EFFECT OF CH₄ ADDITION ON THE CATALYTIC COMBUSTION OF SYNGAS AT HIGH PRESSURE

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Abstract
Catalytic combustion has attracted renewed interest as an alternative route to homogeneous combustion of low BTU mixtures (H₂, CO). Moreover, the thermal power of the fuel could be easily managed by methane addition. On the other hand, syngas and methane show very different reactivity. In this work we investigate the effect of the partial substitution of H₂/CO mixtures (representatives of syngas) with CH₄ over a perovskite based structured catalyst. The tests were carried out under self-sustained and high pressure conditions (up to 10 bar). The mixtures studied are characterized by the same overall heating value.

Introduction
Catalytic combustion has attracted renewed interest as an alternative route to homogeneous combustion of low BTU mixtures (H₂, CO). Moreover, the thermal power of the fuel could be easily managed by methane addition. On the other hand, syngas and methane show very different reactivity. In this work we investigate the effect of the partial substitution of H₂/CO mixtures (representatives of syngas) with CH₄ over a perovskite based structured catalyst. The tests were carried out under self-sustained and high pressure conditions (up to 10 bar). The mixtures studied are characterized by the same overall heating value.
emissions are higher too [8, 9]. In this context, catalytic combustion has been proposed as an alternative route to the homogeneous combustion of low BTU mixtures. Despite of the above considerations, up to date the most part of the studies related to catalytic combustion at conditions relevant for gas turbine applications (i.e. at pressure above the atmospheric one) have been performed on noble metals and in particular on Pt [10-14]. Very recently we have reported the behaviour of a perovskite based catalyst in the high pressure combustion of methane, showing that fuel ignition can be obtained by increasing the operating pressure and numerically reproduced by a CFD code including a simple fractional reaction rate [15]. Moreover, in [15] the double role of the catalyst during self-sustained combustion has been highlighted. In particular, under non ignited conditions partial fuel conversion occurs by heterogeneous reactions, leading to complete fuel ignition. Under ignited conditions, the catalyst stabilizes the homogeneous reactions.

In this work, self-sustained methane/hydrogen/carbon monoxide combustion over a 20 wt % LaMnO$_3$/La-γ-Al$_2$O$_3$ monolith was experimentally studied at pressure up to 10 bar in a lab-scale test rig. The work focuses on the effect of the partial substitution of H$_2$/CO mixtures (representatives of syngas) with CH$_4$ on the ignition phenomenon for mixtures characterized by the same overall heating value.

**Experimental**

Lean syngas-methane combustion under self-sustained conditions was performed over a 20 wt% LaMnO$_3$/La-γ-Al$_2$O$_3$ catalyst supported on 600 cpsi honeycomb cordierite monolith (NGK) in shape of cylinder (length, 20 mm; diameter, 9 mm). The preparation procedure has been described elsewhere [16]. The catalyst amount deposited onto the substrate was about 0.54 g. The catalytic monolith was placed between two inert mullite foams (45 ppi; the first 20 mm long and the latter 10 mm long) acting as thermal shields and wrapped in a ceramic wool tape before being inserted in the cylindrical cavity of a stainless steel reactor. A heating jacket (Tyco Thermal Controls) equipped with a PID controller provided for the reactor pre-heating.

Combustion tests were conducted in a lab-scale home-made set-up designed to work at pressures up to 12 bar [15]. Water was condensed upstream the analysing system; as a consequence, in order to calculate the wet composition of the reacted gases, water has been calculated through the oxygen balance, carbon and hydrogen balances providing the overall quality of the experiments. Carbon and hydrogen balances were always closed within ±4%.

The tests, carried out under self-sustained condition, were conducted at fixed pre-heating conditions and increasing the pressure from approximately 1 bar up to 10 bar. The mass flow rate was kept constant (i.e., the volumetric flow rate was decreased by increasing the pressure). The mixtures studied are characterized by the same overall heating value equivalent to that of a 2% methane mixture. Experimental conditions are reported in Table 1.
Table 1. Operating conditions adopted for experimental tests

