Nanocrystalline Mixed Oxides Containing Magnesium Prepared by a Combined Sol-Gel and Self-Combustion Method for Catalyst Applications

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ABSTRACT

MgFe₂O₄ spinel ferrite and La₀.₆Pb₀.₂Mg₀.₂MnO₃ perovskite nanopowders were synthesized by a combined sol-gel and self-combustion method and heat treatment. The morphological and structural characterization of the obtained powders has been performed with various techniques: X-ray diffraction (XRD), SEM observations, EDAX spectroscopy and BET analysis. The samples have been catalytically tested in flameless combustion reaction of acetone, benzene, propane and Pb free gasoline at atmospheric pressure. The results revealed a higher catalytic activity of La₀.₆Pb₀.₂Mg₀.₂MnO₃ perovskite than that of MgFe₂O₄ ferrite. This higher catalytic activity can be ascribed to smaller crystallite size (27 nm), larger surface area (8.5 m²/g) and the presence of manganese cations with variable valence (Mn³⁺ - Mn⁴⁺). The current results suggest that La₀.₆Pb₀.₂Mg₀.₂MnO₃ perovskite is preferable to the Mg ferrite and that it can be a promising catalyst for acetone and propane combustion at low temperatures.

Keywords: Oxides; Sol-Gel-Self-Combustion; Microstructure; SEM; XRD; Catalytic Properties

1. Introduction

The aim of the present work is to comparatively estimate the physical and catalytic properties of two magnesium containing oxide compounds prepared by sol-gel-self-combustion: MgFe₂O₄ spinel ferrite and La₀.₆Pb₀.₂Mg₀.₂MnO₃ perovskite. The role of the Mg ion in a ceramic is to prevent the growth of the grains by reducing the grain boundary mobility.

In the last years, the use of perovskite or spinel type oxide compounds as catalyst has been widely investigated in order to find a catalyst with high thermal stability [1] and low temperature activity [2]. Transition metal perovskites as LaMnO₃ are known to be very good oxidation catalyst. The partial substitution of La³⁺ ions by lower valence ions (such as Pb²⁺, Mg²⁺, Ca²⁺) produces the partial oxidation of Mn³⁺ to Mn⁴⁺ ions and the increase in oxygen vacancies which enhance the catalytic activity of the perovskite. The stability of Mn⁴⁺ ions seems to be the most important factor in the catalytic activity of perovskite manganites [3]. Saracco et al. [4] reported the positive effect of the Mg substitution in the basic LaMnO₃ perovskite on the catalytic activity of the resulting perovskite.

Oliva et al. [5] found that the preparation procedure can have a remarkable effect on the physico-chemical characteristics and the catalytic properties of perovskites. In the present work we applied a nonconventional procedure which is a combined sol-gel and self-combustion method [6] followed by thermal treatment. In this procedure the heat generated by an exothermic combustion reaction was used for synthesis reaction of the oxide ceramics. The intimate mixing of constituent ions so that nucleation and crystallization can occur at relatively low temperature is the main feature of this method. Sol-gel-self-combustion method offers a number of advantages including homogeneous mixing (on the atomic scale), low energy cost, easy manufacturing and the control of the grain size by subsequent heat treatments.

The phase composition, microstructural features, compositional homogeneity, specific surface area and pore size of the obtained powders were studied by X-ray powder diffraction analysis (XRD), scanning electron
microscopy (SEM) coupled with energy dispersive X-ray analysis (EDAX) and nitrogen adsorption/desorption at ~77 K. The obtained nanopowders (La0.6Pb0.2Mg0.2MnO3 and MgFe2O4) have been tested as catalysts for the catalytic flameless combustion of acetone, benzene, propane and Pb free gasoline. The effect of the phase composition and structure on the performance of the two catalyst samples has been investigated.

