

## **NEW METHOD FOR CATALYST POWDER MANUFACTURING BASED ON SOLVENT COMBUSTION**

*G. Saracco, F. Geobaldo, D. Mazza and G. Baldi*

Dipartimento di Scienza dei Materiali ed Ingegneria Chimica – Politecnico di Torino, Corso  
Duca degli Abruzzi, 24 – 10129 Torino, Italy

### **Abstract**

A new method for the synthesis of fine catalyst powders is presented. Catalyst precursors are dissolved in an ethanol-water mixture which is burned through a nozzle-type burner. As a result, catalyst powders are formed and removed from flue gases through a filter.  $\text{LaMnO}_3$  catalysts for the catalytic combustion of methane have been prepared, characterised (TEM, XRD) and compared with a reference manufacturing method (the citrates one) showing promising, though improvable, results.

**Keywords:**  $\text{LaMnO}_3$  perovskite catalyst, methane combustion, solvent combustion, spray pyrolysis

### **Introduction**

Catalytic combustion of methane outperforms conventional flame combustion in terms of either lower emissions (HC, CO and  $\text{NO}_x$ ) or easier controllability (a wider range of air-to-fuel ratios is allowed). The most promising applications of catalytic combustion are nowadays foreseen upstream gas turbines (required ignition temperature:  $450^\circ\text{C}$ ; maximum operating temperature:  $1300^\circ\text{C}$ , [1]) or in catalytic burners for heat generation purposes (m. o. t.:  $1000^\circ\text{C}$ , [2]). Since these rather high operating temperatures cannot be tolerated by conventional oxidation catalysts such as noble metals or simple metal oxides, catalytic materials (among others: perovskites hexa-aluminates, etc.) with suitable thermal stability are being developed all over the world. In the present paper, perovskite-type catalysts oxides ( $\text{A}_{1-x}\text{A}'_x\text{B}_{1-y}\text{B}'_y\text{O}_{3\pm\delta}$ , where  $A, A' = \text{La, Sr, Ba, ...}$  and  $B, B' = \text{Co, Mn, Cr, ...}$ ), and the  $\text{LaMnO}_{3+\delta}$  compound in particular, will be considered for their prevalent catalytic activity towards methane combustion [3].

A major hurdle to be faced in this context lies in the rather low specific surface areas (hardly exceeding  $20 \text{ m}^2 \text{ g}^{-1}$ ) of such materials, after exposure to calcination temperatures at least as high as those to be tolerated in the practical application envisaged. Besides, the higher is the calcination temperature, the faster the desired phases are obtained, even though sinterisation becomes a more and more severe hurdle to the conservation of high specific surface areas and catalytic activities. A trade off between catalyst stability and activity has to be faced. Several methods are being investigated to by-pass this problem, all aiming at keeping the crystal size as small as possible despite the achievement of the desired crystal lattice from the precursors.

According to the citrates method [4], suitable amounts of catalyst precursors (generally nitrates) are dissolved in small volumes of distilled water and added with citric acid. While heating at about 150–200°C, the citric acid reacts with the nitrates giving rise to a sudden formation of gases ( $\text{NO}_x$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , etc.) which blow up the precursors to form a fragile, highly porous foam of fine crystals. Such crystals, after high temperature calcination, acquire a perovskite structure with specific surface area often exceeding  $10 \text{ m}^2 \text{ g}^{-1}$ . A variation of this method was recently proposed and tested at Politecnico di Torino: the goal is to promote the simultaneous formation of the perovskite and of a phase (textural promoter [5]) whose crystals, in thermodynamic equilibrium with the perovskite ones, hinder their sinterisation by simple interposition. Such concept was proven for  $\text{LaCr}_{1-x}\text{Mg}_x\text{O}_3$  ( $0 < x < 0.5$ ) compounds prepared with excess  $\text{MgO}$ , which allowed to obtain  $20 \text{ m}^2 \text{ g}^{-1}$  powders [6].

Freeze-drying can also be adopted to obtain high-surface area perovskite catalysts [7]. The method is based essentially on freezing an aqueous solution of the precursors (once again mostly nitrates) and on drying them under vacuum. By these means a highly porous and fragile layer of fine catalyst precursor salts can be obtained, which turns into perovskite crystals after adequate stay at high temperatures. On the basis of the pioneering efforts by some researchers at the Bell Laboratories (Murray Hill, NJ [7]), a group at the Ecole Polytechnique de Montreal recently optimised a freeze-drying route to the preparation of a highly active perovskite catalyst  $\text{La}_{0.66}\text{Sr}_{0.34}\text{Ni}_{0.3}\text{Co}_{0.7}\text{O}_3$  with surface areas slightly exceeding  $20 \text{ m}^2 \text{ g}^{-1}$  [8].

