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Catalytic partial oxidation of methane in a novel heat-integrated wall reactor

Theophilos Ioannides and Xenophon E. Verykios*

Department of Chemical Engineering, University of Patras, GR-265 00 Patras, Greece

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A novel reactor has been developed and applied in the reaction of partial oxidation of methane to synthesis gas. The reactor consists of a ceramic tube in the inner and outer surface of which a metal catalyst film is deposited. The CH_4/O_2 feed enters into the tube and a large fraction of the heat generated on the wall by methane combustion is transported across the tube wall towards the outer catalyst film, where the endothermic reforming reactions take place. In this way, the temperature in the combustion zone is controlled and hot spots are significantly reduced in magnitude. Initial results presented in this work demonstrate the feasibility of the concept.

Keywords: synthesis gas, methane partial oxidation, wall reactors

1. Introduction

Catalytic partial oxidation (CPO) of methane has been the subject of extensive research efforts in recent years, as an alternative process to steam reforming for the production of synthesis gas. Work in this field has been recently reviewed by Pena et al. [1]. The reaction is catalyzed by group VIII metal catalysts, such as Ni, Rh, Ru, Pt, Ir and Pd. In the majority of cases, synthesis gas is produced indirectly, i.e. via the following reaction scheme [1,2]:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (1)$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad (2)$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (3)$$

according to which part of methane is initially combusted by supplied oxygen towards CO_2 and H_2O and reforming of the remaining methane with CO_2 and H_2O produced primarily takes place subsequently, leading to formation of synthesis gas. Direct formation of synthesis gas via reaction of CH_4 and O_2 has been reported in the case of Ru/TiO_2 catalysts [3,4] and of Rh- or Pt-loaded monoliths operating at high temperatures (1000°C) and short contact times ($\sim$10 ms) [5,6].

A major issue in the process of partial oxidation of methane is the heat management of the reactor. Methane combustion (reaction (1)) is strongly exothermic ($\Delta H \approx 800$ kJ/mol CH_4) and the heat produced at the first part of the catalytic bed can result in hot spots of considerable magnitude, considerably exceeding 1000°C. Simulations of an adiabatic fixed-bed reactor containing a Ni/Al_2O_3 catalyst show that for a CH_4/O_2 feed with a ratio of 1.67 the hot-spot temperature can be as high as 1500°C [7]. The strongly endothermic reforming reactions which take place at downstream sections of the bed lead to cooling of that part of the reactor. This highly uneven temperature profile in a fixed-bed CPO reactor raises serious questions related to catalyst and reactor durability, catalyst stability and to the maximum obtainable methane conversion.

Several types of catalytic reactors have been considered for this reaction, in addition to conventional fixed-bed reactors. Fluidized-bed reactors seem promising because of their good heat transfer properties. Studies of CPO of methane in such reactors have been reported by Bharadwaj and Schmidt [8] and Olsbye et al. [9]. Alternative catalyst bed configurations, such as dual-bed or mixed-catalyst bed reactors have been examined by Ma and Trimm [10], while dense oxygen-selective, as well as porous or dense, hydrogen-selective membrane reactors have been also investigated [11–13]. Reactors of the monolithic type have been extensively studied by Schmidt and co-workers [5,6,14]. Rh-loaded monoliths have been found to be the most selective and stable for synthesis gas formation.

In the present work, a new reactor concept is proposed which can resolve the heat management problem of the CPO reaction in an efficient manner. In addition, the proposed reactor is simple to construct and operate. This is the *heat-integrated wall reactor* (HIWR), which, in its simplest form, is shown schematically in figure 1. The reactor comprises of a non-porous ceramic tube of high thermal conductivity (i.e. alumina) in the inner and outer surface of which a metal catalyst is deposited in the form of a film. The reactor design offers the flexibility to deposit different catalysts on the inner and outer surface

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* To whom correspondence should be addressed.

