Digest Journal of Nanomaterials and Biostructures Vol. 8, No. 2, April - June 2013, p. 581 - 587

NANOSTRUCTURED LANTHANUM MANGANITE PEROVSKITES IN CATALYST APPLICATIONS

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Finding less expensive alternatives to noble metals catalysts is vital for implementing catalytic combustion on a wide scale, and lead substituted lanthanum manganites are a promising option. Nanometer particles of $La_{0.6}Pb_{0.4}MnO_3$ and $La_{0.6}Pb_{0.4}MnO_3$ + 0.2MeO (where Me = Mg or Ca) with perovskite structure were prepared by self-combustion method followed by heat treatment at 1000 ^oC in air. The effects of excess divalent ions (Ca^{2+} and Mg^{2+}) in $La_{0.6}Pb_{0.4}MnO_3$ manganite perovskite on the catalyst properties were investigated. The morphological and surface properties are of great importance in the catalyst activity. Structure, specific surface area and grain size were determined using XRD, nitrogen adsorption (BET) and SEM analysis. X-ray diffraction evidenced the crystallinity and the nanosize of the perovskite crystallites. Following Mg or Ca addition to $La_{0.6}Pb_{0.4}MnO_3$, a decrease in the grain size was detected by SEM. Rather large values for specific surface areas were obtained (of about 8 m^2/g).The perovskite manganite powders have been tested in the catalytic combustion of three diluted gases: acetone/air, ethanol/air and methanol/air. The experimental results revealed that it was possible to start the catalytic combustion of the gases over the surface of the three perovskite at much lower temperatures than catalyst-free combustion.

(Received February 27, 2013; Accepted March 26, 2013)

Keywords: Perovskite; Microstructure; Self-combustion; Catalyst

1. Introduction

The high cost of the noble metal (Pt, Pd) based catalysts determined many researchers to search for alternative materials as inexpensive catalysts. Some of the most promising materials for the catalyst applications are part of the perovskite group (ABO_3), where A and B are cations of different sizes. The catalytic properties of perovskite-type oxides depend on the nature of A and B ions and on their valence states.

Recently, lanthanum containing mixed oxides with perovskite structure, $LaBO_3$ (B = Mn, Co or Fe) have been studied extensively with the aim to develop combustion catalysts and environmental purification catalysts. Volatile organic compounds (VOCs) are the main source of air polluting and the most effective method for the removal of VOCs is catalytic combustion [1–5]. By lowering the combustion temperature, catalytic combustion allows a reduction in emissions of NO_x, CO and unburned hydrocarbons.

Lanthanum manganite perovskites, $LaMnO_3$, are studied because of their important catalytic activity during methane combustion [6]. The stable structure of the perovskites allows the partial substitution of La^{3+} or Mn^{3+} with foreign cations with different size and shell configurations, which can improve the perovskite structure and its properties. Thus, the partial substitution of La^{3+} with Sr^{2+}, Ca^{2+}, Pb^{2+} or Ba^{2+} can force a large amount of Mn^{3+} to oxidize to

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Mn^{4+} generating ionic vacancies to maintain electroneutrality. Ponce et al. [7] found that the stability of Mn^{4+} ions seems to be the crucial factor determining the catalytic activity of manganites in the oxidation of methane in the temperature range 200 – 800 °C.

Previous research [7,8] has focused on strontium substituted lanthanum manganites as promising catalysts for VOCs combustion. Less attention has been paid to the catalytic properties of the lead substituted lanthanum manganites. The partial substitution of La^{3+} in $LaMnO_3$ with Pb^{2+} decreases the temperature of the synthesis, stimulates a high ratio Mn^{4+}/Mn^{3+} by changing the oxidation state of manganese from +3 to +4 and improves the conductivity of the perovskite [9-11].

In this study, modified $LaMnO_3$ was investigated as potential catalyst for low temperature flameless combustion of some combustible gases. Modifications were carried out by the partial substitution of Pb^{2+} for La^{3+} and by addition of Ca^{2+} or Mg^{2+}.

Several techniques have been used to produce perovskite-type catalyst materials. The preparation procedure has a remarkable effect on the properties of the perovskites. Among the known methods, the self-combustion method allows a good control over the size of the material particles, which in turn decides structural properties [12]. This method has the advantage of producing ultra-fine, homogeneous and reproducible, multicomponent ceramic powders with precise stoichiometry. The preparation way is relatively simple, implies a low energy cost by utilizing an exothermal reaction and allows a controlled growth of the crystallites by subsequent heat treatments.

