

Transient Operation of a Perovskite Partially Coated Monolith at High Pressure

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This work deals with the experimental study of transient ignition during high-pressure combustion of CH₄-enriched syngas. The structured catalyst is a monolith where only the external channels are coated with 20 wt. % LaMnO₃/La-γAl₂O₃ (catalyst coating degree of 80 %). This novel core-shell configuration has shown the opportunity to get complete methane conversion thanks to the occurrence of homogeneous reactions also in the uncoated central channels. Here, homogeneous combustion is stabilized by catalytic combustion occurring in the external channels. In this work, experimental tests were carried out under high pressure conditions (up to 9 bar).

It has been found that the time required to get ignition increases as the coating degree decreases. The longer time is related to the time required by homogeneous reaction to be activated and stabilized in the uncoated channels. High CO₂ content in the feed mixture retards ignition due to CO₂ adsorption over the catalyst surface at temperature lower than 600 °C which negatively affects the catalytic reaction.

1. Introduction

Syngas blends are typically composed by H₂, CO, CO₂ and water and low amount of methane (Ruoppolo et al., 2013). Dilution of the feed stream with CO₂ and H₂O inhibits homogeneous combustion, leading to an increase in the lean blow-out limit of more than 150 K (Griffin et al., 2005). The combustion reaction rate is significantly reduced when CO₂ is present in the feed, leading to an incomplete burnout of the combustion intermediate CO, and increasing CO emissions when stoichiometric O₂/fuel ratios are used (Griffin et al., 2005).

Recently, it has also been showed that the use of CH₄/O₂/CO₂ mixtures even at high CO₂ concentrations is unsafe (Di Benedetto et al., 2014). Indeed, it has been found that when igniting a CH₄/O₂/CO₂ mixture at stoichiometric ratio, even in the presence of 40 % CO₂, an anomalous behaviour arises leading to over-adiabatic peak pressures up to hundreds of bars (the cRPT phenomenon). In order to overcome the technological (flame stabilization, combustion efficiency) and the safety (preventing cRPT phenomena) issues, catalytic combustion (CC) can be proposed.

As a matter of fact, CC allows converting fuels at relatively low temperatures and with very high combustion efficiency, thus avoiding NO_x formation and CO and HC emissions. It is then considered as an alternative route to produce power with low environmental impact in the field of gas turbine (GT) applications (Lee and Trimm, 1995). In particular, Major and Powers (1999) demonstrated that catalytic combustion is very attractive where ultra-low NO_x levels are required and for small size GT, for which secondary measures turn out to be very expensive. Among different types of metal oxides, perovskites (general formula ABO₃) have been extensively proposed as total oxidation catalysts (Seiyama, 1992). Formulations in which A sites are occupied by La or La-Sr and B sites are occupied by Co, Fe, or Mn (Arai et al., 1986) are claimed as the most active phases for methane combustion, Mn-based perovskite providing the best performance (Saracco et al., 1999). However, their application is limited by their low surface area and sintering phenomena occurring at temperatures above 800 °C. As possible solutions to these problems, the active phases have been dispersed over high surface area supports like La-stabilized alumina with a resulting increase in activity and thermal

stability (Cimino et al., 2000). Up to now, this catalyst represents the best compromise combining high reactivity at low temperature and stable operation at relatively high temperature.

According to our previous works, the occurrence of homogeneous reactions is not only unavoidable but also sustains the combustion process and allows to overcome mass transfer limitations, generally occurring within monolithic reactors (Barbato et al., 2012). As a consequence, the novel idea we proposed (Di Benedetto et al., 2012) was to burn methane in a partially coated monolith, catalyst being deposited only onto the external channels (core-shell configuration). We checked the behaviour of this novel configuration by developing a multichannel CFD model. Simulation results allowed us to identify an optimal reactor configuration in which heterogeneous reaction is activated in the external coated channels (with a minimum coating degree corresponding to 40% of channels) and is responsible for the temperature increase and, thus, for the on-set of homogeneous reaction both in the coated and uncoated channels (Di Benedetto et al., 2012). Recently, we prepared and tested "core-shell" partially coated monoliths at pressure up to 10 bar, verifying that by this configuration complete and stable methane conversion without pollutant emissions can be obtained with a reduced catalyst amount (Barbato et al., 2015).

In this work, ignition and quenching behaviour of a perovskite-based catalytic combustor is investigated at high pressure, focusing on the effects of carbon dioxide concentration and syngas-to-methane ratio.

