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Development of a novel heat-integrated wall reactor for the partial oxidation of methane to synthesis gas

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Abstract

A novel reactor has been developed and applied in the reaction of partial oxidation of methane to synthesis gas. The reactor consists of a hollow ceramic tube with its inside and outside surfaces coated with a metal catalyst film. 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. The performance of the novel reactor has been compared to that of a conventional wall reactor, containing the catalyst film on the inner surface of the reactor tube only. The main parameters which influence reactor operation are: the ratio of the amount of catalyst deposited on the inner and outer surface of the reactor tube, catalyst loading, temperature and feed flow rate. The position and magnitude of hot spots can be readily controlled by proper adjustment of the aforementioned parameters. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Natural gas; Synthesis gas; Partial oxidation; Heat-exchange reactor; Rhodium; Catalyst

1. Introduction

The catalytic partial oxidation (CPO) of methane (reaction (1)) is a promising alternative process to steam reforming for the production of synthesis gas.

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2 \quad (\Delta H = -22\,\mathrm{kJ/mol}) \tag{1}$$

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. It is generally accepted that synthesis gas is produced indirectly, via the following reaction scheme [1,2]:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (\Delta H = -801\,\mathrm{kJ/mol}) \tag{2}$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad (\Delta H = +260\,\mathrm{kJ/mol}) \tag{3}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (\Delta H = +227\,\mathrm{kJ/mol}) \tag{4}$$

according to which, part of the methane is initially combusted with oxygen forming CO_2 and H_2O. Subsequently, reforming of the remaining methane with the produced CO_2 and H_2O takes place leading to formation of synthesis gas. Direct formation of synthesis gas via reaction of CH_4 and O_2 has been claimed

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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 (~10 ms) [5,6].

A major issue in the development of a process based on partial oxidation of methane is the heat management of the reactor. Related to that, issues of catalyst and reactor durability and thermal stability of the catalyst have also to be taken under consideration. Methane combustion (reaction (2)) is strongly exothermic and the heat produced at the first part of the catalytic bed can result in hot spots of considerable magnitude, (>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, on the assumption that methane combustion and reforming takes place in series [7].

Several types of catalytic reactors have been considered for this reaction. 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]. Bharadwaj and Schmidt [8] obtained methane conversions higher than 90% over Ni and Rh catalysts with CO and H_2 selectivities as high as 95%, at contact times of 0.1-0.5 s and temperatures of the order of 800°C. A potential problem under operating conditions was agglomeration of catalyst particles, which occurred at high temperatures (>850°C for Ni and Pt catalysts and >950°C for Rh catalysts). Olsbye et al. [9] obtained equilibrium conversion of CH_4 over a Ni/Al_2O_3 catalyst at a contact time of 0.048 s and temperature of 800°C. Nearly isothermal behavior of the fluidized-bed reactor was observed under reaction conditions. Alternative catalyst bed configurations, such as dual-bed or mixed-catalyst bed reactors have been examined by Ma and Trimm [10]. Their goal was to identify possible advantages of different arrangements of combustion (Pt) and reforming (Ni) catalysts for the enhancement of mass and heat transfer in the reactor. A qualitatively similar concept, the Hot Spot reactor, developed by Johnson Matthey [11], uses two beds arranged concentrically and the feed is point-injected at the center of the reactor. The Hot Spot reactor has been studied in the reactions of partial oxidation of methanol and hydrocarbons for hydrogen production. Dense, oxygen-selective, as well as porous or dense, hydrogen-selective membrane reactors have also been investigated [12–14]. Reactors of the monolithic type have been extensively studied by Schmidt and co-workers [5,6,15]. Rh-loaded monoliths have been found to be the most selective and stable for synthesis gas formation.

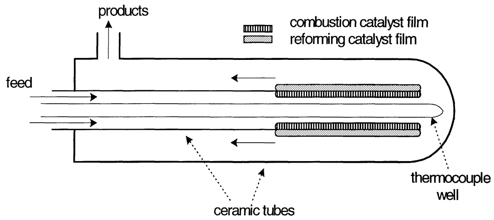

Fig. 1. Schematic diagram of the HIWR.

