Abstract
In this work, we investigated the use of partially coated monoliths as catalytic combustors for syngas/methane mixtures in the presence of significant CO$_2$ partial pressure. In particular, the effects of CO$_2$ content and partial coating degree were studied on perovskite-based monoliths. Results have shown that syngas substitution to methane is effective in improving the resistance to the inhibiting effect of carbon dioxide. It has been found that the operative window of the reactor is dependent on both, catalyst-coating degree and CO$_2$ partial pressure.

Introduction
Catalytic combustion has been mainly used for VOC abatement [1]. As a matter of fact, despite the huge number of papers [see, e.g., Refs. 2-7], power generation by catalytic combustors has been limited due to several issues, mainly related to catalyst durability, cost and maximum operating temperature. The development of novel combustion technologies, such as oxy-fuel and/or syngas combustion, has renewed the interest towards catalytic combustion. This is due to the opportunity to overcome the drawbacks associated with peculiar phenomena related to oxy-fuel combustion (Combustion-induced Rapid Phase Transition [8]), and/or with the low heating value of syngas generally requiring lower dilution [9].

In this context, we have recently proposed “core-shell” partially coated monoliths for methane combustion [10,11]. Due to the heat generated in the catalytic section, homogeneous reaction can be activated and sustained in the uncoated channels. Such configuration ensures complete methane combustion with reduced catalyst load and also with reduced thermal stress for the catalyst itself [10].

On the other hand, we have found that CO$_2$ partial pressure reduces the operative window of methane fueled catalytic combustors [11]. Conversely, the presence of syngas enhances CH$_4$ reactivity [12], thus enlarging the operating window of fully perovskite-coated monolithic reactors.

In this work, we investigated the opportunity to reduce the impact of CO$_2$ on the reactivity of CH$_4$/O$_2$/N$_2$/CO$_2$ mixtures by adding syngas. Catalytic combustion was studied over 20 wt % LaMnO$_3$/Al$_2$O$_3$ catalyst deposited onto cordierite monoliths. The effect of partial coating was addressed by comparing the behavior of a “core-shell” monolith to that of a fully coated
configuration. The final aim was at demonstrating the opportunity to use a partially coated reactor as an effective pilot for homogeneous combustion in the presence of high CO\textsubscript{2} contents.

**Experimental**

Lean methane-syngas mixtures were burnt under self-sustained conditions over 20 wt % LaMnO\textsubscript{3}/La-\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst supported on honeycomb cordierite monoliths (NGK; 900 cpsi; L = 5 cm; D = 1.2 cm). The performance of a fully coated monolith and two “core-shell” partially coated monoliths were compared. Catalyst-coated monoliths were prepared by a dipping procedure [13]. The preparation of the partially coated monoliths is described in [14]. In Figure 1, pictures of substrates and partially/fully coated monoliths are shown. Table 1 summarizes relevant features of the prepared structured reactors. Experimental tests were run in a lab-scale rig designed to work at pressures up to 12 bar and described in [15]. Feed mixtures with different compositions were prepared by mixing controlled flow rates of high purity gases (CH\textsubscript{4}, O\textsubscript{2}, N\textsubscript{2}, CO\textsubscript{2}) or certified mixtures (15 vol.% H\textsubscript{2}/N\textsubscript{2}, 5 vol.% CO/N\textsubscript{2}). The operating pressure was increased from approximately 1 to 12 bar. The mass flow rate was kept constant (i.e., the volumetric flow rate was decreased with increasing pressure). It corresponded to 60 l(STP)/h. The syngas (H\textsubscript{2}/CO = 1.5 v/v) to methane ratio was equal to 1. The effect of CO\textsubscript{2} was studied by increasing its concentration up to 30 vol %. The pre-heating temperature and the oxygen concentration were set to 520°C and 10 vol %, respectively. Some tests were repeated and gave results differing within the experimental error. Mass balances were closed within ±4 %.

![Figure 1. Picture of the prepared monoliths.](image-url)
Table 1. Features of the fully and partially coated monoliths.