For catalytic purposes, the achievement of perovkites with high specific surface areas and nanosized particles is a priority. In nanostructured perovskites, the interface between the nanoparticles and its surrounding media plays a more important role than the bulk. Also, the high curvature of perovskite particles due to their small radius leads to an increased number of structural defects at the nanoparticle surface, enhancing the surface reactivity.

The phase composition, specific surface area, crystallite size and morphology of the perovskite manganites nanopowders prepared by a nonconventional method, self-combustion, were determined using XRD, BET and SEM methods. We performed catalytic tests of perovskite nanopowders in the total oxidation process of three VOCs (ethanol, methanol and acetone) in air.

2. Experimental

Perovskite powders of nominal compositions $La_{0.6}Pb_{0.4}MnO_3$ and $La_{0.6}Pb_{0.4}MnO_3$ + 0.2MeO (where Me = Mg or Ca) were prepared by self-combustion (SC) method [12] followed by heat treatment in air at 1000 °C for 320 min.

In the SC procedure, a solution containing metal (La, Mn, Pb, Ca and Mg) nitrates (reagent grade) is mixed with an aqueous solution of 10 wt% polyvinyl alcohol. Then, a small amount of NH_4OH solution (10% concentration) is dropped to adjust the pH value (pH ~ 8). The result is a sol of metal hydroxides and ammonium nitrate. By drying at 100 °C the sol is turned into a dried gel. The dried gel is ignited in a corner and an exothermic combustion reaction begins. The combustion wave spontaneously propagates through all the gel and an ultra fine powder results. The combusted powder is calcined at 500 °C for one hour to eliminate the residual organic compounds. After calcinations at 500 °C the powders are annealed in air at 1000°C for 320 min, for two major reasons. First, the heat released by the combustion reaction is not sufficient to raise the system temperature to a level that allows the synthesis of the perovskite. Second, La-Pb-Mn-O is an oxide compound and it is possible that the migration of ions required for the formation of the perovskite structure demands some residence time at high temperature.

The phase composition of the heat treated powders was analyzed with diffractometer DRON-2 and CuKα radiation ($\lambda = 0.154$ nm). The average crystallite size was estimated from the full width at half maximum using Scherer's equation. Scanning electron microscopy (SEM) was used to observe the morphology and agglomeration of the grains. Textural characteristics were investigated by means of specific surface area determined by BET (Brunauer-Emmett-Teller) method [13] from the nitrogen adsorption isotherms at 77 K. Total volume of pores was evaluated using desorption isotherms. Adsorption/desorption isotherms were determined with NOVA-2200 apparatus. The pore size distribution (PSD) curves were obtained using BJH (Barret-Joyner-

Halenda) method [13]. The catalytic tests were performed, in the temperature range 200 – 500 °C, with a set-up (described previously in [14]) which allows estimating the lowest combustion temperature of acetone, ethanol and methanol over perovskite surface.

3. Results and discussion

The XRD patterns (Fig. 1) show that all heat-treated powders have the structure of the $La_{0.6}Pb_{0.4}MnO_3$ (LPMO) perovskite and crystallize in cubic (Pm3m) system. The existence of a cubic cell is very similar to the results obtained for $La_{1-x}Sr_xMnO_3$ [15]. In addition, the X-ray patterns show a diffraction peak which belongs to a nonidentified phase, at $2\theta = 27.58^o$. Some broadening of the peaks was evident in all samples due to nanostructuring. Typically, grain growth is reflected in the decrease of the peak width and the increase in the intensity of the peaks. The lattice parameters and average crystallite size derived from XRD data are given in Table 1.

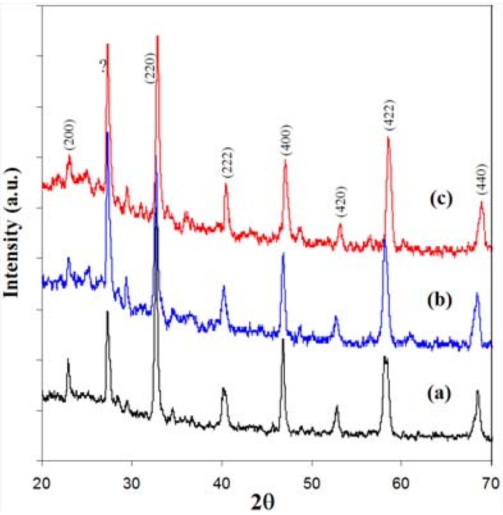

FIG.1 The XRD patterns of perovskites heat treated at 1000 °C: (a) $La_{0.6}Pb_{0.4}MnO_3$; (b) $La_{0.6}Pb_{0.4}MnO_3$ + 0.2CaO; (c) $La_{0.6}Pb_{0.4}MnO_3$ + 0.2MgO.

