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An advanced reactor configuration for the partial oxidation of methane to synthesis gas

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Abstract

The partial oxidation of methane to synthesis gas has been studied in the heat integrated wall reactor (HIWAR). The reactor comprises a ceramic tube on the inner and outer surface of which a metal catalyst film is deposited in the form of a washcoat. The combustion reaction is taking place on the inner catalyst film and the reforming reaction on the outer, absorbing simultaneously the heat of combustion. Thus, the heat integrated wall reactor offers the possibility of reducing the magnitude of hot spots which normally develop during the exothermic combustion of methane in conventional reactors, due to rapid heat transport across the tube wall from the combustion to the reforming zones. The HIWAR can be operated in the adiabatic mode. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Advanced reactor configuration; Partial oxidation of methane; HIWAR

1. Introduction

The partial oxidation of methane may be a promising alternative process to steam reforming for the conversion of natural gas to synthesis gas. Pena et al. [1] have recently reviewed work in this field. The reaction can be carried out over Group VIII metal catalysts such as Ni, Rh, Ru, Pt, Ir and Pd. Methane can be converted to synthesis gas via either the direct or indirect reaction schemes. According to the indirect reaction scheme, part of methane is combusted by supplied oxygen towards CO_2 and H_2O (Reaction 1). Reforming of the remaining methane with CO_2 and H_2O takes place subsequently producing CO and H_2 (Reactions 2, 3)

$$CH_4+2O_2\rightarrow CO_2+2H_2O \quad (\Delta H=-801\,\text{kJ/mol}) \quad (1)$$

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

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

Methane combustion is a strongly exothermic reaction, while the reforming reactions are strongly endothermic. The exothermicity of Reaction 1 may create severe problems of heat management, safety and stability in conventional reactors. According to the direct reaction scheme (Reaction 4), synthesis gas is formed through direct oxidation of methane, without experiencing the CO_2 and H_2O intermediates.

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

The direct reaction scheme has the advantage of being only slightly exothermic, thus alleviating the problems mentioned above. However, the indirect scheme is favored thermodynamially and most catalysts which have been tested seem to promote the indirect scheme, with some notable exceptions which promote both schemes simultaneously [2–4]. Thus, the design of a

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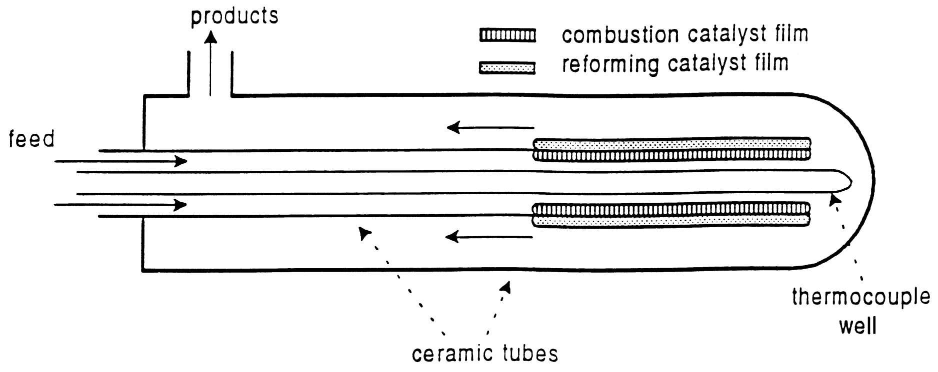

Fig. 1. Schematic diagram of the HIWAR.

conventional fixed bed reactor for carrying out the partial oxidation of methane is posed with a severe heat management problem: very large quantities of heat are released at the first part of the reactor where combustion is taking place, leading to hot spots of such a magnitude which is detrimental for the catalyst and the reactor. De Groote and Froment [5], simulated an adiabatic fixed bed reactor, containing a Ni/Al_2O_3 catalyst. The results showed that for a CH_4/O_2 feed ratio of 1.67, a hot spot of 1782 K can be developed in the catalyst bed assuming that the reforming reactions are consecutive methane combustions. This situation is followed by a rapid drop of temperature as the endothermic reforming reactions take over, leading to relatively low temperatures towards the end of the catalyst bed. This situation is also undesirable since, thermodynamically, CH_4 conversion is reduced with decreasing reaction temperature.

