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Development of a dual functional structured catalyst for partial oxidation of methane to syngas

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Abstract

Rh-$LaCoO_3$ structured catalysts for the oxidative production of syngas from methane were developed by deposition of the active components on La-γ-Al_2O_3 washcoated honeycomb monoliths. SEM/EDS analysis showed a good adhesion of the washcoat layer and a uniform distribution of La and Co, while Rh was favourably located on the outer shell. Catalytic partial oxidation of methane was tested under both isothermal and pseudo-adiabatic conditions showing that the process can be conducted with high yield and selectivity and stable performance at short contact times over the novel catalysts, characterised by a limited content of noble metal and no need for pre-reduction. Further experiments of CO_2 autothermal reforming indicated the possibility to enhance CO production and to reduce the H_2/CO ratio through secondary endothermic reactions consuming CO_2, which are autothermally self-sustained in a single catalytic reactor operated at short contact time by the heat generated through partial oxidation reactions.

Keywords: Catalytic partial oxidation; Autothermal dry reforming; Syn-gas; Rh-perovskite; Stuctured catalyst; Short contact time

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1. Introduction

Syngas is currently produced by catalytic steam reforming (SR) of hydrocarbons through a highly endothermic reaction, which suffers of heat transport limitations and thus requires contact times on the order of seconds with large energy input at elevated temperature [1–3]. Catalytic dry reforming (DR) of methane with CO_2

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \Delta H^\circ = 247.2\ \text{kJ/mol}$$

allows to produce syngas with a lower H_2/CO ratio, which is a preferable feedstock for gas to liquid processes [4,5]. Moreover, it represents a way to chemically utilize two abundant concomitant gases into higher value products more easily transported, but DR catalysts can be strongly deactivated due to carbon deposition. Otherwise, catalytic partial oxidation of methane (CPO)

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \quad \Delta H^\circ = -36\ \text{kJ/mol}$$

could allow the production of syngas through an exothermic reaction but its application has been limited by oxygen production costs, process control and stability of catalysts typically based on precious metals [6,7].

A promising route to overtake actual limitations and to develop a flexible and advantageous process for CO_2 utilization with high yields to CO might come from coupling catalytic partial oxidation (CPO) together with dry reforming (DR), called CO_2-autothermal reforming (CO_2-ATR). The basic idea is that at least part of the hydrocarbon feed is catalytically oxidized to produce a CO rich gas while unconverted CH_4 in the feed is dry reformed to produce further quantities of syngas, without the formation of solid carbon due to the presence of oxygen and water. In principle, by having a dual-functional catalyst, the heat generated by the CPO can be used to drive dry reforming reaction which is endothermic. The heat exchange might be more effectively managed in an adiabatic reactor, i.e. in an autothermal reactor, lowering the costs of the process by reducing the catalyst volumes, carrying out the reactions at short contact times and using a suitable catalyst formulation.

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In fact, it has been reported that Rh based structured catalysts can lead to high yields to syngas through autothermal methane CPO run at very short contact times [8–10], but Rh is also active for dry reforming [11–14].

In this work bi-functional structured catalysts based on Rh and $LaCoO_3$ perovskite supported on alumina have been developed for methane conversion into syngas. The aim is to better disperse Rh and reduce the amount of noble metal required, ensuring high activity and stability, through its strong interaction with the perovskite matrix and possible formation of solid solutions. At the same time, the remarkable deep oxidation activity displayed by $LaCoO_3$ perovskite in its oxidized form [15] should help providing in situ the heat necessary to drive CO_2 dry-reforming reaction while preventing catalyst deactivation due to coke formation. Moreover, metallic cobalt, eventually present on the catalyst surface under rich high temperature operating conditions might well contribute to activate both CPO and DR reactions [14].