In the present work, the results of the application of a novel reactor type in the reaction of catalytic partial oxidation of methane are presented. The heat-integrated wall reactor (HIWR), in its simplest form, is shown schematically in Fig. 1. The reactor comprises a non-porous ceramic tube of high thermal conductivity, 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 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 can be 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 a series of ceramic tubes placed in a bundle inside an insulated vessel. In this configuration, the HIWR can be easily operated in the adiabatic mode. The performance of the HIWR 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 OD×4 mm ID×51 cm length (Alsint, ETK). The outer ceramic tube (Pythagoras, ETK) had dimensions of 12 mm OD×8 mm ID×41 cm length, while the thermocouple well, which was placed in the center of the inner tube, was an alumina tube of dimensions 3 mm OD×2 mm ID. A Rh/Al_2O_3 catalyst was used throughout this work. The Rh/Al_2O_3 catalyst film was deposited on the wall of the reactor tube by dip-coating of a $Rh\text{-}Al_2O_3$ sol, which corresponded to a Rh loading of 4.6 wt.% in the final catalyst. The procedure of preparation of the $Rh\text{-}Al_2O_3$ sol can be found in [16]. Following calcination at 500°C for 2 h, the surface area of the Rh/Al_2O_3 catalyst in powder form was 250 m^2/g and the dispersion of Rh was 0.5. Calcination at 1000°C for 2 h caused a reduction of the surface area of the catalyst to 59 m^2/g. 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 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-1. Additional amounts of the Rh/Al_2O_3 catalyst were deposited both on the inner and outer surfaces of the same reactor tube by consecutive dip-coatings. The characteristics of all reactors, which were tested, are shown in Table 1.

Based on the dimensions of the tubes used in the reactor, the void volume of the inner side (bore) of the reactor tube is 0.55 cm^3, while the volume of the annulus is 2.2 cm^3. For the range of flow rates used in the present work, (60–1200 cm^3/min), the calculated residence time of the gas (at STP conditions) is 0.027–0.55 s at the inner side of the tube and 0.11–2.2 s at the annulus. The true contact time is estimated to be 3–6 times lower than the above values, depending on reaction conditions (reactor temperature and conversion).

Table 1
Wall reactor characteristics

Reactor	Catalyst film	Catalyst loading
CWR	One coating on inner surface	1.5 mg
HIWR-1	One coating on both inner and outer surfaces	3 mg
HIWR-2	Two coatings on both inner and outer surfaces	5 mg
HIWR-3	Three coatings on both inner and outer surfaces	7 mg
HIWR-4	Three coatings on inner surface – four coatings on outer surface	8 mg
HIWR-5	Four coatings on inner surface – five coatings on outer surface	10 mg

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 60–1200 cm^3 STP/min and was controlled by thermal mass flow controllers (MKS instruments). In specific reactor tests, such as the test of the CWR, the range of flow rate employed was narrower, because of the occurrence of hot spots exceeding 1000°C. Experiments were carried out at nominal furnace temperatures in the range of 600–750°C. The temperature variation along the catalyst film under nitrogen flow at a nominal temperature of 700°C was approximately 30–40°C, whereas the temperature at the middle of the film was 700°C and 660–670°C at the ends. Temperature profiles along the bore of the reactor were measured by a thermocouple, as shown in Fig. 1. Two gas chomatographs were used for the analysis of reactants and products. 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.

Prior to each run, the catalyst film was reduced under hydrogen flow at 700°C for one hour. Tests were always performed starting from the lowest flow (60 cm^3/min), by introducing CH_4 first, followed by oxygen. It was found that the catalyst ignited instantaneously, when the furnace temperature was higher than 550–570°C. Experiments with a blank reactor tube showed that the rate of homogeneous reactions is negligible at furnace temperatures lower than 850°C.

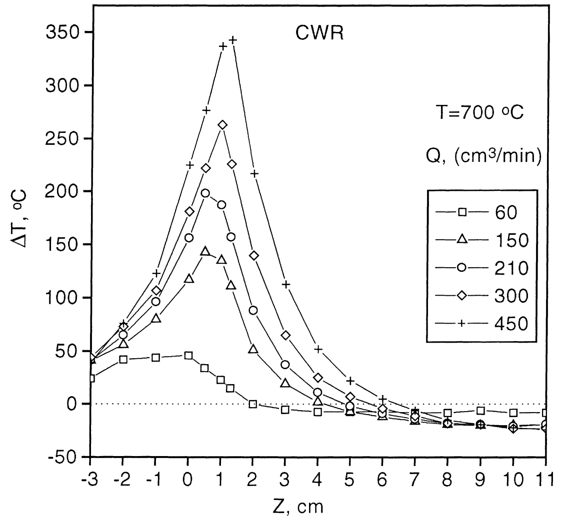

Fig. 2. Temperature profiles along the CWR under reaction conditions with varying feed flow rate, (furnace temperature: 700°C).

