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Partial oxidation of methane to synthesis gas on a Rh / TiO_2 catalyst in a fast flow porous membrane reactor

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The partial oxidation of methane to synthesis gas has been studied over a 3% Rh / TiO_2 catalyst in a fixed bed and a novel membrane reactor under autothermal conditions using O_2 as oxidant. The membrane reactor allows the partial oxidation reaction to be performed without premixing the reactants reducing the risk of explosion even at low methane / oxygen ratios. The membrane reactor can operate autothermally and at millisecond residence time. Methane conversions of up to 65% with CO and H_2 selectivities of 90 and 82% respectively have been achieved. The low methane / oxygen ratio and the high flow rates are the key factors to attain autothermal behavior. The most sensitive factor to attain high conversion and selectivities appears to be short contact time but high temperature. A kinetic model was used to interpret the experimental results.

Keywords: membrane reactor, partial oxidation, methane, synthesis gas, Rh / TiO_2, kinetic model

1. Introduction

The partial oxidation of methane (POM) to synthesis gas has recently received increasing attention as an alternative reaction pathway to the steam reforming of methane. The POM pathway has several advantages. The product gas ratio (H_2 / CO) of the reaction is 2, which can be directly used as feed for the Fischer–Tropsch synthesis or methanol synthesis. Furthermore, since the POM reaction is slightly exothermic, a process based on this reaction would be much more energy efficient than the energy intensive steam reforming reaction [1,2]. Recently, several investigators have studied the POM reaction on Ni [3–6], Ru [7,8], Pt [9–11] and Rh [12–16] supported catalysts. Schmidt and coworkers [11,17,18] have studied the POM reaction using various noble metal catalysts in a monolith reactor at fast flow rates. It was possible to achieve high methane conversion and syngas selectivities with the monolith reactor operated under autothermal conditions.

Despite the impressive results achieved in the POM, a major difficulty still exists. For autothermal behavior to be attained, a low methane / oxygen mixture is fed to the reactor. When a mixture with a low methane / oxygen ratio contacts a high temperature catalyst, the potential for an explosion exists. The goal of this work was to design a reactor which will allow for an overall low methane / oxygen ratio mixture to be fed at high flowrates without premixing the methane and oxygen feeds before the catalyst bed. Based on our previous studies concerning the distribution of oxygen during the methane oxidative coupling reaction [19], we designed a configuration that uses a porous membrane reactor.

The objective of this study was to determine the conversion and selectivity of the methane partial oxidation reaction when using high feed rates, millisecond residence times and low methane / oxygen feed ratios in the membrane reactor configuration.

A Rh supported catalyst was chosen because Rh has been shown to be one of the most active and selective catalysts for methane partial oxidation [11,17,18]. Results in our laboratory using $LaRhO_3$ also showed that Rh containing catalysts are selective for syngas production [20]. A 3% Rh / TiO_2 was found to be the most active catalyst, igniting at 320°C in a fixed bed reactor using methane and oxygen feed rates of 500 and 250 cm^3 / min respectively. Experiments were performed initially in a fixed bed reactor to compare results with those obtained in the membrane reactor [21].

Finally, in order to understand the results obtained, a computer simulation was conducted based on a proposed mechanism by Schmidt and coworkers [22].

2. Experimental

2.1. Catalyst and membrane reactor

The 3% Rh / TiO_2 catalyst was prepared by the wet impregnation technique. The required amount of $RhCl_3 \cdot 2H_2O$ (Sigma Chemical) was dissolved in deionized water. Then the TiO_2 (mostly anatase) was added. The solution was stirred for approximately 30 min, then slowly heated so that all of the water evaporated. The resulting solid was then calcined in oxygen for 2 h at 600°C.

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The catalysts were characterized by XRD (Diano XPG-2X), XPS (Kratos XSAM-80) and H_2 chemisorption (pulse technique) before and after reaction.

The membrane reactor consists of a porous permeable ceramic membrane tube placed concentrically inside a quartz reactor (figure 1). The membrane tube (US Filter) is a porous alumina tube capable of achieving high permeation rates and withstanding high temperatures. The average pore diameter of the membrane tube is 5.0 μm which provides a permeability of 40,000 ℓ/(m^2 h). Methane is fed to the reactor on the shell side and flows in the annular space between the membrane tube and the reactor wall. Oxygen is fed to the tube side and flows exclusively inside the membrane tube whose upper portion has been made impermeable by a ceramic glaze. The end at the lower portion of the membrane tube is closed, leaving the permeable length at the bottom of the membrane tube as the only exit for the oxygen. The permeable length is surrounded by the catalyst powder on the outside of the tube allowing the oxygen and methane to be mixed only over the catalyst surface.

2.2. Procedure

The catalyst is externally heated to the expected ignition temperature under the flow of methane corresponding to the experiment. Upon reaching the expected ignition temperature, the reaction is ignited by initializing the flow of oxygen. Ignition occurs almost simultaneously to the introduction of oxygen. Therefore, for safety reasons, the oxygen concentration is maintained at a low value until the temperature stabilizes. After ignition, the furnace is turned off as the heat generated by the reaction is enough to sustain the reaction under autothermal behavior. Accordingly, the reaction condition was nearly adiabatic. When the experiments were repeated under the same conditions the results were reproducible within 5% on the average.

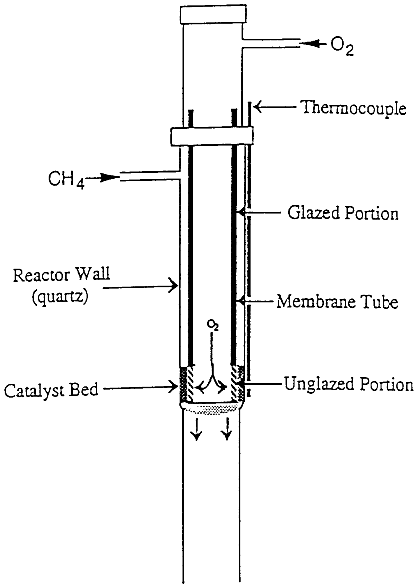

Figure 1. Schematic diagram of the membrane reactor.

Effluent gases first flowed through a water trap in an ice bath to condense water produced by the reaction. Water is further removed by using a drierite trap. The dry effluent flow rate was measured using a soap film bubblemeter and the effluent concentration was analyzed by gas chromatography (GC) using a 5 m × 1/8″ molecular sieve column to determine CH_4, O_2, H_2 and CO. CO_2 was determined using an infrared analyzer. Conversions were calculated as the difference between the inlet and outlet molar flow rates of methane or oxygen, divided by their inlet flow rates. The CO and H_2 selectivities were calculated as the molar flow rates of CO and H_2 in the effluent divided by the total amount of carbon oxides and H_2 and H_2O in the effluent respectively. Water flow rates were calculated by mass balance.