2. Experimental

2.1. Sample Preparation

MgFe2O4 spinel ferrite and La0.6Pb0.2Mg0.2MnO3 perovskite have been prepared by sol-gel-self-combustion method [6], using metal nitrates, ammonium hydroxide and polyvinyl alcohol as starting materials. This method included the following steps: 1) dissolution of metal nitrates in deionized water; 2) polyvinyl alcohol (10% concentration) addition to nitrate solution to make a colloidal solution; 3) NH4OH (10% concentration) addition to increase pH to about 8; 4) stirring at 80°C to turn the sol of metal hydroxides into gel; 5) drying the gel at 100°C; 6) self-combustion of the dried gel; 7) calcinations at 500°C for 30 min of the burnt powder to eliminate any residual ceramic compound; 8) heat treatment of the powders. MgFe2O4 powder was treated at 900°C for 10 min and La0.6Pb0.2Mg0.2MnO3 was treated at 1000°C for 320 min. The higher temperature for longer time interval for perovskite was preferred 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 growth of the perovskite crystallites. Second, La0.6Pb0.2Mg0.2MnO3 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. In Figure 1 is given the flow diagram for preparing process by sol-gel self-combustion and heat treatment. By this procedure oxide compounds can be prepared at much lower temperature than by the conventional solid state reaction method.

2.2. Characterization Techniques

Crystal structure and phase composition of the samples were analyzed by XRD. X-ray diffraction measurements of the powders were performed at room temperature using PANANALYTICAL X’ PERT PRO MPD powder diffractometer and CuKα radiation (λ = 1,542,512 Å). The spectra were scanned between 20 and 80° (2θ) at a rate of 2°/min. The average crystallite size was evaluated based on XRD peak broadening using the Scherer equation D = 0.9 λ/βcosθ, where λ is radiation wavelength (0.15405 nm) of CuKα, β is the half width of the peak and θ is the Bragg diffraction peak angle. A scanning electron microscope (JEOL-200 CX) was used to observe the surface morphology. Textural characteristics were investigated by means of specific surface area determined by BET (Brunauer-Emmett-Teller) [7] method from the nitrogen sorption isotherms at 77 K. Adsorption/desorption isotherms were determined with NOVA-A-2200 apparatus. The pore size distribution (PSD) curves were obtained from sorption isotherms using BJH (Barret-Joyner-Halenda) method [7]. The chemical composition of the surface particles was examined with Energy Dispersive X-ray Spectrometer (EDS).

3. Results and Discussion

The XRD patterns at room temperature of the heat treated samples are shown in Figure 2. Results revealed that all samples were monophase without any other second phase. Cubic spinel structure (Fd3m space group) was identified for MgFe2O4 sample and cubic perovskite structure (Fm3m space group) for La0.6Pb0.2Mg0.2MnO3. The broadening of the peaks implies the generation of crystallites in the nanosize range. The lattice parameters and average crystallite size derived from XRD data are given in Table 1. The values of the lattice parameters almost coincide with those presented in the literature in analogous compounds [8]. It is evident the nanosized crystallinity and that the crystallite size and density behave inversely to each other with respect to Mg concentration. Smaller crystal size (27.28 nm) and higher density (8.33 g/cm³) were found in La0.6Pb0.2Mg0.2MnO3 perovskite which contains 20% molar Mg only.

SEM micrographs showing surface morphology of the
two powders are shown in Figure 3. One can note significant differences in the microstructure of the two samples. Small agglomerates of fine grains with irregular shape can be observed in the perovskite powder, whereas MgFe₂O₄ spinel powder is characterized by the presence of dense and larger agglomerates.

The EDAX patterns confirm the homogeneous mixing of atoms in both samples and the purity of the chemical compositions. Figure 4 shows EDAX spectrum for MgFe₂O₄ and Table 2 shows the elemental composition. The Mg/Fe ratio is found close to the theoretical value (0.5) and this is proof of homogeneous distribution of the elements in the solid.

