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Structural and catalytic characterization of nanostructured iron manganite

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ABSTRACT

In this work the self-combustion method was applied to synthesize simple iron manganite ($FeMnO_3$) nanopowders. Among the various methods known, the self-combustion method allows a good control over the size of the material particles. According to this method the thermal energy for the synthesis of manganite crystallites is supplied by a fast exothermic combustion reaction. The final product is a finely divided powder. The procedure offers the advantage of producing ultra-fine, homogeneous reproducible multicomponent ceramic powders with precise stoichiometry.

We determined a series of structural and catalytic properties of nanostructured materials obtained by this method. The catalytic activity of the nanocrystalline iron manganite for the combustion of acetone vapors and of some hydrocarbons diluted in air was studied. The perovskite thus obtained has a favorable microstructure for obtaining catalysts for the combustion of the gases and vapors.

1. Introduction

The methods for the preparation of oxide compounds were continuously refined and was discovered new methods and procedures that provide a shorter processing time, smaller energy consumption, a higher purity of the final product and technical characteristics more satisfactory for the desired application. New applications of these materials were investigated, such as humidity sensors, gas sensors or catalysts [1–5].

The iron manganese oxides prepared through various methods, simple or doped, has been remarked having good catalytic properties for certain gases, such as hydrogen and carbon monoxide [6,7]. Ponce et al. [8] 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. In general, high surface areas imply small particle sizes. The smaller the particle size, the larger the surface area exposed to gases, for a given mass of particles. The control of morphology will be one of the first requirements for improving the catalyst activity [9,10]. The perovskite-type oxide compounds obtained by self-combustion method proved their successful implication in various applications [4,11–13].

In this work the simple nanocrystalline iron manganite ($FeMnO_3$) was synthesized by self-combustion method [14,15] using polyvinyl alcohol as colloidal medium. The procedure offers the advantage of producing nanosized, homogeneous and reproducible ceramic powders with high specific surface area and precise stoichiometry. The catalytic properties of the nanocrystalline iron manganite in the combustion reaction of acetone and of some hydrocarbons, benzene and liquefied petroleum gas (LPG), diluted in air were studied.

2. Experimental

2.1. Synthesis and characterization of materials

Nanopowders of $FeMnO_3$ were prepared by a self-combustion method using polyvinyl alcohol as colloidal medium. The method included the following procedures: (1) dissolution of the metal nitrates, $Fe(NO_3)_3{\cdot}9H_2O$ and $Mn(NO_3)_2{\cdot}4H_2O$ in deionized water, (2) addition of polyvinyl alcohol solution, (3) ammonia addition to increase pH to about 8, (4) stirring at 80 °C, (5) drying the gel at 120 °C and (6) self-combustion. The combusted powders were (7) calcined at 500 °C for 30 min to eliminate any residual carbon and organic compounds.

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The reactions for $FeMnO_3$ can be schematized as follows:

$$Fe(NO_3)_3 + 3 \cdot NH_4OH \rightarrow Fe(OH)_3 + 3 \cdot NH_4NO_3 \quad (1)$$

$$Mn(NO_3)_2 + 2 \cdot NH_4OH \rightarrow Mn(OH)_2 + 2 \cdot NH_4NO_3 \quad (2)$$

$$C_2H_3OH + 5 \cdot NH_4NO_3 \rightarrow 2 \cdot CO_2 \uparrow +12 \cdot H_2O \uparrow +5 \cdot N_2 \uparrow +Q \quad (3)$$

$$2Fe(OH)_3 + 2Mn(OH)_2 + 0.5 \cdot O_2 \rightarrow Fe_2O_3 + Mn_2O_3 + 5 \cdot H_2O \uparrow \quad (4)$$

$$Fe_2O_3 + Mn_2O_3 \rightarrow 2FeMnO_3 \quad (5)$$

After calcination the powders were heat treated in air at 1000 °C for 5 h at a heating/cooling rate of 20 °C/min. The method used by us allows obtaining a purely single-phase material as the result of this treatment.

X-ray diffraction (XRD) studies of the material were carried out at room temperature within the Bragg angle range $25° \leqslant 2\theta \leqslant 75°$ at a scan speed of $2° \min^{-1}$ by an X-ray diffractometer (PANALYTICAL X'PERT PRO MPD) using Cu Kα radiation ($\lambda = 1.54251$ Å). Crystalline phases were identified by using the "Crystallographica" program. The unit cell parameters of the crystalline phases were determined with XLAT-Cell Refinement program. The average crystallite size D_x was evaluated based on XRD peak broadening using the Scherrer equation [16]. The X-ray density, $d_x = M/Na^3$ [15,17] (where M is the molecular weight, N is Avogadro's number, and a is the lattice constant) was determined. The specific surface area S_{BET} was determined by BET method (NOVA 2200 apparatus) [18]. The morphology and elemental chemical composition were analyzed by using a JOEL-200CX scanning electron microscope (SEM), equipped with an energy dispersive X-ray spectrometry (EDX).