3. Results and discussion

3.1. Fixed bed reactor

To design the membrane reactor we first conducted an initial study of the operation of a fixed bed reactor under fast flow rates. All fixed bed reactor experiments were performed using the 3% Rh/TiO_2 catalyst. In all cases, ignition occurred at 320°C upon introduction of the oxygen flow. Ignition was followed by a rapid temperature increase to the steady state temperature. In addition, 100% oxygen conversion was achieved in all experiments and there was no evidence of hydrocarbon production.

The effect of catalyst loading was studied using methane and oxygen feed rates of 500 and 250 cm^3/min respectively (figure 2). Although methane conversion started at 43% at a loading of 7.5 mg, and reached a maximum of 77% at 60 mg, the conversion remained between 50 and 60% even with a seven-fold increase in catalyst loading. CO selectivity remained around 90% at all loadings, but hydrogen selectivity varied from about 50% at low loadings to around 75% at the higher loadings. The most notable observation is that oxygen conversion remained at 100% in all the experiments. At higher loadings, an increase in methane conversion would be expected, however, conversion remains fairly constant. The most likely reason for this result is that there is no longer any oxygen available to react with methane. Oxygen conversions of 100% were achieved in every experiment, and since increasing the amount of catalyst did not provide additional oxygen to react with the unconverted methane, its conversion remained constant. At low catalyst loading methane conversion is lower because the bed is not uniformly covered by the catalyst and some methane could pass through the bed without

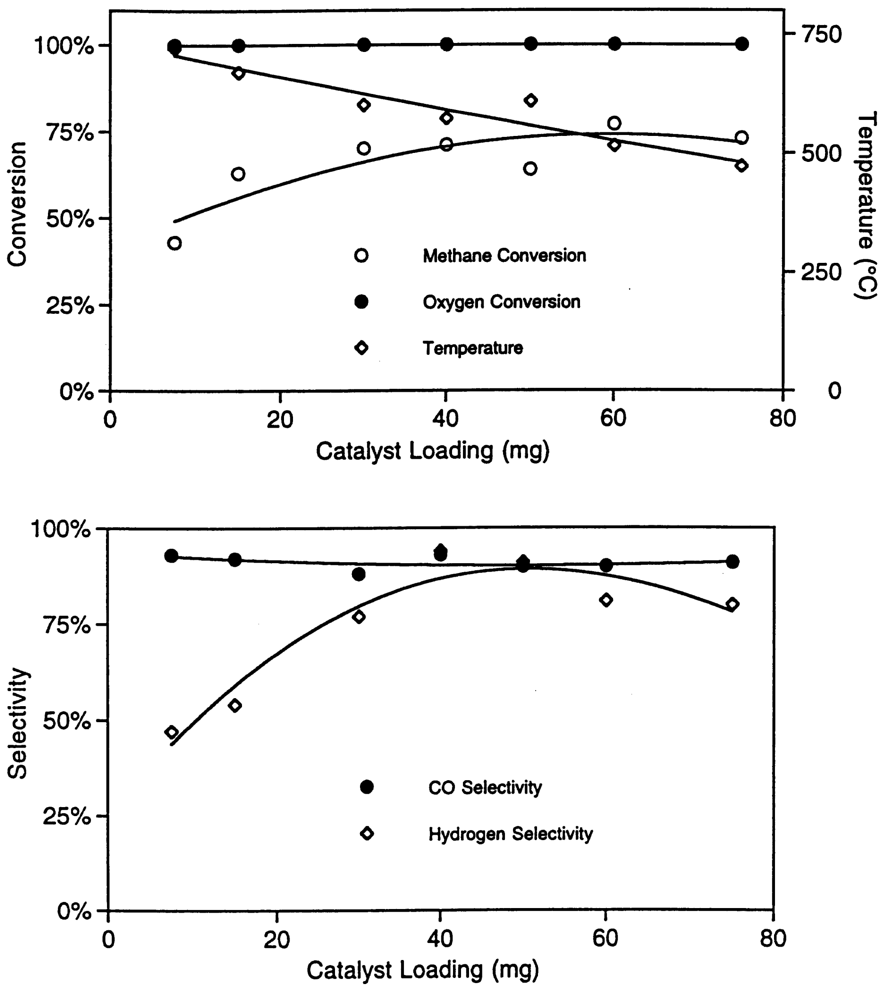

Figure 2. Effect of catalyst loading using the fixed bed reactor. The methane and oxygen feed rates were 500 and 250 cm^3/min respectively and the ignition temperature was set at 320°C.

contacting the catalyst. Despite the fact that hydrogen selectivity varied greatly, CO selectivity was unaffected by catalyst loading and remained around 90%. This would indicate that methane is converted primarily to syngas, but hydrogen could be oxidized to form water. The temperature appears to decrease linearly with increasing catalyst loading. At 7.5 mg, the temperature rose to 721°C and gradually decreased to 472°C at 75 mg. This could be due to the fact that more hydrogen (and therefore less water) is produced at higher loadings, and that the heat generation is spread out in a larger volume as loading increases.

The effect of varying the total feed rate in the fixed bed reactor while maintaining a 2/1 methane/oxygen feed ratio was studied using 30 mg of catalyst. The conversions and selectivities are shown in figure 3. The total feed rate was varied between 250 and 1500 cm^3/min which corresponds to residence times varying between 2.3 and 0.3 ms. As in the previous results with varying loadings, the hydrogen selectivity is the variable that is most sensitive to changes in operating conditions. For a three-fold increase in flow, hydrogen selectivity varied from 35 to 50%, and reached a maximum of 77% at 525 cm^3/min. Methane conversion increased from 54% at low flow rates to around 70% at higher flow rates, but it remained constant at flow rates greater than 500 cm^3/min. As in the results shown in figure 2, 100% oxygen conversion is achieved for all flow rates and CO selectivity remained constant near 90%. It was expected that the methane conversion would decrease as the residence time decreased. The lack of variation of methane conversion with feed rate is probably due to the fact that, at 100% oxygen conversion, the reaction occurs in a very narrow volume at the entrance of the bed. Increasing the flow rate in the range studied does not significantly affect the oxygen concentration profile in the catalyst bed and, therefore, the methane conversion remains nearly constant. The slight increase of methane conversion at the low flow rate is probably due to the initial temperature increase which promotes secondary reactions between methane and CO_2 or water. Once again it appears that at feed rates of 750 cm^3/min and above, the methane that reacts is primarily converted to syngas, but as the feed rate increases, more water is formed. At the