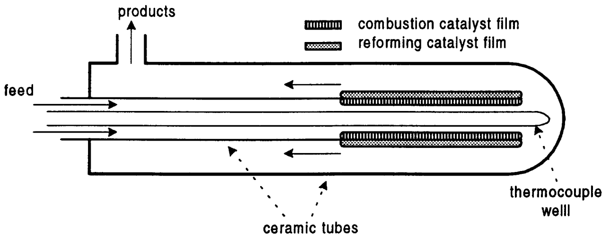

Figure 1. Schematic diagram of the heat-integrated wall reactor (HIWR).

of the tube. Thus, a catalyst highly active for combustion, such as Pt or Rh, may be deposited on the inner surface, while a reforming catalyst, such as Ni or Rh, may be deposited on the outer surface. The catalyst may be deposited directly on the reactor wall or on a washcoat which is anchored to the reactor wall. The ceramic tube is enclosed in a larger ceramic tube of low thermal conductivity. The feed enters into the inner tube where the exothermic methane combustion takes place. A large fraction of the heat generated on the wall (where the catalyst is) is transported across the tube wall towards the outer surface where the endothermic reforming reactions take place. In this way the temperature in the combustion zone is controlled and runaway conditions can be avoided. The feed to the reactor is also preheated by the products, as they are carried away from the reactor. In an industrial scale application, the reactor may comprise of a series of ceramic tubes placed in a bundle inside an insulated vessel. In this configuration, the HIWR can easily be operated in the adiabatic mode.

In the present communication, the results of the application of this reactor in the reaction of partial oxidation of methane are presented and the feasibility of the concept is demonstrated. The performance of the heat-integrated wall reactor is compared to the performance of a conventional wall reactor (CWR), which contains the catalyst layer on the inner surface of the reactor tube only.

2. Experimental

The reactor tube employed in the construction of the laboratory-scale HIWR is a non-porous alumina tube of dimensions 6 mm o.d. × 4 mm i.d. × 51 cm length (Alsint, ETK). The outer ceramic tube (Pythagoras, ETK) had dimensions of 12 mm o.d. × 8 mm i.d. × 41 cm length, while the thermocouple well, placed in the center of the inner tube, was an alumina tube of dimensions 3 mm o.d. × 2 mm i.d. The catalyst employed in this work was Rh/Al_2O_3. It has been reported that rhodium is an active and stable catalyst for the reaction of partial oxidation of methane [5,6,13]. The Rh/Al_2O_3 catalyst (4.6 wt% Rh) was deposited on the wall of the reactor tube by dip-coating of a $Rh–Al_2O_3$ sol, prepared according to the following procedure [15]: Aluminum isopropoxide was added under vigorous stirring into excess water (molar ratio $H_2O/\text{alkoxide} = 100$) at the temperature of 75°C. After stirring for 20 min, a $Rh(NO_3)_3$ solution in HNO_3 was added to the slurry. The amount of the rhodium salt corresponded to 4.6 wt% Rh in the final catalyst. The molar ratio $HNO_3/\text{alkoxide}$ was 0.1. After peptization, the formed clear red-brown sol was stored in a closed container.

The catalyst film was deposited over a length of 10 cm at one end of the alumina tube. As a first step, a quantity of catalyst of 1.5 mg was deposited on the inner surface *only* by a single dip-coating. The term conventional wall reactor (CWR) is used to denote this reactor configuration. After testing under reaction conditions, a single catalyst layer was also deposited on the outer surface of the reactor tube. This reactor configuration is called HIWR-A. As a final step, an additional amount of catalyst was deposited both on the inner and outer surfaces of the same reactor tube. This reactor is denoted as HIWR-B. The characteristics of the three reactors are shown in table 1. It is estimated that the thickness of the catalyst film is of the order of 100–300 nm. Regarding the homogeneity of the distribution of the catalyst film, it was observed that there were patches along the outer surface which appeared more black than the rest of the surface. This inhomogeneity was random along the reactor and is most probably due to the non-perfect cylindrical surface of the alumina tube. Adhesion of the film on the tube was excellent.

