1. Introduction

It is well known that fossil fuel reserves are becoming exhausted at an alarming rate. Moreover, the combustion of such fuels results in the emission of noxious pollutants which threaten the survival of life in this planet. The role of existing internal combustion engines needs to be reviewed now in the context of these two major crises aforementioned.

In view of the versatility of internal combustion engines, they will continue to dominate the transportation sector. There is a considerable limitation for the battery and fuel-cell powered vehicles with regard to range and acceleration [1]. It has also been demonstrated that, despite the conversion losses, the power to weight ratio of the internal combustion engine (including the tank and the fuel) exceeds that of the battery powered or fuel-cell operated vehicles.

Under such circumstances it becomes essential that environment-friendly technologies should be developed and alternatively fuelled internal combustion engines be designed to ensure safe survival of the existing engine technology. The other problem with the unrestricted combustion of fossil fuels is the level of CO₂ emission into the Earth's atmosphere. There are various alternative fuels that are being seriously investigated in several parts of the world. Since the present work is based on evaluating only CNG for engine application, no discussion is made here on the characteristics of other alternative fuels, such as methanol, ethanol, electricity, liquefied petroleum gas (LPG), biogas and vegetable oils. At this point it would perhaps be appropriate to discuss the potential of CNG as an alternative fuel for the S.I. engine. The difference between the operation of the conventional gasoline fuelled and CNG engine system arises from the physical and chemical properties of the two fuels.

Natural gas (NG) is a largely available form of fossil energy and therefore non-renewable. Natural gas is composed primarily of methane (CH₄) but includes other HC compounds in small amounts (e.g. propane, butanes and pentanes). NG has a high octane number (RON = 110–130) and therefore can be easily employed in spark-ignited internal combustion engines. It has also a wider flammability range than gasoline and diesel oil. Advanced natural gas engines have considerable advantages over conventional gasoline and diesel engines from an environmental perspective. Natural gas low flame temperature of lean-operated CNG engines helps to limit the formation of NOₓ. Furthermore, since NG contains only 75 wt% carbon versus 86–88 wt% of gasoline or diesel, it produces less CO₂ per unit of energy released. Other benefits lie in the fact that NG is neither toxic, carcinogenic, nor caustic. CNG is likely to be safer than gasoline or diesel, owing to its low density, high ignition temperature (540 °C) and high flammability limits which play in favour of a comparatively fast dispersion of CH₄ losses and render it less likely to ignite [2].

As above underlined, from the environmental viewpoint, CNG engines could lead to very low pollutant emissions. However, unburned methane is harder to oxidise than gasoline-derived unconverted HCs. The strong greenhouse effect of methane (more than one order of magnitude higher than that of CO₂) induces increasing concern at a legislation level and the development of tailored after treatment technologies [3-5]. Catalytic combustion of methane on honeycomb converters similar to those used for the treatment of gasoline engine exhaust gases is the way to go. Particular demands are imposed on the catalysts for methane
combustion. They must resist thermal and mechanical shocks and exhibit high activity, which is not trivial owing to the high stability of CH₄ and the low temperature of the exhausts of CNG vehicles (hardly exceeding 500 °C). Commercial catalysts are mostly based on γ-Al₂O₃-supported Pd [6-9], having at least a three-fold higher noble metal loading compared to that of conventional three-way catalysts. However, besides being expensive, the latter easily sinters. A possible solution could be the insertion of the noble metal in the structure of perovskite-type transition metal oxide mixtures, that when properly prepared, showed comparably active, highly resistant to deactivation and much cheaper.

Perovskites are mixed oxides of general formula ABO₃±δ, where A is usually a lanthanide ion and B is a transition metal ion. Both A and B can be partially substituted, leading to a wide variety of mixed oxides of general formula A₁₋ₓA’ₓB₁₋ᵧB’ᵧO₃±δ, characterized by structural and electronic defects, owing to their non-stoichiometry, indicated by the δ subscript in the formula. For full oxidation reactions, such as methane combustion, cation B is considered responsible for catalytic activity [10], while the cation A, especially when partially substituted with a cation A’ of different valence, governs the formation of crystal lattice vacancies and can stabilize unusual oxidation states for B, leading to different catalytic performance [10–12]. The oxidation activity of perovskites has been ascribed to their ionic conductivity, to oxygen mobility within their lattice [11], to their reducibility and to their oxygen sorption properties [13]. Indeed, two possible mechanisms, a suprafacial and an intrafacial one, were proposed since long time [14] and now widely accepted for oxidation reactions over these catalytic materials. The former mechanism rises from the interaction of surface oxygen with reactants and it is operative at low temperature (< 600°C). The latter is effective at higher temperature (> 600°C) and involves a Mars–Van Krevelen redox cycle. In it, bulk oxygen migrates towards the surface, becoming available for the oxidation of the adsorbed substrate and it is quickly replaced by oxygen coming from the gaseous phase. The mobility of O²⁻ ions within the crystalline framework determines the mechanism of the catalytic reaction [12].

