Partial oxidation of methane to synthesis gas over unpromoted and (0.1–0.5 wt%) Ni-promoted calcium aluminate catalysts

A.A. Lemonidou [b,*], A.E. Stambouli [a], G.J. Tjatjopoulos [a,*] and I.A. Vasalos [a,b]

[a] *Chemical Process Engineering Research Institute, PO Box 361, 57001 Thermi, Thessaloniki, Greece*
E-mail: gjt@aliakmon.cperi.forth.gr
[b] *Chemical Engineering Department, Aristotle University of Thessaloniki, PO Box 1517, 54006 University City, Thessaloniki, Greece*
E-mail: lemonido@alexandros.cperi.forth.gr

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The partial oxidation of methane towards synthesis gas is catalyzed over calcium aluminate ($CaO{\cdot}2Al_2O_3$) catalysts, either unpromoted or promoted with small amounts of Ni (0.1–0.5 wt%), at medium temperatures (800°C) and methane-to-oxygen ratios of 2 : 1. Carbon monoxide and hydrogen appear to be primary products of the reaction, along with carbon dioxide and small amounts of C_{2+} hydrocarbons. Methane conversions of 35% and carbon monoxide-to-carbon dioxide ratios of 0.5–0.6 are obtained with the unpromoted or 0.1 wt% Ni-promoted catalysts at complete oxygen consumption. Near thermodynamic equilibrium synthesis gas mixtures are realized with the 0.5 wt% Ni-promoted calcium aluminate catalyst at sufficiently long gas contact times.

Keywords: methane, partial oxidation, synthesis gas, calcium aluminate ($CaO{\cdot}2Al_2O_3$), nickel (Ni)

1. Introduction

Synthesis gas formation by catalytic conversion of stoichiometric methane/oxygen mixtures ($CH_4 : O_2 = 2 : 1$) has been reported several times in the literature [1] with various catalysts, such as Ni dispersed on different supports [2–4], mixed metal oxides of Ru [5] and supported transition metals [6,7]. The reaction over these catalysts usually proceeds via the indirect partial oxidation route which involves a combustion step, i.e. production of CO_2 and H_2O by complete conversion of oxygen, followed by reforming of the residual methane with steam and carbon dioxide to synthesis gas. This reaction scheme leads to steep temperature gradients and severe hot spots in the front region of the catalyst bed due to the occurrence of the strongly exothermic combustion reactions.

Considerable research efforts over the past few years have been directed towards the development of active and stable catalysts for the direct catalytic partial oxidation of methane to carbon monoxide and hydrogen, without the intermediate formation of deep oxidation products, thus avoiding the severe temperature excursions which characterize fixed-bed reactors of indirect partial oxidation catalysts. Formation of carbon monoxide and hydrogen as primary products has been reported by Hickman and Schmidt [8,9] with Pt- and Rh-coated monolith reactors at contact times of 0.1–10 ms and temperatures of about 1000°C. Choudhary and co-workers [10] also reported high synthesis gas yields at low temperatures over various catalysts, but their findings are probably due to the difference between the actual reaction temperature inside the catalyst particles and the measured bed temperature [11]. Parallel formation of carbon monoxide and carbon dioxide during the partial oxidation reaction of methane has been found over transition metals supported on metal oxides [12] and a Ru/SiO_2 catalyst [13]. Primary formation of carbon monoxide and hydrogen over Pt and Rh sponges is supported by recent TAP experiments [14,15], whereas production of carbon monoxide over a $Rh/\gamma\text{-}Al_2O_3$ catalyst via the fast reverse Boudouard reaction of primarily formed surface carbon species and carbon dioxide has been suggested by Baerns and co-workers on the basis of TAP and in situ DRIFTS studies [16,17].