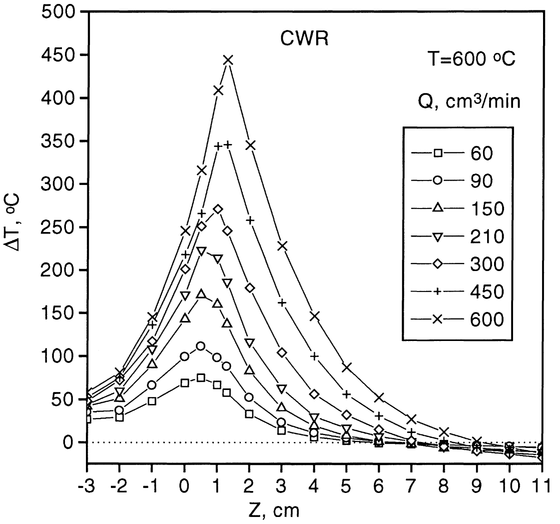

Fig. 3. Temperature profiles along the CWR under reaction conditions with varying feed flow rate, (furnace temperature: 600°C).

3. Results and discussion

3.1. Temperature profile of CWR

A reactor containing the catalyst on the inner surface of the reactor tube only, named CWR, (Table 1), serves as the reference reactor for the assessment of the performance of the heat-integrated reactors. The temperature profiles under reaction conditions for the CWR are presented in Figs. 2 and 3 for nominal furnace temperatures of 700°C and 600°C, respectively, and CH_4/O_2 feed flow rates in the range of 60–600 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 end of the outer tube, which encloses the reactor tube.

A hot spot is observed, in all cases, at the first part of the catalyst film, due to the occurrence of the exothermic reaction of methane combustion. The hot spot becomes larger with increasing flow rate. This can be understood by the increase of the rate of heat production with increasing flow rate. The position of the hot spot does not change appreciably with flow rate, although it shifts slightly towards the right, as the flow rate increases. For example, the hot spot is at z=0.6 cm for a flow rate of 150 cm^3/min and at z=1.2 cm for a flow rate of 450 cm^3/min. Another important observation is that the temperature profiles in the reactor are similar, regardless of the furnace temperature (600 or 700°C). 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 (Figs. 2 and 3). The behavior of the reactor with respect to temperature demonstrates the problems associated with the heat management of the reaction of CPO of methane. These problems relate to the very rapid release of large quantities of heat at the first part of the catalyst film or bed and the subsequent control of the significant hot spot in this region. At the same time, high temperatures must be maintained at the end of the catalyst film, so as to maximize methane conversion.

3.2. Demonstration of the concept of the heat-integrated reactor

The temperature profiles of the reactor HIWR-1 under reaction conditions are presented in Fig. 4 for a nominal furnace temperature of 700°C and feed flow rate in the range of 60–840 cm^3/min. The reactor HIWR-1 contains one catalyst coating on both the inner and outer surfaces of the reactor tube. The observed temperature profiles show that deposition of catalyst on the outer surface of the reactor tube has

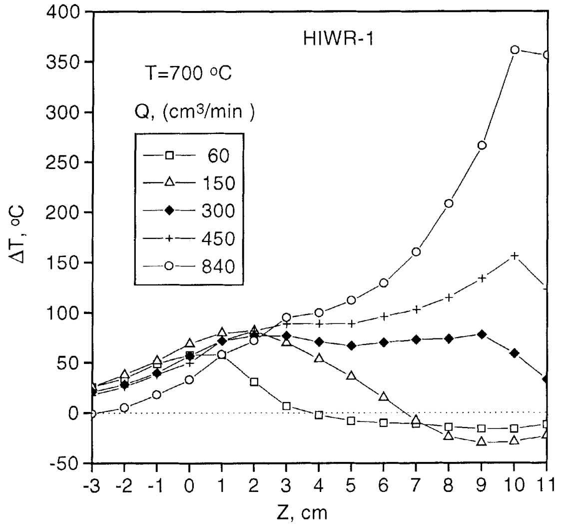

Fig. 4. Temperature profiles along the HIWR-1, under reaction conditions with varying feed flow rate, (furnace temperature: 700°C).

led to a drastic alteration of the shapes of the temperature profiles at high flow rates, compared to those observed in the CWR. 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 a 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 maximum ΔT of 265°C (Fig. 2). As flow rate is increased further, a hot spot develops at the end of the catalyst film (z=10 cm).

The observed behavior of the reactor HIWR-1 can be explained as follows:

1. At low flow rates the contact time is sufficiently large and the exothermic methane combustion is completed at the first part of the catalyst film. In this case, the endothermic reforming reactions already start on the inner surface, as evidenced by the negative ΔT observed after the first part of the catalyst film.
2. As flow rate increases, the temperature profiles become gradually more uniform and at the flow rate of 300 cm^3/min the temperature is almost constant along the catalyst film. In this case, methane combustion apparently takes place throughout the entire length of the inner catalyst film. 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. The basic difference between the CWR and HIWR-1 reactors is that, in the former case, increase of the feed flow rate causes increase of the rate of heat production which raises the catalyst temperature. This leads to enhancement of the combustion rate and so on. This does not happen in the latter case because of the consumption of heat, generated by combustion, by the reforming reactions taking place on the outer surface of the reactor tube.
3. As the flow rate is increased 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 situated at the end of the reactor tube.