Several types of catalytic reactors have been considered for this reaction, such as fixed bed reactors, fluidized-bed reactors, dual-bed or mixed-catalyst bed reactors [6], the hot spot reactor [7], which is an autothermal system using two beds arranged concentrically and the feed is point-injected at the center of the reactor, hydrogen-selective membrane reactors [8–10] which separate H_2 from the reaction mixture and monolithic reactors [2,3,11].

In the present study, the partial oxidation of methane has been studied in the heat integrated wall reactor (HIWAR) [12]. The HIWAR offers the possibility of reducing drastically the magnitude of hot spots which develop during the exothermic combustion of methane, by heat integration of the combustion reaction and the endothermic reforming reactions. The HIWAR is shown schematically in Fig. 1. The reactor comprises of 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 offers the possibility to deposit the same or different kinds of catalyst on the inner and outer surfaces. The ceramic tube is enclosed in a larger ceramic (or quartz) tube. The feed enters into the inner tube where exothermic methane combustion takes place. A large amount of the heat generated is transported through the tube wall towards the outer surface of the tube, where the endothermic reactions take place, absorbing the heat of combustion. As a result of this, temperature in the combustion zone can be controlled and the magnitude of hot spots can be reduced. Furthermore, the highest rate of heat transport occurs near the entrance to the inner catalyst zone. This corresponds to the exit of the reforming zone, at the outer tube surface. It is exactly at this location where the highest temperature is desirable in order to drive the thermodynamic methane conversion towards higher levels. Finally, as is illustrated in Fig. 1, the feed is preheated as the products of the reaction are carried away from the reactor.

New results of experiments using 10% Rh/Al_2O_3 as a catalyst carried out in the HIWAR are presented in the present communication.

2. Experimental

The reactor tube employed in the construction of the laboratory scale HIWAR is a non-porous alumina tube of dimensions 6 mm o.d., 4 mm i.d. and 51 cm length (Alsint, ETK) The outer tube which encases the inner one is made out of quartz and has dimensions of 12 mm o.d., 8 mm i.d. and 41 cm length. The thermocouple well, which is placed in the center of the inner tube, is an alumina tube of dimensions 3 mm o.d. and 2 mm i.d. The catalyst film was deposited on the inner and outer surface of the wall of the reactor tube by dip-coating of a Rh/Al_2O_3 sol, which corresponded to Rh loading of 10% in the powder catalyst. It has been found that Rh is a stable and active catalyst for this reaction. The procedure of preparation of the Rh/Al_2O_3 sol can be found elsewhere [12]. The catalyst film was deposited over a length of 11 cm at one end of the ceramic tube. At first a quantity of catalyst of 2 mg was deposited only on the inner surface of the tube. This reactor configuration is designated as conventional wall reactor (CWR). After testing this configuration under reaction conditions, additional catalyst layers were deposited on the outer as well as on the inner surface of the reactor tube. The characteristics of the reactors which were tested, are shown in Table 1.

The feed flow rate was in the range of 60–1950 cm^3/min and was controlled by mass flow controllers (MKS instruments). The maximum feed flow rate employed depended on the magnitude of hot spot which developed. Thus, in the case of the CWR the maximum feed flow rate employed was 450 cm^3/min because the hot spot temperature in this case was over 1000°C. The reaction feed consisted of CH_4 and O_2 with a 2:1 ratio and the concentration was 66.67% CH_4 and 33.33% O_2. Experiments were carried out at furnace temperatures of 600 and 700°C. The catalyst film was reduced under hydrogen flow at 500°C before testing. The reactor was placed inside a furnace. Temperature profiles were measured along the reactor tube by a thermocouple which was placed inside a thermocouple well as shown in Fig. 1. The thermocouple was moved inside the themocouple well, along the length of the tube. Two gas chromatographs were used for the analysis of reactants and products. CH_4, O_2, CO, and CO_2 were analyzed in a Carboxene 1000 column with He as a carrier gas while hydrogen was analyzed in the second chromatograph with N_2 as a carrier gas. H_2O produced in the reaction was condensed in a condenser located downstream of the reactor.