Other potential techniques in this context are based on spray pyrolysis [9] or on aerosol methods [10]. In the first case, the pyrolysis of volatile catalyst precursors is accomplished after spraying them in a hot zone of the reactor; typical materials obtained by this route are nanosized titania (exceeding  $100 \text{ m}^2 \text{ g}^{-1}$ , [11]) or silica (trade name: cabosil, [12]), but to the authors knowledge complex oxide materials such as perovskite ones have never been produced by these means. In the second case, a highly dispersed aerosol of an aqueous solution of the catalyst precursor is generated and then forced to pass through a flame or a hot furnace where the solvent is rapidly evaporated and the intimately mixed metal salts decomposed to their metal oxides; in this case, on the grounds of earlier studies for the development of perovskite catalysts for the Fisher-Tropsch reaction [13], investigations are in progress at the University of Milan for the synthesis of perovskite catalysts for methane combustion, even if the related results are premature, so far [14].

The method here presented can be regarded as a sort of a variation of the spray pyrolysis or the aerosol one, since it is based on the production of fine perovskite powders by combustion of an alcoholic solvent in which suitable catalyst precursors are dissolved. Basically, the combustion of the solvent itself provides the heat for its evaporation and for the calcination of the catalyst precursors into the final perovskite powders.

## Materials and methods

Pure lanthanum nitrate ( $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  by Fluka) and manganese acetate ( $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  by Merck) were dissolved in a commercial denaturated ethanol (90 wt% ethanol, 10 wt% water) up to a concentration of 37.3 and  $21.1 \text{ g l}^{-1}$  (1:1 La:Mn molar ratio), respectively. Such conditions are very close to saturation. The

choice of technical ethanol was made owing to economic reasons, in an industrial perspective. However, it was previously verified that such a fuel could give rise to a self-sustaining flame in the experimental apparatus described hereafter, despite the significant presence of water. On the other hand, water played a positive role on enhancing the precursor solubility.

The pilot plant in which catalyst preparation was accomplished is schematically represented in Fig. 1. The core of the plant is the burner section, where the solution is sprayed through a nozzle (Schlick) and burns out in a flame confined in an alpha-alumina sintered tube, whose role is that of providing some thermal insulation which helps flame stability and prevents extinction. After some optimisation runs, the nozzle diameter was set equal to 0.2 mm and operated with a pressure difference of 8.5 bar (obtained by pressurizing the solution reservoir with nitrogen). The resulting flow rate of alcoholic solution was  $2.1 \text{ l h}^{-1}$ . The use of an 0.1 mm nozzle, the smallest-in-size available on the market, capable of spraying only  $1 \text{ l h}^{-1}$  at the above  $\Delta P$  conditions, entailed rapid nozzle plugging due to the formation of precipitates, whereas an 0.3 mm nozzle was found to deliver a flow rate of alcohol ( $3.5 \text{ l h}^{-1}$  at 8.5 bar pressure difference) too large for the heat removal capacity of the apparatus. The cooling of the flue gases and, to some extent, the flame temperature control, can be obtained by two means: i) by modulation of the flow rate of primary and secondary air flow, dosed from the net through Venturi-meters; ii) a water cooling system (sprayed on the external walls of the stainless steel reactor). In a first run (named hereafter run A), the primary air flow rate was set equal to  $400 \text{ l min}^{-1}$ , a value slightly higher than the stoichiometric one. Conversely, in a second run (named run B in the following), the above figure was increased up to  $1000 \text{ l min}^{-1}$  in order to check whether it could modify the flame temperature, eventually causing variations in the crystal habit of the produced crystals. Lanthanum manganate can indeed crystallize according to a low temperature rhombohedral structure, rich of cation vacan-