The corresponding temperature profiles under reaction conditions for the reactor HIWR-3 are presented

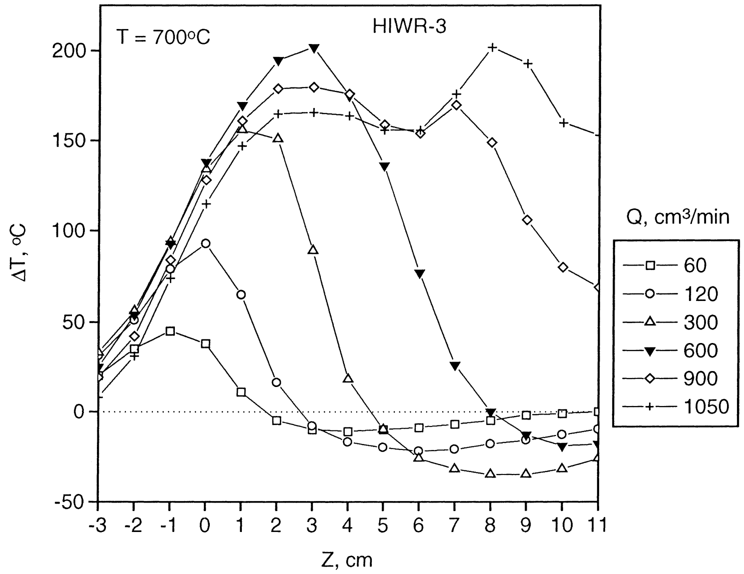

Fig. 5. Temperature profiles along the HIWR-3, under reaction conditions with varying feed flow rate, (furnace temperature: 700°C).

in Fig. 5 for feed flow rates in the range of 60–1050 cm^3/min. The reactor HIWR-3 contains three catalyst coatings on both surfaces of the reactor tube. Therefore, the basic difference of the reactors HIWR-1 and HIWR-3, is that the latter contains a larger amount of catalyst (Table 1). The main points of interest regarding the alteration of temperature profiles with flow rate are described below:

1. In the flow rate range of 60–600 cm^3/min, increase of the flow rate causes an increase of the hot spot temperature and a shift of the position of the hot spot towards the middle of the catalyst film. In any case, the hot spot is considerably smaller (approximately 50%) compared to the CWR reactor.
2. As flow rate becomes larger than 600 cm^3/min, the hot spot does not increase further, but rather a uniform temperature profile develops along the catalyst film. The appearance of two maxima in the temperature profiles is, most probably, due to inhomogeneities of the catalyst distribution along the inner and outer surface of the reactor tube.

The observed differences in the temperature profiles of the reactors HIWR-1 and HIWR-3 may be attributed to the higher catalyst loading of the HIWR-3 reactor. For example, if one compares the corresponding profiles at the flow rate of 300 cm^3/min, it can be seen that in the case of HIWR-3, which contains more catalyst, the reforming reactions already start on the inner surface, as evidenced by the negative ΔT at z>5 cm. In the case of the HIWR-1, on the other hand, the observed temperature profile indicates that only methane combustion takes place on the inner catalyst film. The aforementioned results suggest that the temperature profile along the heat-integrated reactor depends on the amount of catalyst deposited on the inner and outer surface of the tube. The effect of the relative quantity of catalyst on the inner and outer surface of the tube on the development of the temperature profiles along the reactor is discussed in the following section.

3.3. *Effect of relative quantity of catalyst on the inner and outer surface of the reactor tube on temperature profiles*

The effect of the relative quantity of catalyst on the inner and outer surface of the reactor tube on the observed temperature profiles can be understood by comparison of the performance of reactors HIWR-3 and HIWR-4. Reactor HIWR-4 contains one addi-

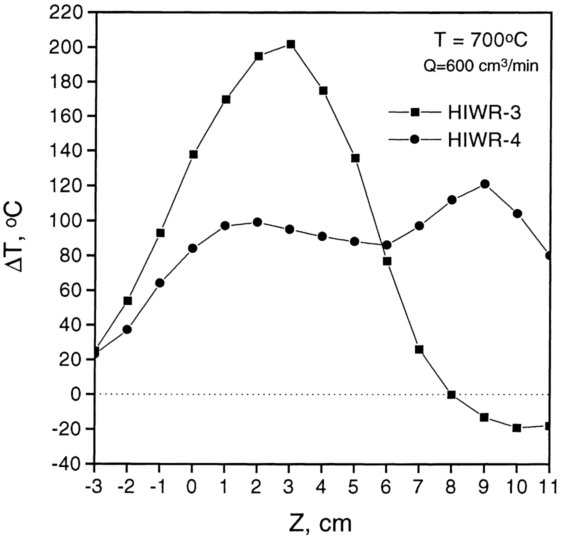

Fig. 6. Temperature profiles along the HIWR-3 and HIWR-4, under reaction conditions at a furnace temperature of 700°C and feed flow rate of 600 cm^3/min.