Table 1
Characteristics of reactors employed in the present study

Reactor	Surface	Catalyst (mg)	
		Inner surface	Outer surface
CWR	Inner	2	
HIWAR1	Inner+outer	2	3
HIWAR2	Inner+outer	2	6
HIWAR4	Inner+outer	4	9

3. Results and discussion

3.1. Temperature profiles

The temperature profiles of the CWR reactor and the HIWAR reactors at a furnace temperature of 600°C at a feed flow rate of 450 cm^3/min, are shown in Fig. 2. Qualitatively similar temperature profiles were also obtained at a furnace temperature of 700°C. In all cases, a hot spot is observed to develop near the entrance of the catalyst film, due to the combustion of methane. In the case of the CWR, in which there is no catalyst on the outer surface of the ceramic tube, the hot spot temperature exceeds 1000°C. In the case of the HIWAR1, in which 3 mg of catalyst were

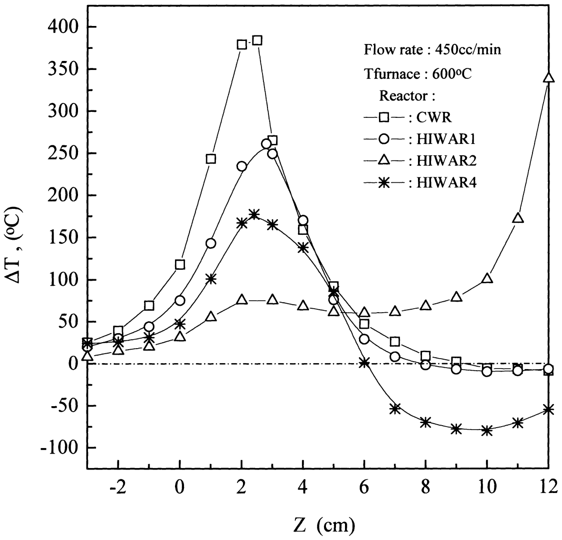

Fig. 2. Temperature profiles along the CWR and the HIWAR under reaction conditions with varying flow rate at a furnace temperature of 600°C (z=0, refers to the entrance of the catalyst film).

deposited on the outer surface of the reactor tube, the magnitude of the hot spot is reduced by at least 150°C, compared to that observed in the CWR. This is because of the endothermic reforming reactions which take place on the outer surface of the reactor tube absorbing a fraction of the heat of combustion which is transported across the tube wall. In the case of HIWAR2, deposition of additional 3 mg of catalyst on the outer surface of the reactor tube results in a drastic alteration of the temperature profile. As a result of the larger quantity of catalyst in the outer tube surface, the temperature near the catalyst film entrance is reduced, which results in lower rates of methane combustion and lower rates of heat release. Thus, the combustion zone is moved toward the end of the catalyst film and, in most probability, combustion is also taking place at the outer catalyst film as well. As a result, a significant hot spot appears at this location of the reactor. The nearly flat temperature profile which is observed over a large fraction of this reactor is due to the fact that the rate of methane combustion is low (the catalyst has not fully ignited) when temperature is controlled at levels below approximately 700°C, and due to rapid transport of heat from the inner tube surface, across the tube wall to the outer surface.

The temperature profile is altered again when the amount of catalyst in the outer tube surface is increased to 9 mg and that in the inner tube to 4 mg (HIWAR4). In this case, the hot spot appears again near the entrance of the catalyst film, but it is low in magnitude due to heat transport across the tube wall to the reforming zone. It is also observed in this case that significant endotherms develop towards the end of the reactor tube. This implies that most of the oxygen has been consumed in the region where the exotherm appears and reforming takes place, to a certain extent, over the inner catalyst film. The reforming reactions continue over the outer catalyst film, as indicated by the well-controlled exotherm.

It is apparent from the temperature profiles shown in Fig. 2 that the performance of the HIWAR is very sensitive to the quantity of catalyst placed in the inner and outer tube surfaces. As expected, the magnitude and location of hot spots is also affected by furnace temperature. The reactor performance is also sensitive to the feed gas flow rate, as is illustrated in Fig. 3.

