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Combustion synthesis of perovskite-type catalysts for natural gas combustion

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Abstract

Combustion synthesis has been applied to $LaMnO_3$ production with a view to boosting its activity towards natural gas combustion by enhancing its specific surface area. With a highly exothermic and self-sustaining reaction, this oxide can be quickly prepared from an aqueous solution of metal nitrates (oxidisers) and urea (fuel).

The favourable conditions for $LaMnO_3$ formation were sought: only fuel-rich mixtures are effective, but carbonaceous deposits are formed when too much urea is used. In the field of operating conditions in which the combustion synthesis reaction takes place, the specific surface areas were not dramatically higher than those obtained with traditional methods; moreover, even short thermal treatments have been found to rapidly deactivate the catalysts by rapid sintering. With a view to tackling these problems, NH_4NO_3 was chosen as an additive for its low costs, highly exothermic decomposition and because it generates gaseous products only, without altering the proportion of the other elements in the catalysts. With ammonium nitrate, specific area was enhanced from $4\,m^2/g$ up to about $20\,m^2/g$. A short thermal treatment at 900 °C partially deactivates also the NH_4NO_3-derived catalysts. It was found that NH_4NO_3-boosted mixtures produce materials whose activity, after a similar thermal treatment, behave practically as the perovskites obtained by the "citrates" method.

Combustion synthesis is though rather cheap—in terms of reactants employed—and quick, given that the process requires few minutes at low temperature without successive calcination. However, the main drawback of this method is that hazardous or polluting compounds are emitted during the synthesis (mainly NH_3 or NO_x).

The MgO introduction, which should act both as a structural promoter and as a sulphur poisoning limiting agent, has proved to be harmful: since MgO does not physically interpose between perovskite grains, it does not offer resistance to deactivation induced by high temperatures.

Keywords: Combustion synthesis; Perovskite; $LaMnO_3$; Natural gas; Catalytic combustion

1. Introduction

Over the last decades catalytic combustion has drawn growing attention as, for several reasons, it represents an appealing alternative to conventional thermal combustion. Not only does catalytic combustion allow a wider range of air-to-fuel ratios, but also the total conversion being attained at lower temperatures, NO_x emissions can be remarkably reduced. In a world-scale scenario where laws set up stricter and stricter standards for environmentally hazardous emissions, natural gas catalytic

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combustion is therefore object of many research projects.

Perovskite-type oxides appear to be a promising alternative to noble metal catalysts in view of their low cost, thermochemical stability at relatively high temperatures and catalytic activity [1]. Many perovskite-oxides can be considered, given that the general ABO_3 structure—where a rare-earth metal A and a transition metal B are in the +3 oxidation state—is compatible with a number of different combinations. Any A and/or B replacement with non-equivalent ions is likely to stabilise an unusual oxidation state or a mixed valence state in the transition metal ions in the B site, thus changing the electronic properties and therefore modifying the catalytic performance of the so-formed perovskite [2]. Previous studies on $LaCr_{1-x}Mg_xO_3$ [3] and $LaMn_{1-x}Mg_xO_3$ [4] have shown a promoting effect of the substitution on the catalytic activity of the resulting perovskite.

The rather low values of specific surface area of perovskites, together with their susceptibility to sulphur dioxide poisoning, have limited to some extent the degree of their application in industrial processes. Further recent studies [5,6] have proved, though, that with $LaMn_{1-x}Mg_xO_3 \cdot yMgO$ perovskites a good resistance to high temperatures (900–1000 °C) can be attained; the loss in catalytic performance caused by sulphur poisoning is much slower and can be even completely recovered with a simple regeneration procedure.

In this paper combustion synthesis for the preparation of perovskite-type oxides has been considered, with a view to boosting catalytic performance by enhancing the catalyst specific surface area. Particularly, the catalyst compositions developed in earlier papers of ours ($LaMnO_3$, $LaMnO_3 \cdot 17MgO$) [4–6] by other preparation procedures will be considered so as to set a proper basis for the assessment of the potential of this unconventional synthesis route.

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 [7–18] to produce homogeneous, very fine, crystalline powders, without the intermediate decomposition and/or calcining steps which other conventional synthesis routes would require. Such characteristics are interesting also for use in catalysis as a support for noble metals [19–21] or as a standalone catalysts. This latter application was not yet exploited, at the authors' knowledge.

Hydrate nitrates were chosen as the metals precursors: not only are they fundamental for the method, the NO_3^- groups being the oxidising agents, but also their high solubility in water allows a proper homogenisation. Urea seems to be the most convenient fuel to be employed, given that it is cheap and readily available commercially.

A theory of *combustion synthesis* has been developed following the works of other researchers [8] and the dictates of propellant chemistry. According to both the propellant chemistry and to our own thermodynamical calculations, CO_2, H_2O and N_2 are the most stable products of the combustion synthesis reaction with respect to other theoretically acceptable combinations that might be considered, including the formation of nitrogen oxides, CO and so forth. Jain et al. [22] introduced a simple method of calculating the oxidising/reducing character of the mixture. In this picture, carbon and hydrogen are considered as reducing elements with the corresponding valencies +4 and +1, oxygen is seen as an oxidiser with the valence −2 and nitrogen is considered with valence 0. Extrapolating these concepts to the combustion synthesis of ceramic oxides means considering metals as reducing elements with their corresponding valences (e.g. +3 for lanthanum, +2 for magnesium). In the case of multiple valence elements, the valence of the element in the product is used in the calculation; henceforth, in our case manganese in the perovskite was accounted for in the oxidation state +3. It is known that in rhombohedral form of $LaMnO_3$ the Mn cation can easily pass to +4 state [23]; our samples, however, were crystallised in the orthorhombic system, that is typical of compositions closer to stoichiometry. For this reason the possibility of having Mn^{4+} in the product was neglected.