2. Experimental

2.1 Catalyst preparation

Preparation of fully (Barbato et al., 2013 a) and partially Barbato et al., 2015). coated monoliths is described elsewhere. Briefly, 20 wt. % $\text{LaMnO}_3/\text{La-}\gamma\text{-Al}_2\text{O}_3$ catalyst was supported on 900 cpsi cordierite honeycomb monoliths (NGK) in shape of cylinder (length, 50 mm; diameter, 12 mm) by modified dip coating procedure. In order to obtain the "core-shell" monoliths, before catalyst deposition, a parallelepiped hole with square section was created in a monolith previously cut as a cylinder; subsequently, the catalyst has been deposited onto the surface of the hollow monolith. A non-coated monolith has been cut with square section and dimensions corresponding to the hole and has been then inserted in order to occupy the void volume of the coated part (Figure 1a). The adopted procedure allowed us to deposit about 1.83, 1.36 and 1.11 g of catalyst onto the substrate respectively of the fully coated monolith (denoted as F) and the partially coated ones (denoted as P1 and P2).

2.2 Catalytic tests under pressure

The lab-scale set-up, designed to work at pressures up to 12 bar, has been described elsewhere (Barbato et al., 2013 b). Briefly, it can be ideally divided into three sections: gas feed preparation and control, reaction zone and gas analysis. The latter is at atmospheric pressure. Gas feeding is provided by 5 mass flow controllers (Brooks SLA5850) independently controlling the flow rate of O_2 , N_2 , CH_4 (pure gases from different cylinders: CH_4 : 99.995 %; O_2 : 99.7 %; N_2 : 99.998 %), H_2 and CO (as certified mixtures: H_2/N_2 and CO/N_2 respectively at 15 % and 5 %). Besides, a pressure transducer (ABB 261G) is placed just downstream of the gasses mixing point, thus allowing the on-line monitoring of the pressure in the first section of the rig.

A system of three two-way remote-controlled electron valves simulates a four-way valve allowing the analysis of both reacting mixture and reactor off products. A second pressure transducer (ABB 261G) is positioned just upstream of the reactor, thus allowing the pressure measurement at the reactor inlet also when the reactor is bypassed.

The catalytic monolith was placed between two mullite foams acting as thermal shields and wrapped in a ceramic wool tape before being inserted in a cylindrical stainless steel reactor depicted in Figure 1b. As shown in Figure 1b, 6 thermocouples were used to measure the axial profile of the whole reactor including the monolithic section. In particular, three thermocouples provided the temperature measurements inside the monoliths and were positioned at 5 mm from the inlet of the monolith (T_3), at the middle (T_4) and at 5 mm to the end of the monolith (T_5) in the central channel. It should be noted that the central channel is coated for F and uncoated for P monoliths.

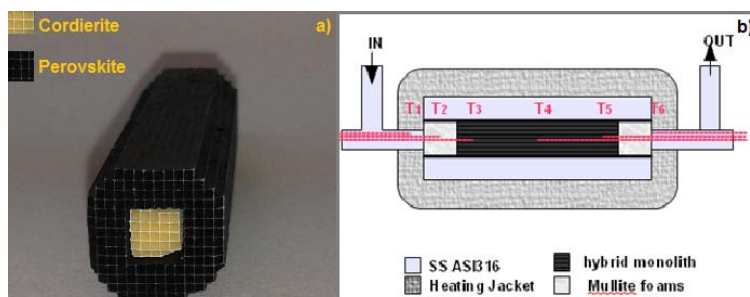


Figure 1: a) Pictures of the assembled partially coated monolith P1; b) Schematic drawing of the catalytic reactor for honeycombs with indications of flow path and thermocouple placement

Reactor pre-heating is provided by an heating jacket (Tyco Thermal Controls); water produced by combustion is condensed and the dry gasses flow through the pressure controller (Brooks SLA5820), which regulates the upstream pressure in the range of 0-15 bar gauge. The remainder of the plant is, then, at a pressure slightly above the atmospheric one. A constant fraction of the gas flow rate is further dried by means of a CaCl_2 chemical trap before entering the analysis system (ABB AO2000), provided with seven equipment for the on-line and continuous analysis of the main gas species (CH_4 , CO_2 and CO by infrared detectors, O_2 by paramagnetic detector, H_2 by thermo-conductivity detector, NO and NO_2 by ultraviolet detector).

Operating pressure was increased from approximately 1 to 12 bar. The mass flow rate was kept constant (i.e., the volumetric flow rate decreased with increasing pressure). A syngas/methane volumetric ratio (50/50) and three CO_2 concentrations (0, 5 and 30 vol.%) were investigated at fixed H_2/CO (1.5 v/v) and pre-heating temperature (520°C). Oxygen concentration was fixed to 10 vol.%; the total flow rate was equal to 60 L(STP)/h.