2. Experimental

2.1. Catalyst preparation

Commercial cordierite monoliths (Corning) with a cell density of 400 or 600 cpsi were coated using a modified dip-coating procedure with a thick γ-Al_2O_3 layer, successively stabilised with La_2O_3 (~7%, w/w) by impregnation, followed by calcination in air at 800 °C. $LaCoO_3$ precursors were deposed on the stabilised alumina washcoat through impregnation with an aqueous equimolar solution (0.23 M) of $La(NO_3)_3{\cdot}6H_2O$ (Aldrich, >99.99%) and $Co(NO_3)_2{\cdot}4H_2O$ (Aldrich, >99%), followed by drying in MW oven and in stove at 120 °C with periodic rotation on the axis and calcination at 800 °C for 3 h under flowing air. The process was repeated 10 times in order to achieve a perovskite loading of ~30% (w/w) with respect to the active washcoat layer, monolithic substrate excluded (in the following quoted as LC monolith). Rh-containing samples (named LCR) with a 1% (w/w) target loading with respect to active washcoat, monolithic substrate excluded, were prepared adding $Rh(NO_3)_2{\cdot}2H_2O$ (Fluka, purum.) in the desired amount (0.027 M) to the solution containing both Co-nitrate and La-nitrate. All the three elements were deposed at the same time by repeated impregnations of alumina coated monoliths. Monoliths were dried and calcined as described above. Table 1 reports catalysts denomination, loading of active washcoat and its nominal weight composition.

2.2. Catalyst characterisation

Physico–chemical characterisation was performed directly on monolith catalysts, opportunely sectioned when needed. Specific surface area of the samples was assigned only to the active washcoat layer (SSA of cordierite substrate $\leq 1\ m^2/g$): it was evaluated by N_2 adsorption at 77 K according to the BET method using a Carlo Erba 1900 Sorptomatic apparatus after degassing under vacuum at 200 °C. SEM analysis was performed using a Philips XL30 microscope equipped with an EDAX detector for EDS microanalysis. Metals content in monolith catalysts were checked by inductively coupled plasma spectrometry on a Agilent 7500 ICP-MS instrument, after MW-assisted dissolution of samples in nitric/hydrochloric acid solution.

2.3. Thermodynamic calculations

Thermodynamic equilibrium was calculated using CHEMKIN 4.0.1 [16] software either at constant T and P (isothermal) or H and P (adiabatic, initial temperature required), taking into account the possible formation of solid carbon.

2.4. Experimental set-up

Methane CPO experiments were carried out on monolith catalysts in either of two ways:

- Pseudo-isothermally (low CH_4 flow rate, large N_2 dilution) in order to obtain reliable data for intrinsic activity of catalysts taking advantage of the favorable enhanced heat and mass transfer characteristics of monoliths with controlled fluid dynamics and low washcoat depths. Monoliths 400 cpsi (with 8 out of 25 open channels on the section) were cut to a standard length of 35 mm and positioned inside a lab scale quartz reactor (inner $d = 10$ mm), externally heated by a three zone electrical tubular furnace. The central monolith channel was blocked for catalyst wall temperature measurement with two K-type thermocouples ($d = 0.5$ mm). Standard feed composition was $CH_4/O_2/N_2 = 2/1.2/96.8$, F/W = 150–400 N l/($g_{cat}$ h)

Table 1
Denomination, morphology, active phase content, nominal composition and specific surface area of monolith catalysts

Catalyst	Cell density (cpsi)	Number of cells	d_h (mm)	L (mm)	Active layer (g); (% wt.)	Nominal composition (% wt.)[a]			B.E.T.[a] (m^2/g)
						La-γAl_2O_3	$LaCoO_3$	Rh	
LC1	400	25	1.09	36	0.51 (35.7)	69.60	30.40	0	70.2
LCR1	400	25	1.09	35	0.49 (35.6)	67.50	31.45	1.05	69.7
LCR2	600	210	0.96	11	0.94 (52.6)	69.50	29.52	0.98	69.2

[a] Referred to the weight of active layer, monolithic substrate excluded.

