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Catalysis Today 100 (2005) 275–281

www.elsevier.com/locate/cattod

Optimal compositional and structural design of a $LaMnO_3/ZrO_2/Pd$-based catalyst for methane combustion

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Abstract

The aim of this work was to identify the optimum synthesis conditions and the most effective technique for noble metal deposition in a perovskite/palladium-based catalyst for natural gas combustion. The solution combustion synthesis (SCS) of perovskite/zirconia-based materials was investigated, by starting from metal nitrates/glycine mixtures. Characterization and catalytic activity tests were performed on as-prepared powders and then repeated after calcination for 2 h at 900 °C in calm air. Calcination appeared to be beneficial in that, despite lowering the specific surface area, it promoted the simultaneous crystallization of both $LaMnO_3$ and ZrO_2 and the half-conversion temperature (T_{50}), regarded as an index of catalytic activity, was lowered. Two phases, both active towards methane oxidation – lanthanum manganate and palladium oxide – were combined so as to evaluate their synergism in terms of catalytic activity. Pd was therefore added either via *incipient wetness impregnation* on $LaMnO_3{\cdot}2ZrO_2$ or through a one-step SCS-based route. Characterization and catalytic activity tests followed suit. Optimal composition and preparation routes were found: T_{50} was lowered from 507 °C – pure $LaMnO_3$ prepared via SCS – to 432 °C attained with a 2% (w/w) Pd load on pre-calcined $LaMnO_3{\cdot}2ZrO_2$.

Keywords: Catalytic combustion; Methane; Perovskites; Palladium; Solution combustion synthesis (SCS)

1. Introduction

Perovskite-type oxides (ABO_3) containing a transition metal ion (B) have received remarkable attention over the last years in view of their activity and significant thermal resistance in the catalytic complete oxidation of hydrocarbons. Above all, particular interest has been raised by the opportunity to exploit the catalytic combustion of methane as a way to generate power with very limited emissions. Particularly, the formation of nitrogen oxides, rather significant at the high temperatures entailed by flame combustion, would remarkably be lowered.

What makes perovskites attractive with respect to noble metals, traditionally employed for this kind of application, is their lower cost and the absence of problems such as sublimation and volatilization. The perovskite structure allows for a number of substitutions and compositional modifications, so that different oxidation states for the transition metal are possible, as well as anionic or cationic defectivity [1]. However, one of the main drawbacks of perovskites is their limited specific surface area, especially when they are prepared with solid-state reactions between the oxide precursors at high temperatures [2]. The simultaneous synthesis of a perovskite phase such as $LaMnO_3$, which was found to be remarkably active towards methane oxidation [3], and of a suitable second oxide with good thermal resistance that can act as a structural promoter (e.g. MgO), was investigated and found beneficial both in terms of higher specific surface area and better resistance to high temperatures [4]. In particular, the potential benefits of ZrO_2 as support to enhance the temperature stability of $LaMnO_3$ perovskite has been broadly demonstrated [5].

Very promising results were obtained when considering low-environmental-impact premixed metal fiber burners as the final application for these catalytic materials [6]. Radiant premixed burners offer superior performance compared with the traditional diffusive-type ones, in terms of thermal efficiency, environmental impact, and design flexibility [7,8]. Due to the considerable heat exchange between the

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doi:10.1016/j.cattod.2004.09.062

reacting gas and the porous medium and the radiative characteristics of the latter, lower flame temperatures can be achieved, thus allowing a remarkable reduction of NO_x emissions. Coupling the radiant-premixed burners technology with perovskite-based catalysts proved to be an interesting strategy to further improve their performance [9].