Table 1. Lattice parameters, average crystallite size (D_{XRD}) and Mn^{4+} concentration (%)

Sample composition	Lattice parameter (nm)	D_{XRD} (nm)	Mn^{4+} concentration (%)
$La_{0.6}Pb_{0.4}MnO_3$	0.7752	24.05	34.8
$La_{0.6}Pb_{0.4}MnO_3$ + 0.2 CaO	0.7742	25.05	35.9
$La_{0.6}Pb_{0.4}MnO_3$ + 0.2 MgO	0.7749	27.28	36.7

One can note that the lattice parameter of $La_{0.6}Pb_{0.4}MnO_3$ is almost insensitive to the addition of Ca or Mg, its decrease being very small, between 0.7752 nm and 0.7742 nm. This means that the excess of Me^{2+} (Ca or Mg) in $La_{0.6}Pb_{0.4}MnO_3$ was incorporated in the perovskite structure in a small amount. The perovskite structure remained intact and this can be attributed to the presence of a large number of Mn^{4+} cations (Table 1) with small ionic radius ($5.3 \cdot 10^{-2}$ nm) [16], which compensated the electronic effect of Mg and Ca doping.

The crystallite size (D_{XRD}) was found to be of about 24 – 27 nm (Table 1) attesting that perovskite powders with nanosized crystallites have been synthesized.

Generally, nitrogen adsorption/desorption at liquid nitrogen temperature (~77 K) is used to obtain information about the specific surface area S_{BET} and pore volume of the perovskite particles. Fig. 2 (a, b and c) presents the characteristic isotherms. These isotherms are identical in shape to the standard isotherm of type II in IUPAC classification [13]. It can be clearly seen that the width of hysteresis loop decreases and almost disappears for the Ca or Mg doped manganites, indicating nonporous adsorbents [13]. Systematic studies revealed that pore size influences the occurrence of hysteresis: a decrease in pore size leads to a decrease in the width of hysteresis loop. In this study, the pore size distribution PSD graphs (given inset Fig. 2) obtained from N_2 desorption isotherm by BJH method [13] show that the pore sizes decreased by Ca or Mg addition to LPMO, but these are within the mesopores region (2 – 50 nm) [13].