Temperature profiles obtained over the HIWAR2 as a function of feed flow rate at furnace temperatures of 700 and 600°C are shown in Fig. 3(a) and (b), respectively. As expected, at the furnace temperature of 700°C (Fig. 3a), temperature increases with increasing feed flow rate due to the larger quantities of methane converted and, therefore, the larger quantities of heat released. In nearly all feed rates, two temperature maxima are observed, which tend towards a nearly uniform temperature profile as feed rate increases to fairly high

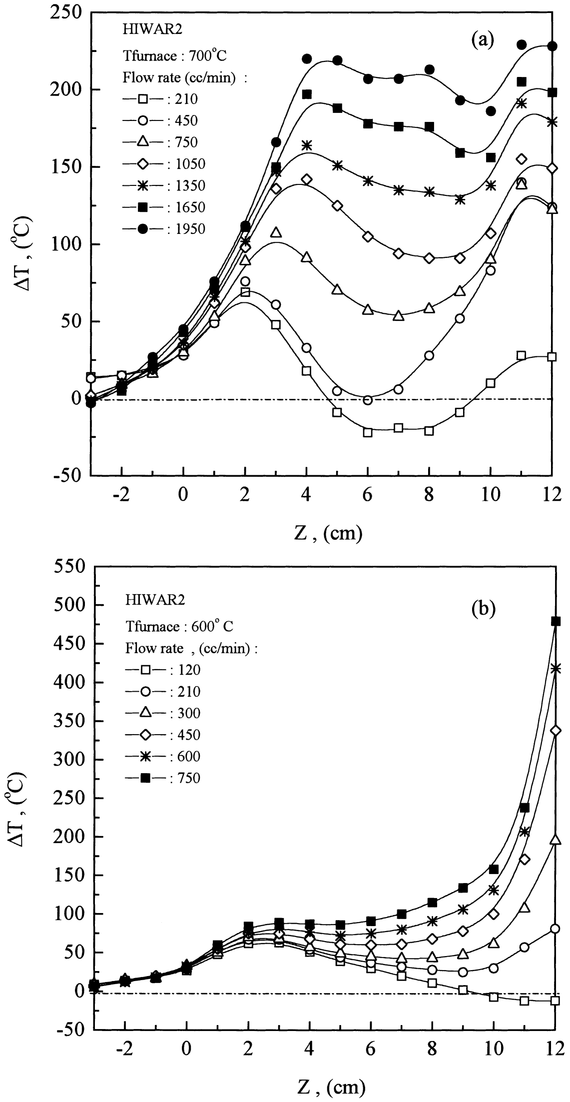

Fig. 3. Temperature profiles along HIWAR2 under reaction conditions with varying flow rate, at furnace temperatures of (a) 700°C and (b) 600°C (z=0, refers to the entrance of the catalyst film).

levels. The two temperature maxima are due to different rates of heat generation and heat transport at different locations within the reactor tube. The maximum near the catalyst film entrance is due to high rates of methane combustion at this location. The second maximum at the end of the catalyst film is probably due to the fact that combustion is taking place at both the inner and outer tube walls. Because temperatures are controlled at low levels, the rate of combustion is low and accelerates in this region of the tube. As the flow rate is increased, temperature tends to increase and combustion takes place over the entire inner tube surface, resulting in more uniform temperature profiles, as shown in Fig. 3a for feed rates exceeding 1 l/min. It is interesting to note that when the HIWAR2 was operated at a furnace temperature of 700°C, the maximum feed flow rate used was 1950 cm^3/min and the hot spot temperature was only 225°C above the furnace temperature (higher feed flow rates were not used due to limitation of the mass flow controllers). This temperature profile compares very favorably with that obtained over the CWR, which, at the flow rate of 450 cm^3/min shows an exotherm which exceeds 300°C.

The temperature profiles obtained over the HIWAR2 at a furnace temperature of 600°C are shown in Fig. 3(b). In this case the temperatures which develop along the catalyst film are significantly lower for all feed flow rates used. It is apparent that, because the entrance temperatures are low, the catalyst has difficulty to ignite. As flow rate increases, ignition takes place towards the end of the catalyst film, where a strong exotherm appears. Combustion of methane takes place in this region of the reactor at both the inner and outer catalyst films. Comparison of Fig. 3b with Fig. 2 shows that ignition of the catalyst film depends not only on the feed temperature but also on the quantity of catalyst per unit length of tube. The latter parameter defines the rate of reaction and, therefore, the rate of heat release. Apparently, a critical rate is required for the catalyst to ignite and combustion to proceed rapidly.