The global reaction between lanthanum and manganese nitrates to form $LaMnO_3$ can be written as

$$2La(NO_3)_3 + 2Mn(NO_3)_2 + 8CO(NH_2)_2 \rightarrow 2LaMnO_3 + 16H_2O + 13N_2 + 8CO_2 \quad (1)$$

The hydration of both lanthanum and manganese nitrates was neglected since the reactants are dissolved in water. The stoichiometric ratio between nitrates and urea corresponds to five groups of NO_3^- per four molecules of urea.

Following the method proposed by Jain et al. [22] it is possible to calculate the so-called elemental stoichiometric coefficient φ as the ratio between the total valencies of fuel (urea) and the total valencies of oxidisers (nitrates):

$$\varphi = \frac{n[+4_{(C)} - 2_{(O)} + 2(0_{(N)} + 2 \times 1_{(H)})]}{x[3_{(La)} + 3(0_{(N)} + 3 \times -2_{(O)})] + y[3_{(Mn)} + 2(0_{(N)} + 3 \times -2_{(O)})]}$$

where n is the mole of $CO(NH_2)_2$, x the mol of lanthanum nitrate and y the mol of manganese nitrate (in our case obviously $x = y$). Under stoichiometric conditions, $\varphi = 1$; $\varphi < 1$ means oxidant-rich conditions, $\varphi > 1$ fuel-rich conditions. In the following this ratio will be referred also as fuel-to-oxidisers ratio.

It should be noted that this calculation is based on a theoretical reaction equation that neglects all secondary phenomena such as urea hydrolysis and thermal decomposition, as well as nitrates decomposition, that would alter the initial fuel-to-oxidisers ratio. This simplified reaction equation is by no means intended to describe comprehensively the complexity of the reacting system, but allows one to identify a stoichiometric operating condition that can be used as a reference, especially when comparing the effect of fuel-rich/fuel-lean mixtures on the synthesis of different materials.

To produce any metal oxide by combustion synthesis, an aqueous solution containing the nitrates of the desired metals and the appropriate amount of urea is brought to the boil; shortly thereafter the mixture ignites and the fast self-sustaining redox reaction takes off.

3. Experimental

3.1. Catalyst preparation

A series of perovskite catalysts ($LaMnO_3$ and $LaMnO_3 \cdot 17MgO$) was prepared by combustion synthesis. An aqueous solution containing the metal-precursors, dosed in stoichiometric ratio, was prepared from $La(NO_3)_3 \cdot 6H_2O$ (from Fluka) and $Mg(NO_3)_2 \cdot 6H_2O$ (from Aldrich), whereas Mn metallic powder (from Aldrich) was used as a source of manganese, once dissolved with the addition of the suitable amount of HNO_3 (65%, w/w solution, from Aldrich). The excess NO_3^- anions introduced when dissolving Mn powder were accounted for in the calculation of the initial fuel-to-oxidisers ratio of every batch of catalyst. This slightly less straightforward route was chosen because the commercially available manganese salt does not have a well-defined hydration degree. Different amounts of $CO(NH_2)_2$ (from Aldrich), corresponding to various fuel-to-oxidisers ratios, were added to the required volumes of solution that would lead to the formation of 1 g batches of catalyst. For some preparations, a varying amount of NH_4NO_3 (from Aldrich) was also added and kept into account in the fuel-to-oxidisers ratio.

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 400–800 °C. First, the aqueous solution underwent dehydration. At some stage, then, the mixture frothed and swelled, until a fast and explosive reaction took off, and large amounts of gases evolved. At very low fuel-to-oxidisers ratios the presence of NO_x can be detected, while when a large excess of urea is used the flue gases leaving the system contain a certain percentage of ammonia. The whole process was over after 5–6 min, but the time between the actual ignition and the end of the reaction was less than 10 s. Different operating conditions affected the duration of the process as well as its intensity, and resulted in differences in the morphology of the products obtained: some had a foamy structure and easily crumbled to give a fine and volatile powder, whereas others were denser and needed proper grinding.

A series of frames were extracted from a video recording of the process: the resulting images that