<table>
<thead>
<tr>
<th></th>
<th>H₂ᵃ</th>
<th>COⁱ</th>
<th>CH₄ᵃ</th>
<th>H₂/CO</th>
<th>(H₂+CO):CH₄</th>
<th>O₂ᵃ</th>
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</thead>
<tbody>
<tr>
<td>Mix1</td>
<td>3.7</td>
<td>2.5</td>
<td>-</td>
<td>1.5</td>
<td>100:0</td>
<td>10</td>
</tr>
<tr>
<td>Mix2</td>
<td>1.6</td>
<td>1.1</td>
<td>1.14</td>
<td>1.5</td>
<td>70:30</td>
<td></td>
</tr>
<tr>
<td>Mix3</td>
<td>0.9</td>
<td>0.6</td>
<td>1.5</td>
<td>1.5</td>
<td>50:50</td>
<td></td>
</tr>
<tr>
<td>Mix4</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>0:100</td>
<td></td>
</tr>
</tbody>
</table>

Heating value: 18 Wₜₜₜ
Qₑₑₑₑₑₑₑₑ: 100 slph
Pre-heating temperature: 460°C

Results and discussion
In Figure 1 (a), (b), and (c) are reported hydrogen, carbon monoxide and methane conversions as a function of the total pressure obtained during the combustion of the Mix2, Mix3 and Mix4 respectively. Mix1 (not reported) has an almost complete H₂ and CO conversions also at the lowest pressure investigated (i.e. the atmospheric one).

![Figure 1](Image)

Figure 1. Hydrogen (■), carbon monoxide (▲) and methane (●) conversions as a function of the pressure during the ignition tests of different fuel mixtures: (a) Mix 2; (b) Mix3; (c) Mix4.

As shown in Figure 2 (a), high fuel reactivity is detected already at atmospheric pressure, syngas and methane conversions being complete and 90% respectively. The mixture complete conversion is approximately attained at 2 bar.

The behaviour of Mix3, characterized by a 50% syngas substitution, appears interesting. As shown in Figure 2 (b), CO is mostly converted at atmospheric pressure, while hydrogen conversion appears lower than 50%. It is known the good activity of perovskites towards CO oxidation, usually used as model reaction [17]; moreover perovskite-type oxides have been recently tested in the preferential oxidation of carbon monoxide in H₂-rich streams, showing an higher reactivity towards CO with respect to H₂ [18, 19]. Moreover, by increasing the pressure CO and mainly H₂ conversions increase allowing a temperature on the surface catalyst.
high enough to ignite methane at 4.5 bar. On the other hand, when methane is fed alone, fuel conversion progressively increases by raising the pressure from approximately 3% at 1 bar to 19% at 8 bar. This behaviour is expected since the pressure has a positive effect on kinetics and contact time is increased at constant mass flow rate [15]. A further slight increase of pressure causes a steep conversion rise up to 100%, associated with ignition occurrence.

In Figure 2 ignition pressures (P_{ig}) have been reported as a function of substitution degree, i.e. the ratio between methane (CH\textsubscript{4}) and overall fuel (H\textsubscript{2}+CO+CH\textsubscript{4}) concentrations. P_{ig} monotonously increases by increasing the methane content in the mixture and an almost linear dependence can be detected. In conclusion, the detected increase of the ignition pressure is related to the lower reactivity of methane on the perovskite catalyst; on the other hand, the heat produced by CO and H\textsubscript{2} combustion enhances the temperature along the reactor since until CH\textsubscript{4} ignition can occur. In this case it clearly appears that the highest reactivity belongs to carbon monoxide, whose oxidation drives the combustion of hydrogen first and methane later.

![Figure 2](image)

**Figure 2.** Ignition pressure as a function of the substitution degree (CH\textsubscript{4})/(H\textsubscript{2}+CO +CH\textsubscript{4}).

**Conclusions**

The effect of the co-feeding of hydrogen and carbon monoxide (representative of syngas) with methane was successfully studied under self-sustained conditions at pressures relevant for small size gas turbines (P up to 10 bar) and over a non noble metal and high temperature resistant active phase such as LaMnO\textsubscript{3}/La-\gamma-Al\textsubscript{2}O\textsubscript{3} deposited onto an honeycomb monolith. It has been demonstrated that partial substitution of syngas with methane causes the ignition occurrence under more severe conditions (i.e. at higher pressure keeping constant the pre-heating temperature). On the other hand, co-feeding of syngas and methane allows to obtain full ignition of the fuel mixture under intermediate values of pressure. In this
case, methane can be completely burnt at conditions not usable when it is fed alone. The increase of the pressure ignition with the substitution degree was found to be linear under the reaction condition explored in this work.

Acknowledgments
This work was financially supported by MiSE-CNR “CO2 capture- Carbone pulito” Project (Italy).

References


