

Ignition and Quenching Behaviour of High Pressure CH₄ Catalytic Combustion over a LaMnO₃ Honeycomb

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In the present work, we report experimental results for the behaviour of a LaMnO₃-based honeycomb in the catalytic combustion of methane, in particular during the start-up and shut-down operations at different pressures. Methane ignition is mainly driven by heterogeneous reactions. The temperature increase due to the heat developed on the catalyst surface is responsible for ignition of homogeneous reactions, allowing the complete fuel consumption. On the other hand, during quenching, the homogeneous reaction front moves towards the exit of the catalytic reactor; a rapid drop in the mean reactor temperature and methane conversion is detected. According to our results, quenching appears to be related to the decrease in the heat generated by homogeneous reactions.

1. Introduction

The reduction of pollutant emissions from gas turbines is still a major concern about power generation systems (Kanniche, 2009). Catalytic combustion allows converting light hydrocarbons 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; Barbato and Landi, 2012). 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.

Amongst different types of metal oxides, perovskites (general formula ABO₃) have been extensively proposed as total oxidation catalysts (Seiyama, 1992). Moreover, their structure robustness permits the partial substitution of A and B cations by metals with a different oxidation state (A_xA'_{1-x}B_yB'_{1-y}O_{3-δ}). The partial substitution results in a profound modification of the activity, since it leads to the formation of structural defects promoting the catalytic activity of the material (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 or La-stabilized MgO or spinels with a resulting increase in activity and thermal stability (Cimino et al., 2000). In order to increase the perovskite activity, bi-functional catalysts, containing small amounts of noble metals, have been proposed (Uenishi et al., 2005; Giebler et al., 2007; Scarpa et al., 2009). Up to now, this catalyst represents the best compromise combining high reactivity at low temperature and stable operation at relatively high temperature.

Even though, in all the possible applications, catalytic combustors operate at high pressure (up to 20 bar), most of the literature studies have been performed at atmospheric pressure. Pressure affects several phenomena such as transport of reactants and products between gas phase and catalytic surface (including diffusion in the catalyst pores), surface reaction (including several steps, such as species adsorption and desorption, reactions among adsorbed species, etc.) and heat transfer between gas and solid phases. Moreover, it has been demonstrated that, under high pressure conditions, homogeneous

gas-phase chemistry is coupled with heterogeneous surface-phase chemistry for several fuels, such as methane, hydrogen and CO/H₂ mixtures (Mantzaras, 2010; Barbato et al., 2012).

Andrae et al. (2005) performed high-pressure catalytic combustion experiments with synthetic gasified biomass fuel in a monolith reactor over Pt/ γ -Al₂O₃. They found that the combustion efficiency decreases with increasing pressure, concluding that the increased surface reaction rate due to pressure increase cannot compensate for increased mass transfer limitations. On the other hand, results obtained at constant mass flow rate showed that a decrease in combustion efficiency can be compensated for by increased residence time in the monolith. In some cases, it has been shown that the increase in catalytic reaction rate due to the pressure increase has a positive effect on the performance of a combustor in terms of operating window (Carroni et al., 2003; Karagiannidis et al., 2011).

It is worth underlying that the most part of the above studies have been focused on noble metals as active phases.

Very recently, we performed a kinetic study of the combustion of different fuels (methane, hydrogen, carbon monoxide) over 20 % wt LaMnO₃/La- γ -Al₂O₃ catalyst with pressure varying in the range of 1-12 bar. From this study, a kinetic rate expression was derived for each fuel (Landi et al., 2013).

We also reported experimental results for the behaviour of methane (Barbato et al., 2012) and methane-added synthesis gas (Barbato et al., 2013) catalytic combustion over a 20 % wt LaMnO₃/La- γ -Al₂O₃ monolith under conditions relevant to small size GT applications (pressure up to 12 bar) showing that, as pressure increases, ignition is attained. In particular, in the case of methane combustion, we coupled a CFD model of a single channel showing that homogeneous reaction plays a significant role in affecting fuel conversion (Barbato et al., 2012). Subsequently, the study was extended to get insights into the combined effects of flow rate and operating pressure on the interplay between heterogeneous kinetics, homogeneous kinetics and transport phenomena and, at the same time, a CFD model of the monolith was developed in order to perform a parametric investigation (Di Benedetto et al., 2012). More precisely, a multi-channel configuration was modelled to test the relevance of homogeneous reaction. We demonstrated that the effect of pressure is to decrease the mass transfer from the bulk phase to the catalyst, thus preventing the complete methane conversion. However, this effect was counter-balanced by the activation of homogeneous reaction which is favoured by increasing pressure.