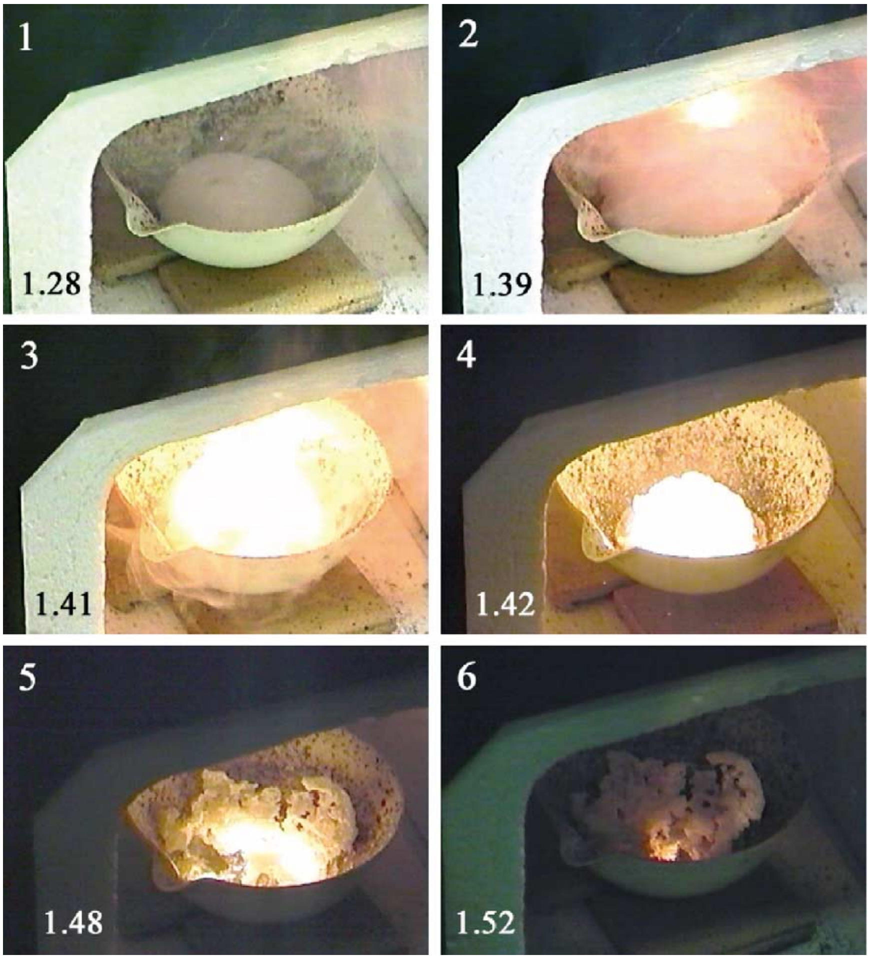

Fig. 1. Combustion synthesis of Al_2O_3 in stoichiometric conditions at 600 °C. The number in the bottom right-hand corner refers to the time elapsed since the time the dish was placed in the oven (expressed in minutes and seconds).

depict the most relevant steps of the process, for the model case of alumina preparation, are shown in Fig. 1.

In a few cases the temperature profile in the capsule during the reaction was monitored with a thermocouple placed within the starting solution. A typical temperature versus time plot can be found in Fig. 2.

The main steps of the transformation can be easily detected: at the beginning, a constant temperature is reached that corresponds approximately to the boiling point of the solution, then a ramp with a moderate slope can be seen. When a thermal level sufficient to trigger the main reaction is reached, a dramatic increase is recorded, resulting in a neat temperature peak. It must be emphasised that the peak temperature measured by the thermocouple does not correspond to the value actually reached within the reacting system. Due to some delay of the thermocouple signal in the case of a sudden change in the system temperature, the values recorded are significantly lower than those actually reached by the reacting mixture. An indirect sign of this is the formation of crystalline phases, as detected by XRD analysis (see Section 3.2), despite the short duration of the combustion synthesis reaction.

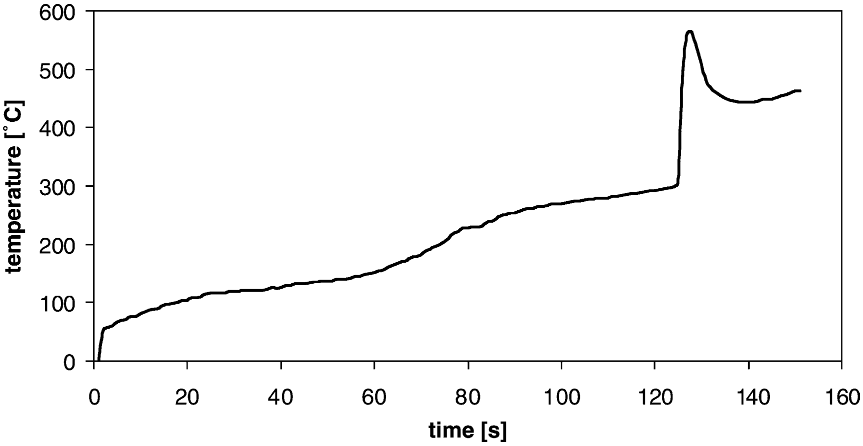

Fig. 2. Temperature versus time plot during the synthesis of $LaMnO_3$; oven temperature 500 °C, fuel-to-oxidisers ratio $\varphi = 2.5$.

3.2. Characterisation

XRD analyses (Philips X'PERT; Cu Kα radiation) were performed on all fresh samples to assess the presence and purity of the expected phases and to gather information about their degree of crystallisation. The same analysis was repeated on a number of samples that had undergone a short ageing treatment to verify to what extent they had been affected, both in terms of further crystallisation and/or of appearance of new phases.

BET specific surface area was measured (Micromeritics ASAP 2010 M apparatus, employing N_2) on most fresh perovskites and on a few selected aged samples, with a view to verifying how this feature can be affected when the catalyst deals with temperatures comparable to the actual operating conditions.

Perovskites obtained under different synthesis conditions were examined by scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) (Philips, 515 SEM equipped with EDAX 9900 EDS) to define the morphology and verify the elemental composition of the catalysts. Transmission electron microscopy (TEM, Philips EM 400 apparatus) was employed to obtain indications about the microscopic structure of the powders.

Catalytic activity tests were performed on catalysts that had 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 SiO_2 (0.2–0.7 mm 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 $50\,N\,cm^3/min$ ($CH_4 = 2\%$, $O_2 = 16\%$, He = balance) was 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 CO_2, CO, CH_4 and O_2 concentration (by means of a Hartmann and Braunn URAS 14 continuous analysers). The typical sigma-shaped curves were obtained when plotting methane conversion versus temperature and the half-conversion temperature (T_{50}) was regarded as an index of the catalytic activity.