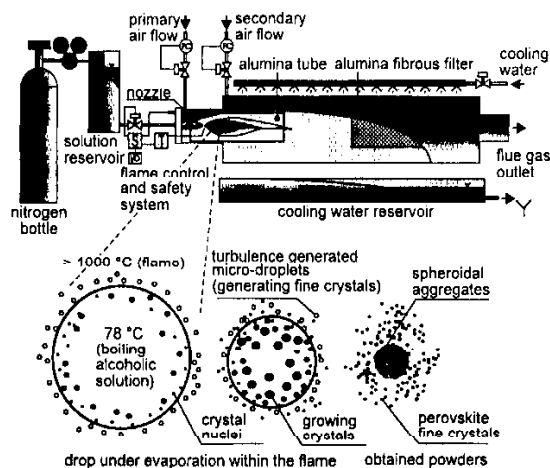


Fig. 1 Scheme of the experimental apparatus and tentative model of catalyst powder formation

cies and correspondingly characterised by a high oxygen excess with respect to  $\text{LaMnO}_3$  stoichiometry ( $\delta=0.1-0.2$ ), or to a high-temperature orthorhombic phase, well ordered ( $\delta<0.05$ ) and therefore much less active towards methane combustion than its rhombohedral counterpart [15]. The secondary air flow rate was in any case set equal to  $1000 \text{ l min}^{-1}$  in order to prevent filter damaging. In fact, too high flue gas temperatures ( $>800^\circ\text{C}$ ) would promote solid state reactivity between the filtered catalyst powders and the filter constituting material (alumina). The filter used for catalyst recovery was indeed assembled by wrapping an alumina fibre mat (Nextel by 3M) around a drilled stainless steel tube exposing a filtering area of about  $8 \cdot 10^{-2} \text{ m}^2$ .

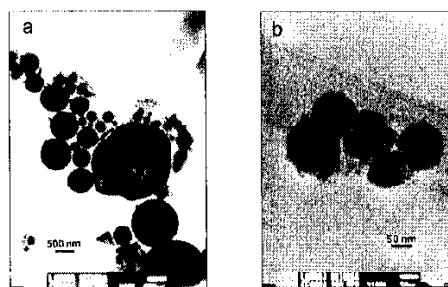
Each run was started through an automatised system acting contemporary both on the solution feed through an electrovalve and on the ignition electrodes. The run duration was prolonged to at least one hour so as to recover a sufficient catalyst amount for characterisation purposes. Finally, a photovoltaic flame detector caused immediate electrovalve closing whenever, for exceptional reasons (e.g. unexpected nozzle plugging), the flame extinguished.

Characterisation of the obtained perovskite powders was performed by TEM observation (JEOL), X-ray diffraction (PW1710 Philips diffractometer equipped with a monochromator on the diffracted beam  $\text{CuK}_\alpha$  radiation), BET specific surface area measurement (Sorptomatic Series 1800 – Carlo Erba Instruments), and through a test of the catalytic activity towards methane combustion. The experimental apparatus employed in this last context was described in detail in [6]. Briefly, it consists of a one-through fixed-bed of 1 g of catalyst particles (obtained by pressing the perovskite powders into tablets, then crushed into 0.2–0.5 mm granules), enclosed in a quartz tube (internal diameter: 4 mm) and sandwiched between two quartz-wool layers. The reactor temperature was varied, via a PID regulated oven enclosing the reactor, from  $850^\circ\text{C}$  (a pre-treatment temperature at which any chemisorbed gas such as  $\text{CO}_2$  leaves completely the sample) down to  $300^\circ\text{C}$  at a  $3^\circ\text{C min}^{-1}$  linear rate. Meanwhile, a  $100 \text{ Ncm}^3 \text{ min}^{-1}$  flow rate of a mixture of methane (2 vol%) – oxygen (17 vol%) – helium (balance) was continuously fed to the reactor (outlet pressure: 1 bar) and the flue gases analysed by means of a  $\text{CO}_2$  IR analyser (Hartmann & Braun URAS 10E) and a gaschromatograph (Hewlett Packard, mod. 5890 series II, equipped with a Porapak QS column and both TCD and FID detectors). Mass balances were verified by these means with a maximum deviation of 5%,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  being the only reaction products detectable. As a consequence methane conversion ( $\xi_{\text{CH}_4}$ ) could be monitored as a function of temperature. The higher the catalyst activity the lower the temperature range at which it could still promote methane combustion, the half-conversion temperature ( $T_{50}$ ) being generally regarded as the simplest index of catalytic activity. A reference run was also performed in a non-catalytic bed (1 g of 0.3–0.7 mm silica granules) to set a proper basis for the evaluation of the catalytic effect.

Finally, a reference rhombohedral  $\text{LaMnO}_3$  material was prepared through the earlier described standard citrates method with a final calcination treatment at  $900^\circ\text{C}$  for 2 h. The activity of this compound was checked and compared to that of the prepared materials.

## Results and discussion

The major results obtained are shown in Figs 2–4, where the outcomes of TEM observation, of XRD analysis and of the catalytic activity tests are shown, respectively.