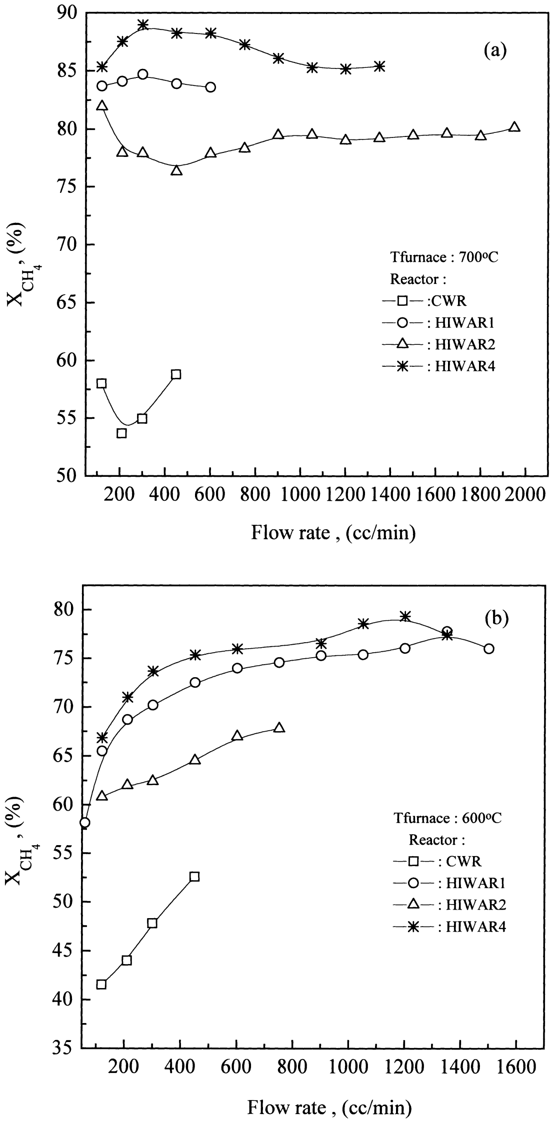

Fig. 4. Methane conversion obtained over the CWR and the HIWAR as a function of feed flow rate, at furnace temperatures of (a) 700°C and (b) 600°C.

3.2. Conversion

Methane conversions recorded under operation of the CWR and the HIWAR reactors at furnace temperatures of 700 and 600°C as a function of feed flow rate are presented in Fig. 4(a) and (b), respectively. Methane conversion was measured at the exit of the catalyst film, i.e. at z=11 cm in the case of the CWR and at z=0 cm in the annulus side, in the case of HIWAR. Methane conversion is primarily influenced by the magnitude of the hot spot and the average temperature within the reactor. This parameter is strongly influenced by the feed flow rate (Fig. 3), the quantity of catalyst deposited in the inner and outer tube wall surfaces (Fig. 2) and by the furnace temperature. Another parameter which influences methane conversion is contact time, which, in the present experimental scheme is defined by feed flow rate. The results shown in Fig. 4 can be explained on the basis of these two variables, temperature and contact time. In the case of HIWARs, at low feed rates the residence time within the reactor is high enough so as to reach equilibrium conditions. Thus, the methane conversion which is observed is close to that predicted by equilibrium considerations, at the temperature which exists at the reactor exit. In the case of the CWR, methane conversion is limited by the fact that sufficient catalyst is not available in the reactor to promote the reforming reactions. As is illustrated by the temperature profile of Fig. 2, combustion is completed over a large fraction of the inner catalyst film and very little reforming is taking place. Heat is transported towards the reactor annulus but, in this case, there is no catalyst on the outer tube furnace to promote reforming. As a result, overall methane conversion is low.

