

# Effects of thermal treatment on physico-chemical and catalytic properties of lanthanum manganite $\text{LaMnO}_{3+y}$

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## ABSTRACT

Lanthanum manganite oxides were prepared by citric acid gel process. The precursor gel was thermally decomposed in four steps allowing high composition homogeneity and textural stabilisation. As the calcination temperature increased, the lattice constants increased whereas the average oxidation state of manganese decreased resulting in lower cation vacancies (lower  $y$  values in  $\text{LaMnO}_{3+y}$ ). The specific surface area (SSA) was found to decrease from 13 to  $1.5 \text{ m}^2 \text{ g}^{-1}$  when the sintering temperature was raised from 600 to 1000 °C. Well characterized (XRD, ATD-ATG, chemical analysis, surface area, SEM, XPS) perovskite phase  $\text{LaMnO}_{3+y}$  synthesized after calcination at 700–1000 °C was tested for total methane oxidation in a fixed bed reactor with feed containing 1% methane, 4% oxygen and the balance helium. The catalytic activity was found to decrease with increasing calcination temperature and correlates not only with the bulk structure of the perovskite phase and consequently oxygen mobility but also with the content of manganese and its surface concentration. At low temperature (<600 °C), the decrease of catalytic activity with the increase of calcination temperature is correlated to the increase of surface Mn deficit. At higher temperature (>600 °C), the redox system is assumed to occur with the oxygen ions being transported through the lattice to the reduction site for reaction. This mechanism seems to be favoured by the increase of bulk cation vacancy amount.

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## 1. Introduction

$\text{LaMnO}_3$  first attracted attention more than 50 years ago [1], but widespread interest in this system was generated first by the emergence of Sr-doped lanthanum manganite as the cathode material of choice for the solid oxide fuel cell [2] and by the discovery of colossal magnetoresistance in those compounds with mixed Mn valence [3,4]. Moreover, their utilisation as prominent catalytic systems in many reactions [5–8] appeared very promising, because they could become cheaper materials in substitution of noble metal supported on alumina, silica and other inert solids.

In all these fields of research, the defect chemistry and the oxygen non-stoichiometry are of considerable importance. Most of the perovskite oxides exhibit some oxygen non-stoichiometry, usually oxygen deficiency; but lanthanum manganite oxide is somewhat unusual in comparison to most other perovskite oxides in that the non-stoichiometry is positive and is dependent of temperature and oxygen partial pressure [9–11]. Furthermore, the excess of oxygen,  $y$  in  $\text{LaMnO}_{3+y}$ , is not caused by hyperstoichiometry,

but by the ability of manganese to exist in tetravalent state. Because the perovskite lattice cannot accommodate interstitial oxygen ions, electroneutrality of the lattice is maintained by formation of cation vacancies [11–16]. Then, the real formula should be written as  $\text{La}_{1-\varepsilon}\text{Mn}_{1-\varepsilon}\text{O}_3$  (with  $\varepsilon = y/(3+y)$ ), a notation which indicates a fully oxygen lattice, showing however, cation vacancies.

It is well known [17,18] that catalytic total oxidation of hydrocarbons is supposed to occur on perovskite surface by means of a redox mechanism in which catalyst oxygen species are partly consumed by hydrocarbon and then regenerated by means of uptake from gaseous phase during a continuous cycle. Fluctuation of the Mn cation between two stable oxidation states  $\text{Mn}^{3+} \leftrightarrow \text{Mn}^{4+}$  is of considerable importance for the progress of this mechanism. Moreover, different types of oxygen are involved in the oxidation process at low and high temperatures. At high temperature, the oxidation process involves lattice oxygen as active species for substituted as well as unsubstituted samples. This mechanism is connected to the presence of lattice species in the layers near to surface. Then, the evolution of these species, was attributed to the reduction of the Mn site cations to lower oxidation state [19,20]. At low temperature, weakly adsorbed or surface oxygen species are involved. These species are accommodated in the oxygen vacancies

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which concentration is increased by partial substitution of the La or Mn site cations by lower valence ions or by increasing vacancies in the La or Mn site cations. This mechanism is connected to the presence of anionic vacancies on the surface.

In this communication, we refer about the possibility of altering the activity of oxygen species not by substitution of low valence ions on La or Mn sites as it was proposed by us [8], nor by altering the La/Mn ratio in the same perovskite lattice, but by annealing the lanthanum manganite oxides with La/Mn = 1:1 at different temperatures. First, the thermal decomposition behaviour of the gel precursor was studied in order to determine the best synthesis conditions of  $\text{LaMnO}_{3+y}$  oxide. The influence of calcination temperatures on the defect structure and the oxygen excess has been studied. The last part of the investigation concerns the effect of the surface Mn concentration and bulk cation vacancy amount on the redox catalytic activity in methane combustion reaction measured at low (<600 °C) and high (>600 °C) temperatures.

## 2. Experimental

### 2.1. Catalysts preparation

Bulk LM perovskite was synthesized by the citrate method using lanthanum nitrate hexahydrate  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Prolabo) and manganese nitrate  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Prolabo). The water content in lanthanum nitrate was determined by thermogravimetry. The formulae weight of manganese nitrate is determined by a potentiometric titration with 0.02 M potassium permanganate.