Tests under reaction conditions were carried out employing an undiluted CH_4/O_2 feed of 2 : 1 ratio at atmospheric pressure. The feed flow rate was in the range of 60–1050 cm^3 STP/min and was controlled by thermal mass flow controllers (MKS instruments). The reactor was operated inside a single-zone tubular furnace. Experiments were carried out at a furnace tem-

Table 1
Wall reactor characteristics

Reactor	Catalyst film		
	length (cm)	position	catalyst loading (mg)
CWR	10	on inner surface only	1.5
HIWR-A	10	on both inner and outer surfaces	3
HIWR-B	10	on both inner and outer surfaces	8

perature of 700°C. The temperature variation along the catalyst film under nitrogen flow was 30–40°C, whereas the temperature at the middle of the film was 700°C and 660–670°C at the beginning and end of the film. Temperature profiles along the bore of the reactor were measured by a thermocouple, as shown in figure 1. Two gas chromatographs were used for the analysis of reactants and products, which were calibrated with certified standards. The error of the experimental results is estimated to be 1–2%. CH_4, O_2, CO and CO_2 were analyzed in a Carboxen 1000 column with He as a carrier gas, while hydrogen was analyzed in the second chromatograph employing N_2 as the carrier gas. H_2O produced in the reaction was condensed in a condenser located downstream of the reactor. No appreciable amounts of C_{2+} hydrocarbons were observed in the reactor effluent under any circumstances.

3. Results and discussion

3.1. *Temperature profile of conventional wall reactor (CWR)*

Initial experiments were conducted with a reactor containing the catalyst on the inner surface of the reactor tube only (CWR, table 1). The temperature profiles under reaction conditions for the CWR are presented in figure 2 for a nominal furnace temperature of 700°C and CH_4/O_2 feed flow rates in the range of 60–450 cm^3 STP/min. The catalyst film starts at $z = 0$ cm and is 10 cm long. The point at $z = 11$ cm denotes the position of the outer tube enclosing the reactor tube. A large rise in temperature is observed in all cases at the first part of the catalyst film, due to the exothermic reaction of methane combustion. The hot-spot temperature becomes higher as the flow rate increases. At a flow rate of 450 cm^3/min the hot-spot temperature is 1032°C. Higher flow rates were not employed to avoid runaway conditions and damage of the reactor materials. Tests were also conducted at a lower furnace temperature (600°C). The temperature profiles were similar to those measured at 700°C but a hot-spot temperature of 1030°C was now obtained at a flow rate of 600 cm^3/min. Towards the end of the catalyst film the reactor temperature becomes lower than the furnace temperature (negative ΔT) due to the endothermic reforming reactions, which take place in this region (figure 2). The behavior of the reactor with respect to temperature demonstrates the problems associated with the heat management of the CPO of methane reaction. These problems relate to the very rapid release of large quantities of heat and the subsequent control of the significant hot spot at the first part of the catalyst film or bed. At the same time, maintaining high temperatures at the end of the catalyst film, so as to maximize methane conversion, is an additional important requirement which must also be satisfied.

3.2. *Temperature profile of heat-integrated wall reactors (HIWR-A and HIWR-B)*

The temperature profiles of the reactor HIWR-A under reaction conditions are presented in figure 3 for a nominal furnace temperature of 700°C and feed flow rates in the range of 60–840 cm^3/min. The observed profiles show that deposition of catalyst on the outer surface of the reactor tube has led to a drastic alteration of the shapes of the temperature profiles at high flow rates,

