ON THE PARTIAL CATALYST-COATING OF MONOLITHS FOR HIGH PRESSURE METHANE COMBUSTION: AN EXPERIMENTAL AND MODELING APPROACH

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Introduction

Catalytic combustion (CC) was proposed as an alternative route to produce energy in an environmental-friendly and safe manner [1]. However, CC is commercially used for pollution abatement, like TWCs and DOCs. This is due to the features required by power production, generally not fulfilled by CC. In particular, ignition temperatures should be close to the compressor outlet temperature (290-450°C depending on load), thus requiring high activity at low temperatures. On the contrary, steady state temperatures should be relatively high (at least 900-1000°C, but the turbine inlet temperature should be higher), thus requiring high thermal stability of the active phase. Other required features are mechanical resistance and low pressure drops, suggesting the use of structured catalyst [2].

Among the proposed active phases, perovskites, in particular $LaMnO_3$, are interesting for methane total oxidation [3], showing a good compromise between intrinsic activity and thermal stability.

In the last years, we have investigated, through both experimental and modeling (CFD) approaches, into the high pressure behavior of a catalytic combustor based on $LaMnO_3$ perovskite catalyst [4-7]. In those works, we have shown the role of homogeneous reactions in the complete fuel consumption, in particular due to the overcoming of mass transfer limitations, and that of the catalyst in ignition and steady state stability of the combustion process.

Coupling heterogeneous and homogeneous combustion in different sections of the burner has been suggested in order to increase the inlet temperature to the turbine; in particular, staged combustion, realized by a post-catalytic flame stage, has been proposed [8]. As a consequence, we have proposed [6], on the basis of CFD and experimental results, a novel reactor configuration, consisting of a partially coated monolith, the catalyst being deposited only onto the external channels (core-shell configuration).

In this work, we review the most relevant results of our modeling/experimental campaigns, highlighting the importance of CFD when coupled with appropriate experimental testing.

Materials and methods

Details of the two-dimensional CFD model are given in [6]. Briefly, each channel

consists of two parallel (infinitely wide) plates (gap distance, d = 783 µm; catalytic wall thickness, d_w = 45 µm; total length, L = 50 mm). The model solves the steady-state and transient mass, momentum, chemical species and energy conservation equations in the fluid (coupled to the ideal-gas equation), along with the energy equation in the solid walls. Heat losses at the outer surface of the monolith were considered. Single-step homogeneous [9] and heterogeneous [10] reaction rate equations were used. Computations were performed by means of the ANSYS FLUENT code (release 13.0) [11].

Monoliths with different coating fractions were prepared and tested [12]. In particular, a fully coated, as a reference, and two partially coated ''core-shell'' samples were prepared, the features of which are reported in Table 1.

Preparation of the fully and partially coated monoliths is reported elsewhere [12]. A picture of a partially coated monolith (P1) is reported in figure 1: perovskite is deposited only onto the external channels.

Details of the experimental rig are reported in [12].

Table 1. Features of the fully and partially coated monoliths.

Monolith	D, mm	L, mm	Cell density, cpsi	Total channels	Coated fraction	Catalyst weight, g
F					1	1.83
P1	12	50	900	172	0.79	1.36
P2					0.63	1.11
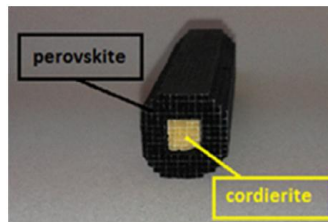
**Figure 1.** "Core-shell" partially coated monolith (adapted from [12]).

Results
Steady state behavior
In [6], we first proposed a "core-shell" partially coated catalytic combustor and compared the steady state conditions of this configuration to the corresponding ones of a fully coated monolith. Figure 2 compares the steady state distributions of temperature, fuel molar fraction and homogeneous reaction rate for fully and partially coated configurations.

Homogeneous combustion is activated in all the channels even if, in the center channels, the front is shifted downstream. It is worth noting that the fuel