Nitrogen adsorption/desorption isotherms at ~77 K were used to obtain information about the specific surface area S_{BET}, the pore volume and the pore size in the ceramic particles. The isotherms for the both samples are presented in Figure 5. As can be seen, the desorption branch does not follow the adsorption branch, but forms a hysteresis loop of type H3 according to the International Union of Pure and Applied Chemistry (IUPAC) classification [9]. H3 type hysteresis is typically for materials with an interparticle mesoporosity (pore size 2 - 50 nm) [7]. However, a clear decision with regard to the type of hysteresis loop is not always possible. The factors which determine the shape of the hysteresis loop are still not fully known for disordered pore system [10].

Pore size distribution curves (PSD by BJH method) for both samples obtained from N₂ (~77 K) sorption isotherms are given inset of Figure 5. There are two distinct ranges for pore size distribution for MgFe₂O₄. These are between 2.7 and 3 nm and between 5.5 and 6.3 nm. The pore size distribution of La₀.₆Pb₀.₂Mg₀.₂MnO₃ was found to be different from that of MgFe₂O₄. Four ranges with different pore sizes were evidenced: two narrow ranges, from 3 to 3.5 nm and from 4.8 to 5.2 nm, and two wider pore ranges, from 6.8 to 8.5 nm and from 13 to 15 nm. But all the pore sizes are within the mesoporous region.

The BET surface area, pore volume and average pore diameter are given in Table 3. BET specific surface area (8.5 m²/g) of La₀.₆Pb₀.₂Mg₀.₂MnO₃ is higher than that of MgFe₂O₄ (4.0 m²/g). Larger pore volume and smaller particle size determine the increased S_{BET} value of the perovskite. The characteristics of MgFe₂O₄ are comparable to those of other spinel ferrites reported in [11].

The catalytic testing of the two catalyst samples in the flameless combustion of four VOCs (acetone, propane, benzene and Pb free gasoline) was carried out at atmospheric pressure in a flow-type set-up previously described by us [12]. The catalyst powder (0.3 - 0.5 g) was sandwiched between two layers of quartz wool in a quartz tubular micro-reactor (Φ = 7 mm) placed in an electrical furnace. The increase of the temperature was made stepwise. At every predetermined temperature, as a result of catalytic combustion, the gas concentration at the exist of reactor will be smaller than the inlet gas concentration. The degree of conversion of gases over catalysts at a certain temperature was calculated as:

\[
\text{Conv} = \frac{c_{\text{in}} - c_{\text{out}}}{c_{\text{in}}} \times 100\% ,
\]

where c_{in} and c_{out} are the inlet and outlet gas concentration, respectively, measured by a photo-ionization detector (PID-TECH) for VOCs. Data were collected when the flameless catalytic combustion had reached a steady state, after about 20 minutes at each temperature. These ex-
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Figure 3. SEM micrographs for La$_{0.6}$Pb$_{0.2}$Mg$_{0.2}$MnO$_3$ and MgFe$_2$O$_4$ nanopowders.

Table 2. EDAX analysis of MgFe$_2$O$_4$ powder.

<table>
<thead>
<tr>
<th>Element</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>50.34</td>
</tr>
<tr>
<td>Mg</td>
<td>17.60</td>
</tr>
<tr>
<td>Fe</td>
<td>31.99</td>
</tr>
<tr>
<td>Mg/Fe</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Figure 4. EDAX spectrum for MgFe$_2$O$_4$ ferrite heat treated at 900°C for 10 min.