2. Experimental

2.1 Catalyst preparation

The transient behaviour of lean methane combustion was studied over a 20 wt % LaMnO₃/La- γ -Al₂O₃ catalyst supported on 900 cpsi honeycomb cordierite monolith (NGK) in shape of cylinder (length, 50 mm; diameter, 11 mm). The commercial cordierite monolith cut in the desired shape was previously coated with a La₂O₃-stabilized γ -Al₂O₃ layer, by a dip-coating procedure, and calcined in air at 800 °C (Barbato et al., 2009). Perovskite precursors were deposited on the stabilized alumina washcoat through impregnation with an aqueous solution of La(NO₃)₃·6H₂O (Aldrich, > 99.99 %) and (CH₃CO₂)₂Mn·4H₂O (Aldrich, > 99 %). The samples were dried in stove at 120 °C, and calcined at 800 °C for 3 h under flowing air. The process was repeated 10 times in order to achieve the target loading (\approx 20 wt % perovskite with respect to the active washcoat layer, monolithic substrate excluded). The adopted procedure allowed us to deposit about 1.4 g of catalyst onto the substrate.

2.2 Catalytic tests under pressure

The lab-scale set-up, designed to work at pressures up to 12 bar, has been home-made and can be ideally divided into three sections: gas feed preparation and control, reaction zone and gas analysis. The latter is at atmospheric pressure. O₂, N₂, and CH₄ from gas cylinders at high purity (CH₄: 99.995 %; O₂: 99.7 %; N₂: 99.998 %) have been independently controlled through mass flow controllers (Brooks SLA5850), operating at 15 bar and each one having downstream their own two-way electrovalve operated by remote control in order (i) to block the gas flow of unused gasses and, (ii) to interrupt the flow of all gasses for safety reason. 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 electrovalves 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.

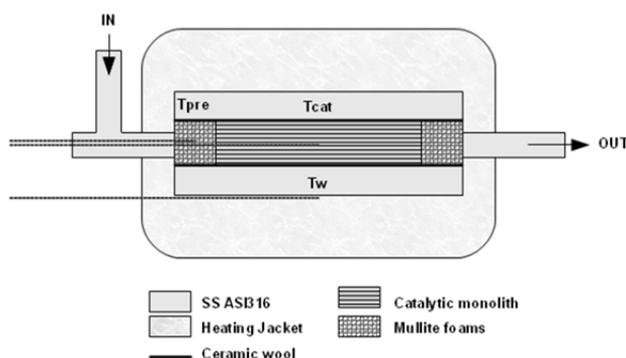


Figure 1: schematic drawing of the catalytic reactor for honeycombs with indications of flow path and thermocouple placement.

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 1. Two thermocouples were placed inside the reactor at the centre of the first thermal shield (or pre-heater) (T_{pre}) and at the centre of the monolith (T_{cat}). Moreover, a third thermocouple (T_w) was placed close to the external steel wall and the heating jacket, approximately in correspondence to T_{cat} (figure 1). The thermocouples inside the reactor were sealed thanks to a Multiple-Hole Ceramic gland feedthrough connected at the end of the reactor (Conax Buffalo, MHC series).

An heating jacket (Tyco Thermal Controls) was equipped with a PID controller for the initial reactor temperature. In order to avoid water condensation, the reactor exit line was maintained at 120°C till the entrance of a condenser (Parker), which consists of two co-axial steel tube coils, the inner for the gas flow and the outer for the cooling water counter-flow. The condensed water was collected in a tank. Finally, the dry gasses or the reacting mixture 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 four equipments for the on-line and continuous analysis of the main gas species (CH_4 , CO_2 and CO by infrared detectors and O_2 by paramagnetic detector).

Auto-thermal experiments were conducted at fixed pre-heating conditions and by first increasing and then decreasing the pressure in the range of 1-10 bar. The catalysts were previously aged in air at 800 °C for at least 12 hr, thus providing stable performance (Scarpa et al., 2009). The mass flow rate was kept constant (i.e., the volumetric flow rate was decreased by increasing pressure).

The methane concentration has been fixed to 3.7 % which is out of the flammability limits at all the test conditions. In all the experiments, the oxygen concentration has been set to 10 %, lower than the minimum oxygen concentration (MOC = 12 %), thus allowing inherently safe run conditions.

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 ± 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 (± 5 %).

3. Results

As reported in our previous papers (Barbato et al., 2012; Di Benedetto et al., 2012), by increasing the operating pressure, methane ignition is obtained at fixed pre-heating temperature. In particular, at 450 °C pre-heating temperature, corresponding to about 500 °C measured in the middle of the monolithic reactor, and using 60 slph of total flow rate, ignition occurs at 5.5 bar (by increasing the pressure).