**Fig. 2** TEM micrographs of  $\text{LaMnO}_3$  powders obtained by the solvent combustion method during run A: a) a set of large spheroidal crystal aggregates; b) fine crystals

Figures 2a and 2b show TEM micrographs of the powders obtained during run A, similar views were obtained for the powders obtained during run B. From these pictures two different classes of particles can be distinguished:

- Spheroidal crystal aggregates with a size ranging from 200 to 2000 nm, in some cases appearing as rather dense and particularly close to a perfectly spherical geometry, in others rather unhomogeneous and porous as the large aggregate shown in the middle of Fig. 2a.
- Small-size perovskite crystals (<200 nm), as those represented in the high-magnification micrograph shown in Fig. 2b.

As a first approximation, one might think that each single catalyst particle should originate independently, through evaporative crystallization and subsequent high-temperature calcination, from each single droplet generated by the nozzle. However, this hypothesis immediately fails on the grounds of simple calculations based on data derived from the nozzle manufacturer. The droplet-size range in the given operating conditions should be, in fact, almost entirely confined within 20 and 100  $\mu\text{m}$ . As a consequence, on the basis of the above hypothesis and of the precursor concentration in the alcoholic solution, it can be easily calculated that the particle size range should vary between 2 and 20  $\mu\text{m}$ , when 2  $\mu\text{m}$  is just the dimension of the largest particles detected in practice. Conversely, on the basis of the actual particle size observed, it can be deduced that each single droplet should give rise to about  $10^4$  perovskite particles on average.

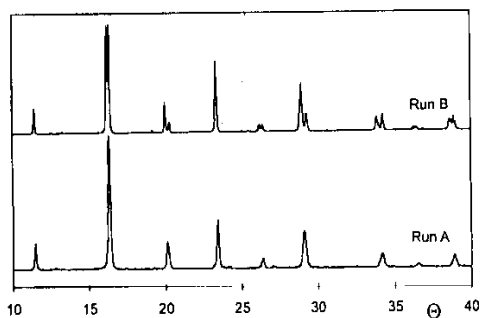
Following these considerations a tentative and, so far, qualitative model can be proposed to explain how the different kinds of particles are generated during solvent combustion. Such model is sketched in Fig. 1. It is assumed that each single droplet once sprayed into the flame zone undergoes two phenomena which progressively diminish its size:

i) evaporation: the droplets are inside a burning gas phase in which temperatures higher than  $1000^{\circ}\text{C}$  are likely; therefore they immediately start boiling at the temperature of about  $78^{\circ}\text{C}$  (azeotrope); as a consequence of the rapid evaporation which causes a local oversaturation, crystal nuclei of the catalyst precursor are formed close to the droplet surface;

ii) fragmentation: owing to the flame turbulence and to the boiling process the droplets divide into smaller ones, each one carrying a certain amount of nuclei and crystals already grown up to a certain extent.

The smallest droplets generated by this process evaporate quickly and are likely to give rise to fine crystals as those shown in Fig. 2b. Conversely, after a certain lifetime, the oldest and largest droplets are characterised by the presence of considerable amounts of grown-up crystals, which turn into a spheroidal perovskite aggregates as long as the residual solution is evaporated and calcination takes place. The nearly spherical shape of some particles might suggest the occurrence of some melting process that originates liquid droplets which acquire a spherical geometry to minimize surface tension and become solid when the flue gases are rapidly quenched. XRD analyses do not seem to support this hypothesis since no amorphous phases were detected in both runs. In fact, owing to the rapid particle quenching, at least partial formation of such phases from the molten droplets should likely be expected.

The XRD results (Fig. 3) clearly point out that rather pure crystalline phases were generated in both runs: during run A (low air excess, hot flame) orthorhombic  $\text{LaMnO}_3$  was formed, whereas the product obtained from run B (low air excess, cold flame) was rhombohedral. It is quite surprising that in both cases, despite the small residence time of the catalyst precursors in the hot flame zone (a few tenths of a second), well crystallised particles are obtained and complete reaction amongst the lanthanum and the manganese occurs, as suggested by the complete absence, in the XRD spectra, of any peak ascribable to unreacted lanthanum or manganese oxides. Further, it has been demonstrated that, by playing on the operating conditions at which the solvent combustion process is carried out, and, particularly, on the excess of primary air employed, a certain control of the crystal habit of the product can be achieved. Confirmations to this positive feature of the process are being obtained in the synthesis of both transition- and  $\alpha$ -alumina powders.