In the present contribution the reaction of methane with oxygen is investigated over unpromoted and Ni-promoted calcium aluminate catalysts ($CaO{\cdot}2Al_2O_3$) at a methane-to-oxygen ratio of 2, atmospheric pressure and nominal temperatures in the range of 800–900°C. These catalyst materials were selected on the basis of previous reports [18,19] which demonstrated that mixtures of alumina with at least one compound selected from the group of alkaline earth oxides are active for the steam/hydrocarbon catalytic cracking reaction, and also for the steam-reforming reaction when promoted by nickel. Although the synergy of the catalyst components has not been elucidated yet, it is speculated that the alkaline earth metal oxides regulate the reactions of hydrocarbon dehydrogenation and inhibit the progress of thermal polymerization towards carbonaceous deposits.

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[*] To whom correspondence should be addressed.

2. Experimental

2.1. Catalysts

Calcium aluminate was prepared from $CaCO_3$ (Mallincrot) and γ-Al_2O_3 (Catapal) with a molar ratio of $CaO : Al_2O_3 = 1 : 2$. The samples were calcined at a temperature of 1100°C for 20 h and crushed to 180–212 μm particles. Details on the preparation and calcination procedures of $CaO \cdot 2Al_2O_3$ have been reported in the literature [19]. X-ray analysis of the samples revealed the formation of two crystalline phases comprising $CaAl_4O_7$ and $CaAl_4O_4$. The incipient wetness technique was applied for the deposition of 0.1 and 0.5 wt% Ni on the calcium aluminate substrate. An aqueous solution of $Ni(NO_3)_2$ was the precursor of NiO. The catalyst samples were calcined in air at a temperature of 600°C for 4 h to decompose nickel nitrate, and then at 900°C for another 10 h.

2.2. Experimental unit

The experiments were conducted at atmospheric pressure in a fixed-bed microreactor made of quartz. The internal diameter of the reactor tube in the catalytic zone is 9.5 mm with a nominal length of 50 mm, whereas the internal diameter in the pre- and post-catalytic sections is 4 mm to minimize the extent of gas phase reactions. The temperature profile along the catalyst bed was measured by a thermocouple shielded in a quartz thermowell. The reactor was heated electrically by a furnace with three independent zones.

High-purity gases CH_4 (99.95%), O_2 (99.99%), H_2 (99.99%), and He (99.95%) were used in the experiments. The effluent stream was cooled down to 0°C for steam removal by condensation. The products were analyzed on line by a Varian 3700 gas chromatograph equipped with a TC detector. A molecular sieve 5A column and a Porapak Q column in a series–by pass configuration were used in product analysis. The carbon, oxygen and hydrogen atomic balance were satisfied within a maximum absolute deviation of less than 2%.

In all experiments the $CH_4 : O_2$ molar ratio was fixed at the partial oxidation stoichiometric value of 2 : 1. The reactants were diluted with He (90 vol%) to minimize the axial temperature gradients. The catalyst particles were also diluted with inert quartz beads of the same size at a ratio of catalyst : inert = 1 : 5. The partial oxidation experiments were conducted at temperatures of 800–900°C and at various contact times corresponding to W/F_t values in the range of 0.1–5 kg s/mol. The variation of the contact time was achieved by changing the catalyst weight and/or the total flow rate of the reactants while keeping the $CH_4 : O_2$ ratio and partial pressures constant. Catalyst weights of 25–400 mg were employed in the experiments. Prior to testing the catalysts were reduced in a H_2/He mixture (50/50) for 1.5 h at 750°C. The contribution of gas phase reactions was assessed by performing comparative experiments at temperatures of 800, 850 and 900°C with the reactor filled with quartz particles. It was confirmed that the extent of gas phase reactions was negligible under the operating conditions applied in the catalytic experiments.

3. Results

3.1. Unpromoted calcium aluminate catalyst

Activity measurements of the unpromoted $CaO \cdot 2Al_2O_3$ catalyst were performed at various temperatures as a function of the gas mean contact time, defined as the ratio of the catalyst layer volume (including the inert particles) to the feed volumetric flow rate (including the He diluent) evaluated at reaction conditions.