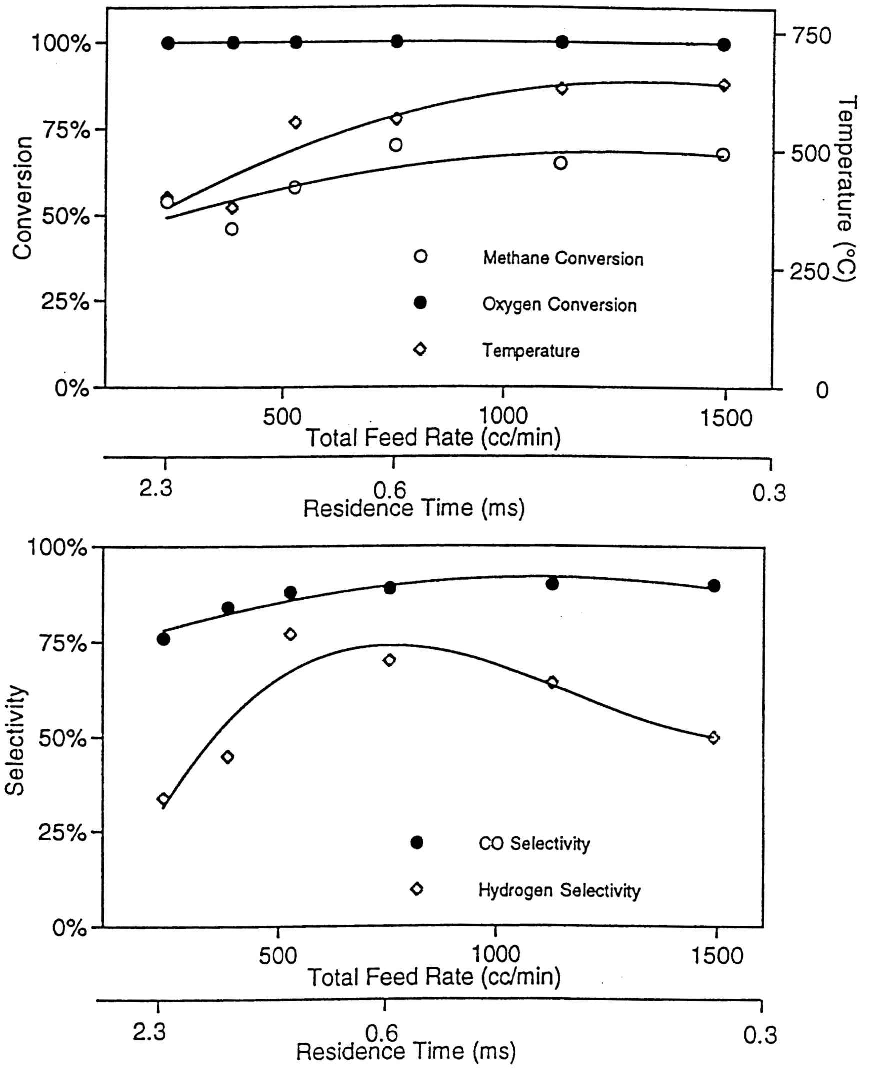

Figure 3. Effect of total feed rate using the fixed bed reactor. The methane/oxygen feed ratio was 2/1, 30 mg of catalyst were used and the ignition temperature was set at 320°C.

lower flow rates, conversion is lower because the temperature is lower. H_2 selectivity is lower at the lower flow rates because at higher residence time H_2 is oxidized to water. Temperature follows the same trends as methane conversion. At flow rates below 750 cm^3/min it increases with flow rate. At flow rates above 750 cm^3/min it increases only slightly. This is because as feed rates increase there is a higher total heat generation and therefore the reactor temperature increases. At the higher feed rate the rate of heat generation and heat removal are similar and the temperature remains almost constant with increasing flow rate.

The effect of reaction temperature on conversion and selectivities at a slow flow rate (methane and oxygen flow rates were 100 and 50 cm^3/min respectively), using external heating, was studied with a loading of 60 mg of catalyst. As in the previous results, oxygen conversion is 100% as shown in figure 4. Conversion and selectivities are comparable to those obtained under fast flow. Under autothermal condition, the temperature was determined by the energy balance and did not exceed 600°C at this slow flow rate. The external heating provided the additional energy required to reach higher temperatures and higher methane conversions. Figure 4 shows that oxygen conversion is 100% and methane conversion increases with temperature. At 800°C, methane conversion is 80%. Both H_2 and CO selectivities also increase with temperature. At 800°C, H_2 and CO selectivities are around 80 and 90% respectively. From this result, it is clear that, under the fixed bed conditions used, one of the most sensitive factors to get high methane conversion and high H_2 and CO selectivities is not only a short contact time, but high temperature. The high methane conversion and high H_2 and CO selectivities observed at short contact time are partly due to the exothermicity of POM reaction, which at short contact time (fast flow rate) leads to high catalyst temperature.

