CORRELATION OF THE Sr-DOPANT CONTENT IN La$_{1-x}$Sr$_x$CoO$_3$ WITH CATALYTIC ACTIVITY FOR HYDROGEN PEROXIDE DECOMPOSITION

Florica PAPA,[a] Daniela BERGER,[b] Gianina DOBRESCU,[a*] Razvan STATE [a] and Niculae I. IONESCU[a]

[a] "Ilie Murgulescu" Institute of Physical Chemistry, Roumanian Academy, 202 Splaiul Independenței, 060021 Bucharest, Roumania
[b] "Politehnica" University of Bucharest, Faculty of Applied Chemistry and Materials Science, 1-7 Gheorghe Polizu St., Sector 1, 011061, Bucharest, Roumania

La$_{1-x}$Sr$_x$CoO$_3$ (x=0-0.3) samples were prepared by solution combustion method from metal nitrates and α-alanineand were characterized by X-ray diffraction (XRD), scanning electron microscopy-energy-dispersive X-ray analysis (SEM-EDX), adsorption isotherms and temperature programmed reduction (TPR). The fractal analysis using adsorption isotherms was performed.
The catalytic activity of La$_{1-x}$Sr$_x$CoO$_3$in H$_2$O$_2$ decomposition as test reaction in alkaline medium was investigated. The kinetic results analysis shows the presence of so-called compensation effect for this group of catalysts.
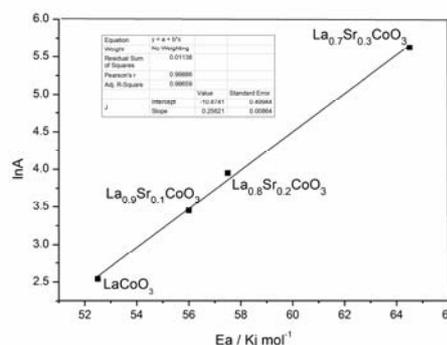
INTRODUCTION

The oxides with perovskite structure, with general formula ABO$_3$, can be used for numerous catalytic applications[1-5] been studied for their attractive physical and chemical properties.[6] By varying either the A-site or the B-site cations, one can generate a extensive class of catalysts. The partial substitution of A-site with a lower valence metal cation can be varying the chemical and catalytic properties by introducing the lattice defects. This substitution requires a charge compensation, which is achieved by increasing the M-site cation oxidation state and/or formation of positive holes. The property offers the opportunity to obtain catalysts for specific reactions.

Perovskite oxides La$_{1-x}$Sr$_x$CoO$_3$ (x=0-0.3) have been tested for numerous catalytic applications. A considerable interest has been focused on lanthanum cobaltite perovskites for their use as catalysts for light hydrocarbons oxidation,[7,8] combustion of volatile organic compounds,[9] the control of automotive emissions[10] and catalytic hydrogen peroxide decomposition.[11-15] The partial substitution of lanthanum ions with strontium cations can strongly change catalytic activity in a range of reactions due to the stabilization of the unusual oxidation state of cobalt cations and defects formation. The catalytic hydrogen peroxide decomposition has been widely studied because it is a very simple, but important reaction in term of theoretical and practical point of view. The kinetic studies of catalytic decomposition

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* Corresponding author: gdobrescu@icf.ro

of on oxide-type perovskite as catalyst has been reported in several papers.

Yang *et al.*[13] investigated the influence of the systematically lanthanum substitution by strontium in $La_{1-x}Sr_xMnO_3$ (0<x<0.8) toward the catalytic activity for hydrogen peroxide decomposition. Lanthanum substitution by copper in lanthanum manganites for hydrogen peroxide decomposition and CO oxidation was investigated by Das*et al.*[14] and the surface area of $La_{1-x}Sr_xMO_3$ (M=Co, Mn) for different *x*-values was studied by Yasutake *et al*[15]. Correlations between the catalytic hydrogen decomposition, the surface chemical composition and the oxigen non-stoichiometries were found by Y. N. Lee *et al.*[12]

Ariafard *et al.*[11] has investigated the influence of the Sr and Cr content as dopant in the $La_{1-x}Sr_xNi_{1-x}Cr_xO_3$ catalysts toward H_2O_2 decomposition. The correlations between the oxidation state of Ni and the electronic conductivity of $(R,A)NiO_{3-x}$ (R = lantanide, A = alkaline earth) perovskite, and the catalytic activity of hydrogen peroxide decomposition were considered by Alonso*et al.*[16]

The goal of this paper is to study the correlation of the Sr-dopant content, the influence of surface chemical composition and fractal dimension for $La_{1-x}Sr_xCoO_3$ with catalytic activity for hydrogen peroxide decomposition reaction in alkaline medium.