conversion at the reactor outlet is 100%, regardless of the catalyst coating degree. On the other hand, the shift of the reaction front and the absence of heterogeneous reaction in the core zone modify the temperature distribution. The maximum surface temperature in the catalytic (external) channels is lower than 1400 K, while in the fully coated configuration, the wall temperature reaches about 1600 K. In the partially coated monolith, higher temperature values (up to 1700 K) are obtained only in the bulk gas phase of the non-catalytic channels. Thus, partial coating is a good strategy to redistribute the heat generated by combustion and reduce the thermal stress of the catalytic layer without a reduction of the fuel conversion.
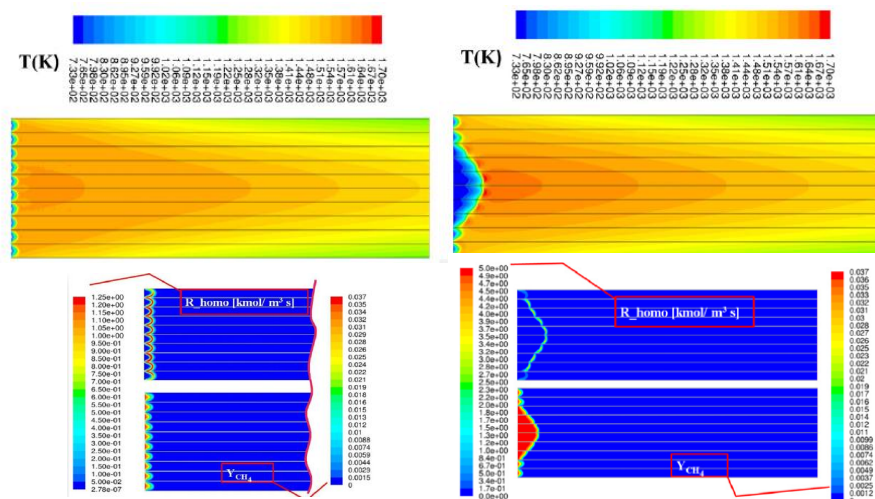
Figure 2. Computed maps of temperature, homogeneous reaction rate and methane molar fraction: Q = 88 slph; P = 9 bar. Fully coated (left) and partially coated (right; four external channels are catalyst-coated) configurations (adapted from [6]).

The above results suggested to realize a lab-scale partially coated combustor, as reported in the previous paragraph and depicted in figure 1. In [12], a fully coated and two partially coated monoliths were tested. In particular, the operating maps of the catalytic burners were obtained as a function of the operating pressure and coating degree (figure 3). Three zones can be identified: ignited zone, steady state multiplicity zone and not ignited zone. It is worth noting that the pre-heating temperature significantly affects the operating window of the catalytic burners. Under the reaction condition reported in [12], quenching conditions are realized only for partially coated monolith at low flow rates. The decrease of quenching pressure by increasing the flow rate suggests that the quenching mechanism is extinction, as expected at low flow rates [6]. On the other hand, ignition pressures increase with decreasing coating degree. This agrees with the results reported in [6] suggesting that the catalyst not only plays a major role in fuel ignition, but also

contributes to stabilize the reaction front under ignited conditions. It is noteworthy that experimental results confirm that complete fuel conversion can be obtained in partially coated combustors. However, the different operating maps suggest that the coating degree should be tuned according to the specific size of the burner. Large reactors, with a high adiabaticity degree, can significantly benefit by partial coating, due to their low cost (due to the reduced catalyst amount), without a performance reduction. On the contrary, at small scales, as those of micro-combustors, heat losses cannot be neglected and thus a more stable system would be preferable, i.e., a fully coated or a partially coated monolith with a high coating degree.
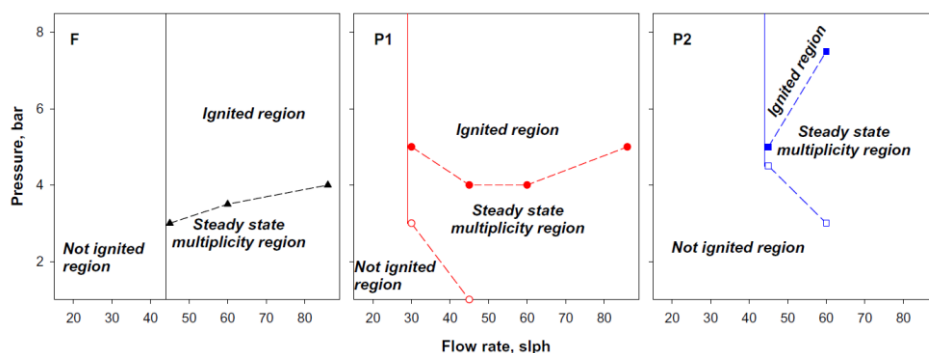

Figure 3. Operating maps in the plane pressure/flow rate for F (▲), P1 (●) and P2 (■) monoliths. $O_2 = 10\%$; $CH_4 = 3.7\%$; N_2 = balance. Pre-heating temperature = 520°C. (adapted from [12]).

Transient behavior
The knowledge of the time evolution of temperature and heat wave during start-up is crucial for the design of a catalytic combustor mainly for hot-spots and then thermal stresses, time length and associated pollutant emissions. As a consequence, we studied the transient response of partially coated monoliths during ignition [13]. In Figure 4, the maps of temperature, CH_4 concentration and homogeneous reaction rate are shown as obtained for the fully (left) and partially coated (right) reactor at different times. In both cases, during the first part of the ignition transient, the temperature values are low and methane is converted exclusively by heterogeneous reactions. It is trivial that no reaction occurs in the core section of the partially coated reactor. The heat produced by catalytic fuel conversion causes a temperature increase. Then, the temperature is high enough to allow the activation of the homogenous reaction pathway. The corresponding time (t_{ig}) increases with decreasing catalyst coating degree. In the fully coated monolith, the reaction front is developed along all the channels, shifts upstream and is anchored at the entrance of the monolith. The behavior of the partially coated monolith shows both analogies and differences. The reaction front developed in the coated channels