The evolution of the conversions of methane and oxygen, measured at 800°C, is presented in fig. 1. It is clearly seen that oxygen is consumed more rapidly than methane, especially at relatively high contact times, despite the fact that a stoichiometric CH_4/O_2 ratio was used. The dependence of the product distribution on methane conversion (fig. 2) seems to indicate that carbon monoxide and hydrogen are primary products, while carbon dioxide is either formed simultaneously with carbon monoxide or is a secondary product over the unpromoted calcium aluminate surface. Twice as much carbon monoxide than carbon dioxide is formed at the lowest methane conversion of ca. 5% which was possible to realize in the experimental setup without serious analytical errors. At higher conversions of methane the carbon monoxide selectivity, defined as the ratio of the CO moles produced to the CH_4 moles consumed, decreases in favor of carbon dioxide, which implies that carbon monoxide, being a primary product, is partially converted to carbon dioxide as the reaction progresses

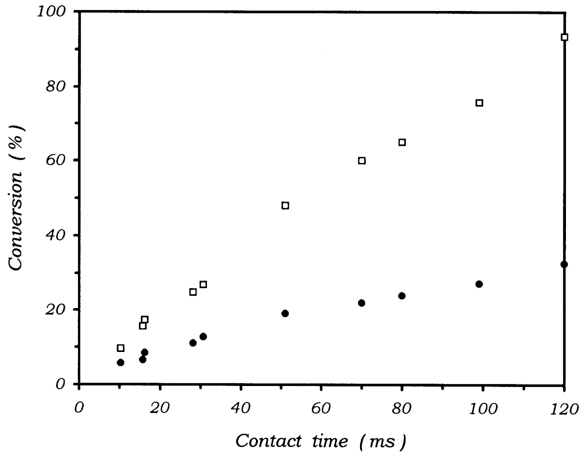

Fig. 1. Effect of contact time on the methane (●) and oxygen (□) conversions with the unpromoted $CaO \cdot 2Al_2O_3$ catalyst ($T = 800°C$, $CH_4 : O_2 = 2 : 1$, 90% He).

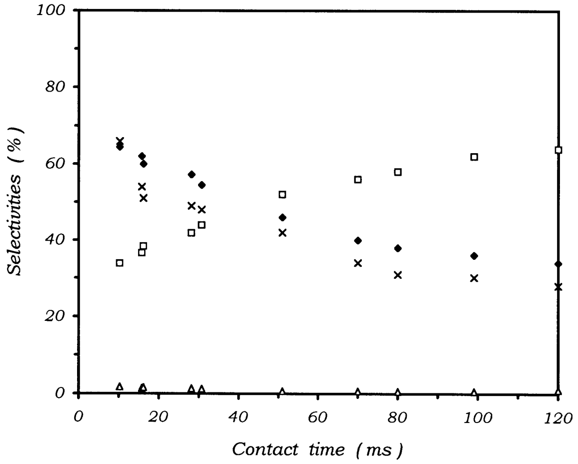

Fig. 2. Product selectivities as a function of contact time with the unpromoted CaO·2Al$_2$O$_3$ catalyst ($T = 800$°C, $CH_4 : O_2 = 2 : 1$, 90% He). Symbols: (×) hydrogen, (◆) carbon monoxide, (□) carbon dioxide, (△) hydrocarbons.

further. The hydrogen selectivity, defined as the ratio of the H_2 moles produced to twice the CH_4 moles consumed, also decreases due to combustion with oxygen towards water. Even at high conversions of methane, C_{2+} hydrocarbons (mainly C_2H_6) were clearly detected at the reactor outlet whereas the C_2H_4/C_2H_6 ratio increased with contact time.

As expected, increasing the reaction temperature above 800°C results in higher rates of methane and oxygen consumption at a fixed contact time (see table 1). At high enough temperatures where oxygen is almost completely consumed, the conversion of methane exhibits a saturation-type behavior reaching a plateau value of about 35%, whereas the carbon monoxide-to-carbon dioxide ratio approaches a limiting value of 0.55 at 850°C and remains nearly constant thereafter.