EXPERIMENTAL

$La_{1-x}Sr_xCoO_3$ (x=0-0.3) samples were prepared by solution combustion from metal nitrates and α-alanine. The synthesis steps are:(i) dissolution of stoichiometric amounts of metal nitrates and organic substance; (ii) heating the reaction mixture for water evaporation; (iii) heating to ignite the reaction mixture and its combustion with as prepared powders formation; (iv) calcining of the as prepared powders to obtain single phase compound. More details about the catalysts synthesis have been presented elsewhere[17]. The experimental conditions of $La_{1-x}Sr_xCoO_3$ (x=0-0.3) synthesis are summarized in Table 1.

Fractal dimensions of different samples of pure and strontium doped lanthanum cobaltite, $La_{1-x}Sr_xCoO_3$ (x=0-0.3), were computed using both single adsorption isotherm method and scanning electron (SEM) micrograph analysis was presented in details our paper.[18] The experimental data of isotherm were fitted using the Dubinin–Radushkevitch fractal model.[19] Fractal isotherms were used to fit directly the experimental nitrogen

adsorption data. SEM micrographs were analyzed using correlation function method.

The H_2-TPR measurements were performed using a CHEMBET Quantachrome instrument equipped with thermal conductivity detector (TCD). The fresh calcined samples (50 mg) were heated up to 800 °C at the constant rate of 10 °C min^{-1} in the stream of the 5 vol. % H_2/Ar gas and a flow rate of 70 mL min^{-1}. A silica gel water trap was placed between the analyzed sample and TCD detector in order to ensure a good stability and sensitivity of the detection system. The hydrogen consumption was estimated from the surface area of recorded peaks.

The catalytic activity of $La_{1-x}Sr_xCoO_3$ (x=0-0.3) perovskites for hydrogen peroxide decomposition was investigated by a conventional gasometric[1] in the temperature range of 288-323 K (288 K, 298 K, 308 K and 323 K)at atmospheric pressure. A amount of 50 mg catalyst was dispersed in 100 mL of 0.1 M NaOH solution, 0.8 mol L^{-1} H_2O_2 placed in the thermostated vessel reaction. The volume of liberated oxygen was measured as a time function at a given temperature, the temperature of the reactor being stabilized ±1° C.

RESULTS AND DISCUSSION

The XRD data of all pure and strontium doped lanthanumcobaltite powders present a single phase with distorted perovskite structure and rhombohedral symmetry, space group R3m. No secondary phase was observed in the annealed samples. For all $La_{1-x}Sr_xCoO_3$ (x=0-0.3) samples, the crystallite size are in nano scale range and SEM micrographs show that primary fine particles have the tendency to agglomerate, leading to irregular shapes and pores as we reported elsewhere.[17]The substitution of lanthanum by strontium ions determines an increasing of the specific surface area values.

The H_2-TPR profiles in temperature range of 200-800°C of $La_{1-x}Sr_xCoO_3$ (0-0.3) perovskite catalysts are presented in Fig. 1.It can be observed several reduction peaks, which can be assigned to Co^{3+} ions because reduction Sr^{2+}. La^{3+} do not change their oxidation state in this temperature range[20].The first two peaks below 380° -450°C can be attributed to the removal of the adsorbed oxygen species on oxygen vacancies concurrently with the Co^{3+}/Co^{2+}reduction, and the peak at high temperature (550°-750°C) was assigned to the Co^{2+}/Co^0 reduction.[21]

