Methane/Hydrogen/Air Mixture Combustion in a Catalytic Microcombustor

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1. Introduction

The combustion of methane, hydrogen or other gaseous hydrocarbons in a very little space can represent an innovative method to produce thermal and electrical energy. The idea consists to confine a catalytic oxidation in a microcombustor because in this way allows to control easily the energy generation in a short dimensions with versatile destinations. The aim of this work has been focalized to study new type of catalysts for the oxidation of methane in drastic conditions (in order of temperatures and space dimensions). The catalysts proposed are all been produced by combustion synthesis method, and a long discussion has been related to the chemical adsorption and desorption of oxygen for every catalyst and a catalytic activity has test towards methane combustion has been realized. The work includes a preliminary simulation step for the microreactor (a point of view about fluidodynamic property) in which the catalyst proposed will be used for the aim described below.

2. Combustion synthesis fundamentals

The combustion synthesis method takes advantage of exothermic, fast and self-sustaining chemical reactions between metal salts and a suitable organic fuel. Since most of the heat required for the synthesis is supplied by the reaction itself, the mixture of the reactants only needs heating up to a temperature that is significantly lower than the actual phase formation temperature. The energetic expense involved is therefore limited. In recent years this technique has been used [1-3] to produce homogeneous, very fine, crystalline powders, without the intermediate decomposition and/or calcining steps which other conventional synthesis routes would require.

The global reaction between lanthanum and manganese nitrates to form LaMnO$_3$ can be written as:

$$3\text{La(NO}_3\text{)}_3 + 3\text{Mn(NO}_3\text{)}_2 + 10\text{COOH-CH}_2\text{-NH}_2 \rightarrow 3\text{LaMnO}_3 + 20\text{H}_2\text{O} + 14\text{N}_2 + 25\text{CO}_2 \quad (1)$$

The hydration of both lanthanum and manganese nitrates was neglected since the reactants are dissolved in water.

3. Experimental

3.1. Catalyst preparation

The series of oxides has been prepared by combustion synthesis. An aqueous solution containing the metal precursors, dosed in stoichiometric ratio, once dissolved with the addition of the suitable amount of HNO$_3$ (65%, w/w solution, from Aldrich). This slightly less straightforward route was chosen because the commercially available. After a few minutes stirring on a heating plate, to ensure proper homogeneity, the so-prepared solution was transferred in a ceramic dish, which was placed into an oven preheated and kept at a constant temperature in the range of 450°C.
3.2. Characterization
XRD analyses (Philips X’PERT; Cu K radiation) have been performed on all fresh samples to assess the presence and purity of the expected phases and to gather information about their degree of crystallisation. BET specific surface area has been measured (Micromeritics ASAP 2010 M apparatus, employing N₂).
Catalytic activity tests have been performed on catalysts that has previously undergone a short thermal ageing (2 h at 600 °C + 2 h at 750 °C). A fixed-bed of 0.1 g of catalyst powder and 0.9 g of SiO₂ (0.2–0.7mm granulate, from Unaxis) was enclosed in a quartz tube (internal diameter: 4 mm) and sandwiched between two quartz wool layers. The reactor was placed in a PID-regulated oven and a thermocouple was inserted alongside it, while a gas flow rate of 50Ncm³/min (CH₄ = 2%, O₂ = 16%, He = balance) has been fed to it. Temperature was raised to a value between 680 and 850 °C at a constant rate, then lowered by turning the oven off. As the temperature decreased the conversion of methane was monitored, by analysing the outlet flow in terms of CO₂, CO, CH₄ and O₂ concentration (by means of a Hartmann and Braunn URAS 14 continuous analysers). The sigma-shaped curves have been obtained when plotting methane conversion versus temperature and the half-conversion temperature (T50) has been regarded as an index of the catalytic activity.

3.3. Investigation of combustion reaction mechanism
The capability of catalysts to act as an oxygen pump has been investigated by both temperature programmed oxidation and temperature programmed desorption (TPD) tests, carried out in a Termoquest TPD/R/O 1100 analyzer, equipped with a thermal conductivity detector (TCD). A fixed bed of catalyst was enclosed in a quartz tube and sandwiched between two quartz layers; then an oxidation pre-treatment of this sample was carried out. To this purpose the catalyst was heated under an oxygen flow (40 Nml/min) up to 900°C then, after a 60-min stay at this temperature under O₂ flow, the reactor temperature has been lowered down to room temperature under oxidizing atmosphere, thereby allowing for complete oxygen adsorption over the catalyst. Afterward, helium has been sent into the reactor at 10 Nml/min flow rate for one hour at room temperature, thus purging out any excess of gaseous oxygen.
The temperature programmed desorption test has performed by heating the catalyst up to 900°C at a 10°C/min rate under helium flow. The oxygen desorbed during heating has been detected in the outlet flow by a TCD detector