In this work a $LaMnO_3/ZrO_2$-based catalyst composition was investigated, both as an intrinsic catalyst and as the support for the deposition of a noble metal (Pd), so as to assess and study their catalytic synergism. In view of this aim, solution combustion synthesis (SCS) was chosen as the synthesis route. In the past, perovskite-structured oxides have been prepared by numerous wet-chemical methods: co-precipitation; hydrothermal sol–gel synthesis [10]; the so-called citrates method [11]; reactive grinding [12]; freeze-drying [13]. Powders prepared via SCS generally have higher specific surface areas, as well as pure phases and the desired chemical compositions [14]. The wider the specific surface area, the more effective the Pd dispersion over the perovskite and the easier the detection of Pd-perovskite synergetic effects, whose understanding would though require a more thorough and specific analyses than those described in the following. A higher specific surface area would also favor the formation of small-size Pd particles, a key factor for catalytic activity enhancement, as demonstrated recently for the reference $Pd–ZrO_2$ catalytic system [15]. Besides, SCS represents an interesting preparation route for other potential advantages: relatively cheap starting reactants (metals nitrates); simple and easily available organic molecules as fuel; highly exothermic and self-sustaining reactions. Furthermore, a SCS-based technique for the deposition of perovskite catalysts on the metallic fiber mats of premixed burners was successfully developed very recently [16].

2. Experimental

$LaMnO_3 \cdot 2ZrO_2$ powders were prepared via *solution combustion synthesis*, using lanthanum, manganese and zirconyl nitrates (from Aldrich) as precursors and glycine (from Aldrich) as the fuel. The organic molecule plays a double role: it reacts with the precursors (metal nitrates) and, by forming complexes with metal cations in aqueous solution, it guarantees a good solution homogeneity, presumably preventing the preferential precipitation of ionic species. The overall combustion reactions can be written as follows:

$$\begin{aligned} &La(NO_3)_3 + Mn(NO_3)_2 + 2ZrO(NO_3)_2 \\ &\quad + nH_2NCH_2COOH + (\tfrac{9}{4}n - 11)O_2 \rightarrow LaMnO_3 \cdot 2ZrO_2 \\ &\quad + 2nCO_2 + \tfrac{5}{2}nH_2O + (\tfrac{9}{2} + \tfrac{1}{2}n)N_2 \end{aligned}$$

A stoichiometric fuel/oxidizer ratio can be defined ($\varphi = 1$), corresponding to the situation where $LaMnO_3 \cdot 2ZrO_2$ can be formed from the SCS reaction without additional oxygen. Likewise, it can also be pointed out as the condition for which the ratio of total oxidizing and reducing valencies of the reactants [17] is equal to unity; this ensures a maximum specific heat evolution. Consequently, for the reaction considered, $\varphi = 1$ corresponds to $n = 44/9$.

The precursors and fuel, dosed in the stoichiometric amount, were dissolved in distilled water and the resulting solution, thoroughly stirred to ensure complete dissolution of all reagents, was then transferred in a ceramic dish and placed into an electric oven set at 350 °C. After water evaporation and a significant increase in the system viscosity, the heat released in the fast reaction allowed the formation of the perovskite/zirconia powder.

Pure ZrO_2 powders were also synthesized by following the same route, in the presence of just the $ZrO(NO_3)_2$ and H_2NCH_2COOH precursors.

The surface area and the pore size distribution of the prepared materials were determined by nitrogen adsorption at the liquid N_2 temperature in a Micrometrics ASAP 2010 M instrument. The surface area was determined according to the Brunauer–Emmett–Teller theory. The samples were degassed in vacuum for at least 4 h at 250 °C before analysis.

The crystal phases of the various catalysts were detected by X-ray diffraction (Philips PW1710 apparatus equipped with a monochromator for the Cu Kα radiation).

The morphology and grains size of perovskite/zirconia powders were studied using a scanning electron microscope (Philips, 515 SEM) and a high resolution transmission electron microscope, Jeol TEM 2010 apparatus. The granulometric distribution of the powder aggregates resulting from the SCS preparation route was analyzed by means of a Micromeritics SediGraph5100 Particle Size Analysis System.

Pd was firstly deposited on the prepared supports via *incipient wetness impregnation* (IWI) using $Pd(NO_3)_2$ solutions. As for the $LaMnO_3 \cdot 2ZrO_2$ and pure ZrO_2, the deposition was performed both on the as-prepared support and on samples of the same powder calcined for 1 h at 900 °C in calm air. When $Pd(NO_3)_2$ solution is slowly added to a porous solid powder, it is first adsorbed in the internal pores of its particles and the powder will behave as if it was dry. Once the pores have been filled, the outer surface of the grains rather suddenly becomes wet, and the particles tend to stick together, thus causing powder lumps formation. The condition under which the pores have been filled but the outer surface of the grains is still dry is called *incipient wetness* and it can easily be detected by shaking or stirring the powder. As soon as this condition was reached, the deposition was interrupted and the sample was put back into the oven until complete dryness was reached. The procedure was repeated until consumption of the volume of solution corresponding to the desired noble metal load. This preparation route normally allows for a rather good dispersion of the metal over the support, although very high metal loads may not be possible. The Pd cluster size