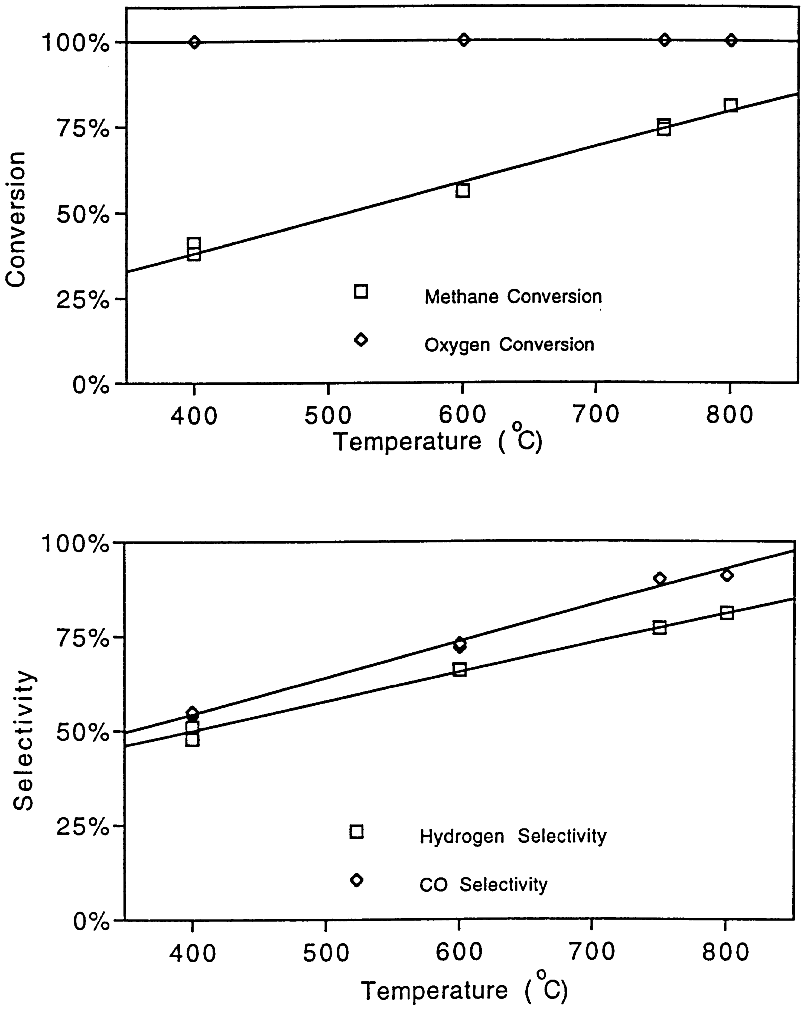

Figure 4. Effect of temperature on conversions and selectivities. $CH_4/O_2 = 2$, 60 mg of catalyst, total flow rate = 150 ml/min.

3.2. Membrane reactor

In all experiments wit 3% Rh/TiO_2 in the membrane reactor, the reaction ignited at 340°C, only 20°C higher than the fixed bed experiments. As with the fixed bed results, 100% oxygen conversion was achieved in every experiment, and there was no evidence of hydrocarbon production. Upon ignition, the temperature of the reactor increased until it reached a steady state value that depended on the operating conditions.

The first variable studied was the effect of catalyst loading. In these experiments methane and oxygen feed rates were maintained at 500 and 250 cm^3/min respectively. As in the fixed bed, the results (figure 5) show that oxygen conversion (100%) and methane conversion (60%) remain fairly constant even when the amount of catalyst was almost doubled. CO selectivity also remains nearly constant at around 80%, reaching 90% when using 60 mg of catalyst. The hydrogen selectivity shows the most dependence on catalyst loading. Hydrogen selectivity reached a maximum of 82% using 60 mg and decreased slightly as loading increases or decreases. The optimal condition in the membrane reactor occurred when the catalyst loading was just large enough to completely cover the permeable section of the membrane tube. Conversion was highest at loadings which are just over this minimum. At the higher loadings, methane conversion and hydrogen selectivity both decreased, which is an indication of oxygen reacting with the hydrogen product rather than with methane. It is clear that oxygen is the limiting reactant in this reaction. Increasing the catalyst loading exposes only a small fraction of the additional catalyst to the methane/oxygen mixture because the height of catalyst bed is higher than the permeable section of the membrane tube. Simulation results for a fixed bed reactor, presented later on, predicted that the reaction occurs only in a small region at the bed entrance. In the case of the membrane reactor, the active region is located near the wall of the membrane tube. Accordingly, increasing the catalyst loading did not significantly increase the active region as shown by the experimental observations. The temperature remained constant near 515°C throughout, regardless

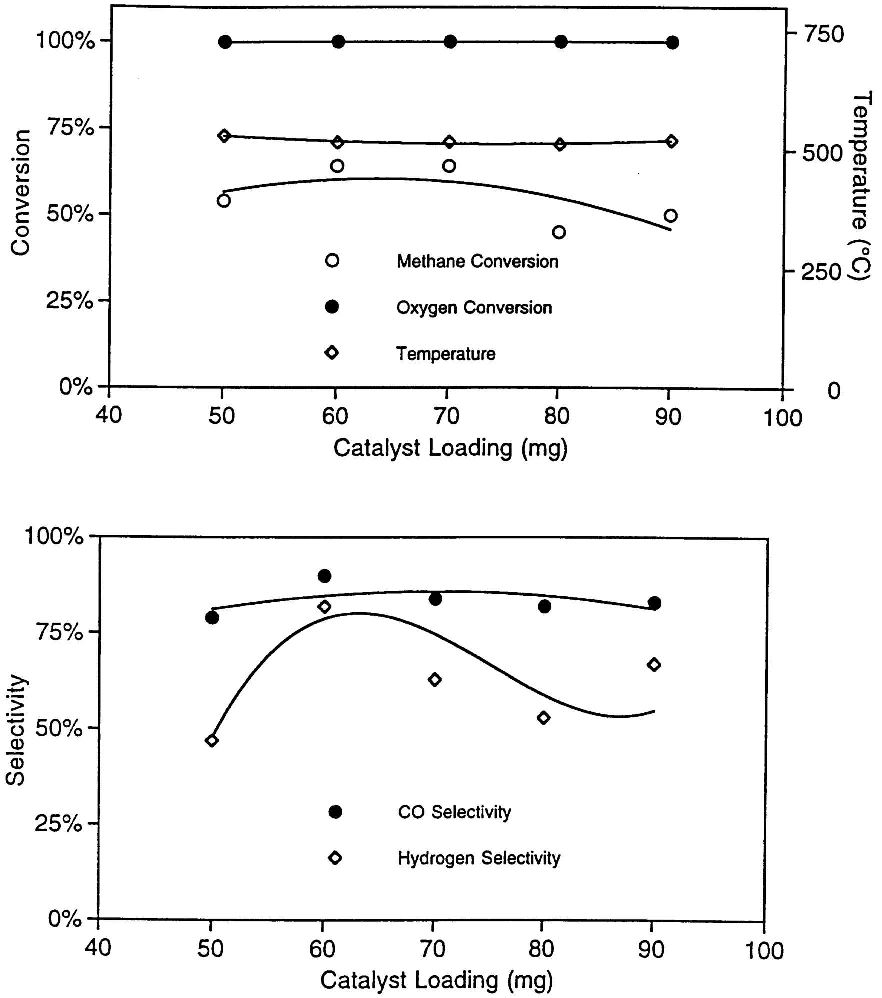

Figure 5. Effect of catalyst loading using the membrane reactor. The methane and oxygen feed rates were 500 and 250 cm^3/min respectively and the ignition temperature was set at 340°C.

of the loading. This indicates a higher thermal stability for the membrane reactor.