4. Results and discussion

Following the previous studies on combustion synthesis of aluminium oxide, the first syntheses of $LaMnO_3$ were carried out in stoichiometric conditions; while aluminium oxide was formed when employing the stoichiometric conditions, in this case no visible reaction took place for $LaMnO_3$. Non-stoichiometric conditions were needed for a proper combustion synthesis reaction. A fuel-to-oxidisers ratio larger than 2 at an oven temperature of 600 °C proved effective. A wide variety of synthesis conditions were tested, by varying both temperature and fuel-to-oxidisers ratio, in order to outline which were

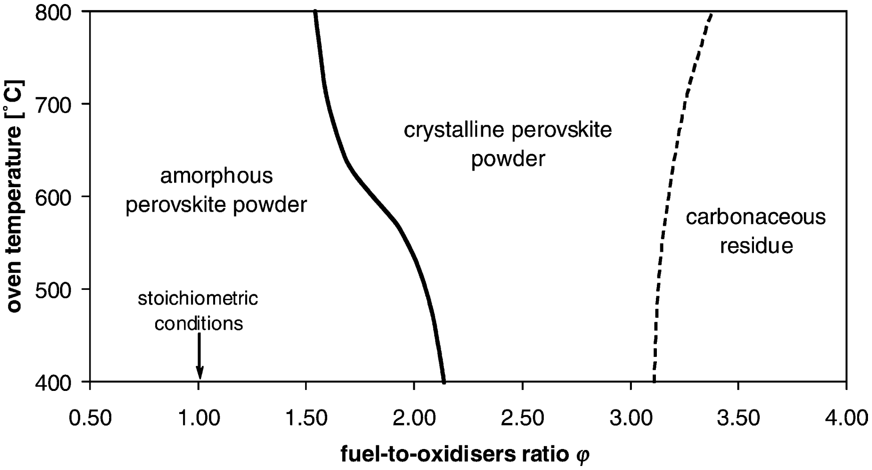

Fig. 3. Operating conditions map, in terms of temperature and fuel-to-oxidisers ratio, for the formation of the $LaMnO_3$ perovskite.

favourable to the reaction. Results are summarised in Fig. 3.

This figure shows that at low urea concentration no crystalline perovskite was formed, and that higher temperatures led to an easier achievement of a perovskite crystal structure. However, when too high a concentration of urea was used, a carbonaceous residue remained after the synthesis.

In order to find the optimum synthesis conditions, BET surface area measurements were made in most of these conditions. Some results are shown in Table 1: it can be seen that these materials always have rather low specific surface area. Higher oven temperatures seem to have a positive effect on BET area, at least for not too high fuel-to-oxidisers ratios, but the gain is not dramatic. It is thought that this small increase in specific surface area is due to a faster reaction rate, which promote the nucleation of grains with respect to their growth.

Table 1
Specific surface area (m^2/g) for $LaMnO_3$ synthesised at different temperatures and with different fuel-to-oxidisers ratios

Fuel-to-oxidisers ratio, φ	Oven temperature (°C)			
	500	600	700	800
2	–	–	3.6	4.1
2.5	3.5	3.6	3.8	4.8
3	–	2.2	2.5	2.7
3.5	–	5.2	3.9	5.6

With a growing excess of $CO(NH_2)_2$, specific surface area decreases as a result of sintering. Over a certain threshold value, however, a rise is seen because not all urea reacts completely and some carbonaceous residue is left.

The specific surface area of perovskite synthesised under these conditions is low probably because of the combination of two effects.

Firstly, as shown in Fig. 3, at low fuel-to-oxidisers ratios the heat released by the reaction is not sufficient to raise the system temperature to a level that allows the synthesis of the perovskite. In order to provide the heat required, the temperature of the oven can be raised, but this effect is not dramatic. More effective proves the addition of excess urea in the starting batch: it is thought that some exothermic reaction between fuel and air takes place, internally heating the mixture and allowing the synthesis reaction to reach sufficient speed to provoke the formation of perovskite. However, if quick and effective dispersion of the additional heat generated by urea combustion is not possible, some local sintering occurs, thus limiting the specific surface area.

Secondly, $LaMnO_3$ is a binary oxide and it is possible that the migration of ions required for the formation of the perovskite structure demands also some residence time at high temperature, which leads to the same result as before.

Since variations of both temperature and fuel-to-oxidisers ratio proved ineffective in significantly raising surface area, the introduction of NH_4NO_3 as an additive reactant in the starting batch was considered.

As the amount of ammonium nitrate in the system is increased, the specific area is enhanced from 4 m^2/g to almost 20 m^2/g (see Fig. 4). The latter value is obtained with 1 g of ammonium nitrate per gram of catalyst, which corresponds in reaction (1) to a stoichiometric coefficient 3.03. Once the maximum is reached, specific surface area slowly decreases as a result of further increasing the amount of NH_4NO_3.

The presence of ammonium nitrate in the starting batch accelerates the reaction: instead of 10 s, the reaction lasts in this case only a couple of seconds, it is thought that in these conditions perovskite has the time to form but not to sinter, and the final specific surface area is higher. The probable increase in local temperature due to the acceleration of the reaction is counterbalanced by the reduction of duration and by the release of a larger quantities of gases, which have a boosting effect on surface area. Ammonium nitrate being an oxidiser, it is possible that an excessive quantity of it (over 1.5 g per gram of catalyst) causes a shift of the effective fuel-to-oxidisers ratio towards lower values that lead to smaller specific surface areas.

It is indeed strange that ammonium nitrate does not decompose before the ignition (that is around 300 °C as shown in Fig. 2), since in air its decomposition starts at less than 250 °C. The presence of much urea in the mixture, however, seems to postpone the decomposition of ammonium nitrate to temperatures of about 300 °C, close to the ignition. We think this is due to urea, since in the presence of lanthanum nitrate only, for instance, the effect is not seen. Further details on this topics will be given in a successive paper in preparation, however, it is possible that a novel complex compound is formed on the addition of ammonium nitrate into the urea–nitrate mixture solution.