In Figure 2, the temperature profile and calculated conversion recorded during the ignition are reported as a function of time on stream. The conversion and temperature, starting from approximately 20 % and 500 °C, continue to increase due to an heat accumulation phenomenon. At approximately 15 min, it can be

observed a change in the slope and at 34 min full ignition occurs. In correspondence to this phenomenon, a maximum of about 860 °C is found in the temperature profile; the peak is related to the reaction front movement from the end of the reactor, where the temperature is expected to be higher, to the reactant inlet thanks to the heat retrodiffusion. After ignition, it appears that the thermal level of the reactor is increased as shown by the value of the temperature at the centre of the monolith reaching 700 °C. At ignition, moreover, a low but not negligible CO production was found with a maximum of 70 ppm (low compared to 3.7 vol.% CH₄). It is worth noting that, once the system is ignited, CO emissions immediately decrease to zero. It is well-known (Saracco et al., 1999, Cimino et al., 2000) that perovskites are selective towards CO₂ rather than CO formation as combustion product (also because CO oxidation is rapid (Landi et al., 2013)). Therefore, CO production should be more likely attributed to homogeneous combustion of a fuel fraction. Thus, the behaviour of CO emissions gives further insight into the ignition mechanism, suggesting the onset of homogeneous reactions. From these results, it clearly appears that methane ignition is mainly driven by heterogeneous reaction, occurring at relatively low temperature. Furthermore, at ignition the temperature raise is enough to allow homogeneous reaction to start; the combination of heterogeneous and homogeneous reactions is responsible for the complete fuel consumption and temperature increase. By increasing the flow rate (88 slph), ignition occurs at higher pressure (8 bar), but the transient behaviour is similar (not reported).

By decreasing the pressure at fixed flow rate and pre-heating temperature and starting from ignited conditions, methane conversion is still complete due to the existence of multiple steady state (Di Benedetto et al., 2012). Nevertheless, at a certain pressure (about 1.3 bar at 60 slph and 2.3 bar at 88 slph) quenching occurs. In order to give further insight into the quenching phenomenon, figures 3(a) and (b) show the temporal profiles of CH₄ conversion, temperature and CO emissions recorded during the quenching at 60 slph and at 88 slph respectively. As previously reported (Di Benedetto et al., 2012), these transients exemplify two different quenching modes: extinction and blowout respectively.

As shown in Figure 3, the quenching phenomenology is similar for both the transients: after a drop in the temperature measured in the centre of the monolith, the conversion drops and at the same time there is a maximum in the CO emissions. The major differences in the profiles recorded are the transient duration, which is longer at the lower flow rate, and the behaviour of the temperature, which in the former case (i.e. extinction) goes through a maximum and has a less steep drop. As a matter of fact, in the case of extinction, stability is lost due to a too large heat loss (towards surroundings) compared to the thermal power provided via combustion. Also this quenching mode, however, involves a progressive rearrangement of the system with an enlargement of preheating zone and a shift of the reaction front downstream, causing the presence of a temperature maximum at the centre of the monolith.

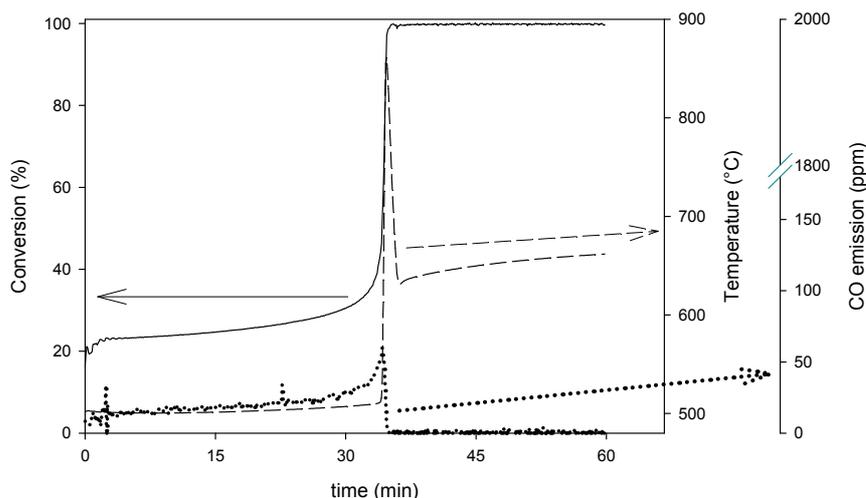


Figure 2: methane conversion (solid line), temperature (dashed line) and CO emissions (dotted line) as function of time on stream during ignition at $P = 5.5$ bar. Flow rate = 60 slph, $T_{pre} = 450$ °C.