The mixed lanthanum–manganese citrate complex was prepared as follows. Lanthanum nitrate  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and manganese nitrate  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  precursors were dissolved in water (atomic ratio La/Mn = 1). Citric acid (Prolabo), used as a complexation agent, was added to the aqueous solution (molar ratio citric acid/metal = 0.25). The obtained solution was maintained under constant stirring for 24 h where gelification occurs in liquid solution. The gel was dried at 80–90 °C under vacuum ( $10^{-1}$  mmHg) for 24 h. Thermal treatment of the dry citrate complex at 400–600 °C in air for 24 h was performed before final sintering of the resulting black powder in air at various temperatures (700–1000 °C) for 24 h.

This procedure is outlined in the flow chart of Fig. 1.

### 2.2. Characterisation techniques

Powder X-ray diffraction patterns recorded on a diffractometer (Philips PW 1710) with  $\text{Cu K}\alpha$  radiation were used to check the phase purity and to determine the unit cell parameters of synthesized oxides. Lattice constants were refined by the least-squares method with the aid of the WINCELL program. From the quoted cell parameters, the volume per unit formula  $V_f$  was evaluated.

Investigations of the particle microstructure were performed on a Philips XL 30 FEG scanning electron microscopy (SEM). The element distribution was analysed by elemental mapping using an energy dispersive X-ray detector (EDX) mounted on the microscope.

The thermal decomposition of the gel under air was studied by differential thermoanalysis (DTA) and thermogravimetric analysis (TGA) with a heating rate  $10^\circ\text{C min}^{-1}$  using a thermobalance SETARAM (accuracy  $\pm 0.04 \mu\text{g}$ ).

BET specific surface areas (SSAs) were determined by  $\text{N}_2$  adsorption at 77 K in a volumetric all glass apparatus. Prior to each measurement, the samples were degassed 4 h at 523 K under vacuum ( $7.10^{-4}$  Pa).

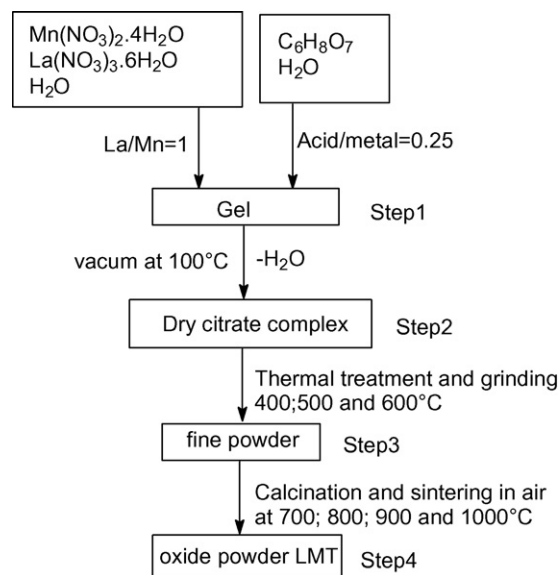
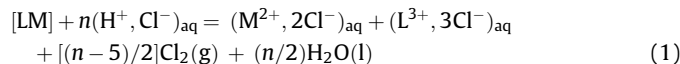


Fig. 1. A flow chart illustrating the preparation procedure of LMT powder.

Concentrations of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions were determined by redox titration [21,22]. The following procedure was used. Potassium iodide solution (0.1 M.) and concentrated hydrochloric acid solution were successively added, under stirring, to a given mass of a finely powdered sample. Upon treatment of tri and tetravalent manganese with hydrochloric acid, the evolved chlorine was reduced in situ with potassium iodide. The liberated iodine was titrated with standard sodium thiosulfate solution. The following reactions occur:



[LM] indicates the sample containing manganese at different oxidation state and lanthanum in a trivalent state. The evolution of manganese mean oxidation state after each step of the preparation procedure can be followed by the ratio  $R$  of the quantity (in mole) of sodium thiosulfate per mole of used manganese in [LM] sample. The same procedure of redox titration was also used to determine the oxygen excess,  $y$ , when the samples [LM] crystallized in a perovskite lanthanum manganite oxide of formulae  $\text{LaMnO}_{3+y}$ .

XPS spectra were recorded on a VG Scientific ESCALAB 200 R<sub>1</sub> electron spectrometer using  $\text{Al K}\alpha$  as the exciting radiation (1486.6 eV). The base pressure in the analysis chamber was less than  $5.10^{-8}$  Pa. All binding energy (BE) measurements were corrected for charging effects with reference to the C1s peak at 284.6 eV (adventitious carbon). This reference gave BE values with an accuracy of  $\pm 0.2$  eV. Collected data were analysed with a Shirley background subtraction and a least-squares fit routine using the simplex algorithm. For quantitative analysis, the signal intensities were measured by using integrated area under the detected peak. To evaluate the surface atomic ratios, we used sensitivity factors provided by the VG software (inelastic mean free path and transmission function) and the cross section for X-ray excitation as calculated by Scofield [23].

Catalytic activity in the combustion of methane was determined using a catalyst charge of about 0.1 g loaded in a U-shaped quartz microreactor. The reactor was operated in a down-flow

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