in the selectivity to partial oxidation products can be realized through engineering of the reaction environment so that these products are efficiently removed from the catalyst bed instead of being forced to flow the rest of the way through it. Most effort to date has been focused upon engineering the catalyst reactivity. The two approaches are complementary. If a catalyst is found which gives much higher selectivity to formaldehyde than the V_2O_5 used here for modeling purposes, then it should be possible to improve upon that new catalyst's performance by using it in a RSCMR. The RSCMR parameters for methane partial oxidation have not yet been optimized, and still better selectivity is expected as they are. At the same time, catalyst improvements will most likely occur, and perhaps by combining the two approaches (catalyst reactivity improvement and efficient partial oxidation product removal), high selectivity will be obtained at conversion levels which are commercially practical.

Acknowledgments

This material is based upon work supported by the National Science Foundation under Grant No. CBT-8857100. The Government has certain rights in this material. The author would also like to thank Professor J.A. Tsamopoulos for his willingness to help with the finite elements analysis.

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