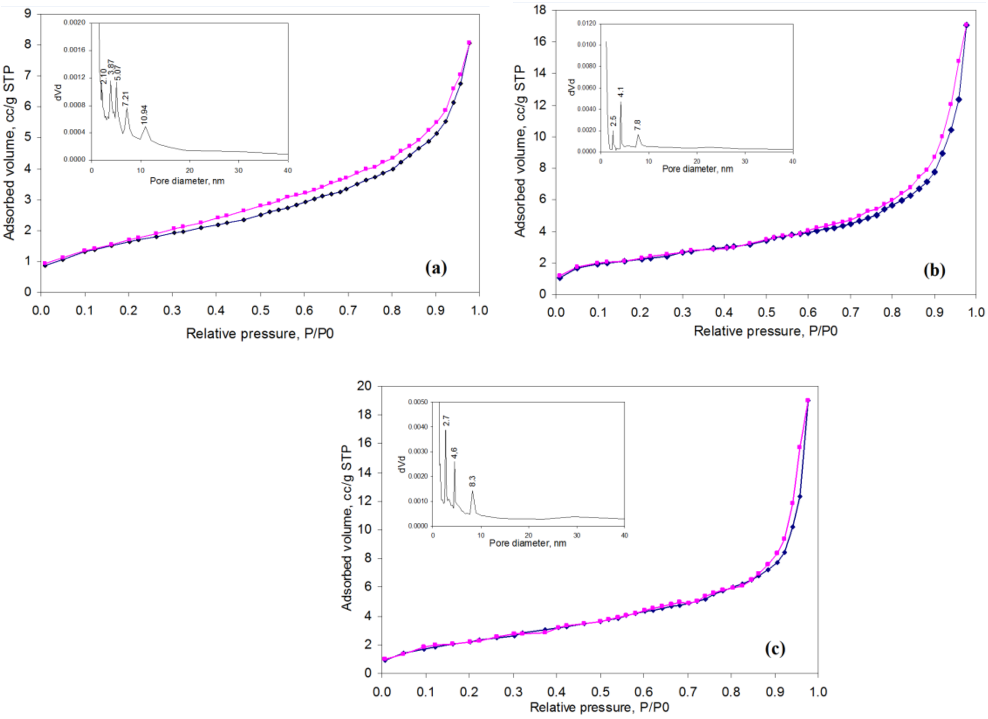

Fig. 2 Nitrogen adsorption/desorption isotherms at 77K for studied perovskites: (a) $La_{0.6}Pb_{0.4}MnO_3$, (b) $La_{0.6}Pb_{0.4}MnO_3$ + 0.2CaO, (c) $La_{0.6}Pb_{0.4}MnO_3$ + 0.2MgO; symbol rhomb (◊) is the adsorption branch and square symbol (□) is the desorption branch. Inset: the pore size distribution graphs.

Table 2 summarizes the structural properties of the investigated manganites. Values of BET area of approximately 6 – 8.5 m^2/g were obtained whereas the porosity was very low. The BET surface area of manganites increased by addition of divalent cations (Mg and Ca) to the parent composition $La_{0.6}Pb_{0.4}MnO_3$. It is possible that excess divalent cations produced very fine crystallites of MgO or CaO during the combustion synthesis, dispersed on the perovskite grain boundaries, contributing to an increase of the BET area [17].

Using S_{BET} data, the particle size D_{BET} was calculated under the assumption that the particles are cubic [13] and the density is 7.8 g/cm^3. It should be mentioned that for all samples, the average particle size (D_{BET}) (Table 2) is substantially greater than the X-ray crystallite size (D_{XRD}) (Table1) estimated by the Scherrer equation. A similar difference between D_{BET} and D_{XRD} for La-Sr-Mn-O composites was found by Ivanov et al. [18], who suggested the results can be explained by the concretion of the crystal domains forming the developed network of grain boundaries.

Scanning electron micrographs of the perovskites without and with addition of Ca and Mg are shown in Fig. 3. One can observe agglomerates of fine grains with irregular shapes. The grain size decreases with the addition of Ca and Mg due to the refinement of the grain size (Table 2).

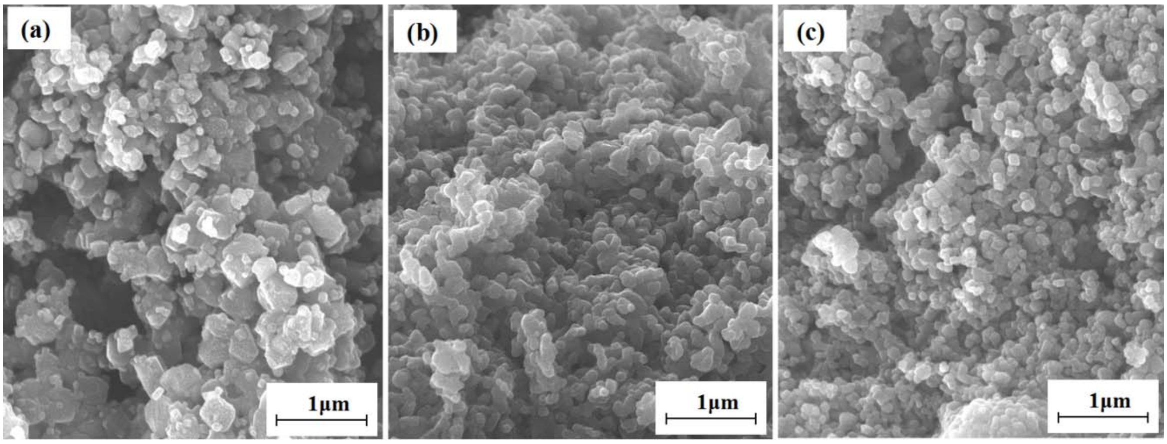

Fig.3 SEM micrographs for heat treated at 1000 °C manganites: (a) $La_{0.6}Pb_{0.4}MnO_3$; (b) $La_{0.6}Pb_{0.4}MnO_3$ + 0.2CaO; (c) $La_{0.6}Pb_{0.4}MnO_3$ + 0.2MgO.