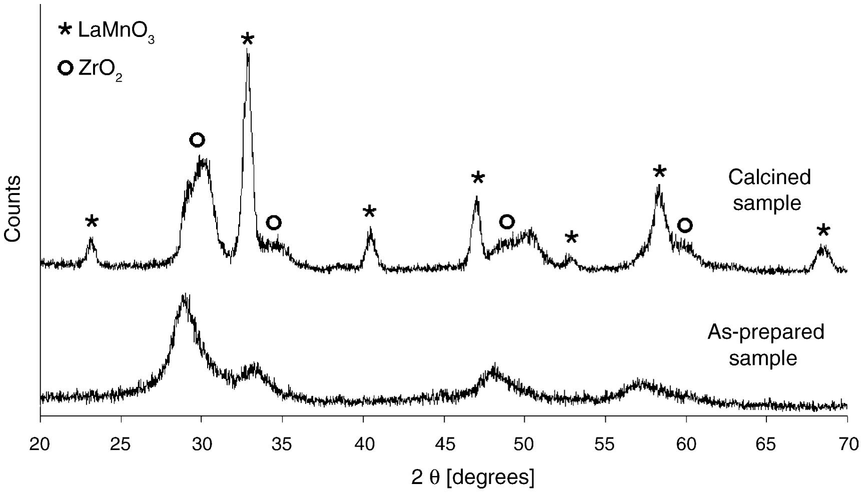

Fig. 1. XRD patterns for $LaMnO_3 \cdot 2ZrO_2$, as-prepared and calcined for 1 h at 900 °C in calm air.

measurement was accomplished through the above mentioned HRTEM apparatus.

Several deposition cycles were performed, so that the target Pd loads (0.5, 1, 2, 3%, w/w) were achieved. Samples were then calcined for 3 h at 600 °C in calm air, so as to favor decomposition of the nitrate precursor. The obtained oxidized palladium form (PdO), which is stable at the lower temperatures and thermally decomposes into metallic Pd when temperature is raised above 800 °C, is generally regarded as the more active phase [18–20].

An attempt was also made to prepare directly a Pd/$LaMnO_3 \cdot 2ZrO_2$ catalyst with a one-step route based on SCS. Palladium nitrate, which was used as the precursor, was expected to react with glycine just as the lanthanum, manganese and zirconyl nitrates. Therefore amounts of $Pd(NO_3)_2$ solution corresponding to the desired loads (again 0.5, 1, 2 3%, w/w) were added to the volume of precursors solution typically used for the SCS of the support. The synthesis was subsequently performed in an electric oven set at 350 °C. Also in this case the resulting powders were calcined for 3 h at 600 °C in calm air.

BET measurements were repeated following the deposition and XRD patterns were also recorded again.

Catalytic activity towards methane oxidation was then evaluated in a lab-scale plant: 0.1 g of catalyst powder mixed with 0.9 g of SiO_2 were inserted in a U-shaped quartz tube (4 mm i.d.), sandwiched between two quartz wool layers. The fixed-bed reactor thus obtained, fed with 50 N cm^3/min of a gaseous mixture containing CH_4 (2%), O_2 (14%) and He (balance), was placed into a PID regulated electrical oven. Starting from 750 °C, the temperature – measured by a thermocouple placed alongside the quartz tube – was decreased at a 2 °C/min rate and the outlet CO_2, CO, CH_4 and O_2 concentrations were determined by continuous NDIR and paramagnetic analyzers (ABB), thus allowing to calculate methane conversion (ζ). By plotting ζ versus temperature the typical sigma-shaped curves were obtained and the half-conversion temperature (T_{50}), easily evaluated from these curves, was regarded as an index of the catalytic activity for comparison purposes.