As feed flow rate increases, the magnitude of the hot spot and the average temperature within the reactor increases (Fig. 3). This factor tends to enhance methane conversion for thermodynamic reasons, when conversions are near the equilibrium value — or kinetic reasons, when the operation is far from the equilibrium value. On the other hand, contact time decreases with increasing flow rate, a factor which tends to decrease methane conversion. These two contradictory factors, and possibly other less important factors, give rise to the conversions reported in Fig. 4a and b. Which of the two factors prevails may depend on furnace temperature. Thus, at the low reactor temperatures which are encountered when the furnace temperature is 600°C, conversion seems to increase with increasing flow rate. In this case, the low temperatures impose severe thermodynamic limitations on conversion, which are alleviated as temperature increases with increasing flow rate. Thus, the thermodynamic factor seems to prevail. On the other hand, at the high temperatures encountered at the furnace temperature of 700°C (Fig. 4a) thermodynamic limitations do not seem to be very critical and conversion seems to be mostly influenced by contact time. At very high flow rates, however, conversion seems to be nearly independent of flow rate. This may be due to the fact that at high flow rates the temperature maximum is shifted to the right while the temperature at the catalyst film entrance (inner side) and exit on the annular side is nearly independent of flow rate (Fig. 3). At that level conversion is then adjusting to the thermodynamic constraints imposed by the prevailing temperature.

The influence of the amount of catalyst deposited onto the inner and outer tube surface on methane conversion is also illustrated in Fig. 4. A very large enhancement of conversion is observed in going from the CWR to HIWAR1, i.e. by addition of 3 mg of catalyst onto the outer tube surface. The reason for this is obvious. When 3 more mg of catalyst is added to the outer surface (HIWAR2) in contrast to what might be expected, conversion drops to lower levels. This can be explained with the aid of Fig. 2 which shows that in this reactor the hot spot at the entrance of the catalyst film is very weak. Thus, in the corresponding annulus side (z=0) low temperatures prevail, giving rise to low methane conversion, controlled by thermodynamic constraints. When more catalyst is added on both the inner and outer tube wall surfaces (HIWAR4), methane conversion is increased to rather high levels at all flow rates. This result may imply that within the range of catalyst loadings employed in this study, mass and/or heat transport resistances within the catalyst film (internal resistances) do not significantly influence reactor performances.

3.3. Selectivity

The selectivity towards CO formation and H_2 formation obtained over the CWR and the HIWARs at the furnace temperature of 700°C as a function of the feed flow rate is presented in Fig. 5(a) and (b), respectively. At low flow rates, CO and H_2 selectivities obtained over all reactors are close to the equilibrium values which correspond to the reactor exit temperature. It should be noted that in the CWR the exit temperature is at z=11 and is rather low, while in the HIWARs the exit temperature is at z=0, on the annulus side, and is high because of the exotherm which develops in the inner surface of the tube. Apparently, at these low flow rates the contact time within the reactor is sufficiently high so as to approach conditions of equilibrium.

In the case of the CWR, CO selectivity increases with increasing flow rate while H_2 selectivity decreases up to a flow rate of 300 cm^3/min, to increase