There are a few differences between the membrane reactor and the fixed bed reactor. The membrane reactor provides for a much safer reaction environment, but it yields slightly lower conversions and selectivities. The fixed bed reactor can achieve CO and hydrogen selectivities of 93% with methane conversions around 70%. The membrane reactor can achieve a methane conversion of 64% with CO and hydrogen selectivities of 90 and 82% respectively. The primary reason for the lower conversion is that the reactant gases distribution in the membrane reactor is different than in the fixed bed. In the latter case, methane and oxygen are mixed at the top of the catalyst bed, and throughout the reactor. In the membrane reactor, oxygen concentration is much greater near the membrane tube than towards the outer wall of the reactor. Consequently, in the design used in this study, some methane might not get in contact with the oxygen. This however is a matter of optimizing the reactor design. Nonetheless, the safer reaction environment that the membrane reactor provided permitted us to study the reaction at conditions that otherwise could be hazardous in a fixed bed reactor. In the membrane reactor, it is possible to lower the methane/oxygen feed ratio without the potential of an explosion.

Figure 6 shows the conversions and selectivities obtained when varying the feed ratio. In the following experiments, 60 mg of catalyst were used, and the methane feed rate was held constant at 500 cm^3/min. The methane/oxygen feed ratio had a much greater effect on reactor behavior than the other variables. Although oxygen conversion remains at 100%, methane conversion, syngas selectivity and temperature were affected by changes in methane/oxygen feed ratio. Methane conversion varied from as high as 64% at a ratio of 1/2 to as low as 44% at a ratio of 3/1. Hydrogen and CO selectivities varied from 22 and 67% at low ratios to 82 and 90% respectively at high ratios.

The important result obtained from these experiments is that both CO and hydrogen selectivities were significantly lower at the lower feed ratios, particularly

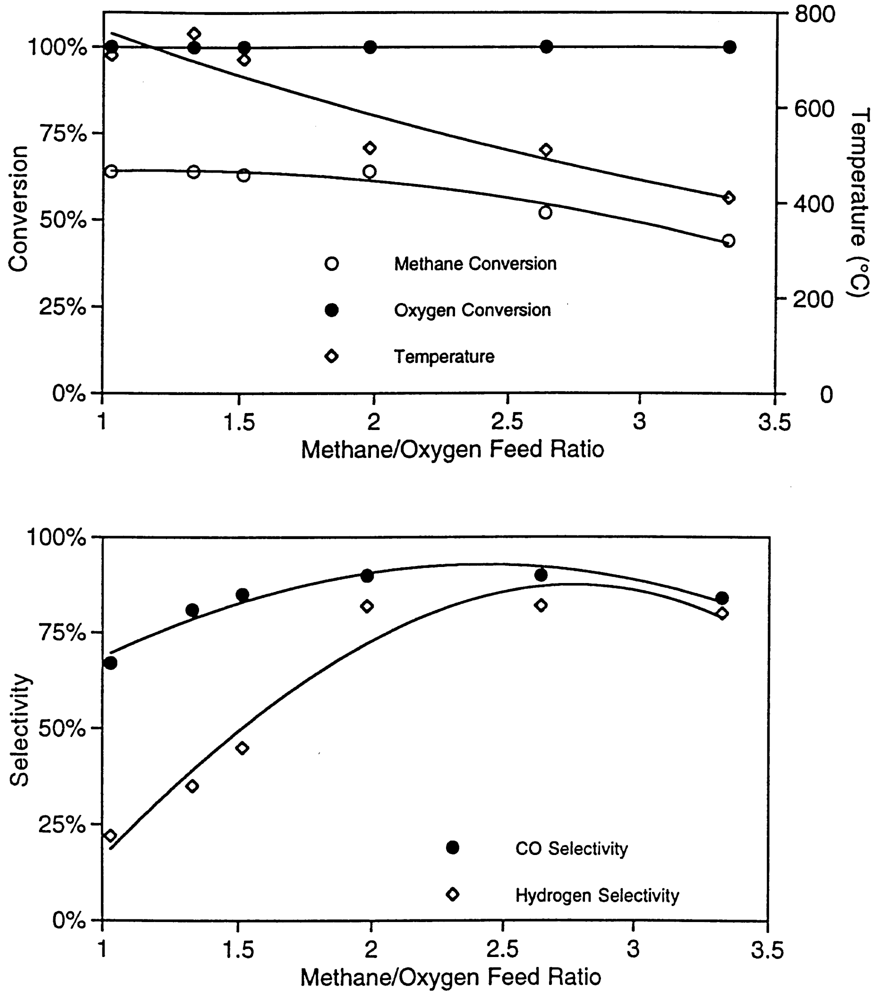

Figure 6. Effect of methane/oxygen feed ratio using the membrane reactor. The methane feed rate was 500 cm^3/min, 60 mg of catalyst were used and the ignition temperature was set at 340°C.

when the ratio was less than 2/1. The hydrogen selectivity fell below 25%, and the CO selectivity fell below 70%. This is an indication that the partial oxidation reaction is no longer dominant, instead, the complete combustion reaction predominates at lower feed ratio. This was corroborated by the large amount of water condensed in the traps and the larger amount of CO_2 detected in the product. This effect can be explained by the fact that at the lower feed ratios, more oxygen is available in the reactor to oxidize H_2 and CO to form water and CO_2. At higher feed ratios, the concentration of oxygen in the reactor is low, therefore the secondary reactions are less significant.

It should be noted, however, that for values of methane/oxygen above 2, the CO and hydrogen selectivities remain nearly constant around 90 and 80%, respectively. The decrease in temperature with increasing methane/oxygen ratio also is consistent with the role of the deep oxidation of the products as the cause of the lower selectivities. At feed ratios less than 2/1, the steady state temperature rises above 700°C, but as ratios equal to or greater than 2/1 the temperature is in the 500°C range. The higher temperature can be accounted for by the complete combustion reaction of hydrogen and oxygen to form water which has a higher heat of reaction than the partial oxidation reaction. As methane conversion decreases the heat generated decreases and the temperature decreases. Although 100% conversion of oxygen is achieved at low feed ratios, the methane conversion levels off at about 65%. Additional oxygen does not convert more methane, but instead it only results in more of the products being converted to CO_2 and water. At higher feed ratios the temperature is lower, further decreasing methane conversion. At a methane/oxygen feed ratio of 2/1, which is the stoichiometric ratio of the direct partial oxidation reaction, methane conversion and both CO and hydrogen selectivities are maximized.