- Pseudo-adiabatically, in order to reproduce conditions of interest for self-sustained high temperature operation. Thus monolithic reactor configuration was changed to a 11-mm long disk with roughly 200 open channels; this assures a higher degree of adiabaticity since the external surface to volume ratio is smaller and the fraction of peripheral channels, which can exchange heat with the surroundings, is minimized. Instead, the front and back faces of the catalyst are larger than the previous configuration, but heat losses are reduced by two blank monoliths (mullite foams, 45 ppi) symmetrically placed upstream and downstream of the catalytic monolith. The catalytic and non-catalytic monoliths were placed in a quartz reactor and tightly sealed with a quartz ceramic wool sheet to avoid gas by-pass and reduce heat losses by conduction. The quartz reactor itself was wrapped with thick layer of ceramic wool and placed in an electric furnace. Three K-type thermocouples ($d = 0.5$ mm), entering from the top of the reactor, were placed respectively above and in the middle of the front radiation shield (T_1, T_2) and in the middle of the central channel of the catalyst in close contact with its surface (T_{cat}); a fourth thermocouple (T_4, K-type with $d = 1$ mm) was used to measure the gas exit temperature downstream of the back heat shield.

High-purity gas flows, controlled with Brooks 5850-MFC, were pre-mixed and fed to the reactor at gas hourly space velocity (GHSV) comprised between 20,000 and 150,000 h^{-1} as evaluated on the basis of monolith volume at standard conditions, corresponding to residence times between 180 and 24 ms. Reactor pressure was kept between 1.12 and 1.3 atm, and feed composition was always above the upper flammability limit at room temperature. Product gases passed through a $CaCl_2$ trap to selectively remove water, prior to splitting to a Hartmann&Braun Advance Optima continuous analyser, employed to measure concentrations of H_2 (Caldos17), CO, CO_2 and CH_4 (Uras14), and to an on line GC (HP5890 Series II). Nitrogen (co-fed or added downstream of the reactor) was used as an internal calibration standard and carbon balance was always closed within ±4%. In these tests O_2 was completely converted and thus the corresponding curve is not reported; moreover no other hydrocarbons were detected apart from unconverted methane.

3. Results and discussion

3.1. Catalyst characterization

SEM analysis revealed that washcoat is uniform and firmly anchored onto the cordierite support due to submicronic nature of the γ-Al_2O_3 powder employed (Akzo CK-300, ~200 m^2/g) and to the network of ramifications deriving from the alumina-based binder. The presence of the washcoat layer leads to a rounding of the initially square channels of the monolith. Average thickness of the washcoat for a 400 cpsi monolith is 20–30 μm at the wall and 80–100 μm in the corners. Specific surface area of active layer, is about 70 m^2/g after calcination at 800 °C for a total of 30 h, either when the alumina was impregnated with Rh + perovskite or perovskite alone (Table 1).

SEM/EDS maps collected on the cross-section of the active layer show that the co-impregnation procedure coupled with MW drying lead to a uniform and homogeneous distribution of La and Co in the whole depth of the washcoat (Fig. 1) without penetrating into the underlying macroporous cordierite substrate. On the other hand, Rh appears preferentially located on the outer shell of the washcoat, limiting its penetration in the porous layer to less than 10 μm starting from the external surface. Such circumstance, probably due to a strong interaction of Rh with the alumina/perovskite surface, does not represent a limit since it actually guarantees a more favourable utilization of the precious metal: especially during high temperature autothermal CPO operation, the reaction is most likely to proceed with a low catalyst effectiveness factor or even under external mass transfer regime with reactants not penetrating deep inside the active layer.

3.2. Pseudo-isothermal tests

Preliminary experiments carried out on LC1 catalyst (not shown for sake of conciseness) revealed a limited methane conversion, below 35% up to 850 °C where thermodynamic equilibrium conversion is >90%. Deep oxidation products (CO_2 and H_2O) prevail, as the selectivity to syngas is lower than 30%; only at total oxygen conversion ($T \geq 800$ °C) a slight increase of H_2 and CO selectivities is detected.