A research line carried out at Politecnico di Torino is aimed at developing nano-structured Pd-perovskite-type-oxide catalysts employing an overall noble metal load markedly smaller or similar to that used in conventional converters. The present manuscript concerns the development of these catalysts. The performance of the most promising developed catalyst, once deposited on a honeycomb catalytic converter and tested in a lab-scale test rig, is also presented and discussed.

2. Experimental section

2.1. Catalyst preparation and characterization

A series of perovskite catalysts (LaMnO₃, LaMn₀.₉Pd₀.₁O₃, LaFeO₃, LaFe₀.₉Pd₀.₁O₃, LaCrO₃, LaCr₀.₉Pd₀.₁O₃) were prepared via a highly exothermic and self-sustaining reaction, the so-called “solution combustion synthesis” (SCS) method [15]. This technique is particularly suited to produce nano-sized particles. A concentrated aqueous solution of various precursors (metal nitrates and urea), placed in a crucible, was located in an oven at 600 °C for few minutes, so as to ignite the very fast synthesis reactions. The adoption of the SCS method entails the formation of pure oxide catalysts with rather high specific surface areas in the absence of any carrier. This allows to better compare the intrinsic catalytic activity of the series of prepared materials.

All the catalysts were then ground in a ball mill and characterized by XRD (PW1710 Philips diffractometer equipped with a monochromator for the Cu-Kα radiation) and FESEM (Leo 50/50 VP with Gemini column) in order to check the achievement of the desired microstructure and chemical composition. The activity of the prepared catalysts were analyzed by Temperature Programmed Combustion (TPC) tests, according to the following
standard screening operating procedures: a gas mixture (2.5 vol.% CH₄; 7.5 vol.% O₂, He = balance) was fed at the constant rate of 0.83 Nml·s⁻¹ to a fixed-bed micro reactor constituted of 100 mg of catalyst and 900 mg of SiO₂ (W/F = 0.12 g·s/cm³). Starting from 950 °C, the inlet temperature, measured by a K-type thermocouple placed alongside the quartz tube, was decreased at a 2 °C/min rate and the outlet CO₂, CO, CH₄ and O₂ concentrations were determined by continuous NDIR and paramagnetic analyzers (ABB), thus allowing to calculate methane conversion and verify the carbon balances closure (relative error: ±4 %). From the obtained typical sigma-shaped curves, methane half-conversion temperatures (T₅₀) were evaluated as an index of catalytic activity towards methane combustion. Each data point was obtained as the average of three twin runs performed on different samples of the same catalytic material. In order to fully appreciate the catalytic effect of the perovskites, blank runs in the absence of the catalyst and in the presence of just SiO₂ were also carried out.

2.2. Catalytic monolith preparation and characterization
The catalytic converters (cylindrical cordierite honeycombs by Chauger; cell density: 200 cpsi; length: 25 mm; diameter: 34 mm) were prepared by a preliminary deposition of a layer of γ-alumina by in situ SCS [16] (10 wt% referred to the monolith weight) and then, again with in situ SCS, 15 wt% (referred to the γ-alumina weight) of LaMn₀,₉Pd₀,₁O₃, the most active perovskite catalyst. Adhesion tests and structural characterization (XRD, FESEM) were carried out. The adhesion properties between the catalyst and ceramic surface was checked by means of an ultrasonic bath test: a piece of the catalytic monolith was weighted before and after a standard ultrasonic treatment [17] to quantify the catalyst loss. Physicochemical characterization was performed on sections of the catalytic monolith; in particular, field emission scanning electron microscopy (FESEM) analyses were performed using a FESEM - Leo 50/50 VP with GEMINI column apparatus equipped with an energy-dispersive spectrometer, in order to investigate the morphology and composition of the deposited catalytic layer. Catalytic combustion experiments were performed in a stainless steel reactor heated in a horizontal split tube furnace with a heating length of 60 cm. The catalyzed monolith was sandwiched between two mullite foams to optimize flow distribution.

![XRD diffraction patterns of the perovskite-type catalysts prepared.](image)
For the temperature control a thermocouple, inserted along one of the central monolith channel, was used to measure the inlet temperature. Lean inlet conditions (0.4% vol. % CH$_4$, 10% vol. % O$_2$, N$_2$ balance) were ensured via mass flow controllers. The reactor temperature gradient measured in the axial direction was not significant. The GHSV was set equal to 10000, 40000 and 80000 h$^{-1}$, whereas the composition of the off-gases was monitored by the same equipment described above.