In order to observe the microstructure of the synthesised perovskites SEM and TEM analyses were performed. Fig. 5a–c shows SEM pictures of perovskite prepared without NH_4NO_3, whereas Fig. 5d–f refers to perovskites synthesised with the addition of ammonium nitrate. In Fig. 5a the sponge-like structure is more evident than in Fig. 5d. Fig. 5b and e shows perovskites synthesised without and with ammonium nitrate at higher magnification. The pores size is of some hundreds of nanometres, and it is also possible to see some more sintered parts. The ammonium nitrate-synthesised perovskite, on the other hand, shows a wider pore distribution (Fig. 5e), but from Fig. 5f the presence of a fraction of pores much smaller (size lower than 100 nm) than in Fig. 5c, can be easily detected. Fig. 6a and b shows TEM images of the same materials synthesised without and with ammonium nitrate, respectively: the powder synthesised without ammonium nitrate is clearly more sintered than the one prepared with the additive.

The crystallinity of the so-synthesised catalysts was assessed by X-ray diffraction and the results are shown

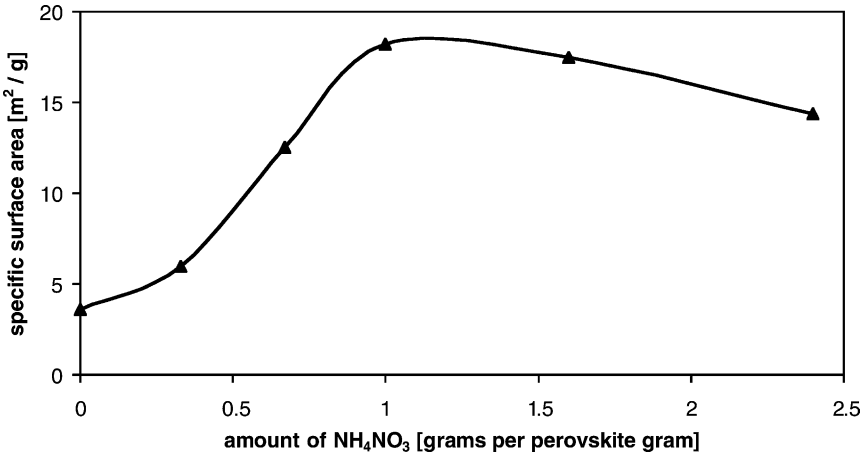

Fig. 4. Effect of different amounts of NH_4NO_3 on the specific surface area of $LaMnO_3$ (fuel-to-oxidisers ratio $\varphi = 2$; oven temperature 600 °C).

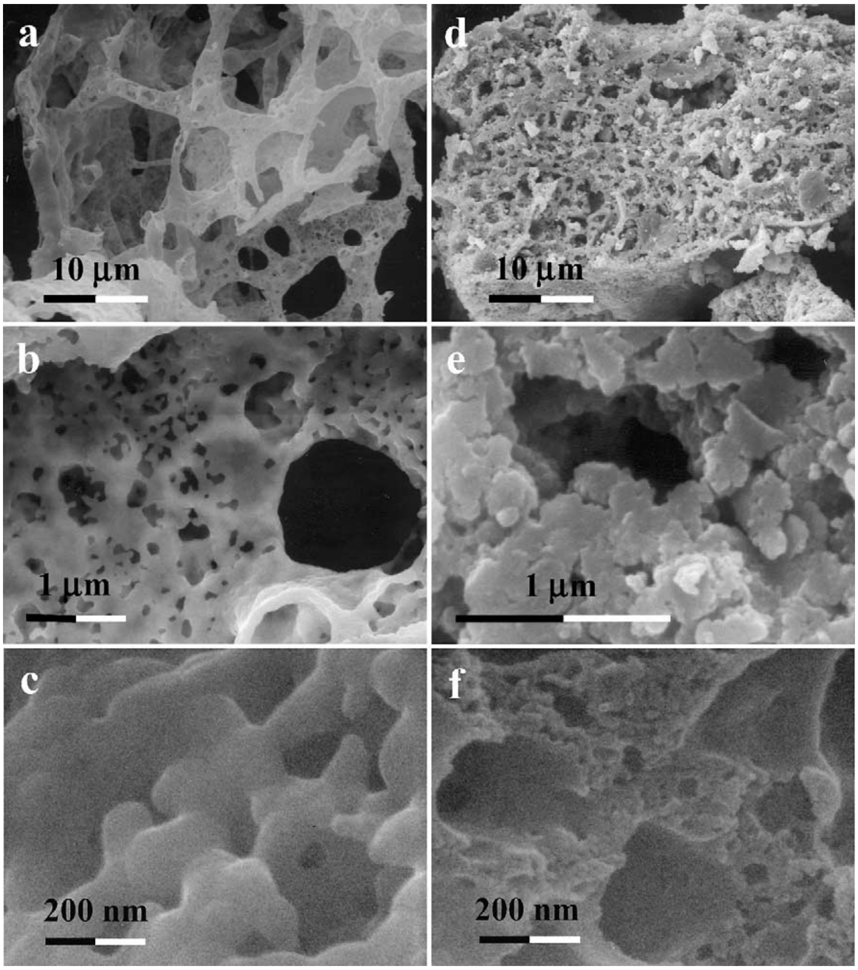

Fig. 5. SEM pictures of $LaMnO_3$ perovskites prepared with a fuel-to-oxidisers ratio $\varphi = 2.5$ at an oven temperature of 600 °C: (a)–(c) absence of NH_4NO_3; (d)–(f) presence of NH_4NO_3 in the starting solution.

in Fig. 7. After a short thermal treatment the perovskite was always well crystallised.