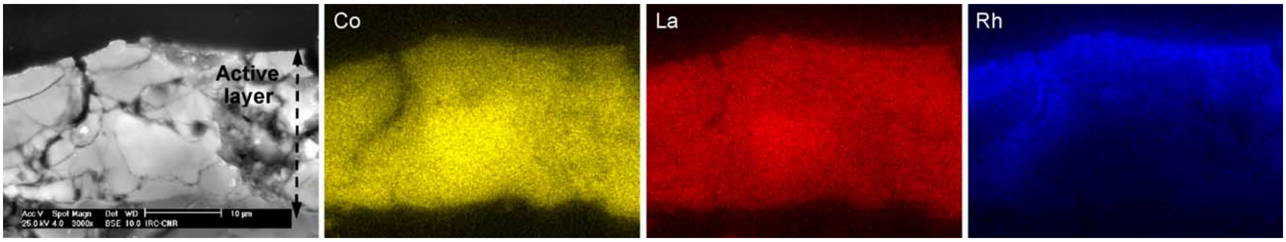

Fig. 1. EDS microanalysis with false colour maps giving elemental distribution inside the active washcoat layer of LCR1 monolithic catalyst.

Decreasing total gas flow, provides higher methane and oxygen conversions, suggesting that surface reaction is the rate-limiting step.

On the other hand, almost total methane and oxygen conversions with high selectivity to CO and H_2 can be obtained at 800 °C over pre-reduced LC1 monolith (1 h in H_2 at 900 °C); however, such catalytic performance is unstable and decreases with time on stream, likely due to the progressive reoxidation of the active metallic Co. Indeed during 3 h under CPO reaction conditions at fixed temperature (800 °C) CH_4 conversion and syngas selectivity progressively decreased from more than 99% and 95%, respectively, down to 50% and the hot reaction front was observed to move along the monolith towards its exit.

Results of CPO reaction tests performed on LCR1 are reported in Fig. 2. For this catalyst it is possible to assign a light-off temperature between 400 and 450 °C, above which both conversion and selectivity to syngas dramatically increase, reaching their corresponding equilibrium values. From this point on the maximum temperature measured on the catalyst (always in the first part of the monolith) was higher than furnace set point by up to 35 °C. Complete CH_4 conversion was obtained for catalyst temperatures $\geq$600 °C.

GHSV had no significant effect on the catalytic performance, probably due to the rapid activation of the catalyst above 400 °C and its high activity that quickly push reactants to thermodynamic equilibrium. No carbon formation was detected after prolonged tests, as confirmed by the absence of CO_x production when feeding O_2 after the catalytic test on the hot monolith. In fact, 8 h long run showed no significant modifications of the catalytic performance, thus the active state of the catalyst appears to be stable under reaction conditions. It must be underlined that no pre-reduction was needed on LCR catalysts to activate the reaction. Thus the perovskite layer appears to be a favourable environment in order to stabilize Rh sites in an active form, giving rise to very good performance even at low noble metal loadings (~0.35% of the total weight of structured catalyst). Furthermore, coke formation is inhibited due to the oxidation properties of the perovskite.

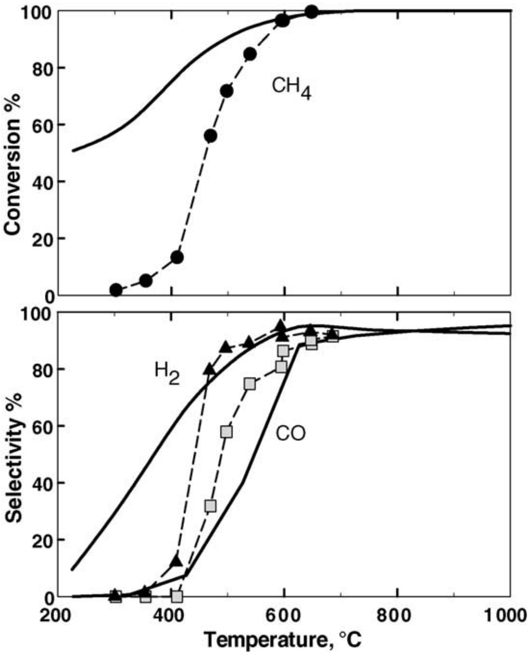

Fig. 2. CH_4 conversion, CO and H_2 selectivity on LCR1 under pseudo-isothermal test conditions as a function of catalyst temperature 10 mm from monolith inlet (solid lines correspond to equilibrium). $CH_4/O_2/N_2$ = 2/1.2/96.8; F/W = 200 N l/(g h).