shifts upstream and reaches the inlet section of the reactor, as found in the fully coated case. On the contrary, in the uncoated section, the temperature is still low to activate homogeneous reactions and here methane conversion remains practically equal to zero. However, this section is continuously heated through the radial heat transfer; thus, the temperature is high enough to activate homogeneous reactions. A second reaction front is then generated and shifts towards the inlet section. By comparing the transients of fully and partially coated monoliths, we can conclude that 1) time to steady state and, consequently, methane emission are lower by increasing the coated degree, 2) ignition on partially coated samples occurs in two-steps (ignition in the coated (first) and uncoated (then) channels).
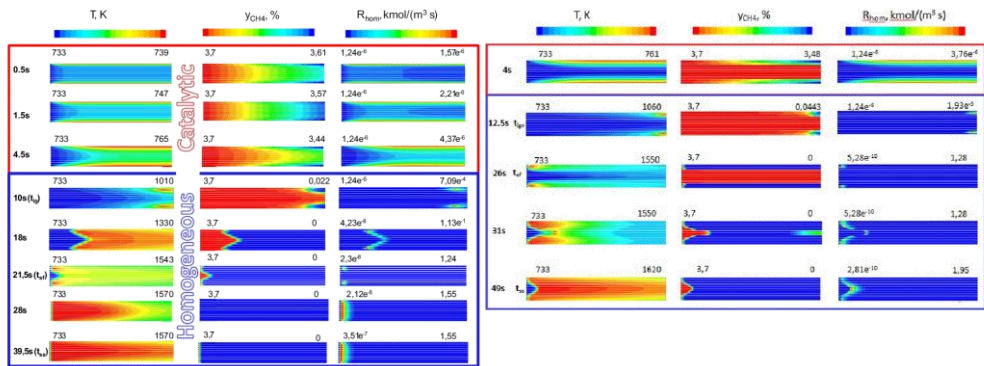

Figure 4. Maps of temperature, methane concentration and homogeneous reaction rate as obtained at different time instances during ignition, when setting the operating pressure equal to 9.5 bar. Fully coated (left) and partially coated (right; four external channels are catalyst-coated) configurations (adapted from [13]).

It is worth noting that, in the uncoated channels where methane is converted by the homogeneous reaction, the maximum temperature is attained in the bulk gas phase, while in the catalytic channels, higher temperatures are reached over the catalyst surface. As a consequence, even if the temperature level is 50 K higher (about 1620 K) in the uncoated channels than in the coated channels (about 1570K), the hot-spots in the uncoated channels are reached in the bulk gas phase, where the homogeneous reaction takes place, rather than on the catalytic walls, thus preserving the solid material.

The study of the transient behavior was carried out experimentally too [14, 15]. In Figure 5, the comparison of the ignition behavior of a fully and a partially coated (P1) monolith is reported. As obtained by modeling, ignition of the partially coated monolith lasts longer. It appears that at ignition, for the fully coated monolith (F), a sharper methane concentration decrease is detected to a value corresponding to methane complete conversion. While in the case of P1 monolith, as obtained by modeling, a peculiar 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. With respect to modeling, experiments revealed the transient production of carbon monoxide (Figure 5). As a consequence, the use of single-step reaction rates fails in the prediction of CO production during the start-up.
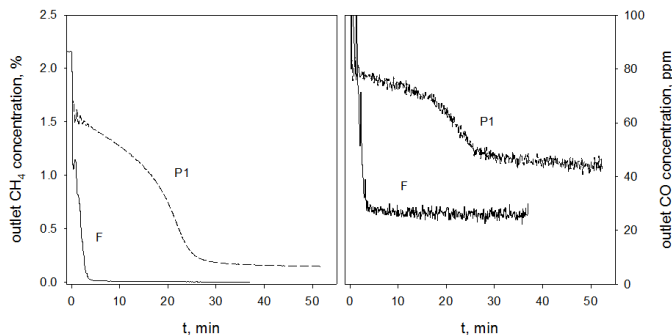
Figure 5. Methane (left) and CO (right) concentration profiles during ignition of fully (F) and partially (P1) coated monoliths (adapted from [15]).

Conclusions

In this work, we have reviewed our results on the partial catalyst-coating of monolith for methane combustion. Under steady state conditions, complete fuel conversion can be obtained in partially coated monoliths with advantageous temperature profiles, causing a reduction of the catalytic peak temperature. However, operating maps are affected by the catalyst coating degree, a wider ignition zone being obtained on the fully coated sample. This suggests that large reactors can benefits by partial coating more than small reactors.

Differences are found in the transient behavior. Partially coated monoliths show longer ignition with larger emissions of methane and carbon monoxide. Thus, partially coated burners are preferable for applications not requiring continuous start-up and shut-down.

Finally, we have clearly demonstrated the benefits of CFD modeling for the design of novel reactor configurations. On the other hand, experimental results offer the opportunity of model validation under real reaction conditions. Phenomena detected in the experiments can be easily explained by comparing modeling results.

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