**Fig. 3** XRD spectra of  $\text{LaMnO}_3$  powders obtained during run A (low excess of air) and run B (high e. o. a.), showing an orthorhombic and a rhombohedral structure, respectively

Finally, in both runs, some catalyst powder was deposited as a by-product all over the inner part of the alumina tube facing the flame. XRD analysis of such material denoted a poorly crystallised cubic structure. Conversely TEM analysis showed the presence of irregular scales with some occasional spheroidal aggregate. It might be thus guessed that such material arises from some precursor solution which reaches the tube wall, wets it and evaporates there generating crystals which slowly undergo calcination at a lower temperature than the flame one. Nonetheless, the catalytic activity of this material, resulting from run A, was also checked.

The results of catalytic activity tests (Fig. 4) clearly show that any prepared material has an appreciable catalytic activity. However, if the orthorhombic perovskite lowers the  $T_{50}$  value from 815 to just 735°C, the catalytic activity of the other prepared catalysts is markedly higher: the  $T_{50}$  values for the rhombohedral perovskites are 485 and 557°C for the citrates and the solvent combustion methods, respectively, whereas the cubic  $\text{LaMnO}_3$  is characterised by a 590°C value of the same parameter. If the scarce activity of the orthorhombic perovskite is not surprising owing to the considerations drawn in the previous chapters [3, 14], the fact that the citrates method gave rise to catalyst samples more active than their solvent-combustion counterparts might be regarded as an upsetting result. A reasonable explanation, lies in the markedly higher BET surface area of the material prepared by the citrates method ( $7 \text{ m}^2 \text{ g}^{-1}$ ) compared to that of the catalyst obtained by the method here proposed (about  $1 \text{ m}^2 \text{ g}^{-1}$ ). Such rather low value is though due to the presence of the rather large spheroidal aggregates which involve a major fraction of the mass of the recovered product. If only fine crystals were obtained it can be easily calculated that the resulting specific surface area should have been markedly higher than  $20 \text{ m}^2 \text{ g}^{-1}$ , i.e. amongst the highest surface areas at which well crystallized perovskite powders have been obtained, according to the available literature [4–8]. This argument renders rather promising the obtained results if the very low filtration efficiency of the fibre filter employed is considered. In fact, on the basis of a simple overall mass balance it could be calculated that the recovered powder was in both runs only about the 5 wt% of the entire amount of perovskite particles produced. It is likely that only the largest particles were caught by the filtering net, meanwhile the fines passed through it almost completely. Therefore, a more efficient filtering apparatus than the one em-

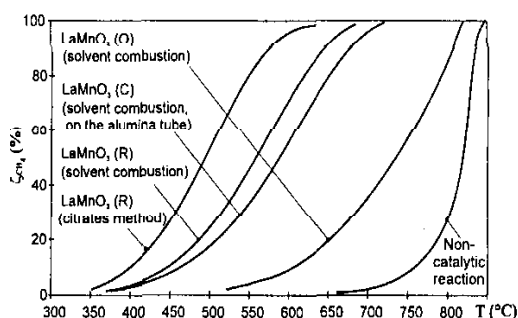


Fig. 4 Results of catalytic activity tests on the recovered catalytic materials, on the sample prepared by the citrates method and in the blank, non-catalytic run

ployed has to be used. The filtration of powders smaller than 50 nm is indeed a serious technological challenge. A special electrical precipitator is currently being designed and assembled for this purpose.

## Conclusions

An innovative method for the synthesis of fine perovskite powders for application in the catalytic combustion of methane has been tested. The obtained results are promising (perovskite crystal size down to less than 20 nm have been achieved on a fraction of the obtained product, a good controllability of the operating conditions can be reached so as to obtain the perovskite in the desired crystal habit), even though further work is needed to improve the overall performance of the experimental apparatus developed at Politecnico di Torino. Particularly, a high efficiency electrofilter is being assembled and some methods for the actual measurement of the flame temperature are being thought of. Once such improvements will be achieved, further studies will be dedicated to at least three directions: i) further reduction of the average particle size of the perovskite catalysts by playing e.g. on the precursor concentration (more diluted solutions than the one here employed may help in this context at the price of lowering the overall throughput of the apparatus) or on the pressure drop over the nozzle (higher values should result in smaller sprayed droplets and eventually in finer crystals); ii) preparation of different materials for different applications (e.g. fine powders are essential for lowering the sintering temperature of a number of ceramic materials for structural and mechanical applications); iii) improvement and quantification of the model here proposed so as to gain a deeper knowledge of the features and potentials of this promising technique.

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