On increasing furnace temperature above the light-off value, a temperature profile developed along the LCR1 catalytic monolith with a maximum progressively moving towards the reactor inlet, while the remaining part of the catalyst became colder than the imposed furnace temperature. Such circumstance indicates the occurrence of a partial indirect mechanism for the syngas production through oxidation reactions (partial and total) followed by endothermic reactions (reforming and reverse WGS).

3.3. Pseudo-adiabatic operation

Fig. 3 shows catalytic performance of LCR2 catalyst as a function of CH_4/O_2 ratio at $T_{furnace}$ = 500 °C without diluting with nitrogen. Solid lines correspond to thermodynamic equilibrium composition and temperature calculated considering an adiabatic transformation of the feed mixture pre-heated at 500 °C.

Selectivities to syngas are very high (about 95%) and quite unchanged in the whole range of compositions investigated, while methane conversion linearly decreases from more than 90% at CH_4/O_2 = 1.8 down to about 80% at CH_4/O_2 = 2.2, thus affecting yields in the same way. As in the case of pseudo-isothermal tests, coke formation does not occur under pseudo-adiabatic operation even at the highest values of CH_4/O_2: indeed CO selectivity remains almost constant, departing significantly from equilibrium which predicts roughly 15% C-atom selectivity to solid carbon at CH_4/O_2 = 2.2.

Catalyst surface temperature is self-sustained in the range 900–1000 °C and progressively decreases at increasing CH_4/O_2 ratio, whereas inlet gas temperature (T_2) appears quite constant. Outlet gas temperature (T_4) is around 700 °C, slightly decreases with the same trend of T_{cat} and indicates a rapid quench of the product mix after the catalytic monolith. As clearly shown in Fig. 3, measured catalyst temperature is generally higher than the adiabatic equilibrium predicted one especially for larger CH_4/O_2, even if methane conversion is lower than the equilibrium value. At the same time, due to heat losses by conduction and radiation from hot catalyst surface, T_{cat} is roughly 100–150 °C lower than the adiabatic temperature corresponding to the measured products distribution ($T_{ad\text{-}mix}$ in Fig. 3). Such behaviour is related to the catalytic total combustion of a part of the feed and further supports the hypothesis that syngas production occurs according to

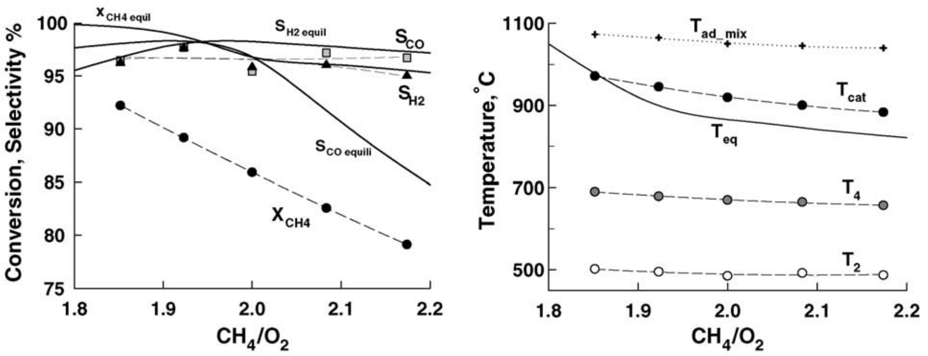

Fig. 3. Catalytic performance and temperature profiles as a function of CH_4/O_2 ratio during pseudo-adiabatic CPO on LCR2 catalyst; $T_{furnace} = 500$ °C; GHSV = 36,000 h^{-1}; no N_2 dilution. (●) CH_4 conversion; (■) selectivity to CO; (▲) selectivity to H_2. Solid lines correspond to calculated adiabatic equilibrium values; $T_{ad\text{-}mix}$ is the adiabatic temperature of the exit gas mixture calculated from the experimental products distribution.

a reaction scheme not excluding indirect formation of H_2 and CO also under self-sustained operation.