tional coating of catalyst on the outer surface of the reactor tube compared to HIWR-3 (Table 1). The corresponding temperature profiles at a furnace temperature of 700°C and a feed flow rate of 600 cm^3/min are shown in Fig. 6. The temperature profile of HIWR-3 is characterized by a hot spot of 200°C at z=3 cm, while towards the end of the catalyst film the temperature is lower than that without reaction (in N_2 flow). This result implies that the reforming reactions have started to take place on the inner surface of the reactor tube. In the case of the reactor HIWR-4, the temperature is more or less uniform along the reactor and the hot spot is significantly reduced compared to reactor HIWR-3 (120°C vs. 200°C).

The observed differences in the temperature profiles of the two reactors must be attributed to the additional catalyst loading on the outer surface of HIWR-4. The additional amount of catalyst has led to an increase of the rate of reforming reactions on the outer surface and, as a consequence, to an increase of the rate of heat absorption. In return, this lowers the temperature of the inner catalyst film and the rate of methane combustion falls accordingly, so that methane combustion is not completed at the first part of the inner catalyst film, as in the case of HIWR-3. In the specific example presented in Fig. 6, methane combustion apparently takes place throughout the entire inner catalyst film. In addition to having lower and more uniform temperatures, HIWR-4 also provides higher methane conversion. The methane conversion for the test shown in Fig. 6, was 77.3% in HIWR-4 and 75.7% in HIWR-3.

3.4. *Effect of furnace temperature on temperature profiles along the reactor*

The performance of the reactors employed in the present work has been studied at various furnace temperatures in the range of 600–750°C. As a representative example, the temperature profiles along the HIWR-3 reactor at furnace temperatures of 600, 700 and 750°C are presented in Fig. 7(a) and Fig. 7(b) for feed flow rates of 300 and 900 cm^3/min, respectively. It can be seen in Fig. 7(a), that the hot spot is located at the beginning of the catalyst film for furnace temperatures of 700 and 750°C, while reforming reactions start on the inner surface, as evidenced by the negative ΔT at $z>4$ cm. At the furnace temperature of 600°C, on the other hand, the temperature increases gradually along the reactor and the hot spot is located at z=8 cm. It is of interest to compare the temperature profile of HIWR-3 with the corresponding profile of the CWR under the same conditions (Fig. 3), which exhibits a hot spot of 270°C at the beginning of the catalyst film. It can be deduced from this comparison that the main factor determining the temperature profile of HIWR-3 at 600°C, is not the lower furnace temperature, but rather the absorption of heat by the reforming reactions.

In the case of the feed flow rate of 900 cm^3/min (Fig. 7(b)), the temperature profiles corresponding to furnace temperatures of 700 and 750°C are similar and they exhibit a rather uniform temperature distribution along the catalyst film. ΔT is lower than 180°C. At the furnace temperature of 600°C, on the other hand, a hot spot of considerable magnitude ($\sim$ 370°C) has developed at the end of the catalyst film (z=9 cm). This result implies that, in this case, methane combustion essentially takes place both on the inner and outer surfaces at the end of the reactor tube. It should be remembered that the direction of gas flow is reversed at the end of the reactor and when methane combustion takes place in this region, development of high temperatures is expected. Needless to say, such a behavior of the reactor is undesirable.