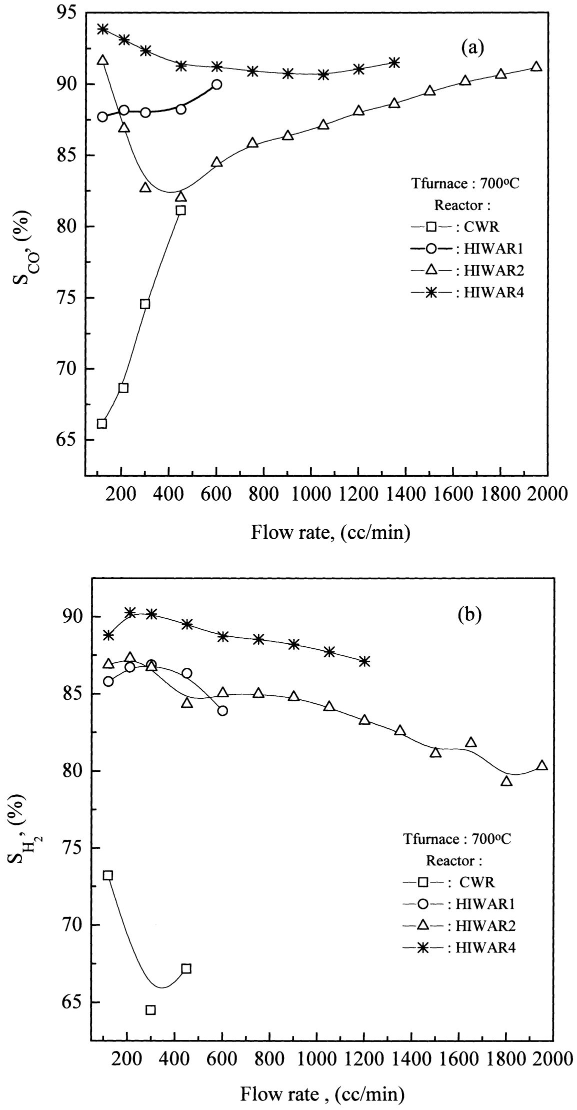

Fig. 5. Selectivity towards (a) CO and (b) H_2 formation, obtained over the CWR and the HIWAR as a function of feed flow rate, at a furnace temperature of 700°C.

again at higher flow rates. The different behavior of the selectivities towards CO and H_2 is probably due to the occurrence of the inverse water–gas shift reaction, which results in enhancement of CO selectivity and reduction of H_2 selectivity. The increase of both selectivities at higher flow rates is due to higher temperatures prevailing in the reactor and higher conversion of methane (Fig. 4).

In the case of the HIWARs, the trends in CO and H_2 selectivities do not seem to follow the variation of methane conversion with flow rate. Furthermore, while H_2 selectivity decreases with flow rate, the opposite seems to be true with respect to CO selectivity. These results may be explained by taking into account two factors: the inverse water–gas shift reaction which results in further production of CO and consumption of H_2, and the possibility that part of CO is produced directly by the interaction of methane and oxygen, without going through CO_2 and H_2O. Direct formation of CO has been reported by Schmidt and co-workers [2,3] over Rh- or Pt-loaded monoliths, and seems to be favored at high temperatures and low contact times. It is conceivable, therefore, that in the present experiments direct formation of CO may be taking place at the regions of the reactor near the exotherms, at high feed flow rates (low contact times). The best syngas selectivity is achieved using the HIWAR4 at a furnace temperature of 700°C. The temperature profiles obtained over the HIWAR4 reactor under reaction conditions at a furnace temperature of 700°C are presented in Fig. 6.

In a different set of experiments, HIWAR4 was modified so as to be able to withdraw samples from the end of the reactor tube (z=11) and analyze them with

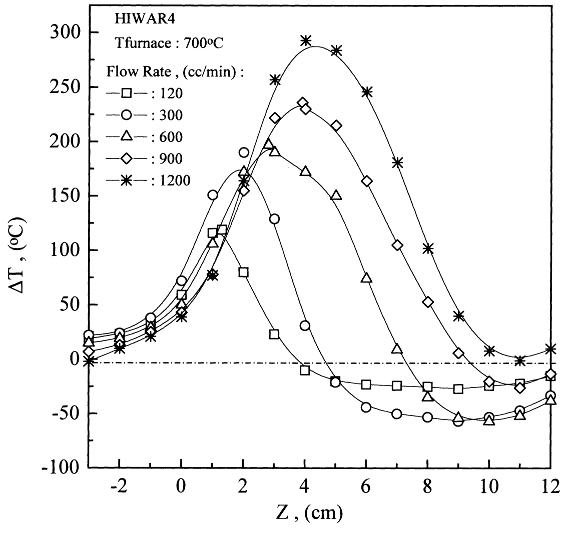

Fig. 6. Temperature profiles along the HIWAR4 under reaction conditions with varying feed flow rate, at a furnace temperature of 700°C (z=0, refers to the entrance of the catalyst film).