It should be noticed that, once the reaction is ignited, the external pre-heating has little effect on the overall performance of the system under partial oxidation with pure methane/oxygen feed mixture: methane conversion and selectivity to H_2 were almost constant for furnace temperatures in the range 300–500 °C, while only selectivity to CO slightly increases with pre-heating. Interestingly also maximum temperatures measured in the catalyst and in the exit gas were not affected by the external pre-heating, which only moved the exothermal reaction front towards the reactor inlet. Therefore, the operating temperature under pseudo-adiabatic operation depends almost exclusively on feed composition and flow rate, while the energy difference necessary to reach this maximum temperature starting from different pre-heating levels is self compensated by a variation in the product distribution (in particular CO/CO_2 ratio).

3.4. CO_2-autothermal reforming

Tests co-feeding CH_4, O_2 and CO_2 were performed in order to evaluate the possibility to obtain syngas with lower H_2/CO ratio coupling in the same reactor exothermic CPO and endothermic CO_2 reforming of methane. Experiments were performed at fixed $CH_4/O_2 = 1.9$ and $T_{furnace} = 500$ °C, starting with roughly 43% dilution of N_2, which was progressively substituted by CO_2 keeping constant the total flow rate. In this way, it was possible to avoid the effects of variable contact times and partial pressures of CH_4 and O_2 and to minimize thermal effects not related to the occurrence of endothermic reactions. Higher O_2 content with respect to stoichiometric for CPO was chosen in order to increase the thermal power available for the reaction and, thus, to sustain the endothermic reforming reactions under autothermal conditions in a single catalytic monolith.

Results reported in Fig. 4 show that methane conversion slightly decreases by increasing CO_2 content in the feed mixture, while more CO_2 is consumed than produced, i.e. CO_2 conversion (defined as $1 - CO_2^{out}/CO_2^{in}$) is always positive, and increases up to about 30% at the highest carbon dioxide content (43% by volume corresponding to $CO_2/O_2 = 2.22$ in the feed).

Selectivity to CO, based only on converted methane, increases continuously, exceeding 100%, i.e. CO is produced through reactions involving not only methane but also carbon dioxide. On the other hand, CO yield,

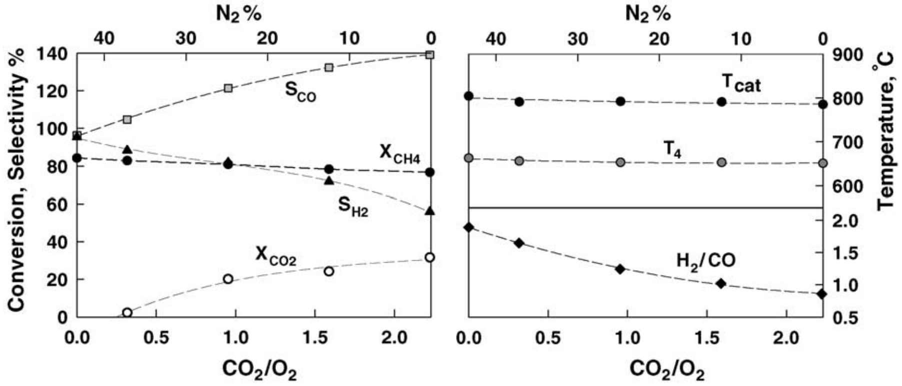

Fig. 4. Catalytic performance and temperature profiles during CO_2-ATR on LCR2 catalyst as a function of CO_2/O_2 ratio varied by progressive substituting N_2 in the feed by CO_2; $T_{furnace} = 500$ °C; GHSV = 40,000 h^{-1}; $CH_4/O_2 = 1.9$; $N_2 + CO_2$ = constant, 43% vol.