For the three perovskite powders we determined the lowest combustion temperature of three diluted gases: acetone/air, ethanol/air and methanol/air (Table 2) over perovskite catalyst surface. The same tests to determine the temperature at which catalytic combustion of gases started were repeated in order to check data accuracy. The results were comparable within ±10 °C. The experimental data are presented in Table 2.

Table 2 Structural properties and the minimum combustion temperature over perovskite

Perovskite composition	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	D_{BET}^* (nm)	Minimum combustion temperature (°C)		
				Acetone	Methanol	Ethanol
$La_{0.6}Pb_{0.4}MnO_3$	6.120	0.0104	125	300	305	290
$La_{0.6}Pb_{0.4}MnO_3$ + 0.2 CaO	8.019	0.0298	96	270	280	265
$La_{0.6}Pb_{0.4}MnO_3$ + 0.2 MgO	8.584	0.0187	89	250	255	260

*Particle size calculated from S_{BET}

The minimum temperature required to ignite the test gases without a spark or catalyst being present is of 465 °C for acetone, 385 °C for methanol and 365 °C for ethanol.

The following observations can be made:

a) In the presence of perovskite catalyst, the combustion of the combustible gases will start at much lower temperatures than the normal combustion temperature;

b) The minimum temperature for gas combustion over Mg and Ca doped LPMO perovskites is inferior to that over LPMO perovskite (without Mg or Ca addition).

c) The lowest combustion temperature was obtained over $La_{0.6}Pb_{0.4}MnO_3$ + 0.2MgO catalyst, which has the smallest D_{BET} (89 nm) and the highest S_{BET} (8.584 m^2/g).

Our results suggest that in the low temperature range (below 500°C) the catalytic activity of the investigated perovskites in oxidation reaction of VOCs may be correlated with the presence of the active oxygen species (O^{2-}, O_2^-, O^-) determined by the structural defects generated by high Mn^{4+}/Mn^{3+} ratio in the perovskite structure. The interaction of surface active oxygen species with reactants constitutes the suprafacial mechanism [19] for gas oxidation over mixed oxide catalysts at low temperature.

The improved oxidation activity of Mg and Ca doped LPMO perovskites indicates an activation of the generation process of punctual defects in the form of oxygen vacancies, which are active sites for oxygen adsorption from the gas phase. More oxygen vacancies involve a larger density of adsorbed surface oxygen species, which are weakly anchored on the perovskite surface and more available for VOCs oxidation when these come into contact with perovskite surface.

Moreover, the formation of oxygen vacancies favors the lattice oxygen mobility (via vacancy mechanism [20]), which can directly affect the catalytic activity of the mixed oxides [21].

Additionally, the role of the specific surface area and particle size is very important. The achievement of high surface area and nanosized particles is a priority for catalyst applications. A larger surface area implies more interactions between perovskite surface and test gases, which can promote gas oxidation at lower temperature. Also, the decrease in particle size in the Mg and Ca doped perovskites leads to the formation of surface defects and, therefore, to a higher number of active sites for oxygen adsorption.

4. Conclusions

In this work, self-combustion method followed by heat treatment at 1000 ^{o}C has been employed to prepare modified perovskite-type oxides with the normal compositions of $La_{0.6}Pb_{0.4}MnO_3$ (LPMO), $La_{0.6}Pb_{0.4}MnO_3$ + 0.2CaO and $La_{0.6}Pb_{0.4}MnO_3$ + 0.2MgO for the catalyst applications. It is a fast and cheap method and the obtained products were pure and presented nanosized crystallinity (24 – 27 nm).

All prepared perovskites had a large specific surface area (6 – 8.5 m^2/g) and very small pores (below 20 nm). The increase of the surface area by Mg and Ca additions to $La_{0.6}Pb_{0.4}MnO_3$ was explained by the formation of very fine crystallites of MgO or CaO dispersed on the perovskite grain boundary.

The catalyst properties of the nanoperovskites were tested in the combustion of three diluted gases: acetone/air, ethanol/air and methanol/air and the obtained results revealed that the starting temperature of the gas combustion over the perovskite surface is much lower than in the case of the normal combustion (without catalyst).

The results of catalytic properties are preliminary, but they show that chemical modifications of the lanthanum manganite perovskite allow producing more active catalysts at low temperature. With the smallest D_{BET} (89 nm) and highest S_{BET} (8.58 m^2/g) among the three samples analyzed here, Mg doped LPMO is a promising catalyst for low temperature combustion of VOCs.

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNST – UEFISCDI, project number PN-II-ID-PCE-2011-3-0453.

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