The effect of total feed rate was studied in the membrane reactor using 60 mg of catalyst and a methane/oxygen feed ratio of 2/1. The total feed rate varied from 300 to 1200 cm^3/min corresponding to residence times of 3–0.8 ms respectively. The results (figure 7) show that,

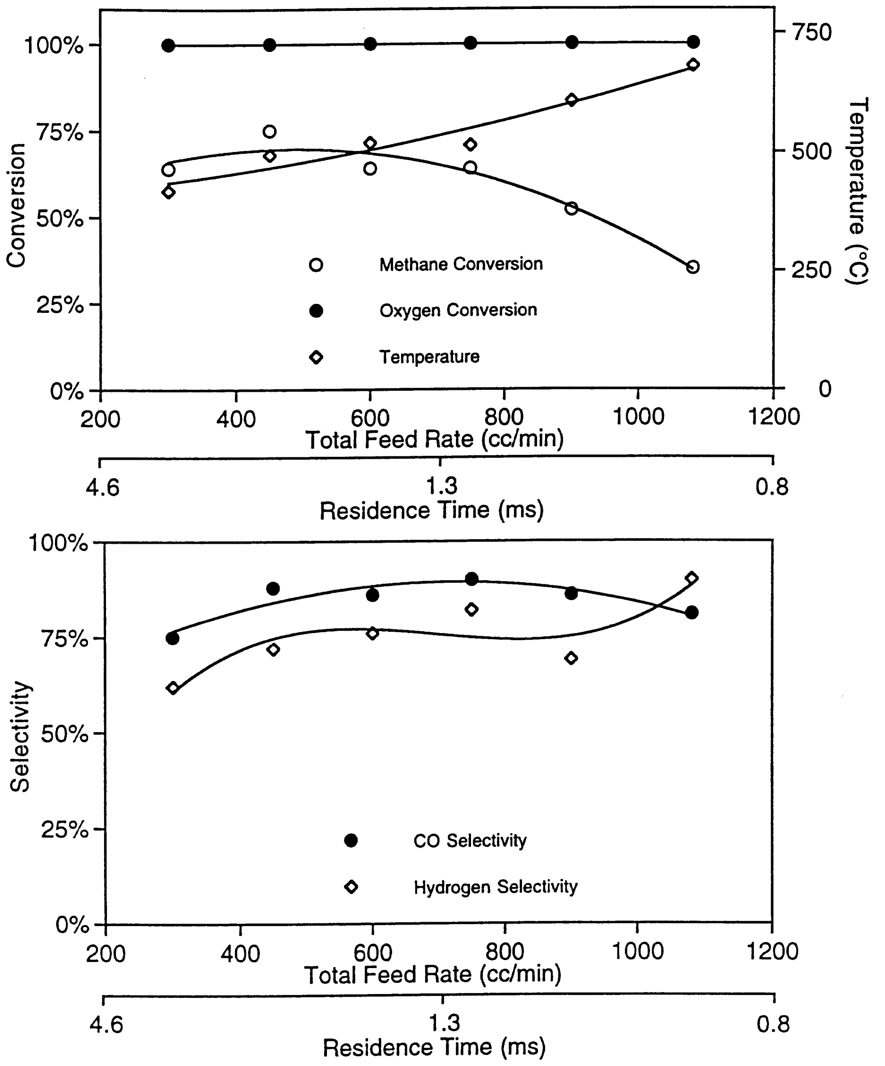

Figure 7. Effect of total feed rate using the membrane reactor. The methane/oxygen feed ratio was 2/1, 60 mg of catalyst were used and the ignition temperature was set at 340°C.

contrary to expectations, upon doubling the flow rate from 300 to 600 cm^3/min, methane conversion and H_2 and CO selectivities remained nearly constant at approximately 65, 70 and 80% respectively. In addition, as in the previous results, oxygen conversion remained at 100%. Methane conversion, which is nearly constant at 65% at feed rates of 600 cm^3/min and below, fell to only 35% when the flow rate was increased to 1080 cm^3/min. The CO and H_2 selectivities remained nearly constant throughout the whole range of flow rates, even when methane conversion decreased. The temperature was nearly constant around 515°C at the lower feed rates but increased to 680°C at 1080 cm^3/min. It would normally be expected that the temperature would decrease with decreasing conversions. However, although conversion is decreasing with increasing flow, overall syngas production is increasing leading to higher heat generation and higher temperature. It should be noted that higher feed rates were attempted, but in such cases the temperature rose out of control due to the large amount of heat evolved from an increased amount of syngas production. The effect of flow rate observed in the membrane reactor is somewhat different than what is observed in the fixed bed reactor. In the latter case, methane conversion remains nearly constant at higher flow rates, but in the membrane reactor, the conversion decreases significantly with increasing flow rate. This is due to the fact that in the fixed bed reactor, the reaction occurs in a narrow region at the top of the bed, but in the membrane reactor, the reaction occurs close to the membrane wall. Thus, it seems that the degree of mixing between the reactant decreases, as total flow rate increases. On the other hand, the decrease in mixing with increasing flow rate also results in higher hydrogen selectivities in the membrane reactor. In this case, there is a lower probability that hydrogen will react with oxygen to form water.

3.3. Catalyst characterization

To determine the phase of the titania during preparation and after reaction, XRD was used. The titania support prior to being impregnated was primarily in the anatase phase. There was a slight drop in the intensity of the anatase peaks for the calcined 3% Rh/TiO_2 catalyst as compared to the pure titania. The XRD results for 3% Rh/TiO_2 after the partial oxidation reaction showed that a phase transformation had occurred. Prior to reaction, the titania was primarily in the anatase phase, but after reaction, the titania was primarily in the rutile phase.

To determine the oxidation state of the rhodium, XPS analysis was performed. Prior to reaction, the Rh 3d peak position was 309.1 eV, but after reaction the peak position was 306.7 eV. This indicates that Rh is in a more oxidized state prior to the reaction. Further analysis of the fresh, unreacted catalyst indicated that the ratio of Rh/Cl was 4/1. This indicates that rhodium exists as some combination of rhodium metal, and rhodium chlorides and oxides because there is not enough chlorine present for rhodium to exist exclusively as Rh_xCl_y. We could also confirm the phase change in the titania after the reaction by XPS.

Chemisorption experiments were performed to determine the dispersion and the particle sizes after calcination. The amount of hydrogen adsorbed on the 3% Rh/TiO_2 corresponds to a dispersion of 56.8% and an average particle size of 1.9 nm.

3.4. *Theoretical reaction model for the fixed bed reactor*

The same elementary step model proposed by Hickman and Schmidt [17], shown in table 1, was utilized to interpret the fixed bed results. The model assumes that methane adsorbs dissociatively forming adsorbed carbon and adsorbed hydrogen (1). Oxygen adsorbs dissociatively (2) and the reaction of adsorbed oxygen and the adsorbed carbon yields CO (3), which then desorbs into the gas phase (4). Recombination of adsorbed hydrogen yields dihydrogen which desorbs into the gas phase (5). Further oxidation of CO yields CO_2 (6) and the reaction of adsorbed hydrogen and adsorbed oxygen yields adsorbed hydroxyls (7). These recombine or react with adsorbed hydrogen to yield adsorbed water (8, 9). It should be noted that chemisorption and dissociation of methane and CO_2 are assumed to occur simultaneously, and that methane chemisorption is assumed irreversible. In this model, it is also assumed that oxygen adsorbs on different sites than the other species. The kinetic equations and rate constants were obtained from the paper of Hickman and Schmidt [17].