The above results suggest that the unpromoted calcium aluminate catalyst exhibits a noticeable activity in the direct partial oxidation reaction of methane, but its activity in the steam and carbon dioxide reforming reactions is rather modest. This was verified by separate steam reforming ($H_2O : CH_4 = 1 : 1$) and carbon dioxide reforming ($CO_2 : CH_4 = 1 : 1$) experiments at contact times of up to 1.5 s, which led to methane conversions of less than 20% at reaction temperatures as high as 1000°C.

Table 1
Activity and selectivity of calcium aluminate in the methane partial oxidation reaction. $CH_4 : O_2 = 2 : 1$; gas contact time 50 ms

T_R (°C)	Conversion (%)		Selectivity (%)		
	CH_4	O_2	CO	CO_2	C_2
800	19.2	48.8	46.2	52.8	1.0
830	29.5	75.3	39.0	59.5	1.5
850	32.6	93.5	35.1	63.2	1.8
910	34.8	100	34.5	63.0	2.5

3.2. Calcium aluminate catalysts promoted with nickel

Activity measurements of calcium aluminate catalysts promoted with 0.1 wt% Ni were conducted at 800°C and contact times of up to 0.12 s (fig. 3). It is seen that oxygen is consumed faster than methane with increasing contact time, whereas the dependence of the product distribution upon the conversion of methane is qualitatively similar to that obtained with the unpromoted calcium aluminate catalyst (compare fig. 4 with fig. 2). At low methane conversions (ca. 5%) the selectivities of carbon monoxide and hydrogen are higher than 70% indicating that these products are formed primarily by partial oxidation of methane. As the reaction proceeds further at 800°C, the selectivities of carbon dioxide and water increase at the expense of carbon monoxide and hydrogen.

To exclude the possibility that carbon monoxide and hydrogen are secondary products formed via reforming reactions, carbon dioxide and/or water were added in the methane–oxygen feed and experiments were conducted at 800°C and at short contact times (less than 10 ms). No change was observed in the product distribution suggesting that the 0.1 wt% nickel added to the calcium aluminate support does not accelerate appreciably the carbon dioxide and steam reforming reactions under the specified operating conditions.

The presence of carbon dioxide and water at low methane conversions is an indication that a portion of methane is fully oxidized on the catalyst surface. Higher hydrocarbons (mainly ethane and ethylene) with selectivities of up to 4% were formed under the conditions investigated. At complete oxygen consumption, nearly 35% of methane has been converted to CO, H_2, CO_2, H_2O and C_2 hydrocarbons, with a carbon monoxide selectivity of about 30%. Note that the above results are very close to those obtained with the unpromoted calcium aluminate catalyst at a much higher temperature of

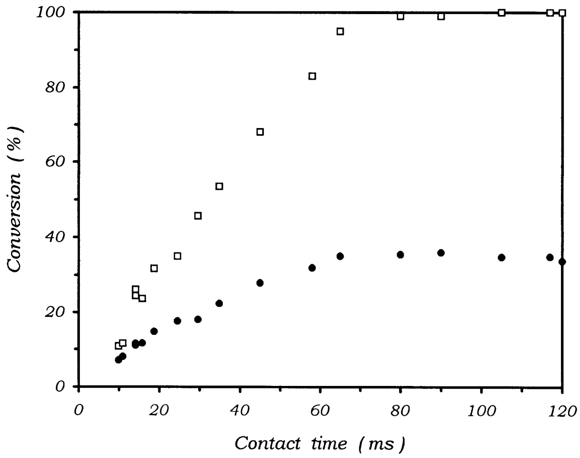

Fig. 3. Effect of contact time on the conversions of methane (●) and oxygen (□) with the 0.1 wt% Ni/CaO·2Al$_2$O$_3$ catalyst ($T = 800$°C, $CH_4 : O_2 = 2 : 1$, 90% He).