3. Results and discussion

The XRD spectra (Fig. 1) of the prepared perovskite catalysts showed diffraction peaks corresponding to the desired catalysts structure (JPCDS card: PDF 24-1016 for LaCrO$_3$, JPCDS card: PDF 74-2203 for LaFeO$_3$ and JPCDS card: PDF 89-0644 for LaMnO$_3$); no diffraction peaks related to other phases were detected. Fig. 2a shows a FESEM micrograph of the LaMn$_{0.9}$Pd$_{0.1}$O$_3$ perovskite-type catalyst. It refers to the catalyst that showed the highest activity among those prepared. Most of the perovskite crystals range between 40 and 100 nm in size, which is in accordance with the B.E.T. specific surface areas measured (10÷30 m$^2$/g).

Fig. 2 FESEM views of LaMn$_{0.9}$Pd$_{0.1}$O$_3$ catalyst: a) in powder; b) deposited as layer over a cordierite honeycomb.

Fig. 3 shows the methane conversion vs. temperature plots. All catalysts guaranteed much lower T$_{50}$ values than the non catalytic combustion system (816°C - not reported). The LaMn$_{0.9}$Pd$_{0.1}$O$_3$ catalyst gave the best performance with a T$_{50}$ value of 425°C. However it is worthwhile to put in evidence that by inducing a partial substitution with 10% of Pd at the B site an improvement of the activity was observed for all catalysts. More in detail the methane half conversion temperature (T$_{50}$) of Pd substituted perovskites was lowered of 5, 40 and 60°C for LaCrO$_3$, LaFeO$_3$ and LaMnO$_3$, respectively.

The SCS technique was adopted to obtain extremely pure perovskites with a good specific surface area despite the absence of any carrier. This will allow a deeper investigation of the mechanistic aspects of the CH$_4$ catalytic combustion over the active phase alone with no interference or synergetic effects of the carrier. The latter was adopted in the catalytic monoliths preparation to maximise the specific amount of active sites. All things considered, after this screening of methane-combustion on perovskite-type catalysts in powder, the best catalyst was found to be LaMn$_{0.9}$Pd$_{0.1}$O$_3$.

Fig. 2b shows a FESEM micrograph of $\gamma$-Al$_2$O$_3$-LaMn$_{0.9}$Pd$_{0.1}$O$_3$ perovskite-type catalyst deposited onto the cordierite monolith channels via SCS. Its microstructure is foamy. During the SCS, the decomposition-combustion of the $\gamma$-Al$_2$O$_3$ and of the LaMn$_{0.9}$Pd$_{0.1}$O$_3$ reacting
precursors generates a large amount of gaseous products in a very short period of time, which leads to a spongy catalyst morphology. This feature favours the formation of large intra layer pores for the catalyst clusters agglomerates, which reduce the mass transfer resistance of the layer itself. The adhesion between the deposited catalyst and the channel walls of the traps was excellent, as the loss of catalyst by ultrasonic treatment was lower than 1%.

Fig. 3 Methane conversion vs T: comparison of the perovskite catalysts developed.

The methane conversion data plotted in Fig. 4 vs. temperature at three different GHSV show that the conversion curve shifted to lower temperature at lower space velocity. The T\textsubscript{50} values are 570°C, 455°C and 385°C at GHSV of 80000, 40000 and 10000 h\textsuperscript{-1}, respectively.
4. Conclusions

Several perovskite-type oxide catalysts (LaMnO$_3$, LaMn$_{0.9}$Pd$_{0.1}$O$_3$, LaFeO$_3$, LaFe$_{0.9}$Pd$_{0.1}$O$_3$, LaCrO$_3$, LaCr$_{0.9}$Pd$_{0.1}$O$_3$) were prepared by SCS, characterized, and tested as catalysts for methane combustion. The comparative analysis of the catalysts activity was carried out with pure perovskites in powder. The best catalyst was found to be LaMn$_{0.9}$Pd$_{0.1}$O$_3$ ($T_{50} = 425^\circ$C) and therefore it was selected to be deposited and tested on a cordierite monolith. Experimental tests on powders and on ad-hoc prepared CNG exhaust gas after-treatment converter demonstrated a superior activity towards methane conversion by inducing a partial substitution of the perovskite B site with Pd. This should entail a reduction of the overall catalyst costs compared to conventional Pd-only catalysts currently employed characterized by high Pd loads. Specific activities are currently in progress either to develop more active perovskite catalysts and to optimize the amount of Pd in order to get a further reduction of this costly noble metal in the catalyst formulation.

5. References

3. web site: www.epa.gov