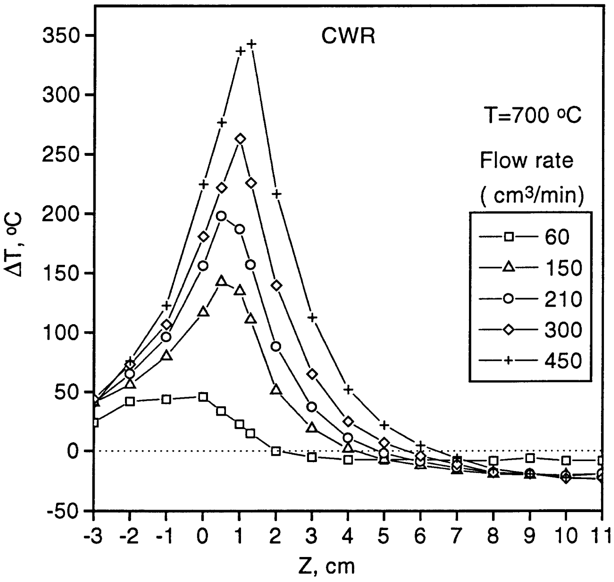

Figure 2. Temperature profiles along the conventional wall reactor (CWR) under reaction conditions with varying feed flow rate.

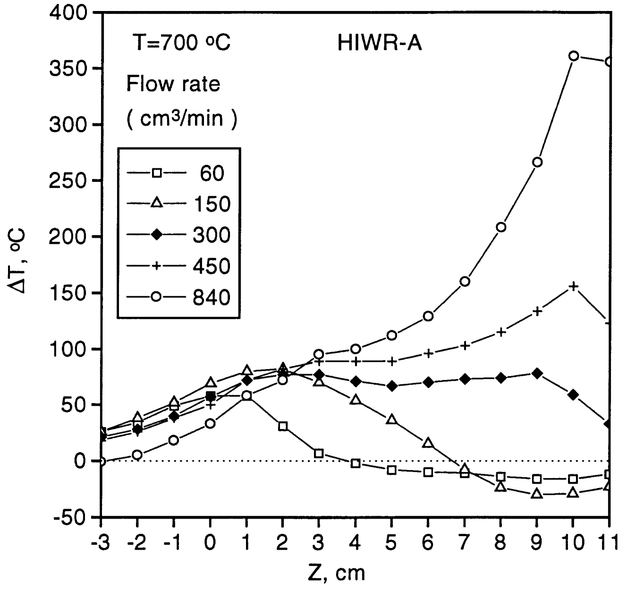

Figure 3. Temperature profiles along the heat-integrated wall reactor (HIWR-A) under reaction conditions with varying feed flow rate.

compared to those observed in the conventional reactor. At low flow rates (60 cm^3/min), the observed profile is similar to that of the CWR. As flow rate increases, there is *no* development of hot spot at the first part of the catalyst film, as in the case of the CWR, but rather a uniform temperature profile develops. The temperature profile at a flow rate of 300 cm^3/min, for example, shows that the catalyst film has an almost uniform temperature, approximately 80°C higher than the furnace temperature, while the corresponding profile of the CWR at the same flow rate exhibits a hot spot of 265°C (figure 2). As the flow rate is increased further, a hot spot develops *at the end* of the catalyst film.

The corresponding temperature profiles under reaction conditions for the reactor HIWR-B are presented in figure 4 for feed flow rates in the range of 60–900 cm^3/min. The observed profiles are qualitatively similar to those observed for the reactor HIWR-A. Due to the larger amount of catalyst loading in HIWR-B, an almost uniform temperature profile is now developed at a flow rate of 600 cm^3/min, compared to a flow rate of 300 cm^3/min for the HIWR-A. The observed uniform temperature rise, in this case, is 100–125°C, while the hot spot in the CWR is larger than 350°C under the same conditions.

The observed behavior of the heat-integrated wall reactors can be explained as follows:

(i) At low flow rates the contact time is sufficiently large and the exothermic methane combustion is completed at the first 2–3 cm of the catalyst film. In this case, the endothermic reforming reactions already commence on the inner surface, as evidenced by the negative ΔT observed after the first part of the catalyst film. This is more clearly seen in the case of the HIWR-B, which contains a larger amount of catalyst.