As reported above, water was condensed upstream of the analysing system; as a consequence, in order to calculate the wet composition of the reacted gases, water has been calculated through the hydrogen balance, carbon and oxygen balances providing the overall quality of the experiments. Carbon and oxygen balances were always closed within $\pm 4\%$.

Some tests have been repeated in order to verify the reproducibility of the results. These tests provided about the same results, errors lying within the experimental error ($\pm 5\%$).

3. Results

In Figure 2, the temperatures measured inside the monolith P1 and methane and carbon monoxide concentrations during ignition in absence (left) and presence (30 vol.%; right) of CO_2 as a function of time-on-stream are reported. Qualitatively, the behaviour is typical of ignition phenomena in both cases (Barbato et al. 2012). A continuous drop of methane concentration, as occurring for methane alone (Di Benedetto et al., 2012) is detected and coupled with temperature increase (Barbato et al. 2013a). After a certain time (about 30 min), methane concentration falls down to a very low value, even though higher pressures are needed for methane complete depletion as reported in Barbato et al. (2015). During start-up, a reaction front moves towards the first part of the reactor, as indicated by the maximum values of temperature in T5 (first) and T4 and the rapid increase of T3 (Landi et al., 2014). This behaviour has been detected also if temperature rather than pressure is increased to get ignition (Barbato et al., 2009).

In order to deeply discuss the transient behaviour of partially coated monoliths and the effect of carbon dioxide, some previous results of ours should be reported and summarised. The catalytic activity of LaMnO_3 perovskite towards the different fuels (i.e. H_2 , CO and CH_4) is different (Barbato et al., 2013b), as suggested by their kinetics too (Landi et al., 2013). In particular, CO combustion shows the most rapid kinetics, while methane is the slowest (Landi et al., 2013). When a fuel blend is used, combustion of CO and H_2 occurs in the first part of the reactor, causing a temperature increase in its second part (Barbato et al., 2013b). Due to the increased temperature, methane ignition is obtained under milder conditions, i.e., lower temperatures (Barbato et al., 2009) and/or pressure (Barbato et al., 2013 b). Independently of the fuel composition, the peak temperature during ignition is generally related to methane activation.

Another important result to report here is the effect of carbon dioxide on the pressure ignition. CO_2 addition to the reacting mixture causes a delay of the ignition conditions (Di Benedetto et al., 2013). In particular, this effect depends on the CO_2 concentration in the feed; low CO_2 concentrations (i.e., 5 vol.%) cause a marginal increase of the ignition pressure, while higher concentrations modify the ignition conditions more significantly.

It is worth noting that the effect of CO₂ is due to both chemical and thermal reasons, related to its adsorption on the catalysts surface (favoured at $T < 550$ °C) and higher specific heat (Di Benedetto et al., 2013).