3. Results and discussion

The XRD spectra for as-synthesized $LaMnO_3 \cdot 2ZrO_2$ powders (Fig. 1) presented weak diffraction peaks corresponding to tetragonal ZrO_2 (JCPDS 50-1089) and a broad shoulder in correspondence with the main peak of the orthorhombic $LaMnO_3$ (JCPDS 35-1353) spectrum. After 1 h at 900 °C in air, peaks corresponding to both phases appeared better developed, suggesting a simultaneous growth of both lanthanum manganate and zirconia crystals. The XRD spectra of the prepared ZrO_2 support showed rather sharp zirconia diffraction peaks already at as-prepared stage. For this reason, no further high temperature calcination was performed on this material. Finally, the XRD spectra on Pd-deposited perovskites gave similar results. No diffraction peaks related to Pd were detected even at the highest noble metal loads, a sign that Pd dispersion was satisfactory. Pd metal clusters were indeed found to be in the range 5–8 nm for any of the prepared materials by HRTEM, the highest cluster sizes being related to the highest Pd loadings. This result is consistent with the findings of Rodriguez et al. [21] and provides a sound basis for the comparison of catalytic activities of the various prepared catalysts.

The BET specific surface areas were around 30 m^2/g for all as-prepared samples (Table 1), which also provides a common background for the comparison of catalytic activities. Conversely, BET SSA values of about 18 m^2/g were obtained for the $LaMnO_3 \cdot 2ZrO_2$ sample calcined for 1 h at 900 °C in calm air. This is not surprising, as a better degree of crystallization does generally entail a loss of BET area. However, this was hampered to some extent because $LaMnO_3$ and ZrO_2 grains, by growing simultaneously, limited their ultimate size and consequently the reduction of

Table 1
Pd deposited via incipient wetness impregnation on as-prepared ZrO_2 and $LaMnO_3 \cdot 2ZrO_2$ supports, as well as on pre-calcined $LaMnO_3 \cdot 2ZrO_2$ (1 h at 900 °C in calm air): BET specific surface area values and methane half-conversion temperatures

Pd (%, w/w) load	Pd/ZrO_2 catalysts		Pd/as-prepared $LaMnO_3 \cdot 2ZrO_2$ $2ZrO_2$ catalysts		Pd/pre-calcined $LaMnO_3 \cdot 2ZrO_2$ $2ZrO_2$ catalysts	
	BET (m^2/g)	T_{50} (°C)	BET (m^2/g)	T_{50} (°C)	BET (m^2/g)	T_{50} (°C)
0	9.00	730	29.82	500	17.91	520
0.5	8.87	515	28.88	460	17.64	509
1	8.91	500	29.30	433	17.53	485
2	8.84	465	28.64	428	17.61	432
3	8.86	460	27.43	449	17.05	461

SiO_2: 775 °C.

specific surface area. Pure $LaMnO_3$ prepared via SCS was found to be remarkably less resistant to high temperatures and suffered from a much more significant loss of specific surface area [22]. Finally, the BET SSA of the Pd-impregnated catalysts was not significantly varied compared to that of the supports. Only for the 3% (w/w) Pd loadings a 5–10% SSA decrease was noticed (Table 1).

The characteristic microstructure of $LaMnO_3 \cdot 2ZrO_2$ powders prepared by SCS with glycine is presented in Fig. 2 (as-synthesized powders). As shown by SEM micrographs, agglomerates appeared to be thin waffles whose surface was perforated by a large number of pores, with a complex high surface area network structure. High resolution transmission electron microscopy was performed on as-synthesized and calcined powders. Fig. 3 shows HRTEM micrographs. The granulometric distribution for the $LaMnO_3 \cdot 2ZrO_2$ calcined for 1 h at 900 °C in calm air was analyzed and the median value of the particle diameter was found to be around 4 μm (Fig. 4). Similar results were obtained for the prepared ZrO_2 support.

On the grounds of the above characterization results, the results of the catalytic activity assessment tests can be properly discussed. Table 1 lists, beyond the discussed BET values, the methane half-conversion temperatures of the fresh- and the calcined-support Pd/perovskite and for the Pd/ZrO_2 catalysts. Fig. 5 shows some methane conversion versus temperature plots as recorded with the most significant catalysts considered (namely 2% (w/w) Pd load on ZrO_2, as-prepared $LaMnO_3 \cdot 2ZrO_2$ and pre-calcined $LaMnO_3 \cdot 2ZrO_2$) together with the corresponding light-off curve obtained when working in the absence of any catalytic phase (only SiO_2 present within the reactor).