The reactor parameters and operating conditions used in this model were all obtained from the experimental reactor conditions: input gas flow rate, 750 cm^3/min; gas temperature, 837 K; active catalyst surface area, 2244 cm^2; cross-sectional area of catalyst bed, 0.7895 cm^2; oxygen partial pressure, 0.35 atm; and methane partial pressure, 0.7 atm.

The results of the simulation were first compared with those reported by Hickman and Schmidt and found to be reproducible within 1% accuracy. Then, the reactor parameters were changed from the values corresponding to the monolith reactor simulated by Hickman and Schmidt, to those of the fixed bed used in this work. Simulation using the same kinetic constants reported by Hickman and Schmidt and our reactor parameters yielded a significant disagreement between the predictions and experimental results. The model predicted that the catalyst was covered mainly by CO. Consequently we decided to decrease the CO desorption activation energy from the value of 31.6 kcal/mol used by Hickman and Schmidt to a value of 25.5 kcal/mol.

As shown in figure 8, the model prediction fitted our

Table 1
Proposed reaction mechanism and kinetic parameters used in the model [a]

Reaction step		Forward			Reverse		
		A [b]	E_a [c]	k [d]	A	E_a	k
$CH_4 + 5S \rightarrow C{\cdot}S + 4H{\cdot}S$	(1)	3×10^4	5	1.4×10^3			
$O_2 + 2S \rightleftharpoons 2O{\cdot}S$	(2)	3.5×10^3	0	3.5×10^3	5×10^{12}	70	2.6×10^{-6}
$C{\cdot}S + O{\cdot}S \rightleftharpoons CO{\cdot}S + S$	(3)	5×10^{13}	15	6×10^9	1×10^{11}	40	3.58
$CO{\cdot}S \rightleftharpoons CO + S$	(4)	4×10^{13}	31.6	2.2×10^5	1.91×10^5	0	1.91×10^5
$2H{\cdot}S \rightleftharpoons H_2 + 2S$	(5)	5×10^{12}	18	9.9×10^7	2.25×10^5	0	2.25×10^5
$CO{\cdot}S + O{\cdot}S \rightleftharpoons CO_2 + 2S$	(6)	1×10^{12}	25	2.96×10^5	0		0
$H{\cdot}S + O{\cdot}S \rightleftharpoons OH{\cdot}S + S$	(7)	7×10^{12}	20	4.19×10^7	1×10^{13}	5	4.9×10^{11}
$2OH{\cdot}S \rightleftharpoons H_2O{\cdot}S + O{\cdot}S$	(8)	4×10^{15}	15	4.84×10^{11}	0		0
$H{\cdot}S + OH{\cdot}S \rightleftharpoons H_2O{\cdot}S + S$	(9)	3×10^{17}	8	2.4×10^{15}	5×10^{14}	37	1×10^5
$C{\cdot}S + H_2O{\cdot}S + S \rightarrow CO{\cdot}S + 2H{\cdot}S$	(10)	1.0×10^{13}	16.9	3.86×10^8			
$C{\cdot}S + CO_2 + S \rightarrow 2CO{\cdot}S$	(11)	1.0×10^5	24.4	4.25×10^{-2}			
$OH{\cdot}S \rightarrow OH + S$	(12)	8.1×10^{11}	34	1.1×10^{13}			
$H_2O + S \rightleftharpoons H_2O{\cdot}S$	(13)	7.4×10^4	0	7.4×10^4	1×10^{13}	10.8	1.5×10^{10}

[a] From Hickman and Schmidt [17].

[b] Preexponential factor.

[c] Activation energy (kcal/mol).

[d] Rate constant at 837 K.

