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Structural and magnetic features of $La_{0.7}Sr_{0.3}Mn_{1-x}Co_xO_3$ nano-catalysts for ethane combustion and CO oxidation

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Abstract

Structural, magnetic and catalytic properties of $La_{0.7}Sr_{0.3}Mn_{1-x}Co_xO_3$ ($x=0.00$, 0.25, 0.50, 0.75, 1.00) nano-perovskites prepared by the citrate method are investigated. The structural characterization of the compounds by X-ray powder diffraction and using X'Pert package and Fullprof program is an evidence for a monoclinic structure (P21/n space group) with $x=0.50$ and a rhombohedral structure (R-3c space group) for other samples. These results have been confirmed by the FT-IR measurements. Crystallite size of the powders obtained from Halder–Wagner method has been compared with the Scherrer method. The structural and magnetic results suggest the presence of different concentrations of various cations of Co^{+2}, Co^{+3}, Co^{+4}, Mn^{+4} and Mn^{+3} in the samples. Activation energy, band gap energy, and electrical conductivity measurements have been employed to explain catalytic performance of the samples. The results of performance tests show that the sample with $x=0.25$ has the highest catalytic activity for CO oxidation, whereas, the sample with $x=0.75$ has the highest catalytic activity for C_2H_6 combustion.

Keywords: Nano-perovskite; Manganite–cobaltite; Magnetic phase transition; C_2H_6 combustion; CO oxidation

1. Introduction

Many efforts have been made to reduce the use of precious metals (Pt, Pd and Rh) in catalytic systems. Finding a suitable replacement for expensive catalysts used in various industries, including the automotive industry, to further reduce environmental pollutants emitted is a main research in the modern world. High activity in reduction–oxidation (redox) reactions, oxygen storage capability and high flexibility to enter other metals in the structure, have proposed perovskite compounds, ABO_3, as a good candidate for this replacement [1]. In addition, being inexpensive and having heat and mechanical resistance properties are some other advantages of these compounds. Among perovskite compounds, lanthalium manganites and cobaltites with the formula of $LaMnO_3$ and $LaCoO_3$ are the famous compounds that are used for complete oxidation of CO to carbon dioxide [1,2].

$LaMn(Co)O_3$ with perovskite structure is an insulator-antiferromagnetic system at room temperature due to the absence of Mn^{4+} (Co^{4+}) ions. Upon replacement of La^{3+} ions with bivalent elements (Sr, Ca, …), trivalent Mn (Co) ions are converted to a mixture of Mn^{3+} and Mn^{4+} (Co^{3+} and Co^{4+}) ions. The measurements reported on polycrystalline samples of $La_{1-y}M_yMn(Co)O_3$, showed insulator-antiferromagnetic behavior in low and high values of y, and metal-ferromagnetic behavior in samples with $y \approx 0.3$ [3,4]. In these compounds, the ferromagnetic–paramagnetic transition associated with a metal–insulator transition below the curie temperature ($100 < T_C(K) < 350$) have been attributed to double-exchange theory between ions of Mn^{3+}–Mn^{4+} (Co^{3+}–Co^{4+}) [5]. Lantalium–strontium cobaltites, like manganites, exhibit complex crystal chemistry, phase separation, but differ from the manganites by the possibility of large oxygen deficiencies and different

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spin states. Phase separation leading to a glassy ferromagnetic behavior for $La_{1-x}Sr_xCoO_3$ is a common feature in cobaltites and plays a very important role in their particular magnetic properties.

The electronic and magnetic properties of colossal magnetoresistance (CMR) materials $R_{1-y}A_yMn_{1-x}B_xO_3$ (where R is a trivalent rare earth and A is a divalent alkali earth, B is a transition metal) have attracted considerable attention during the past decade [6–9]. Effects of Mn site substitution on the T_C and other physical properties of $La_{0.7}Sr_{0.3}Mn_{1-x}B_xO_3$ with different elements such as Cr, Co, Fe, Ni, Mn, etc. have been reported [10–13]. In $La_{1-y}A_yMn_{1-x}Co_xO_3$ compounds, large number of magnetic species present. For example, Co may exist in six possible states, namely, as Co^{2+} with three different spin states (low spin $t_{2g}^6e_g^1$ and high spin $t_{2g}^5e_g^2$), as Co^{3+} with three different spin states (low spin $t_{2g}^6e_g^0$, intermediate spin $t_{2g}^5e_g^1$ and high spin $t_{2g}^4e_g^2$) and as Co^{4+} with three different spin states (low spin $t_{2g}^5e_g^0$, intermediate spin $t_{2g}^4e_g^1$ and high spin $t_{2g}^3e_g^2$). On the other hand, Mn may exist in three possible states, namely, as Mn^{3+} (high spin $t_{2g}^3e_g^1$ and low spin t_{2g}^4) and as Mn^{4+} $\left(t_{2g}^3\right)$ states. Oxidation states of Mn and Co depend on the method of preparation. So, understandably, there are many possible ways for Co–Mn interaction to take place via oxygen. Furthermore, all the structural, electronic and magnetic properties of the samples will depend on the nature of the interaction between the Co and Mn ions via oxygen. Substituting La^{3+} cations with alkaline-earth cations in $LaMn_{0.5}Co_{0.5}O_3$ perovskite increases the average degree of oxidation of Mn and Co and leads to a decrease in magnetization and T_C and a transition to spin-glass or cluster-glass behavior [7].