The perovskite synthesised at 600 °C using fuel-to-oxidisers ratio $\varphi = 1$ was completely amorphous, being prepared either without or with ammonium nitrate (small $LaO(NO_3)$ residual amounts were left in the latter case). This happened probably because the peak temperature value was markedly lower than that needed for perovskite to crystallise.

When a fuel-to-oxidisers ratio $\varphi = 2.5$ was used, the resulting perovskite phase was reasonably pure and well crystallised, as seen in spectra c and d of Fig. 7. Ammonium nitrate apparently had a restraining effect on the crystallisation of perovskite: the sharpest peaks are recorded without the addition of NH_4NO_3.

The catalytic activity measurements carried out with the catalysts gave the results shown in Table 2; the performance of $LaMnO_3$ previously obtained via “citrates” method [3] is also listed.

These results show that as-prepared catalysts obtained by combustion synthesis behave better than “citrates” method. The activity, however, cannot be related for both methods directly with specific surface area; it is thought that combustion synthesis produces more defective catalysts with respect to “citrates” method, due to its peculiar synthesis route.

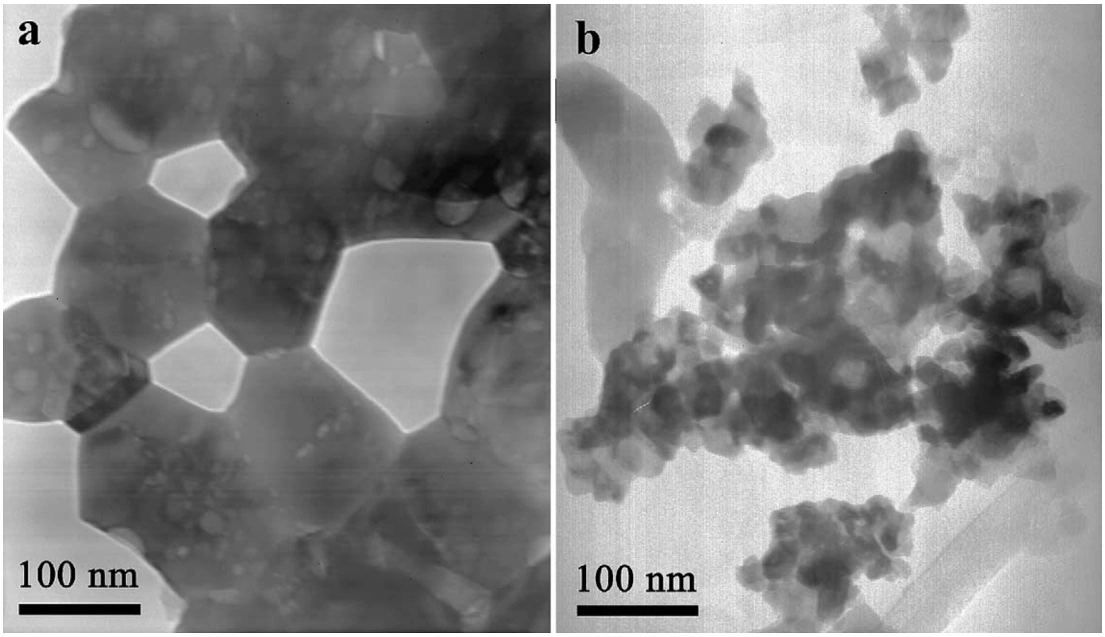

Fig. 6. TEM pictures of the $LaMnO_3$ catalysts prepared with a fuel-to-oxidisers ratio $\varphi = 2.5$ at an oven temperature of 600 °C: (a) absence of NH_4NO_3; (b) presence of NH_4NO_3 in the starting solution.

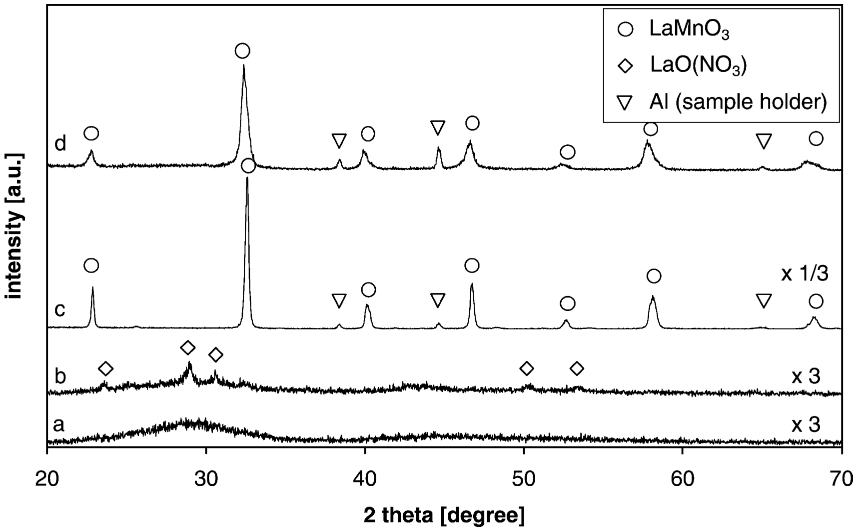

Fig. 7. XRD spectra for $LaMnO_3$ synthesised at an oven temperature of 600 °C: (a) fuel-to-oxidisers ratio $\varphi = 1$; (b) fuel-to-oxidisers ratio $\varphi = 1$, 1 g of NH_4NO_3 per gram of catalyst; (c) fuel-to-oxidisers ratio $\varphi = 2.5$; (d) fuel-to-oxidisers ratio $\varphi = 2.5$, 1 g of NH_4NO_3 per gram of catalyst. Intensities for spectra (a)–(c) were multiplied by the factors on the right-hand side.

