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Short Communication

Structural and catalytic properties of mesoporous nanocrystalline mixed oxides containing magnesium

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ABSTRACT

Oxide compounds are promising catalysts for VOC flameless combustion. In this paper the catalyst properties of two Mg-containing oxide compounds with different crystalline structures and chemical compositions (Mg spinel ferrite and La–Pb–Mg–Mn–O perovskite) were investigated. The samples, prepared by a combined sol–gel and self-combustion method and heat treatment, were characterized using X-ray diffraction, scanning electron microscopy, EDAX spectroscopy, and BET analysis. The two samples have been catalytically tested in flameless combustion reaction of acetone, benzene and propane at atmospheric pressure. The results revealed a higher catalytic activity of the perovskite catalyst that may be ascribed to smaller crystallite size (26 nm), larger surface specific area (8.6 m^2/g) and the presence of manganese cations with variable valence (Mn^{3+}–Mn^{4+}).

1. Introduction

The use of perovskite or spinel type oxide compounds as catalysts for VOCs combustion has been widely investigated to find a catalyst with high thermal stability [1–4] and low temperature activity [5,6]. Mixed oxide systems are promising catalysts for catalytic combustion of volatile organic compounds (VOCs). The catalytic combustion is one of the most effective techniques for the removal of VOCs [7–9].

Many studies have focused on the lanthanum manganite perovskites $LaMnO_3$, which are known to be very good oxidation catalysts [10,11]. Lanthanum, the largest lanthanide ion, forms the most stable perovskite structure [12]. The partial substitution of La^{3+} ions in this stable structure by lower valence ions (such as Pb^{2+} and Mg^{2+} in the present work) can produce the partial oxidation of Mn^{3+} to Mn^{4+} ions and the increase in oxygen vacancies which enhance the catalytic activity of the perovskite [13,14]. Ponce et al. [15] found that the stability of Mn^{4+}ions seems to be the most important factor in the catalytic activity of perovskite type manganites. Previous investigations [16–18] showed a major role of manganese in the catalytic combustion of VOCs. The Mg substitution in $LaMnO_3$ should act as a structural promoter (inhibits the crystallite growth by reducing the grain boundary mobility [19]). Saracco et al. [20] reported on the positive effect of the Mg substitution in $LaMnO_3$ perovskite on the catalytic activity of the resulting perovskite. Rosso et al. [21] also showed the beneficial role of MgO which acts as a sulfur poisoning limiting agent in $LaMn_{1-x}Mg_xO_3$ perovskites, similar to the action observed with addition of noble metals, such as Pd or Pt. The effect of Pb addition in perovskites has been less investigated due to its toxicity. However, several research reports [22,23] have proven that the introduction of Pb^{2+} in the crystal lattice of the $LaMnO_3$ perovskite stimulates a high ratio of Mn^{4+}/Mn^{3+}, decreases the synthesis temperature, and improves the conductivity of the perovskite.

For catalytic purposes, the microstructure has a predominant role. The achievement of spinel ferrites or perovskites with the high specific surface areas and nanosized particles is a priority in the performance of a catalyst. In nanostructured materials, the interface between the nanoparticles and its surrounding medium plays a more important role than the bulk. Also, the strong curvature of nanoparticles due to their small radius leads to an increased number of the structural defects at the nanoparticle surface which enhance the surface reactivity. To obtain perovskites and spinel ferrites with superior microstructures, various chemistry based synthesis methods have been proposed, such as sol–gel [24], coprecipitation [25], hydrothermal [26], spray drying [27], combustion reaction [27], and other methods. Oliva et al. [28] found that the change in the preparation procedure can have a remarkable effect on the physico-chemical characteristics of perovskites. The catalytic activity is correlated with various physico-chemical properties [29].

In the present work we applied a nonconventional procedure, a combined sol–gel and self-combustion method [30] 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