4. Result and discussion
XRD analysis has show a good cristallinity degree and no secondary phases has been detected in all the powders synthesized. Fig.1 illustrates the diffraction spectrum recorded for BaCeO₃
Some oxidation catalysts are believed to act as oxygen pumps, owing to the capability of absorbing oxygen on their surface and releasing it, when they are put in contact with a reducing agent or in a reducing atmosphere, or the capability of changing the oxygen content in their crystalline lattice. A noticeable example of oxidation catalyst acting as an oxygen pump are LaCrO$_3$ and LaMnO$_3$, which proved their effectiveness in carbon combustion, the first one; in methane combustion the second one. [4,5]. The main difference between this two perovskite consists of the range in which they release oxygen. The LaMnO$_3$ promotes the combustion of the gaseous specie because it releases intrafaical oxygen in the range of temperature between 600° and 900°C to the gaseous specie promoting the combustion of gaseous hydrocarbons; the oxygen lost by the perovskite in such a way could be replaced by oxygen coming from the gaseous atmosphere, thus giving rise to a loop for oxygen transfer towards carbon fuel. The TPD test have shown that the BaCeO$_3$ desorbs oxygen in a wide range of temperature becoming at 300°C and going over 900°C and with a higher quantity in terms of detected signals from the TCD sensor (this signal is proportional to the quantity of oxygen detected). In the figure 2 is possible to appreciate a confront respect to the LaMnO$_3$ chosen as a reference.
On the contrary the two oxides analyzed (CeO$_2$ and Pr$_6$O$_{11}$) have not presented a significant quantity of oxygen released. The signal intensity related is lower than the LaMnO$_3$. The ceria presents an interesting desorption phenomena that begins at 250°C and finishes at about 850°C: the widest range temperature found in this experimental analysis; for this reason the cerium oxide can be used both in carbon combustion, when is required a release of oxygen at low temperature (suprafacial oxygen); and gaseous hydrocarbons when are required oxygen in a higher range temperature (intrafacial oxygen).

TPC tests have evidenced that CeO$_2$ has a relatively low T50, but always higher than the LaMnO$_3$ one, on the other hand the T50 for the CeO$_2$ is higher.

In The Table I below are been reported all the values drowned by the TPC tests and correlated with the surface area values by the BET analysis.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET (m$^2$/g)</th>
<th>T$_{50%}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaMnO$_3$·2ZrO$_2$</td>
<td>132.5</td>
<td>471</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>75.2</td>
<td>510</td>
</tr>
<tr>
<td>Pr$<em>6$O$</em>{11}$</td>
<td>7.1</td>
<td>780</td>
</tr>
<tr>
<td>BaCeO$_3$</td>
<td>12.6</td>
<td>540</td>
</tr>
</tbody>
</table>

It is easy to observe as the surface area influences enough the catalytic activity for each catalysts. This is a very important parameter to consider in this type of reaction that occurs in gaseous atmosphere, because favours the contact with both gaseous hydrocarbon and oxygen gaseous molecules. For this reason it will be indispensable to control in future works, the reaction conditions in the combustion synthesis method, to obtain powder of BaCeO$_3$ (that presents a good efficiency as oxygen pump) with a higher surface area therefore a better catalytic activity in the methane conversion.

Fig. 2  TPD plots of BaCeO$_3$, LaMnO$_3$, CeO$_2$, Pr$_6$O$_{11}$
5. Design & study of a micro-reactor for catalysts activity tests

The catalysts developed need to be tested inside a structured module that provide the desired reaction condition for the methane/hydrogen/air mixture combustion study. To reach this goal it has been designed and studied a plug-flow micro-reactor in stainless steel, inside of which has been created a parallelogramic shape combustion chamber where the structured catalyst will be placed.

The reactor posses two orifices, one for the mixture fed to the reactor and another for the combustion gases outgoing form. Also, there exists a mixer before and after the combustion chamber, that stabilizes the flow, and temperature measurement points, as can be seen on figure 3.

![General description of the plug-flow micro-reactor designed for the combustion study](image)

**Fig. 3** General description of the plug-flow micro-reactor designed for the combustion study

Known the geometrical shape and magnitudes, a fluid dynamic study was made to evaluate the influence of the particular geometries, that characterize this reactor, over the velocities and species diffusion inside the combustion chamber. In the study, an methane/hydrogen/air mixture passes throw the combustion chamber, without reacting, at about 0.5 m/s. The results obtained in this simulation shows that the relevant parameters for the reaction are very stable and homogenous. The internal velocities is the same along the reactor length, with a slightly decrease approaching the walls and near the inlet. The distribution of the species is homogeneous and the pressure drop is almost imperceptible. In Figure 4 is show the velocity profiles along the reactor length.

![Velocity profile resulting from the simulation study for the micro-reactor designed](image)

**Fig. 4** Velocity profile resulting from the simulation study for the micro-reactor designed
6. References