Table 2

Specific surface areas and temperatures of half-conversion of methane for $LaMnO_3$ catalysts synthesised in different conditions

Material	Thermal treatment	S_{BET} (m^2/g)	T_{50} (°C)
$LaMnO_3$: 600 °C; fuel-to-oxidisers ratio $\varphi = 2.5$; without NH_4NO_3	Fresh	3.6	506
	1 h, 900 °C	2.3	526
	12 h, 900 °C	1.8	552
$LaMnO_3$: 600 °C; fuel-to-oxidisers ratio $\varphi = 2.5$; 1 g NH_4NO_3 per gram of catalyst	Fresh	18	461
	1 h, 900 °C	4.8	507
	12 h, 900 °C	2.4	533
$LaMnO_3$: "citrates" method [3]	8 h, 900 °C	4.6	535

This defectivity, which improves the catalytic activity for the combustion of methane even if it does not influence specific surface area, is only partially retained after a thermal treatment. This allows for a similar activity of $LaMnO_3$ synthesised by combustion synthesis with respect to the "citrates" method perovskite, even if specific surface is lower. It should be noted that when the latter method is used, a prolonged thermal treatment is necessary, in order to burn away the carbonaceous residue left after the first step of the synthesis, whereas in combustion synthesis no thermal treatment is needed.

Since combustion synthesis employs relatively cheap reactants like urea and ammonium nitrate and given that is faster and more energy saving with respect to the "citrates" method it can be considered a preferable alternative. The main drawback of combustion synthesis is represented, in fact, by the emission of NO_x or NH_3 during the synthesis. Moreover, the very high activity of $LaMnO_3$ obtained from NH_4NO_3-containing mixtures could be interesting for applications like natural gas engines exhaust catalytic converters, where the temperature to which the catalyst is exposed is lower than in the case of the burners.

High-temperature resistance issues have already been dealt with, when using the "citrates" method, by introducing MgO in the catalyst composition [5,6]: small MgO grains among the $LaMnO_3$ seem to dramatically reduce the high-temperature sintering tendency, thus limiting the decrease of the specific area. A similar approach was applied with combustion-synthesised perovskites: a systematic study of the surface area of materials obtained under different conditions was made and some results are presented in Fig. 8.

It is indeed possible to obtain catalysts with very high specific surface area by operating within a relatively wide range of temperatures and fuel-to-oxidisers ratios. The most interesting value obtained to date is slightly lower than 50 m^2/g.

The compositions with the highest specific surface area values were tested with regards to both catalytic activity and temperature resistance, and the results are shown in Tables 3 and 4.

Unfortunately, the expected effect of MgO as a structural promoter was not seen with these materials, since even a 2 h ageing at rather low temperatures caused a marked decrease in the specific surface area.

Table 3

Specific surface areas for $LaMnO_3 \cdot 17MgO$ catalysts synthesised in different operating conditions after different thermal treatments

Material	BET specific surface area (m^2/g)			
	Fresh	2 h, 600 °C	2 h, 750 °C	2 h, 900 °C
$LaMnO_3 \cdot 17MgO$: 600 °C; fuel-to-oxidisers ratio $\varphi = 2$; 1 g of NH_4NO_3 per gram of catalyst	47.8	20.9	13.4	6.6
$LaMnO_3 \cdot 17MgO$: 500 °C; fuel-to-oxidisers ratio $\varphi = 1.2$; 1 g of NH_4NO_3 per gram of catalyst	49.4	22.4	12.4	6.0
$LaMnO_3 \cdot 17MgO$: 500 °C; fuel-to-oxidisers ratio $\varphi = 1.5$; without NH_4NO_3	49.5	25.0	14.0	7.0
$LaMnO_3 \cdot 17MgO$: "citrates" method	After 8 h at 900 °C [3], 7.0			

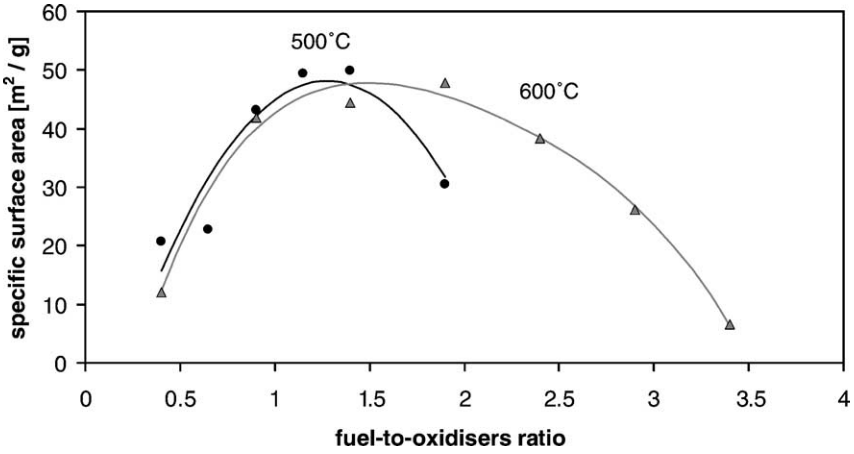

Fig. 8. BET specific surface area for $LaMnO_3{\cdot}17MgO$ synthesised at 500 and 600 °C with varying fuel-to-oxidisers ratios, in the presence of 1 g of NH_4NO_3 per gram of catalyst.