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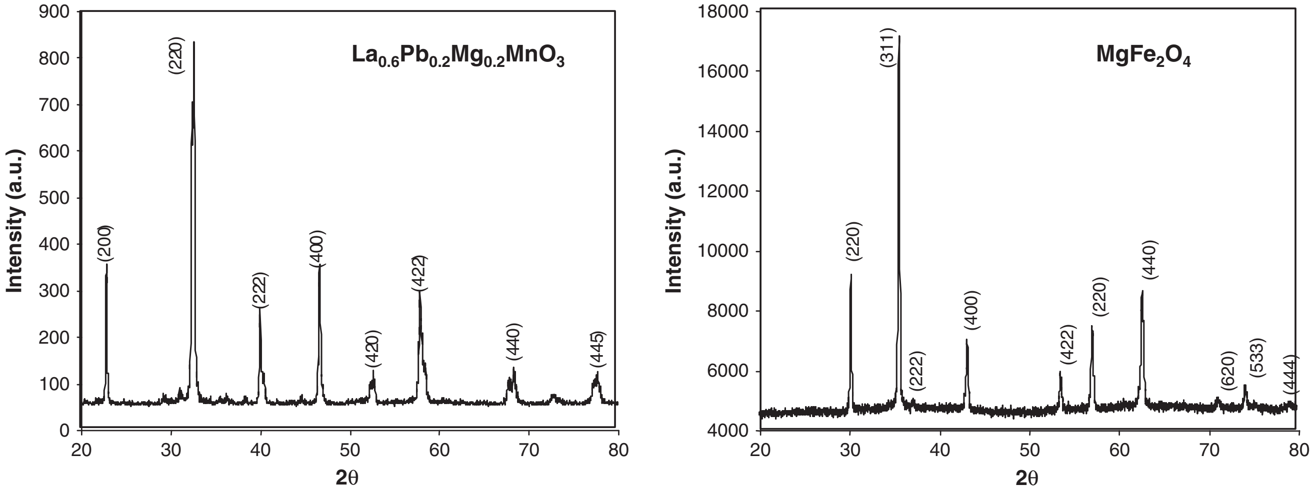

Fig. 1. XRD patterns for $La_{0.6}Pb_{0.2}Mg_{0.2}MnO_3$ and $MgFe_2O_4$ nanopowders.

of advantages including homogeneous mixing (on the atomic scale), high purity, low energy cost, simple equipment, easy manufacturing and the control of the grain size by subsequent heat treatments. By this procedure perovskites can be prepared at much lower temperature (1000 °C) in comparison with the temperature required for the conventional synthesis (1400–1600 °C). Using sol–gel coupled with combustion synthesis method and heat treatment at 950 °C, Tzimpilis et al. [31] prepared lanthanum based perovskites with enhanced catalytic activity in the methane flameless combustion. The main drawback of this method is that polluting compounds are emitted during the combustion (NH_3 or NO_x).

The purpose of this paper is to find new thermally and chemically stable solid state oxide compounds with suitable properties for VOCs combustion at low temperature. Spinel-type ferrite nanopowders of chemical composition $MgFe_2O_4$ and $La_{0.6}Pb_{0.2}Mg_{0.2}MnO_3$ perovskite nanopowders were investigated. We analyzed comparatively the catalyst properties of the two samples, which have different compositions and structures, in the catalytic flameless combustion of some VOCs: acetone, benzene and propane. The influence of various catalyst parameters (chemical composition, crystallite size, surface specific area) and of the process parameters (reaction temperature, conversion degree) on VOC catalytic combustion has been investigated.

2. Experimental

2.1. Sample preparation

$MgFe_2O_4$ spinel ferrite and $La_{0.6}Pb_{0\cdot 2}$Mg0.2MnO$_3$ perovskite have been prepared by sol–gel self-combustion method [30], using metal nitrates, ammonium hydroxide and polyvinyl alcohol (PVA) 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 (metal/PVA ratio = 1).
(3) NH_4OH (10% concentration) addition to increase pH to about 8; a sol of metal hydroxides in polyvinyl alcohol and ammonium nitrate was obtained.
(4) Stirring at 80 °C for 10 min to turn the sol of metal hydroxides into viscous gel.
(5) Drying the gel at 100 °C for 12 h.
(6) *Self-combustion*. The dried gel was locally ignited by an electrically heated wire, triggering an exothermic reaction; once initiated, the combustion wave spontaneously auto propagated (less than 10 s) through the dried gel. During combustion reaction, the temperature is of about 1000 °C and the metal hydroxides convert into metal oxides and the nucleation of very fine crystallites takes place.
(7) Calcination at 500 °C for 30 min of the burnt powder to eliminate any residual organic compound (C, residual PVA).
(8) Heat treatment of the powders to improve the crystallinity of the materials. $MgFe_2O_4$ powder was treated at 900 °C for 20 min and $La_{0.6}Pb_{0.2}$ $Mg_{0.2}MnO_3$ was treated at 1000 °C for 120 min. The higher temperature for longer time interval for perovskite was preferred for two main 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, $La_{0.6}Pb_{0.2}$ $Mg_{0.2}MnO_3$ 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. By heat treatment it was improved the crystallization of the perovskite phase and nanosized crystallites are obtained.

Table 1
Structure characteristics.

Sample composition	Lattice parameter (nm)	Crystal size (nm)	dx (g/cm^3)
$MgFe_2O_4$	0.8379	45.8	4.50
$La_{0.6}Pb_{0.2}Mg_{0.2}MnO_3$	0.7719	25.8	8.38

By this procedure oxide compounds with very fine crystallites can be prepared at a much lower temperature than the temperature required by the conventional ceramic method (1300–1500 °C).

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 PANALYTICAL X' PERT PRO MPD powder diffractometer and CuKα radiation (λ = 1.542512 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 $D = 0.9\lambda/\beta\cos\theta$, were λ is the 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) [32] method from the nitrogen sorption