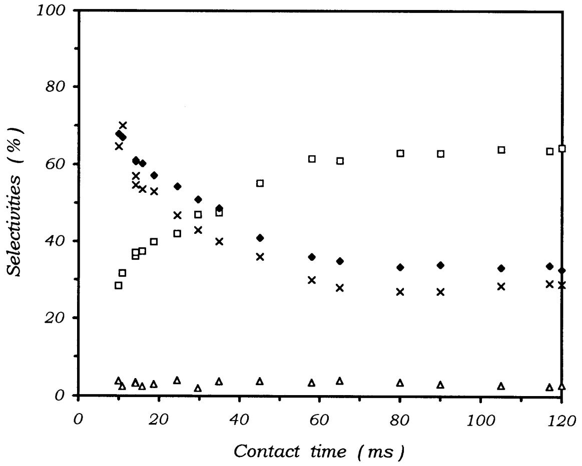

Fig. 4. Product selectivities as a function of contact time with the 0.1 wt% Ni/CaO·2Al$_2$O$_3$ catalyst ($T = 800$°C, $CH_4 : O_2 = 2 : 1$, 90% He). Symbols: (×) hydrogen, (◆) carbon monoxide, (□) carbon dioxide, (△) hydrocarbons.

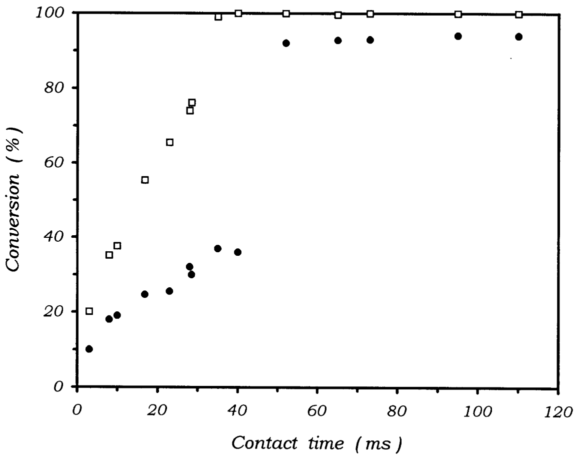

Fig. 5. Effect of contact time on the conversions of methane (●) and oxygen (□) with the 0.5 wt% Ni/CaO·2Al$_2$O$_3$ catalyst ($T = 800$°C, $CH_4 : O_2 = 2 : 1$, 90% He).

900°C, demonstrating the positive effect of nickel in the partial oxidation reaction.

The effect of temperature on the product distribution over the 0.1 wt% Ni/CaO·2Al$_2$O$_3$ catalyst is shown in table 2. For the purpose of comparison, the contact times applied in these experiments were chosen so as to achieve the same conversion of methane (~ 18%) at both temperatures. It is seen that a lower oxygen conversion is obtained at 840°C than at 800°C, which is also reflected on the product distribution characterized by an increase in the carbon monoxide selectivity with increasing temperature. This result suggests that the concentration of adsorbed oxygen species on the catalyst surface decreases with temperature, thus leading to lower rates of oxygen consumption and carbon dioxide formation, as discussed by Hickman et al. [20] for the partial oxidation of methane over Rh and Pt monoliths. A low concentration of adsorbed oxygen species on the calcium aluminate catalyst may be responsible for the primary formation of carbon monoxide and hydrogen.

Different results were obtained when testing calcium aluminate catalysts promoted with 0.5 wt% Ni. As shown in figs. 5 and 6, high conversions of methane and selectivities of carbon monoxide and hydrogen close to thermodynamic equilibrium can be achieved with this catalyst at a temperature of 800°C when operating the reactor at sufficiently long contact times (> 50 ms or $W/F_t > 2$ kg s/mol). A maximum temperature rise of about 10°C along the bed was measured under these conditions. Traces of carbonaceous material were detected on the particles, but the performance of the catalyst samples (~ 100 mg) remained stable without apparent signs of deactivation after 24 h time on stream.