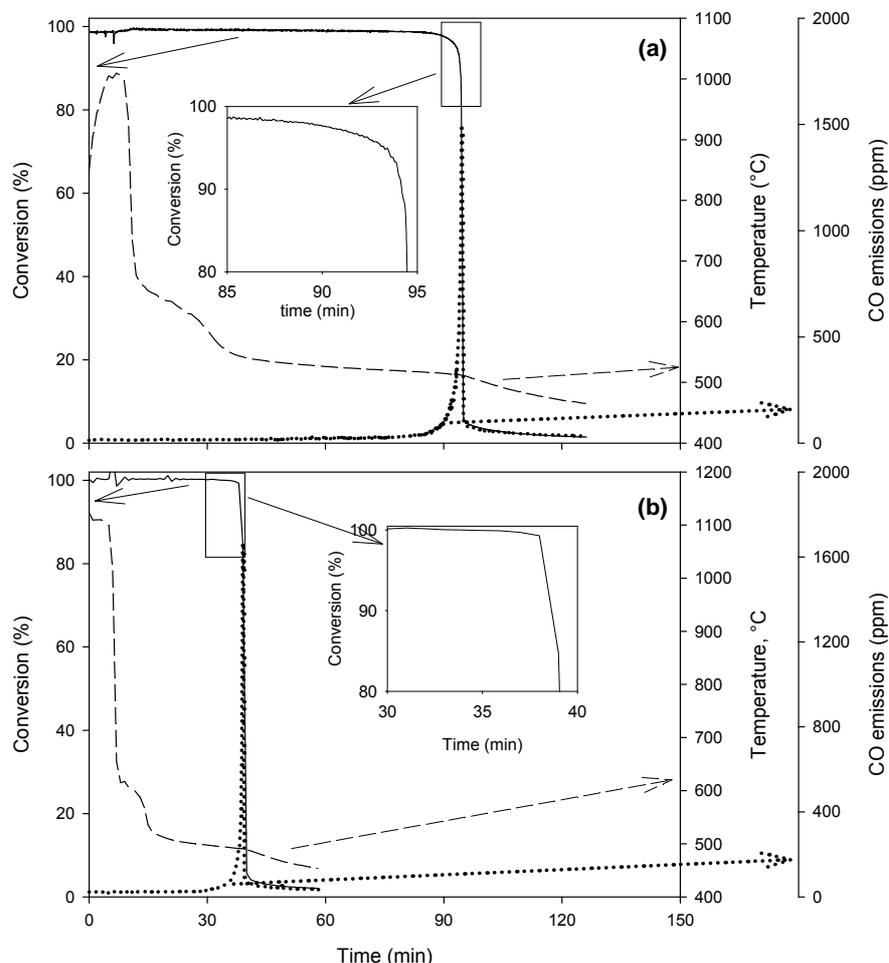


Figure 3: methane conversion (solid line), temperature (dashed line) and CO emissions (dotted line) as a function of time on stream during quenching: $T_{pre} = 450$ °C. (a) $Q = 60$ slph, $P = 1.3$ bar; (b) $Q = 88$ slph, $P = 2.3$ bar.

Moreover, from the enlargement boxes in Figure 3, it appears that the conversion in the case of blowout (Figure 3(b)) has a steeper drop. As a matter of fact, in the blowout mode, quenching occurs because of a too large flow rate, resulting in incomplete fuel conversion for insufficient residence time and a fast shift of the reaction front downstream. In the blowout mode, quenching occurs because of a too large flow rate, resulting in incomplete fuel conversion for both insufficient residence time and a considerable shift of the reaction front downstream, due to insufficient cold feed gas pre-heating. The presence of the CO peak when conversion falls down suggests that the homogeneous reaction front is at the end of the reactor when quenching occurs. Our results show that, regardless of the mode (extinction or blowout), quenching is mainly related to the cut off of the homogeneous reactions, providing a significant fraction of the combustion heat.

4. Conclusions

In this study, experimental results concerning the behaviour of a LaMnO_3 -based honeycomb during the start-up and shut-down operations of methane catalytic combustion at high pressure are reported. Our results show that fuel ignition is mainly driven by heterogeneous reactions; as a matter of fact, the temperature increase related to surface reaction causes ignition of homogeneous reactions, responsible for the complete fuel consumption. According to our results, the ignition is due to a synergistic effect between heterogeneous and homogeneous reactions. During quenching, the homogeneous reaction front moves downstream, reaching the exit of the reactor, regardless of the quenching mode (extinction or

blowout); thus, a rapid drop of temperature and methane conversion is detected. As a consequence, quenching appears to be related to the reduction of the heat generated by homogeneous reaction. Thus, surface (catalytic) reaction is unable to sustain the monolith ignited; it clearly appears the importance of homogeneous reaction in the heat generation allowing self-sustained reaction conditions.

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