Table 3. Surface characteristics of MgFe$_2$O$_4$ and La$_{0.6}$Pb$_{0.2}$Mg$_{0.2}$MnO$_3$ powders.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>MgFe$_2$O$_4$</th>
<th>La$<em>{0.6}$Pb$</em>{0.2}$Mg$_{0.2}$MnO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m$^2$/g)</td>
<td>4.0</td>
<td>8.5</td>
</tr>
<tr>
<td>BJH pore volume (cc/g)</td>
<td>0.006</td>
<td>0.021</td>
</tr>
<tr>
<td>BJH average pore size (nm)</td>
<td>4.25</td>
<td>7.50</td>
</tr>
<tr>
<td>Particle size D$_{BET}^*$ (nm)</td>
<td>33.7</td>
<td>89.2</td>
</tr>
</tbody>
</table>

*D$_{BET}^*$ was calculated using S$_{BET}$ [7].

cantly (Figure 6). From all experiments, La$_{0.6}$Pb$_{0.2}$Mg$_{0.2}$MnO$_3$ perovskite resulted to be more active than MgFe$_2$O$_4$ ferrite. The conversion degree of the gases over perovskite catalyst may even exceed 90% at 500°C, whereas over spinel catalyst the conversion is below 80%. The worst result was obtained for Pb free gasoline combustion over spinel catalyst: 34% conversion at 550°C.

The temperature of the 50% conversion of a gas, T$_{50}$, was used to estimate the catalytic activity of the two catalysts: MgFe$_2$O$_4$ spinel and La$_{0.6}$Pb$_{0.2}$Mg$_{0.2}$MnO$_3$ perovskite. At T$_{50}$ temperature the catalytic activity for the total oxidation of gases is sufficiently high. The lower T$_{50}$ is, the higher the activity. The T$_{50}$ values for each catalyst and each VOC (except for Pb free gasoline) are plotted in bar diagram presented in Figure 7. The T$_{50}$ values for benzene and acetone conversion over La$_{0.6}$Pb$_{0.2}$Mg$_{0.2}$MnO$_3$ are in agreement with those reported by Spinicci et al. [13]. For gasoline conversion over MgFe$_2$O$_4$ catalyst, T$_{50}$ exceeds 550°C.

The catalyst stability of the two materials was studied and no deactivation was observed in any of the samples after 24 hours.

The better catalyst performance of La$_{0.6}$Pb$_{0.2}$Mg$_{0.2}$MnO$_3$ perovskite in comparison with MgFe$_2$O$_4$ spinel can be attributed to smaller crystallite size (27 nm), larger surface area (8.5 m$^2$/g) and the presence of manga-
4. Conclusion

In this work the combined sol-gel and self-combustion method has been employed to prepare MgFe$_2$O$_4$ spinel and La$_{0.6}$Pb$_{0.2}$Mg$_{0.2}$MnO$_3$ perovskite for catalyst applications. It is an inexpensive method and the obtained prod-

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**Figure 5.** N$_2$ adsorption/desorption isotherms at 77 K of the two powders: La$_{0.6}$Pb$_{0.2}$Mg$_{0.2}$MnO$_3$ perovskite and MgFe$_2$O$_4$ spinel ferrite (●: the adsorption branch and □: the desorption branch). Inset: the pore size distribution graphs.

**Figure 6.** Conversion of acetone, propane, benzene and Pb free gasoline vs. temperature over La$_{0.6}$Pb$_{0.2}$Mg$_{0.2}$MnO$_3$ perovskite and MgFe$_2$O$_4$ spinel catalysts.
ucts were pure and presented nanosized crystallinity. Both samples have been tested in the catalytic combustion of acetone, propane, benzene and Pb free gasoline. La$_{0.6}$Pb$_{0.2}$Mg$_{0.2}$MnO$_3$ catalyst is more active at low temperatures compared to MgFe$_2$O$_4$ catalyst. Higher catalytic activity of the perovskite (over 90% gas conversion) is related to smaller crystallite size (27 nm), higher specific area (8.5 m$^2$/g) and the presence of manganese cations with variable valence (Mn$^{3+}$ - Mn$^{4+}$). La$_{0.6}$Pb$_{0.2}$Mg$_{0.2}$MnO$_3$ manganite catalyst can be a promising catalyst for catalytic combustion of acetone and propane at low temperatures (below 300°C).

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