Table 2
Effect of temperature on product distribution at the same methane conversion level. Catalyst: 0.1 wt% Ni/CaO·2Al$_2$O$_3$

	Reaction temperature (°C)	
	800	840
conversion (%)		
CH_4	18.1	17.8
O_2	45.6	37.3
selectivity (%)		
CO	50.9	57.4
CO_2	46.9	37.6
C_2	2.2	5.0

However, when decreasing the contact time below 50 ms the conversion of methane falls off rapidly to the limiting value of 35% obtained with the unpromoted or 0.1 wt% Ni-promoted catalysts at complete oxygen conversion. A similar drastic decline is evident in the carbon monoxide and hydrogen selectivities, whereas at contact

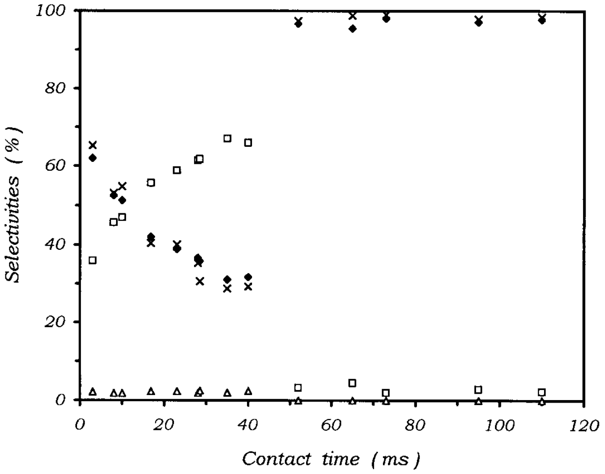

Fig. 6. Product selectivities as a function of contact time with the 0.5 wt% Ni/CaO·2Al$_2$O$_3$ catalyst ($T = 800$°C, $CH_4 : O_2 = 2 : 1$, 90% He). Symbols: (×) hydrogen, (◆) carbon monoxide, (□) carbon dioxide, (△) hydrocarbons.

times smaller than about 35 ms increasing amounts of oxygen are detected in the effluent stream. In the low activity region where oxygen is present in finite concentrations the product distribution and conversions obtained with all three catalysts are qualitatively similar (fig. 7).

Additional experiments were conducted at a temperature of 750°C with the 0.5 wt% Ni/CaO·2Al$_2$O$_3$ catalyst at short contact times and without He diluent. High selectivities to carbon monoxide and hydrogen were obtained at low methane conversion thus confirming the conclusion that carbon monoxide is a primary product even at high oxygen partial pressures, and that the catalytic partial oxidation reaction over these materials proceeds, at least to a significant extent, through the direct route of carbon monoxide and hydrogen production. Carbon dioxide and water are formed simultaneously and the relative rates are controlled by the catalyst composition and the nickel oxidation state.

4. Discussion and conclusions

Based on the above results certain inferences on the mechanism of methane partial oxidation over calcium aluminate catalysts may be drawn. The appearance of ethane and ethylene at short contact times (i.e. at incomplete conversion of oxygen) provides strong evidence that calcium aluminate catalyses the dissociation of the C–H bond of methane molecules thus generating CH$_x$ radicals. The possibility of formation of CH$_x$ species ($x = 2, 3$) over noble metal catalysts at low reaction temperatures has been discussed by Oh et al. [21]. It is speculated that direct formation of carbon monoxide proceeds from CH$_x$ species via the intermediate formation and subsequent rapid decomposition of formaldehyde, much in analogy with the generally accepted mechanism of methane oxidative coupling [22]. The presumption that synthesis gas is produced via adsorbed CH$_x$ ($x = 2$, 3) species and not via totally dehydrogenated carbon species is supported by the value of the apparent activation energy of methane of 110 kJ/mol obtained for CaO·2Al$_2$O$_3$ catalysts over the temperature range of 775–850°C, which is close to the activation energies observed over oxidative coupling catalysts [23]. Direct formation of hydrogen on the catalyst surface is also explained via the generation of CH$_x$ species. The observed decrease in the carbon monoxide and hydrogen selectivities with contact time is due to simultaneous combustion reactions of these species with adsorbed oxygen towards carbon dioxide and water, whereas the enhanced synthesis gas selectivities observed at higher temperatures may be attributed to a decrease in the concentration of adsorbed oxygen species.