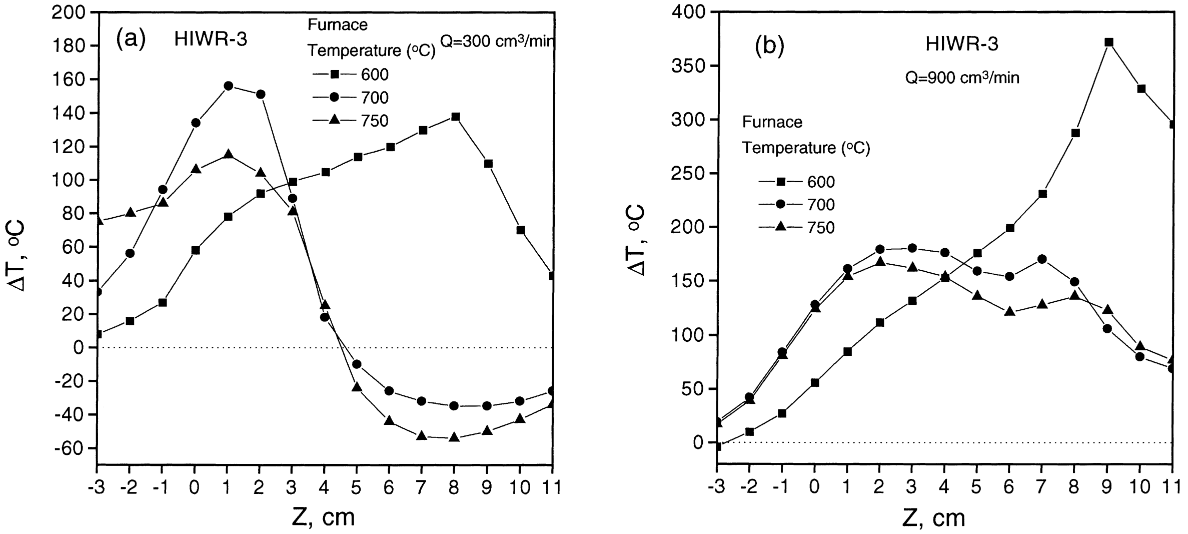

Fig. 7. Temperature profiles along the HIWR-3, under reaction conditions at furnace temperatures of 600, 700 and 750°C and feed flow rate of: (a) 300 cm^3/min and (b) 900 cm^3/min.

3.5. *Comparison of the performance of CWR and HIWR reactors*

The methane conversion obtained over the CWR and the HIWR-1 —HIWR-5 at furnace temperatures of 700°C and 600°C is shown as a function of feed flow rate in Fig. 8(a) and Fig. 8(b), respectively.

The following points regarding the effect of reactor and operating parameters on methane conversion have to be mentioned:

- *CWR vs. HIWR.* It can be seen that in the range of flow rates which were examined, methane conversion in the heat-integrated reactors is consider-

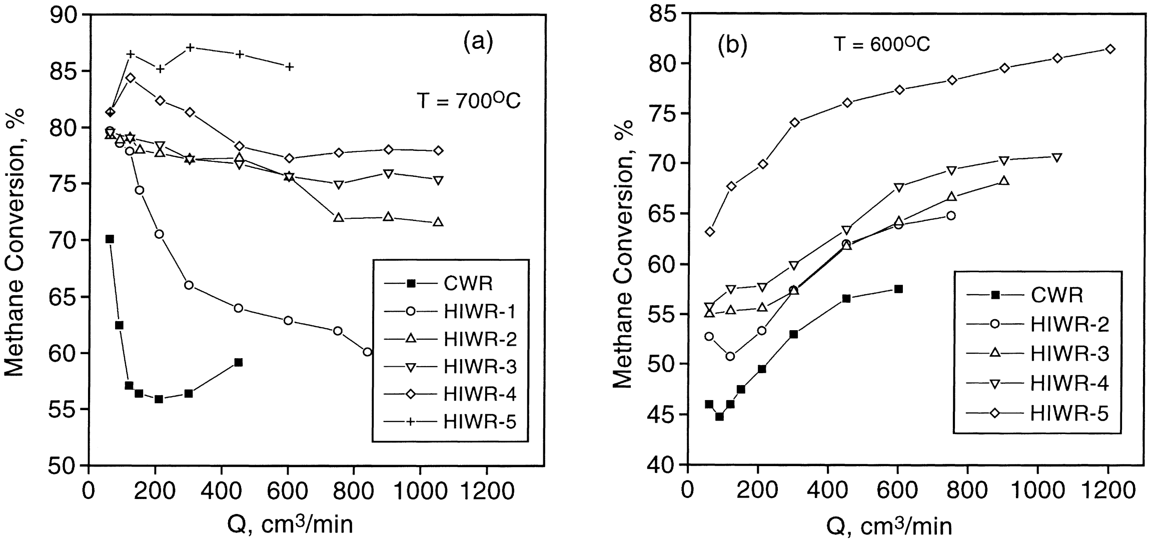

Fig. 8. Methane conversion obtained in the CWR and HIWR-1–HIWR-5, under reaction conditions as a function of feed flow rate at furnace temperatures of: (a) 700°C and (b) 600°C.