(ii) As flow rate increases, the temperature profiles become gradually more uniform. At a specific flow rate, which depends on the amount of catalyst deposited on the reactor tube, temperature profiles are almost flat. This happens because consumption of heat by the reforming reactions, taking place on the outer surface of the reactor tube, lowers the catalyst temperature and the combustion rate is reduced accordingly. As a consequence, a larger catalyst area is required for methane combustion, which in this case corresponds to the entire inner catalyst film.

(iii) As the flow rate increases further, breakthrough of the combustion reaction to the outer catalyst film takes place. At the end of the reactor tube ($z = 9$–10 cm) combustion takes place both on the inner and outer surfaces causing excessive heating of this region and the hot spot is stabilized at the end of the reactor tube. The hot spot is lower in the case of HIWR-B, which contains a larger amount of catalyst.

3.3. Comparison of the performance of conventional wall and heat-integrated wall reactors

The methane conversion obtained over the conventional wall reactor (CWR) and the two heat-integrated wall reactors (HIWR-A and HIWR-B) at a furnace temperature of 700°C is shown as a function of feed flow rate in figure 5. It can be seen that in the range of flow rates which were examined, methane conversion in HIWR-A and HIWR-B is considerably higher than methane conversion in CWR. Methane conversion is also higher in HIWR-B than in HIWR-A, because of the larger cat-

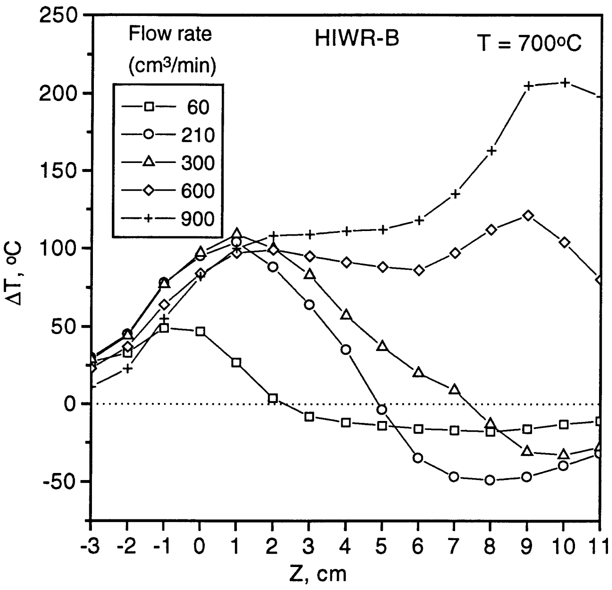

Figure 4. Temperature profiles along the heat-integrated wall reactor (HIWR-B) under reaction conditions with varying feed flow rate.

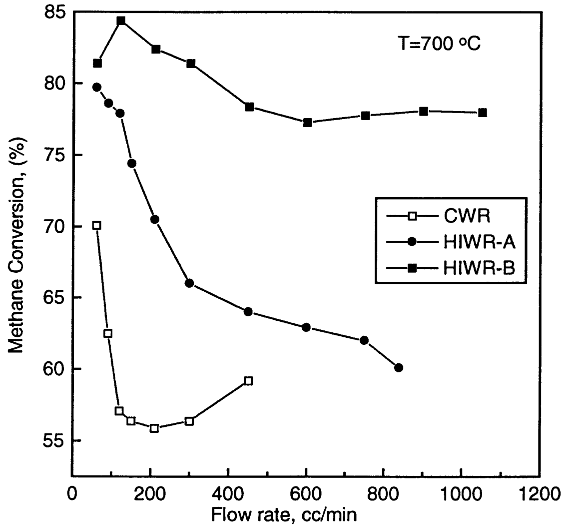

Figure 5. Methane conversion obtained in the conventional-wall (CWR) and the two heat-integrated wall reactors (HIWR-A and HIWR-B) under CPO of methane conditions as a function of feed flow rate.