The results obtained for the reference Pd/ZrO_2 catalyst are in line with those published by other authors [23,24]. The addition of Pd enhanced the catalytic performance in all cases, thus considerably lowering the T_{50}, that reached a minimum in correspondence with the 2% (w/w) Pd load for the Pd/perovskite catalysts. The slight increase in T_{50} observed for these catalysts for a Pd load above 2% (w/w) can presumably be explained considering that the support used in this case offers a relatively limited specific surface area, with respect to stabilized γ-alumina that is more often employed for this application.

As discussed in an earlier paper [25], the amount of palladium with this last support could actually be enhanced up to 8% (w/w) with progressive increase of the overall catalytic activity. However, considering that Pd is very expensive, a 2% as noble metal load seems the best compromise between performances and costs. It is well known that the activity of palladium also depends on the quality of its dispersion over the support: when working with $LaMnO_3 \cdot 2ZrO_2$, higher loads also entailed the impossibility to achieve a good and uniform dispersion, as demonstrated

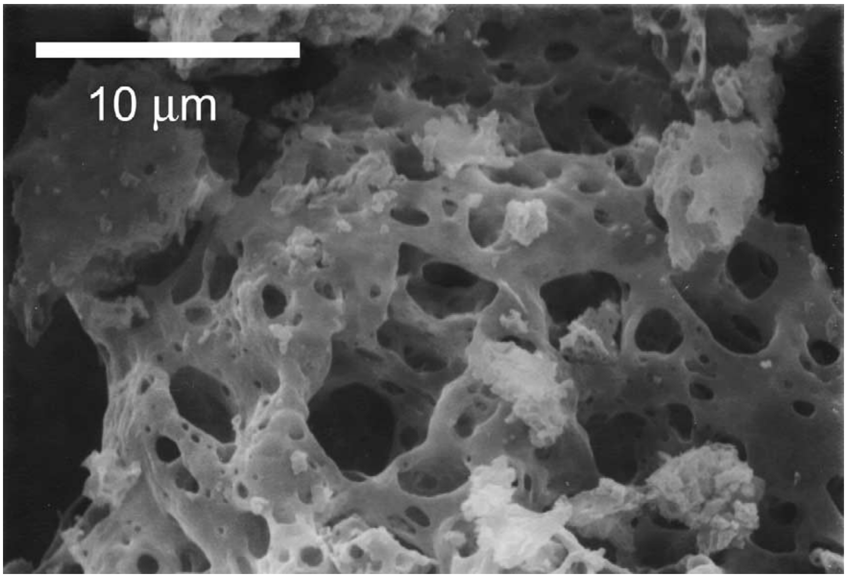

Fig. 2. SEM micrograph of $LaMnO_3 \cdot 2ZrO_2$ prepared via SCS with glycine under stoichiometric conditions.

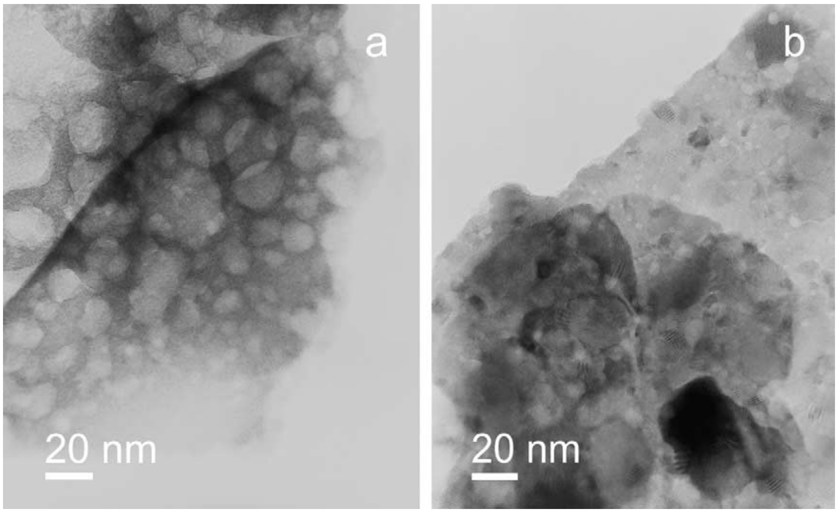

Fig. 3. HRTEM micrographs of $LaMnO_3 \cdot 2ZrO_2$: (a) as-prepared (300,000×); (b) calcined for 1 h at 900 °C in calm air (300,000×).