Table 4
Temperatures of half-conversion of methane for $LaMnO_3{\cdot}17MgO$ catalysts, fresh and after thermal treatments

Material	Thermal treatment	S_{BET} (m^2/g)	T_{50} (°C)
$LaMnO_3{\cdot}17MgO$: 600 °C; fuel-to-oxidisers ratio $\varphi = 2$; 1 g of NH_4NO_3 per gram of catalyst	Fresh	47.8	538
	2 h, 900 °C	6.6	592
$LaMnO_3{\cdot}17MgO$: "citrates" method	8 h, 900 °C	7.0	526

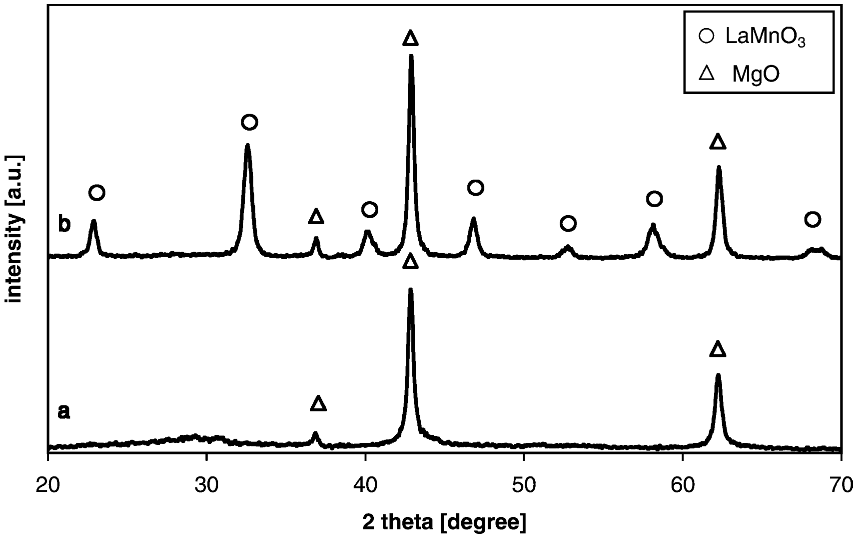

Fig. 9. XRD spectra for $LaMnO_3{\cdot}17MgO$ synthesised at 600 °C with fuel-to-oxidisers ratio $\varphi = 2$, 1 g of NH_4NO_3 per gram of catalyst: (a) as-prepared; (b) after 2 h at 750 °C.

A comparison of Tables 2 and 4 shows that the loss in catalytic activity is remarkably amplified by the presence of MgO.

A possible explanation comes from the XRD analysis: as shown in Fig. 9, in the spectrum of an as-prepared sample (curve a) only peaks relative to MgO can be detected. After a short and mild thermal treatment, the presence of the perovskite phase (curve b) can be easily seen. When both MgO and perovskite grains grow simultaneously, the promoting action of MgO is effective by geometric interposition, the former limiting the growth of the latter. This case apparently does not occur when MgO is already well crystallised right after the synthesis, whereas the $LaMnO_3$ phase is still amorphous.

It is thought that the $LaMnO_3 \cdot 17MgO$ prepared by combustion synthesis consists of two phases that are not intimately mixed; each phase is probably highly porous, as specific surface area measurements suggest, but the sintering effect induced by a thermal treatment is not in any way slowed by structural promotion.

The catalytic performance of these materials is quite poor: fresh, high-surface catalysts behave similar to a thermally treated “citrates” method perovskite, while a short thermal treatment leads to significant deactivation of combustion synthesised catalysts. The reason is probably that in this case MgO represents by far the largest volume fraction of material (>85%), so that perovskite is left with a small fraction of exposed surface. Since the structural promotion does not take place, the reduction of activity due to heat treatment is much more evident than in the case of pure $LaMnO_3$.

5. Conclusions

In this work combustion synthesis has been successfully employed for the preparation of perovskite-type catalysts for the combustion of methane. This method represents an interesting alternative with respect to the traditional techniques previously employed because it is fast, cheap and energy saving. As for the main drawback (the production of pollutant gases, NH_3 or NO_x) combustion synthesis does not represent an improvement with respect to other conventional routes, but the emissions issue does not get any worse, since also “citrates” method, for instance, produces large amounts of NO_x whenever nitrate precursors are employed. The products obtained were pure and presented varying degrees of crystallinity and specific surface areas, depending on the synthesis operating conditions. $LaMnO_3$ samples have been synthesised with a specific surface area that is sensibly higher ($18\,m^2/g$) than that achieved with the so-called “citrates” method. The increase in the specific surface area results in a remarkable improvement of the catalytic activity (the half-conversion temperature for methane combustion on as-prepared samples is 70 °C lower with respect to the samples obtained by “citrates” method). This material is unfortunately prone to temperature deactivation: a heat treatment similar to that used in the “citrates” method causes a reduction of specific surface area to values near to those obtained by this latter technique. However, it should be noted than in “citrates” method the heat treatment is necessary in order to burn away the carbonaceous residue, while in combustion synthesis it is not needed. In the light of these characteristics, these perovskite catalysts might have potential, still to be verified, for applications such as exhaust converters for natural-gas-fired engines that normally work at relatively low temperatures.

$LaMnO_3 \cdot 17MgO$ samples have been synthesised with the goal of verifying the promoting effect of magnesia that had been previously studied. Unfortunately, MgO does not act in this catalyst as a structural promoter, and the perovskite and MgO phases are thought to be mixed not intimately. Therefore, the effect of MgO becomes negative, limiting the active exposed surface area, and reducing the catalytic performance of the material.

The introduction of an alternative oxide phase that can crystallise simultaneously with $LaMnO_3$, e.g. ZrO_2, is now being considered, since some preliminary experiments have shown that ZrO_2 crystallises less easily than MgO.

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