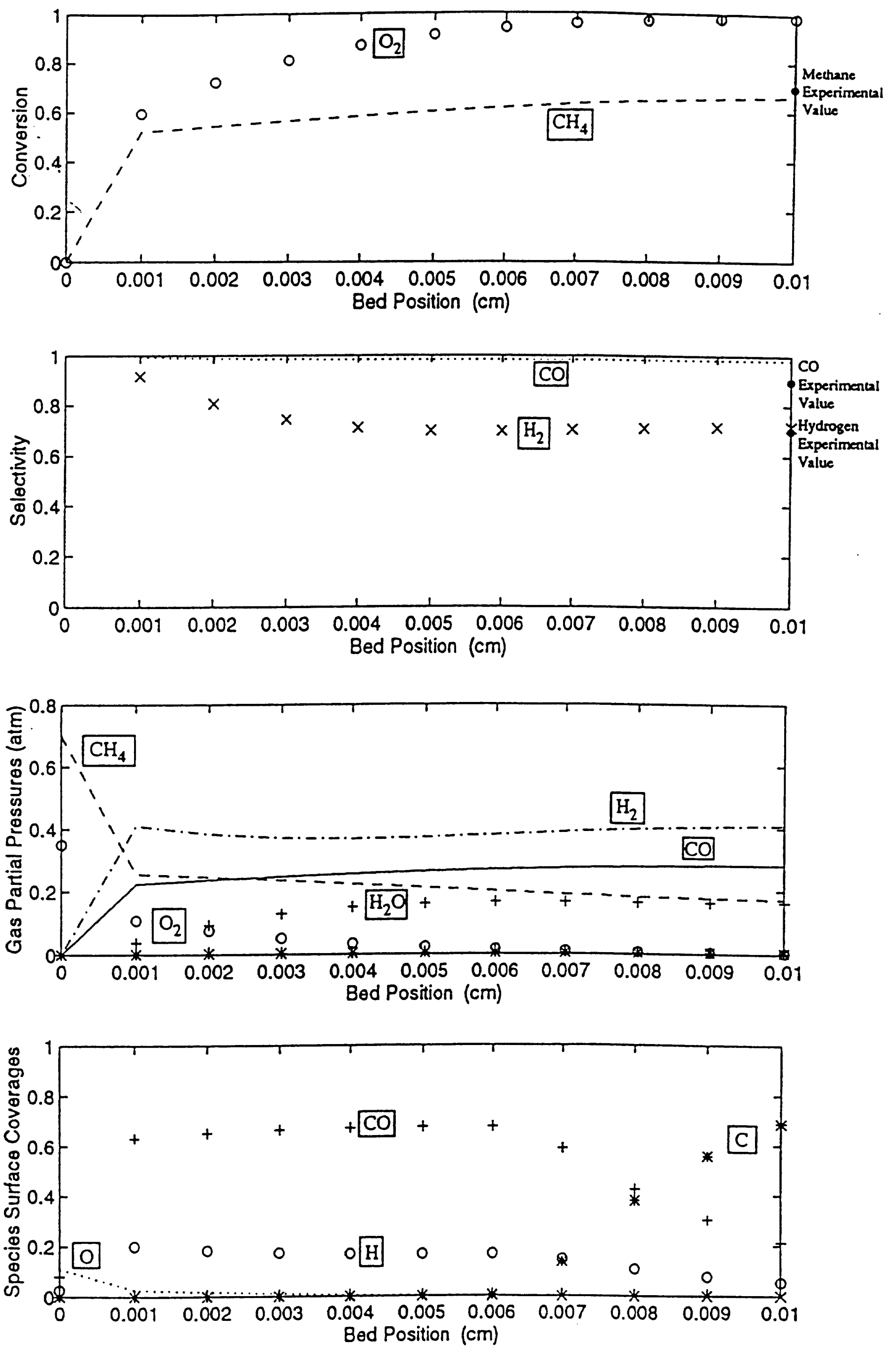

Figure 8. Model simulation of the partial oxidation reaction using the adjusted value for the CO desorption activation energy.

results fairly well using the lower CO desorption activation energy. Oxygen conversion matches the experimental results at 100%, and the methane conversion differs by only 4% (66% model, 70% experiment). CO selectivity differs by 8% (98% model, 90% experiment) and hydrogen selectivity differs by only 2% (72% model, 70% experiment). CO is the primary species on the surface through the first 3/4 of the catalyst bed at which point it begins to decrease and the carbon coverage increases. By the midway point of the bed, there is no longer any oxygen on the surface.

It is obvious that the desorption of CO is one of the key reaction steps in the partial oxidation reaction. A relatively slight variation in the CO activation energy resulted in a significant difference in the model simulation. Not only do the conversions and selectivities provide a better match, but the simulated effluent is much closer to the concentrations obtained in fixed bed experiments. The key observation that can be drawn from the model simulation is that most of the reaction occurs at the beginning of the catalyst bed. After only 10% of the catalyst bed, 53% methane conversion is achieved indicating that 80% of the methane converted, is converted in the first 10% of the bed. As suspected, the main reason that only 70% methane conversion is achieved, is that all of the oxygen is consumed within the first half of the catalyst bed. Past the midway point in the catalyst bed there is no longer any oxygen in the gas stream or on the surface that could react with the methane. This result would explain why all of the changes made to the operating conditions, as performed in both fixed bed and membrane reactor experiments, have only a small effect on conversion and selectivity. Increasing catalyst loading, temperature, or total flow rate does not supply additional oxygen to the second half of the catalyst bed and it does have a negligible effect on syngas productivity.

In order to ascertain the effect of the steam and dry reforming reactions, these two reaction steps were added to the model. The parameters for the reforming reactions were taken from literature [17–22]. Neither the dry nor the steam reforming reaction had a significant effect on conversion or selectivity as the values remained below 30% as before. The kinetic parameters of the dry reforming reaction were then varied in an attempt to raise the conversion, but even when raising the preexponential factor from 1.0×10^5 to 1.0×10^{13} and lowering the activation energy from 24.4 to 17 kcal/mol, the conversion and selectivities remained below 30%. This would indicate that the reforming reactions are not relevant to the autothermal reaction and the necessary modification to the model is the lowering of the CO desorption activation energy. This would also support the hypothesis that methane partial oxidation occurs by direct oxidation in the experiments performed in the fixed bed reactor.

The sensitivities of the kinetic parameters were studied in order to determine which reaction steps are the most important in determining the activity and selectivities of the partial oxidation reaction. Specific reactions were targeted rather than testing all reactions. The study focused on reactions with lower rate constants at 837 K, which is the median temperature throughout the fixed bed experiments. Reactions with low rate constants were chosen because they are the ones which are most likely rate determining. Several reactions were chosen, the most obvious being CO desorption (4) and methane adsorption and dissociation (1). Oxygen adsorption (2) was also chosen because it had a low rate constant. In addition, the steam and dry reforming reactions were tested to determine if they affected the yields.

As suspected, the two steps having the greatest impact on the conversion and selectivities are CO desorption and methane adsorption and dissociation. Small changes in the CO desorption activation energy or in the preexponential factor of the methane adsorption reaction resulted in significant increases in methane conversion and hydrogen selectivity. Oxygen adsorption had a smaller effect on conversion and selectivity, but the conversion and selectivities increased by decreasing the preexponential factor. The steam reforming reaction also had a slight effect on the results, but only when the activation energy was cut in half. Varying the rate of the dry reforming reaction and the OH desorption reaction had no effect on the simulation results.

The results of this study indicate that the key steps in methane partial oxidation are methane adsorption and CO desorption. It would appear that methane adsorption is immediately followed by the reaction with oxygen. As it has been observed experimentally, oxygen is consumed very rapidly. Therefore, a key step in achieving high methane conversion and hydrogen selectivity is fast adsorption of methane, which would result in oxygen reacting with carbon instead of hydrogen. A good partial oxidation catalyst should have a relatively low activation energy for CO desorption and a high rate of methane adsorption. The results of this study support the previous hypotheses by Schmidt and coworkers that CO is formed by the direct oxidation of surface carbon with surface oxygen. The dry reforming reaction, which is the key reaction in the reaction sequence proposed by Baerns and coworkers [23], has little effect on the model simulation. The direct partial oxidation model adequately predicts the experimental data.

4. Conclusion

The catalytic partial oxidation of methane to synthesis gas on a Rh/TiO_2 catalyst has been demonstrated to occur at high conversions and selectivities under fast flow conditions when a porous membrane is used to feed separately the methane and oxygen streams. This configuration allows operation of the reactor at low methane/oxygen ratios and high feed rates eliminating the possibility of a flame flashback which could lead to an explosion. The low methane/oxygen ratio and the high flow rates are the key factors to attain autothermal behavior. One of the most sensitive factors to attain high conversion and selectivities is not only short contact time (high flow rate) but high temperature. The model indicates that 80% of the reaction occurs within the first 10% of the catalyst bed and that the key steps in methane partial oxidation to synthesis gas are the dissociative adsorption of methane and CO desorption. The Rh/TiO_2 catalyst exhibited a low ignition temperature and did not exhibit deactivation during the duration of these experiments.

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