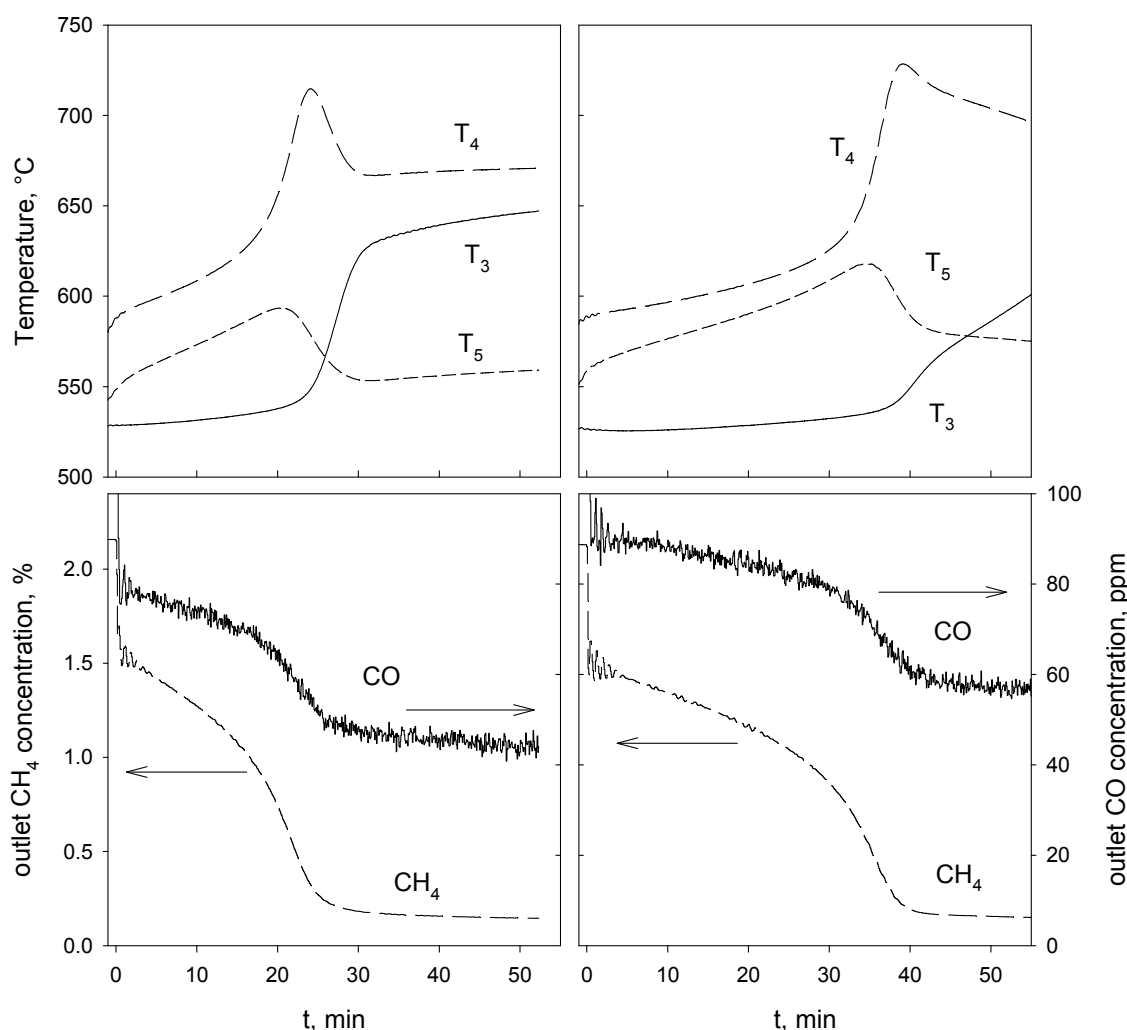


Figure 2: Temperatures (top) and CH₄ and CO concentrations (bottom) profiles during ignition of syngas/methane mixtures. CO₂ concentration: 0 vol.% (left); 30 vol.% (right)

Moreover, from the experimental campaign conducted, it appeared that, while CO successfully competes with CO₂ for adsorption over catalytic active sites, methane does not (Di Benedetto et al., 2013).

As reported above, in Figure 2, ignition transient behaviour at 0 and 30 vol.% CO₂ concentrations is reported; operating pressures correspond to 4 and 5 bar (minimum ignition pressures), respectively. 5 vol.% CO₂ addition does not modify significantly the ignition conditions and the time-on-stream profiles and, thus, has not been reported.

Looking at the temperature profiles, it appears that, before methane ignition, T₄ (i.e., the temperature measured at the centre of the monolith) is the highest. This is due to the heat release related to syngas combustion; as a matter of fact CO concentration is at ppm level.

By comparing the profiles, it clearly appears that the transient at higher CO₂ concentration lasts longer, despite of the higher pressure. This is due to both the CO₂ adsorption on the surface and larger specific heat, causing a reduction of the gas and solid temperatures. This is confirmed by the values of the temperatures; as a matter of fact, before ignition, as CO₂ concentration is increased, T₃ and T₄ decrease and T₅ increases, thus suggesting a shift of the syngas reaction front to downstream. It is worth noting that the temperature inside the uncoated channels is high enough to activate CO and H₂ homogeneous combustion, as demonstrated by the low levels of CO and H₂ (not reported). On the other hand, methane conversion is lower

than that expected if complete conversion is attained in the catalytic section and corresponding to a concentration equal to 0.45 vol.%. This means that only a part of the fed methane is catalytically converted before ignition.