alyst loading of HIWR-B. It is noteworthy that the observed enhancement of methane conversion is accompanied by significant lowering of the hot-spot temperatures, and, generally, higher uniformity in temperature in the case of the heat-integrated wall reactors, as shown in the previous sections. The observed increase in methane conversion in the heat-integrated wall reactors should not be attributed to their larger catalyst loading, but rather to their more efficient heat management characteristics. The observed temperature profiles in the CWR clearly demonstrate that synthesis gas is produced mostly via the indirect route and the reactions of methane combustion and methane reforming take place sequentially at different parts of the catalyst film. As a consequence, the heat generated by methane combustion causes the creation of hot spots and cannot be utilized efficiently to drive the reforming reactions. Increase of the catalyst loading in the conventional reactor would probably do little to change this picture.

The selectivity towards CO formation obtained over the conventional and the heat-integrated wall reactors is presented in figure 6 as a function of feed flow rate. In the case of the two heat-integrated reactors, the dependence of CO selectivity on the feed flow rate is similar. CO selectivity is higher in HIWR-B than in HIWR-A, which is in harmony with the fact that methane conversion is also higher in this reactor. At low flow rates (~60 cm^3/min) the observed CO selectivity over all reactors is very close to the equilibrium values corresponding to the reactor exit temperatures in each case (650°C for the CWR and ~700°C for HIWR-A and HIWR-B). In the case of the CWR, CO selectivity exhibits a rather steep minimum at a flow rate of 120 cm^3/min, while, at a flow rate of 450 cm^3/min, it becomes even higher than the selectivity in HIWR-B. The actual values of CO selectivity at a flow rate of 450 cm^3/min are 87% for the CWR and 82% for HIWR-B, while the corresponding methane conversions are 59 and 78%, respectively. Thus, CO selectivity in the CWR is higher than that of HIWR-B, in spite of the fact that methane conversion is significantly lower in the CWR. This observation might imply that part of CO is produced via the direct route in the CWR, probably at the first zone of the catalyst film where the temperature is of the order of 1000°C (figure 2). The contribution of homogeneous reactions in CO formation (taking place in the hot zone of the reactor) is estimated to be rather small. Experiments with a blank reactor tube showed that the rate of homogeneous reactions is considerably lower than the rate of catalytic reactions under these conditions, although the selectivity towards homogeneous CO formation was comparable (~80%) to that observed in the presence of catalyst. Direct formation of CO has been reported by Schmidt and co-workers [5,6] in the case of Rh- or Pt-loaded monoliths operating at 1000°C. The temperature in the HIWR-B, on the other hand, does not exceed 820°C under the same conditions.

The selectivity for H_2 formation obtained over the conventional and the heat-integrated wall reactors is presented in figure 7 as a function of feed flow rate. Hydrogen selectivity is significantly higher in the case of the heat-integrated reactors, being of the order of 95% in HIWR-B. At low flow rates (~60 cm^3/min), the observed hydrogen selectivity over all reactors is very close to the equilibrium values corresponding to the reactor exit temperatures in each case (650°C for the CWR and ~700°C for the HIWR). Comparison of figures 5 and 7 shows that both methane conversion and selectivity for H_2 formation vary in the same manner