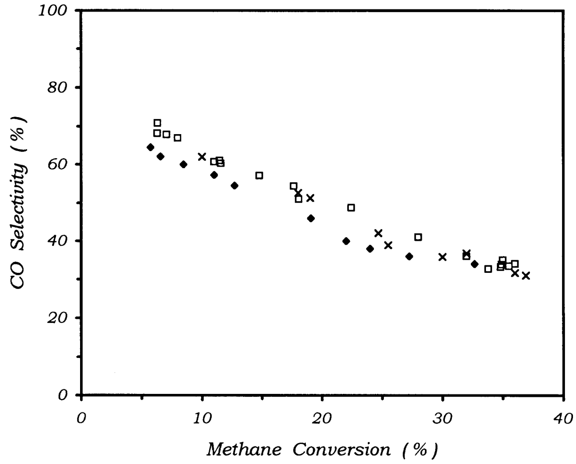

Fig. 7. Dependence of the carbon monoxide selectivity on the conversion of methane over the unpromoted and 0.1, 0.5 wt% Ni-promoted CaO·2Al$_2$O$_3$ catalysts ($T = 800$°C, CH$_4$: O$_2$ = 2 : 1, 90% He). Symbols: (◆) 0 wt% Ni, (□) 0.1 wt% Ni, (×) 0.5 wt% Ni.

The variation in the activity of the 0.5 wt% Ni/CaO·2Al$_2$O$_3$ catalyst with contact time is probably due to the existence of different forms of nickel as discussed in the literature [3,24,25]. At short contact times (incomplete conversion of oxygen) an oxidic form of nickel is established throughout the catalyst bed. In contrast, at longer contact times (complete conversion of oxygen) a metallic form of nickel is likely to be present promoting the secondary reforming reactions of the unconverted methane with steam and carbon dioxide and leading to the formation of equilibrated synthesis gas.

As shown in fig. 7 the oxidic form of nickel which develops on the 0.1–0.5 wt% Ni/CaO·2Al$_2$O$_3$ catalysts in the presence of finite concentrations of oxygen does not lead to enhanced rates of carbon dioxide formation at low methane conversions, even though the catalyst activity is significantly higher than that obtained with the unpromoted calcium aluminate material. Increasing, however, the relative amount of Ni above 1 wt% leads to primary formation of carbon dioxide as evidenced by measured axial temperature profiles displaying a pronounced maximum in the front region of the bed. This behavior is probably due to the existence of significant amounts of NiO.

Synthesis gas production via totally dehydrogenated carbon species is likely to occur over the 0.5 wt% Ni/CaO·2Al$_2$O$_3$ catalyst under the conditions leading to near thermodynamic equilibrium gas mixtures (i.e. at long contact times and complete conversion of oxygen). This possibility is indirectly supported by the formation of traces of carbonaceous material on the catalyst particles, and the absence of C$_2$ products. Formation of CO via fast reactions of surface carbon species with CO$_2$ has been suggested recently [16,17] on the basis of TAP and DRIFTS studies on Rh(1 wt%)/γ-Al$_2$O$_3$ catalysts.

Although the calcium aluminate catalysts investigated in this work (either unpromoted or promoted by small amounts of Ni) are not as active and selective as newly developed direct partial oxidation catalysts [26,27], the fact that synthesis gas is primarily formed in significant amounts at complete oxygen conversion still offers an advantage of these materials over indirect catalysts. Specifically, the temperature excursions which are observed in the entrance zone of fixed beds with indirect partial oxidation catalysts can be moderated by using a dual-bed configuration. In this design concept, an optimized calcium aluminate formulation with a low Ni content is used in the first bed to deplete oxygen and produce as much synthesis gas as possible thus reducing the reaction exotherm, followed by a second catalyst bed to convert the unreacted methane towards synthesis gas via the steam and carbon dioxide reforming reactions. Experimental work on a dual-bed reactor configuration is in progress.

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