Several investigators have reported that in ABO_3 perovskites, the A ions are in general catalytically inactive and the active ions at B position interact with gas molecules readily [1,5,14,15]. It should be noted that substitution of the A-site with a bivalent or a tetravalent cation leads to a different behavior of catalytic activity of manganite–cobaltite compounds. The Sr substitution for La in $La_{1-y}A_yCoO_3$ leads to higher oxidation states of Co, so that the higher the amount of Sr, the higher is the concentration of Co^{4+} [5]. However, since Co^{4+} is unstable, then oxygen release can take place ending in the formation of oxygen vacancies that leads to an increase in the catalytic activity. This behavior is explained considering that at high x values, the amount of unstable Co^{4+} ions and/or of oxygen vacancies increases, which favors the diffusion of lattice oxygen from the bulk to the surface, as charge compensators [5].

The increase in Sr substitution for three series of $Ln_{1-y}Sr_yNiO_3$ (Ln = Pr, Sm, Eu) perovskites showed a strong enhancement in catalytic activity for CO oxidation and this effect was much more marked in $Pr_{0.95}Sr_{0.05}NiO_3$ [5,16]. The changes in the catalytic properties of $AB_{1-x}B'_xO_3$ perovskites, substituting cation B with B′, can be classified in two categories: geometric and electronic structure of cation B′ [6]. The effect of B′ substitution on geometric and electronic factors is considered in the calculation of the structural and magnetic changes. Strontium substituted lanthanum manganite, i.e. $La_{1-x}Sr_xMnO_3$, are known as materials with good oxygen transport properties which make them scientifically interesting as well as technologically useful for many applications [15]. A series of $R_{1-y}A_yMn_{1-x}B_xO_3$ catalysts have been characterized and reported to show proper activities for CO oxidation in a temperature range of 50–400 °C [2,5,6,8,9,14–16]. For the $LaBO_3$ (B is a transition metal) perovskite series, $LaMnO_3$ and $LaCoO_3$ proved to be among the most active and $LaCrO_3$ among the least active catalysts for CO oxidation.

In this paper, we present a systematic study of the structural and magnetic properties of $La_{0.7}Sr_{0.3}Mn_{1-x}Co_xO_3$ ($x = 0.00$, 0.25, 0.50, 0.75, 1.00) nanoperovskites prepared by the citrate method. Moreover, the effect of cobalt substitution is investigated on the catalytic activity of $La_{0.7}Sr_{0.3}MnO_3$ nanoperovskite for CO oxidation and ethane combustion that have been not done so far.

2. Experimental

2.1. Sample preparation

The $La_{0.7}Sr_{0.3}Mn_{1-x}Co_xO_3$ compounds with $x = 0.00$, 0.25, 0.50, 0.75, and 1.00 were prepared by the citrate method (Table 1). Firstly, a solution containing appropriate concentrations of metal nitrates $La(NO_3)_3 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Sr(NO_3)_2$ and citric acid, equal to the total number of moles of nitrate ions, was evaporated at 60 °C, overnight. The homogeneous sol-like substance subsequently dried at 80 °C, overnight. The resulting spongy and friable materials were completely powdered and kept at 200 °C, overnight. The resulting materials were powdered again and calcined at 900 °C for 5 h.

2.2. Materials and physical measurements

All the chemicals were purchased from Merck and used as received without further purification. The FT-IR spectra of samples were recorded in a Perkin-Elmer FT-IR spectrometer in the wave number range of 450–1650 cm^{-1}. The morphology of the samples was studied by the SEM (Philips XL30) analysis. The particle size of the samples was investigated by the TEM (LEO Model 912AB) analysis. Optical absorption spectra of $La_{0.7}Sr_{0.3}Mn_{1-x}Co_xO_3$ samples have been recorded at room temperature using a HP–UV–vis system (Agilent8453, model) in the range of 200–1100 nm wavelengths. Band gap energies have been calculated according to Ref. [17].

Table 1
Moles of the metal nitrates for the preparation of $La_{0.7}Sr_{0.3}Mn_{1-x}Co_xO_3$ samples[a].

Sample	$La(NO_3)_3 \cdot 6H_2O$	$Mn(NO_3)_2 \cdot 4H_2O$	$Co(NO_3)_2 \cdot 6H_2O$	$Sr(NO_3)_2$
$x = 0.00$	0.0093	0.013	–	0.004
$x = 0.25$	0.0092	0.0099	0.0033	0.004
$x = 0.50$	0.0092	0.0066	0.0066	0.0039
$x = 0.75$	0.00915	0.0033	0.0098	0.0039
$x = 1.00$	0.0091	–	0.013	0.0039

[a] Mole of the citric acid is considered to be 0.0615 in all preparation.

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