ably higher than methane conversion in the CWR for both furnace temperatures. At 700°C and a flow rate of 450 cm^3/min, for example, methane conversion in the CWR is 59%, compared to 64% in HIWR-1 and 86.5% in HIWR-5. At 600°C and a flow rate of 600 cm^3/min, methane conversion in the CWR is 57.6%, compared to 63.9% in HIWR-2 and 77.4% in HIWR-5. It is to be noted 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. A critical question is whether the observed increase in methane conversion in the heat-integrated wall reactors should be attributed to their higher catalyst loading or to their more efficient heat management characteristics. It is proposed that the enhancement in methane conversion is due mainly to the latter cause. This can be explained as follows: if one assumes that the CWR has the same catalyst loading and reaction interface area as the HIWR reactors, then its length would be 25 cm. In this case, a hot spot of considerable magnitude would develop at the first few centimeters of the reactor under reaction conditions due to methane combustion, while towards the end of the reactor the temperature would become approximately equal to the furnace temperature. Thus, the maximum achievable methane conversion in the CWR would be the one predicted by thermodynamics for that temperature regardless of catalyst loading. In the HIWR reactors, on the other hand, the reactor inlet (where hot spots appear) is coupled thermally to the reactor outlet. In this way, higher reactor outlet temperatures and, as a consequence, higher methane conversions can be achieved, while at the same time hot spots are reduced due to heat absorption by the endothermic reforming reactions. In a practical application, one would require a methane conversion of the order of 95%, which corresponds to outlet temperatures of 900°C and higher. If a CWR was employed under these conditions hot spots could supposedly be as high as 1500°C [7], which of course is not acceptable.

- *Effect of feed flow rate*. The effect of feed flow rate on methane conversion can be understood by taking into account the fact that the reactors were operated in a non-isothermal (polytropic) mode. At the lowest flow rate employed (60 cm^3/min), the methane conversion obtained is close to the one predicted thermodynamically for the reactor exit temperature (the reactor exit is at $z=10$ cm for the CWR and at $z=0$ cm for the HIWR reactors). As feed flow rate increases, the rate of heat production from methane combustion increases leading to an increase of the hot spot and the average reactor temperatures. The increase of the reactor temperature tends to increase methane conversion due to kinetic and thermodynamic reasons, while, on the other hand, the decrease of contact time with increasing flow rate tends to decrease it. Which factor prevails, depends mainly on the furnace temperature. Thus, at a furnace temperature of 600°C (Fig. 8(b)), methane conversion increases with flow rate. This can be understood by considering that at 600°C methane conversion is restricted by thermodynamic limitations and an increase of the actual reactor temperature removes in part these limitations. Thermodynamic constraints are not so severe at 700°C, and, in this case, methane conversion generally tends to decrease with increasing flow rate due to the stronger effect of decreasing contact time (Fig. 8(a)).
- *Effect of furnace temperature*. Methane conversion decreases at lower furnace temperatures. This is readily understood on thermodynamic grounds by the fact that the reactor temperature is lower at lower furnace temperatures.
- *Effect of catalyst loading*. Increase of the catalyst loading in the HIWR reactors results in enhancement of methane conversion under the same reaction conditions. This implies that in the range of catalyst loadings examined, internal mass and heat transfer resistances do not significantly influence reactor performance. Indeed, the thickness of the catalyst layer in the reactors examined is estimated to be up to 20 μm, assuming that the layer is uniformly deposited and has a porosity of 50%. At such thickness, internal mass and heat transfer resistances are expected to be of minor importance, with the possible exception of the region of the hot spot, where methane combustion takes place.