by the relatively larger cluster size and by the decrease of the specific surface area. However, the simultaneous presence of the perovskite helped providing the catalyst with a higher activity that would not have been reached with higher Pd loadings. This can be clearly understood by comparing the T_{50} values data of the as-prepared $LaMnO_3 \cdot 2ZrO_2$ support (500 °C), of the 2% (w/w) Pd/ZrO_2 catalyst (465 °C) and of the 2% (w/w) $Pd/LaMnO_3 \cdot 2ZrO_2$ one (428 °C).

The T_{50} values for pre-calcined samples were generally higher than those obtained with the fresh powders, which is likely to be explained by considering the different BET areas (nearly 30 m^2/g for the as-prepared $LaMnO_3 \cdot 2ZrO_2$ as opposed to about 18 m^2/g obtained after calcination). Nonetheless, the behavior of the catalyst with a 2% (w/w) load is very interesting, because its catalytic performance was nearly unaffected by the calcinations and in any case higher than that of the reference 2% (w/w) Pd/ZrO_2 catalyst. In view of this result, the pre-calcined catalyst seems perhaps to be a better choice for those applications in which high temperatures have to be withstood steadily (catalytic radiant burners, methane converters for gas turbine cycles). It was actually observed that, upon exposing these powders to high temperatures ($\geq$900 °C), their BET area decreases asymptotically, but most of the loss occurs during the first hour of treatment.

The catalysts prepared via the one-step SCS-based route were also characterized by means of BET measurements and XRD analyses. The BET SSA values of these catalysts were all in the range 15–18 m^2/g, and surprisingly enough, XRD patterns showed the formation of $La_2Zr_2O_7$ (JCPDS 50-0837). As shown in Table 2, where results of the catalytic activity tests are listed, the addition of palladium caused once again a decrease in half-conversion temperatures, once more attaining an optimum value with a 2% (w/w) load. The T_{50} values recorded in this case were always higher than those attained with the same Pd loads on calcined

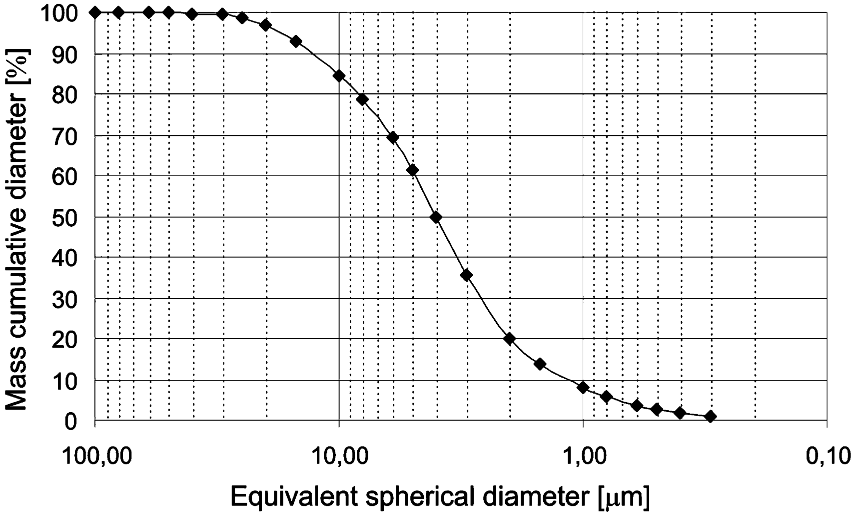

Fig. 4. Granulometric distribution for $LaMnO_3 \cdot 2ZrO_2$ calcined for 1 h at 900 °C in calm air.