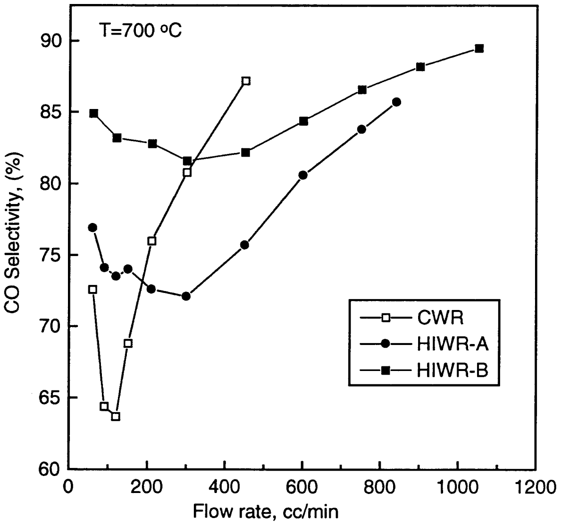

Figure 6. CO selectivity obtained in the conventional wall (CWR) and the two heat-integrated wall reactors (HIWR-A and HIWR-B) under CPO of methane conditions as a function of feed flow rate.

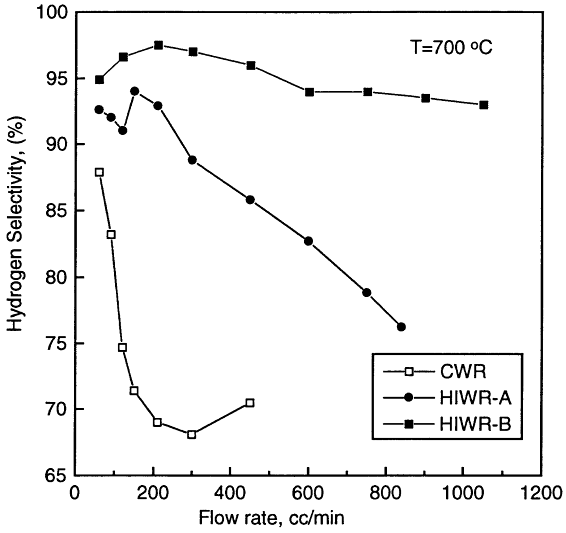

Figure 7. Hydrogen selectivity obtained in the conventional wall (CWR) and the two heat-integrated wall reactors (HIWR-A and HIWR-B) under CPO of methane conditions as a function of feed flow rate.

with feed flow rate. This is not observed in the case of CO selectivity as it can be inferred by comparison of figures 5 and 7 with figure 6. Thus, in the entire range of flow rates examined, hydrogen selectivity almost invariably decreases when methane conversion decreases. CO selectivity, on the other hand, increases at high flow rates despite the fact that methane conversion might decrease. As stated in the previous paragraph, this observation implies that part of CO is produced via the direct route in the hot zone of the reactor. Hydrogen, on the other hand, appears to be produced indirectly via the reforming reactions.

3.4. Further considerations

The results which were presented concerning the application of the heat-integrated wall reactor in the reaction of partial oxidation of methane have demonstrated the feasibility of the concept and its advantages over conventional wall or fixed-bed reactors. Hot-spots can be significantly reduced in magnitude and uniform temperature profiles can be obtained under certain conditions. Based on the design concept of the heat-integrated reactor and the general characteristics of the reaction, the main parameters which should influence reactor operation are: the amount of catalyst per unit length of the reactor, the ratio of the amount of catalyst deposited on the inner and outer surface, the CH_4/O_2 ratio, the temperature and the feed flow rate. Modeling of the reactor will be extremely useful in its optimization. Further improvements in the performance of the reactor can be realized by deposition of additional amounts of catalyst on the reactor tube and this work is currently in progress.

4. Conclusions

The following conclusions can be drawn from the present study:

– A novel type of reactor, namely the *heat-integrated wall reactor*, has been developed and successfully applied in the partial oxidation of methane to synthesis gas. The reactor offers the possibility of reducing the magnitude of hot spots created during partial oxidation of methane and even maintain uniform temperature profiles under specific conditions.

– The Rh/Al_2O_3 catalyst film used in the reactor was found to be stable and very active in the CPO reaction.

– Experimental indications have been obtained suggesting that part of CO is produced via the direct route, when hot spots exist in the reactor. Hydrogen, on the other hand, seems to be produced mainly via the indirect route.

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