<table>
<thead>
<tr>
<th>Monolith</th>
<th>D, mm</th>
<th>L, mm</th>
<th>Cell density, cps</th>
<th>Total channels</th>
<th>Coated fraction</th>
<th>Catalyst weight, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>12</td>
<td>50</td>
<td>900</td>
<td>172</td>
<td>0.63</td>
<td>1.83</td>
</tr>
<tr>
<td>P1</td>
<td>12</td>
<td>50</td>
<td>900</td>
<td>172</td>
<td>0.79</td>
<td>1.36</td>
</tr>
<tr>
<td>P2</td>
<td>12</td>
<td>50</td>
<td>900</td>
<td>172</td>
<td>0.63</td>
<td>1.11</td>
</tr>
</tbody>
</table>

Results

Figure 2 shows the ignition (full symbols) and quenching (open symbols) branches for monoliths with different coating degrees (F, P1 and P2) in the absence of CO\textsubscript{2} in the gas feed. Under not ignited conditions, fuel conversion increases by increasing coating degree. We have previously demonstrated that ignition with activation of homogeneous reaction occurs if a fixed thermal power is developed through fuel conversion \([10,12,16]\). The value of the thermal power is mainly dependent on the heat exchange with the surroundings. Consequently, as the coating degree is decreased, higher pressure is needed to get ignition. Under the adopted conditions, no ignition is attained for P2 monolith.

It should be underlined that CO conversion in the partially coated monoliths is higher than that corresponding to the complete conversion in the coated channels (dashed-dotted lines in Figure 2), suggesting that CO combustion is also activated in the uncoated section. Homogeneous hydrogen combustion is also activated but at pressure higher than 2 bar.

In figure 3, the operating map as a function of the coating degree and CO\textsubscript{2} addition is shown. Regardless of the CO\textsubscript{2} content, the operating window is reduced by decreasing the coating degree. CO\textsubscript{2} addition to the feed mixture results in an increase of both ignition and quenching pressure, as previously reported for methane \([11]\). However, the increase of ignition pressure in the case of P1 monolith is lower than in the case of F monolith. In the partially coated monolith (P1), ignition occurs at higher temperatures and, thus, CO\textsubscript{2} adsorption on the catalyst surface is limited. Consequently, the ignition pressure is slightly affected by the CO\textsubscript{2} content.

The effect of CO\textsubscript{2} on the quenching pressure is mainly related to its high thermal capacity. As a matter of fact, the temperature level decreases by increasing the CO\textsubscript{2} content at fixed thermal power. As a result, on increasing the content of CO\textsubscript{2}, homogeneous reaction becomes less stable especially in the partially coated monolith that, thus, shows quenching at higher pressure.

From Figure 3, it appears that, despite the reduced operating window, the partially coated monolith can operate even in the presence of a large amount of CO\textsubscript{2} (30 vol.%) and under fuel ultra-lean conditions. By comparing the above results with those obtained with methane alone \([11]\), it clearly appears that more stable operating conditions can be obtained when partially substituting methane with syngas, also on a partially coated monolith. In particular, this configuration offers
the advantage to operate with relatively low amounts of catalyst, acting as an effective (homogeneous) combustion igniter and stabilizer.

**Figure 2.** Hydrogen (▲), carbon monoxide (◆) and methane (■) conversion as obtained by increasing (full symbols) and decreasing (open symbols) the operating pressure for monoliths with different coating degree.

**Figure 3.** Operating map of LaMnO$_3$-based monolithic combustor as a function of coating degree and CO$_2$ concentration in the feed.

**Conclusions**
In this work, we tested partially coated monoliths as catalytic combustors fueled with syngas/methane mixtures in presence of carbon dioxide and compared their
performance in terms of operative window with those of a fully coated monolith, to
test the ability of syngas to drive catalytic combustion of methane in the presence
of CO₂.
It has been demonstrated that partially perovskite-coated “core shell” monoliths
can operate with different fuels (i.e., CH₄, H₂, CO) also in the presence of huge
amounts of CO₂. The operative window is dependent on coating degree and CO₂
partial pressure. In addition, it should be considered that the ratio between
produced thermal power and thermal power lost towards the surroundings affects
the operative window as well. The maximum thermal power is related to the fuel
flow rate, while the thermal power lost towards the surroundings is affected by the
combustor size. As a consequence, the coating degree of a perovskite-based
catalytic combustor can be optimized as a function of fuel type and composition,
CO₂ concentration, and combustor size. Partially coated monoliths are preferred at
large size and large syngas concentration, the catalyst acting as igniter and
stabilizer for homogeneous reaction. Conversely, at small scales (i.e., in the case of
micro-combustors) and high methane and carbon dioxide concentrations, high
coating degrees offer improved stability.
It should be underlined that the only link between coated and uncoated section is
the radial heat transfer. Even if the operative windows is dependent on the fuel
composition, we have demonstrated that different fuels can be completely burnt in
a partially coated monolithic combustor. This also means that a partially coated
combustor could be theoretically fed with two different fuels (one for the coated
section, another one for the uncoated section). As a consequence, such a combustor
could be fed with “cleaner” fuels only in the coated (catalytic) section.

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References
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