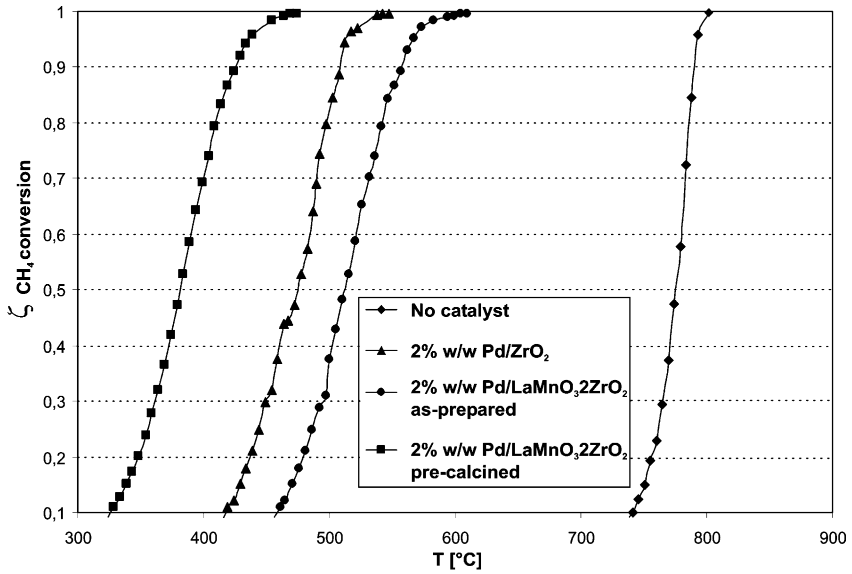

Fig. 5. Methane conversion vs. temperature plots as recorded for the most significant catalysts considered (namely 2% (w/w) Pd load on ZrO_2, as-prepared $LaMnO_3{\cdot}2ZrO_2$ and pre-calcined $LaMnO_3{\cdot}2ZrO_2$) and for non-catalytic combustion (only SiO_2 present within the reactor).

Table 2
$Pd/La_2Zr_2O_7$ prepared via one-step SCS: half-conversion temperatures

Pd (%, w/w) load	T_{50} (°C) of $Pd/La_2Zr_2O_7$ catalysts
0	–
0.5	531
1	518
2	476
3	498

SiO_2: 775 °C.

$LaMnO_3{\cdot}2ZrO_2$, which has a similar value of BET area. While this direct one-step synthesis failed matter-of-factly to produce a catalyst with the desired composition, these results seem to prove that this preparation route has likely to be dismissed as it does not lead to interesting catalysts from the point of view of activity.

4. Conclusions

SCS was successfully employed for the synthesis of a perovskite-based support for the deposition of a noble metal, in the perspective of preparing a combined $Pd/LaMnO_3$ supported catalyst for methane combustion. The introduction of ZrO_2 as a structural promoter enhanced the support thermal resistance and incipient wetness impregnation proved to be an effective preparation route. As for catalytic activity, half-conversion temperatures were lowered down to about 430 °C by the combined and synergetic effect of Pd and $LaMnO_3$ catalytic species.

In view of the rapidity of the SCS method for the perovskite–zirconia support preparation and of its relatively low cost, in terms of starting materials and energetic expense, the best-performing catalyst (2% (w/w) Pd load deposited via incipient wetness impregnation on $LaMnO_3{\cdot}2ZrO_2$ pre-calcined for 1 h at 900 °C in air) represents a very promising and cost-effective alternative to more traditional catalytic systems proposed in the recent past [6,7]. As a disadvantage of the SCS technique it has though to be admitted that during the synthesis formation of NO_x is possible: metal nitrates can undergo a partial thermal oxidation just before the main reaction is ignited, thus releasing nitrogen oxides in the atmosphere, and glycine as well can decompose into a number of simpler molecules. Apparently, the process in this case is very fast and little time is given for thermal decomposition prior to ignition, and only small amounts of NO_x are expected to be released. Without a doubt, NO_x emissions can anyhow become an issue when scaling up the process to the industrial level, where larger production is necessary. In that case a small NO_x abatement reactor by selective catalytic reduction with ammonia might be envisaged.

Investigations are in progress in the application of this catalyst to premixed porous burners for domestic boilers in order to prove this potential.

Acknowledgements

Funding of the European Union is gratefully acknowledged (EU project CAT-NAT no. G5RD-CT2001-00567: cost-effective and durable nanostructured Pd CATalysts for NATural gas vehicle and premixed burners applications). A special thanks to the CAT-NAT partners Centro Ricerche Fiat (Italy) and Ecocat (Finland) for the fruitful cooperation.

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