2.2. Measurement of catalytic activity

The measurements of catalytic activity for the acetone vapors and two hydrocarbons, benzene and LPG were performed at moderate temperatures (50–550 °C). A quartz tubular reactor with the inner diameter of 7 mm was used, able to control the temperature of the introduced material (powder), the inlet gas flow rate and concentration, and to measure the outlet gas concentration [10]. Gas hourly space velocity (GHSV) was 5217 h^{-1}. This value is the result of small volume of the catalyst. The powder catalyst (0.4 g) is placed such that the entire inlet gas flow rate with a concentration of 1–2$^{o}/_{oo}$ in air passes through the entire volume of the powder at a pressure close to the atmospheric one. We also checked if the combustion is complete (if the reactor outlet gases only contain CO_2 and H_2O).

The catalytic activity of the studied $FeMnO_3$ perovskite was evaluated in terms of the gas conversion C calculated as [19,20]:

$$C = \frac{(c_{in} - c_{out}) \cdot 100}{c_{in}} (\%) \quad (6)$$

where c_{in} and c_{out} are the inlet and outlet gas concentration, respectively. The data were collected when the flameless catalytic combustion had reached a steady state, after about 20 min, at each 50 °C step between 50 and 550 °C. These experiments were repeated with decreasing temperature and similar results were obtained. The catalyst was not deactivated during testing.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 shows the XRD pattern for powders calcined and heat treated at 1000 °C for 5 h. After this heat treatment, the diffraction pattern indicates a good crystalline quality of the powder without foreign phases. Referring to the PDF card No. 75 – 894, the compound exhibits a cubic symmetry (space group la3). The structural parameters of the heat treated $FeMnO_3$ powders were determined: the lattice constants $a = 9.400$ Å; average crystallite size $D_x = 59.2$ nm; X-ray density $d_x = 5.08$ g/cm^3 and specific surface area $S_{BET} = 3.20$ m^2/g.

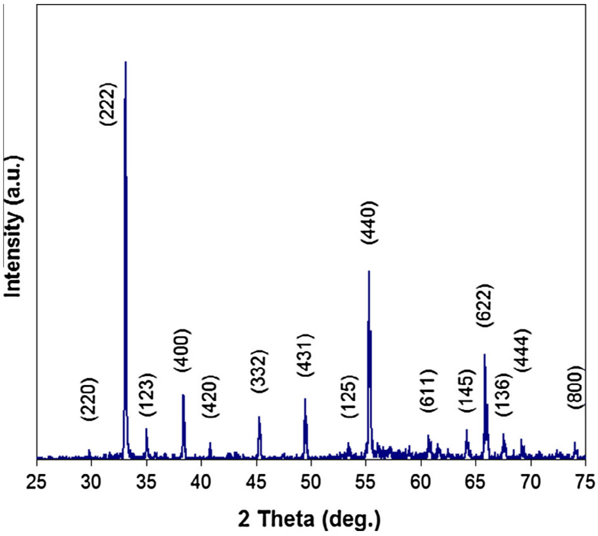

Fig. 1. The XRD pattern of $FeMnO_3$ powders heat treated at 1000 °C for 5 h.

Fig. 2(a) and (b) shows the SEM micrographs, at two different magnitudes on the $FeMnO_3$ powder after the heat treatment at 1000 °C for 5 h. The sample is characterized by a porous structure. In Fig. 2(a) one can notice particle agglomerations with numerous pores of about 200 nm. In Fig. 2(b) one can see facetted polycrystalline particles with irregular shapes with the size of 100–500 nm. A tendency towards agglomerations can be noticed, as the $FeMnO_3$ crystallites are small ($D_x = 59.2$ nm).

The crystallinity of the powder heat treated at 1000 °C for 5 h was confirmed by the energy dispersive X-ray spectra (EDX). The obtained chemical elemental composition is typical for this perovskite (any foreign element is absent). Fig. 2(c) presents the EDX spectrum for this powder. Moreover, the composition of the sample is similar to the nominal one, ABO_3, i.e. the A/(A + B) or B/(A + B) ratio is close to 0.5 (where A is Fe at.%, and B is Mn at.%).

The smaller the particle size (100–500 nm), the larger is the surface area exposed to gases (3.20 m^2/g) for a given mass of particles. The control of morphology will be one of the first requirements for improving the catalyst activity [2,9,10,20–22].

3.2. Catalytic activity

The results of the measurements on the catalytic combustion of the three studied gases (acetone, benzene and LPG) over heat-treated $FeMnO_3$ perovskite are presented in Fig. 3 and Table 1. In Fig. 3 the gas conversion over the catalyst is plotted as a function of reaction temperature for this gases diluted in air. It was found that the catalytic combustion of the three gases is complete, and the gases at the reactor outlet only contain CO_2 and H_2O. The complete combustion (in air) in the acetone and benzene cases can be expressed as complete oxidation:

$$C_3H_6O + 4 \cdot O_2 \rightarrow 3 \cdot CO_2 + 3 \cdot H_2O \quad (7)$$

$$C_6H_6 + 7.5 \cdot O_2 \rightarrow 6 \cdot CO_2 + 3 \cdot H_2O \quad (8)$$

In the case of the bi-component LPG gas, the reactions are given in Ref. [10].

In the case of benzene the catalytic combustion starts at 100 °C, in the case of acetone the catalytic combustion starts at 150 °C, while in the case of the LPG the catalytic combustion starts at 300 °C. In the case of acetone, the conversion factor increases up