calculated on a fed carbon base, diminishes because of relatively low values of CO_2 conversion. Selectivity to H_2 continuously decreases at increasing CO_2 concentration, from about 95% without CO_2 down to 56% for the highest carbon dioxide content, so that also its yield decreases due to the behaviour of selectivity. The H_2/CO ratio in the product stream (Fig. 4) decreases due to the introduction of carbon dioxide, passing from roughly 1.9 under pure CPO conditions down to 0.86 at 43% CO_2 in the feed.

Self-sustained (ignited) operation was achieved with all feed compositions. Fig. 4 also reports temperature values measured on the wall of the catalytic monolith in its central channel and downstream of it in the gas phase (T_{cat} and T_4): they both follow the same trend, only slightly decreasing as a consequence of CO_2 addition, passing respectively from 804 °C to 785 °C and from 663 °C to 651 °C.

All these results suggest that under the used reaction conditions the Rh-$LaCoO_3$ catalyst is more active in the reverse water gas shift reaction (RWGS)

$$CO_2 + H_2 \rightarrow CO + H_2O \quad \Delta H^\circ = 41\ \text{kJ/mol}$$

rather than in the dry reforming of methane. In fact, the occurrence of this reaction, consuming CO_2 and H_2, explains why CO_2 is converted but no positive change of CH_4 conversion is detected, while at the same time selectivity to H_2 decreases and that to CO increases. Moreover, a weak temperature reduction on the catalyst is expected since RWGS is a slightly endothermic reaction. This clearly supports the evidence that CO_2 reforming is not occurring significantly over the present catalyst at temperatures near 800 °C, at contact times near 25 ms and in the presence of oxygen. Indeed CH_4 is probably reacting very rapidly with O_2, and the relatively short contact time (and possibly low temperature) under autothermal operation prevents the remaining CH_4 from reacting with CO_2.

4. Conclusions

Catalytic partial oxidation of methane can be conducted with very high selectivity and stable performances at short contact times over dual functional Rh-$LaCoO_3$ catalysts supported on honeycomb monoliths. Such catalysts are characterised by a low noble metal content (0.35 wt.%) and no need for pre-reduction, indicating a favourable interaction between the two active species. On the other hand, systems based on $LaCoO_3$ in its oxidized form and without noble metal are only moderately active towards total rather than partial oxidation of methane. If pre-reduced, highly dispersed metallic cobalt is active for syngas production but not stable under CPO conditions, since it progressively tends to be reoxidized. Under both isothermal and pseudo-adiabatic conditions H_2 and CO are likely produced through a combination of direct and indirect mechanisms, the latter involving the exothermic total oxidation of a CH_4 fraction, promoted by the perovskite, followed by the endothermic reforming of the unreacted hydrocarbon or reverse WGS, favoured by the noble metal.

In particular, under self-sustained operation of CPO, high syngas selectivities (above 95%) were constantly obtained in the whole range of compositions explored without coke formation, whereas the highest syngas yield (90%) was reached for CH_4/O_2 feed ratios between 1.8 and 1.9. Test conducted with CO_2 added to the feed demonstrated that it is possible to enhance CO production and to modify the H_2/CO ratio, reducing its value well below 1 through secondary (endothermic) reactions consuming CO_2. Such reactions can be autothermally sustained by the catalyst also at the relatively short contact times employed, by taking advantage of the coupling of heat generation and consumption in a single structured reactor. Nevertheless, the main contribution to CO_2 conversion appears to come from reverse water gas shift reaction rather than from dry reforming of the methane, whose unconverted fraction remains almost unaffected even by the addition of large amounts of CO_2.

Acknowledgment

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