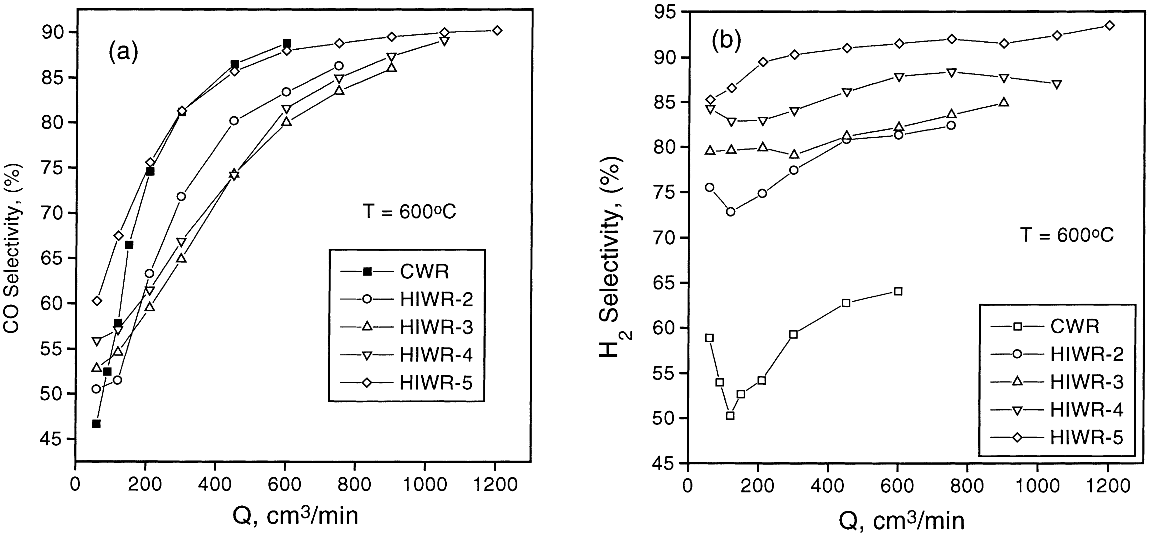

Fig. 9. (a) CO and (b) H_2 selectivity obtained in the CWR and the HIWR-1–HIWR-5, under reaction conditions as a function of feed flow rate, (furnace temperature: 600°C).

Selectivity towards CO and H_2 formation obtained over the conventional and the heat-integrated wall reactors at a furnace temperature of 600°C is presented as a function of feed flow rate in Fig. 9(a) and Fig. 9(b), respectively. At the lowest flow rate employed (60 cm^3/min), the observed CO and H_2 selectivities over all reactors are comparable to the equilibrium values corresponding to the reactor exit temperature in each case (570°C for the CWR and ~ 600–630°C for the HIWRs). In all cases, CO selectivity increases considerably with increasing flow rate, as methane conversion does. A noteworthy observation is that CO selectivity is higher in the CWR than in the heat-integrated reactors (only HIWR-5 has comparable selectivity, but much higher methane conversion), in spite of the fact that methane conversion is significantly lower in the CWR. Hydrogen selectivity, on the other hand, is considerably higher in the heat-integrated reactors compared to the CWR and varies much less with flow rate.In order to gain insight on the effect of reactor and operating parameters on CO and H_2 selectivity, the ratio R = $[CO_2][H_2]/[CO][H_2O]$ in the reactor effluent has been calculated and compared to the value of the equilibrium constant of the water-gas shift reaction, K_{WGS}. Typical results are shown in Fig. 10, where the above ratio is plotted as a function of temperature in the case of CWR and HIWR-4 at a furnace temperature of 600°C. Each straight line connects the highest and lowest temperature measured in the reactors at a specific flow rate. Flow rates increase moving downwards. It can be seen that, in the case of the CWR, the

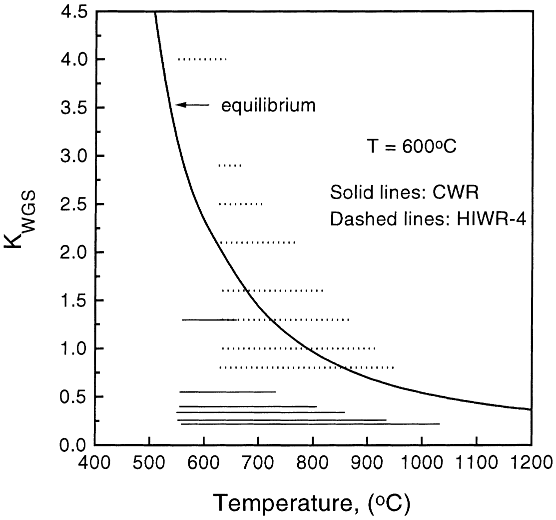

Fig. 10. Comparison of the ratio R = $[CO_2][H_2]/[CO][H_2O]$ in the products of the reactors CWR and HIWR-4 with the equilibrium constant of WGS reaction, (furnace temperature: 600°C).

ratio, R, is significantly lower than the equilibrium constant of the WGS reaction. This result corresponds to production of more CO and less H_2 compared to equilibrium. In the case of HIWR-4, on the other hand, the straight lines generally intersect or are above the equilibrium line, which means that the reactor effluent gas is closer to equilibrium with respect to the WGS reaction and H_2 formation is favoured. Generally, similar trends were found for all other heat-integrated reactors regarding the value of the ratio R.

It might be postulated that the deviation of the composition of products in the case of the CWR towards more CO formation compared to WGS equilibrium is due to direct formation of CO from the reaction of CH_4 with O_2 at the hot spot region of the reactor. 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 with contact time of 10 ms. The contact time in the CWR for the highest flow rate employed is estimated to be 15–20 ms.

4. Conclusions

The following conclusions can be drawn from the present study:

- The results 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 potential advantages over conventional types of reactors.
- The new 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 main parameters which influence the operation of the reactor are: the ratio of the amount of catalyst deposited on the inner and outer surface of the reactor tube, catalyst loading, temperature and feed flow rate. The position and magnitude of the hot spot can be readily controlled by proper adjustment of the aforementioned parameters. The Rh/Al_2O_3 catalyst film used in the reactor was found to be very active in the reaction of CPO of methane.

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