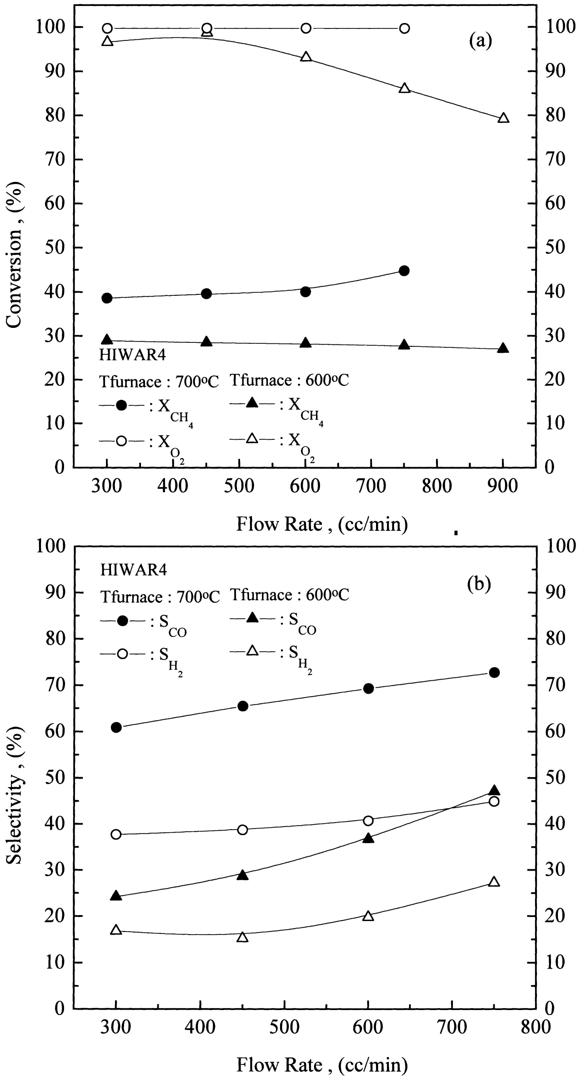

Fig. 7. (a) Methane conversion and (b) CO and H_2 selectivities obtained over HIWAR4 following reaction on the inner catalyst film only as a function of the feed flow rate, at furnace temperatures of 600 and 700°C.

respect to methane and oxygen conversion and CO and H_2 selectivities. The quantity of sample withdrawn was small enough so as not to disturb the steady operation of the reactor. Values of conversion and selectivities, which correspond to reaction occurring over the inside catalyst film only, are shown in Fig. 7(a) and (b), respectively. At the furnace temperature of 600°C, methane conversion is nearly independent of flow rate, varying only between approximately 30 and 25% with variation of flow rate between 300 and 900 cm^3/min. On the other hand, oxygen conversion is complete at low flow rates and drops to approximately 80% at the highest flow rate used. Thus, the combustion reaction is essentially completed within the inside catalyst film, where some reforming also seems to occur. The invariability of methane conversion with contact time may imply that combustion is only taking place at the hot spot region of the catalyst film while the rest of the film is at low enough temperature not to promote methane combustion.

At the furnace temperature of 700°C, complete combustion is occurring over the inside catalyst film, as indicated by the complete oxygen conversion and the relatively high methane conversion. The latter factor also indicates that reforming is also taking place on the inner catalyst film since combustion accounts for 25% methane conversion while the observed values are between 40 and 50%. The variation of CO and H_2 selectivity at the end of the inner catalyst film with feed flow rate, are shown in Fig. 7b. At both temperatures, the variation of H_2 and CO selectivities with flow rate is weak, but sufficiently stronger than methane conversion. This, again, may imply that at high feed rates (i.e. low contact times) and high temperatures, a portion of CO is produced via the direct route, not going through CO_2. Also, at both temperatures, CO selectivity is higher than H_2 selectivity and this may be due to the inverse water–gas shift reaction occurring over the catalyst film.

4. Conclusions

The following conclusions can be derived from the results of the present study:

- The heat integrated wall reactor offers the possibility of reducing significantly the magnitude of hot spots which develop during the partial oxidation of methane in conventional reactors.
- The parameters which influence the operation of the reactor are the relative quantity of catalyst which is deposited on the inner and outer surface of the ceramic tube, temperature and feed flow rate.
- The HIWAR can be operated at very short contact times and nearly uniform temperatures and still

offer nearly equilibrium methane conversions and selectivities.

- There are experimental indications that part of CO and, to a smaller extent H_2, are produced via the direct reaction of partial oxidation of methane.

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