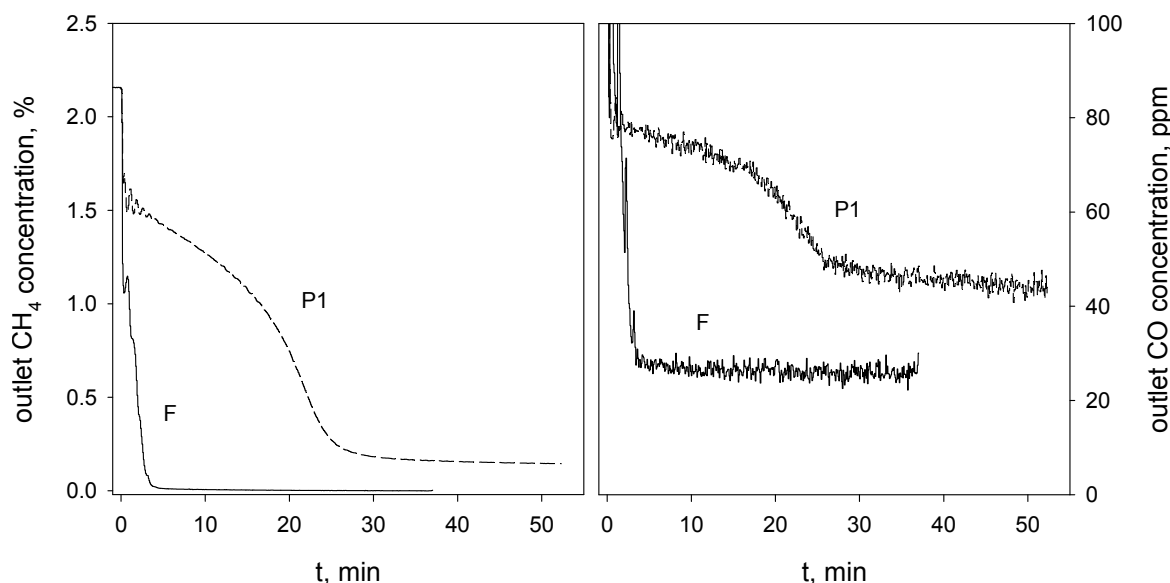


Figure 3: Methane (left) and CO (right) concentrations profiles during ignitions of syngas/methane mixtures on fully (F) and partially (P1) coated monoliths in absence of CO₂. Operating pressures: 3 bar (F), 4 bar (P1)

During the ignition, the temperature increase allows methane to be activated homogeneously, very probably first in the catalytic section and then in uncoated channels, as suggested in Landi et al. (2014) and Di Sarli et al. (2014). The shift of the reaction fronts due to CO₂ addition causes a little but significant increase of CO emissions from 45 to 55 ppm. This could be due to an increase of the unconverted CO or to a larger fraction of methane converted to CO instead of CO₂. Even if it is difficult to distinguish between these two hypotheses, it seems more likely that the higher CO concentration is originated by methane incomplete combustion. As a matter of fact, in our previous work of ours (Barbato et al., 2013 a), over a CH₄-fuelled fully coated monolith, at ignition, a low but non-negligible CO production was found associated with the onset of homogeneous reactions occurring at the end of the monolith, leading to insufficient residence time to convert the produced CO to CO₂.

The methane concentration profiles reported in Figure 2 are characterised by a significant change of the slope in correspondence of the peak temperature. This behaviour seems peculiar of the partially coated monolith. By comparing the transient concentration of methane during ignition on fully and partially coated monoliths (Figure 3, left), it appears that on the fully coated monolith (F) at ignition a sharper methane concentration decrease is detected to a value corresponding to methane complete conversion. The same behaviour is observed on CO concentration (Figure 3, right). While in the case of P1 monolith, a peculiarity change of the slope is observed that is related to the activation at different times of the homogeneous methane combustion in the coated and uncoated channels, as we already reported in a previous modelling work (Landi et al., 2014).

Finally, under the experimental conditions adopted in this work, monolith P2 did not show a full ignition of the fuel mixture. We demonstrated that the operability window is a function of the coating degree (Barbato et al., 2015). Thus, the adopted fuel concentrations are too low to get stable operation on P2.

4. Conclusions

In this study, the experimental start-up operations of a “core-shell” perovskite partially coated honeycomb fuelled with methane enriched syngas at high pressure are reported. Ignition phenomenon is qualitatively similar on both partially and fully coated honeycomb, although several differences are found. First of all, a sharp methane concentration drop to zero is obtained only over the fully coated monolith, while in the case of the partially coated one, even if CO and H₂ conversions are very high (suggesting a non-negligible contribution of gas phase reactions in uncoated channel) methane falls down to a small but not negligible value. Moreover, the shape of the CH₄ time profile, characterised by a significant slope change, suggests a

time-spaced activation of methane homogeneous reaction in coated (first) and uncoated (after) channels, thus confirming our previous modelling results. The impact of 5 vol.% CO₂ does not affect the transient behaviour of the partially and fully coated monoliths while a more different behaviour has been addressed in the case of 30 vol.% CO₂, whose ignition transient lasts longer and is related to larger CO emissions.

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