Table 1

Experimental conditions of $La_{1-x}Sr_xCoO_3$ (*x*=0-0.3) synthesis

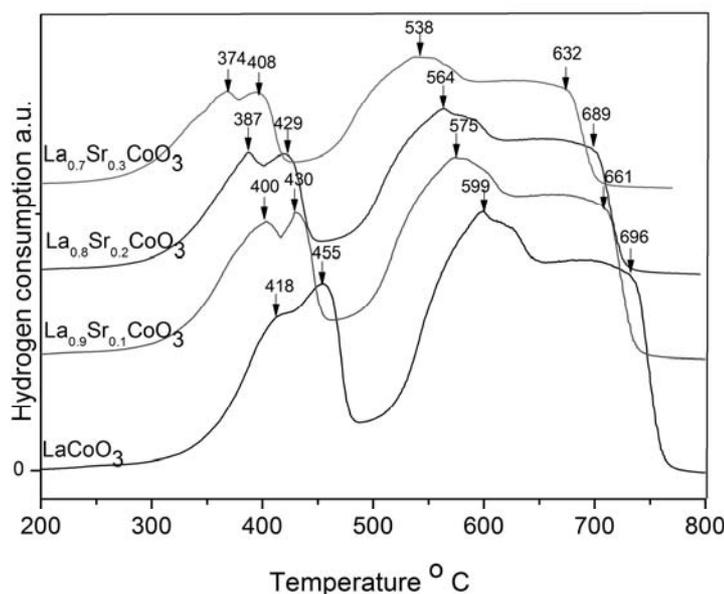| Catalyst	La(NO$_3$)$_3$:Sr(NO$_3$)$_2$: Co(NO$_3$)$_2$: α-alanine molar ratio	Thermal treatment (°C)	Time (h)
LaCoO$_3$	1:0:1:2	600	3
La$_{0.9}$Sr$_{0.1}$CoO$_3$	0.9:0.1:1:2	1000	4
La$_{0.8}$Sr$_{0.2}$CoO$_3$	0.8:0.2::1:2	1000	4
La$_{0.7}$Sr$_{0.3}$CoO$_3$	0.7:0.3:1:2	1000	4

Fig. 1 – TPR profile for $La_{1-x}Sr_xCoO_3$ (x=0-3) catalysts.

The substitution of La^{3+} with Sr^{2+} leads to an improvement in the reduction capacity, the reduction peaks being shifted to lower temperatures. Total hydrogen consumption for reduction of $La_{1-x}Sr_xCoO_3$ catalysts is displayed in Table 2. The amount of consumed hydrogen for the first reduction step varies with the in strontium content, increase in the following order: $LaCoO_3<$ $<La_{0.9}Sr_{0.1}CoO_3<La_{0.8}Sr_{0.2}CoO_3<La_{0.7}Sr_{0.3}CoO_3$, which in good agreement with the literature is, that the number of oxygen vacancies increases with the doping content.[22]

The samples fractal behavior was investigated fitting the experimental adsorption data with the Dubinin-Radushkevitch isotherm.[18]

$$\theta = K\left[\ln(p_) / p)\right]^{-(3-D)} \qquad (1)$$

where θ is the monolayer coverage, p_0 and p are the saturation and equilibrium pressures, and D is the fractal dimension, where for:

$$2<D<3 \qquad (2)$$

K has the following formula:

$$K = \frac{1}{2}C\Gamma\left(\frac{3-D}{2}\right)m^{-(D-3)/2}(RT)^{D-3} \qquad (3)$$

and Γ being the Gamma Function, T, the temperature and C and m, constants.

Equation (1) was used to fit the experimental data for pure and doped lanthanum cobaltite samples and the obtained results are presented in Table 2.

As we have already mentioned, the substitution of lantanum by strontium ions determined an increase of specific surface area value and also, of the fractal dimension, which measures the roughness and the self-similarity of the exposed surface to the adsorption, the increae of fractal dimension D when Sr content is high demonstrates that a part of strontium ions segregates on the surface, increasing the surface roughness.

Table 2

The fractal dimensions obtained using the Dubinin-Radushkevitch isotherm and H_2 consumed from TPR

Sample	Fractal dimension	Determination coefficient	H_2 consumed (µmol/g) from TPR
$LaCoO_3$	2.39±0.03	0.987	240.2
$La_{0.9}Sr_{0.1}CoO_3$	2.45±0.01	0.989	246.23
$La_{0.8}Sr_{0.2}CoO_3$	2.48±0.01	0.999	263.5
$La_{0.7}Sr_{0.3}CoO_3$	2.62±0.03	0.970	271.3

Catalytic activity

The hydrogen peroxide has a dual behaviour: in the non dissociated form, is a strong oxidizing agent, while in the ionized form acts as an electron donor. This duality explains why hydrogen peroxide is not stable in aqueous solutions and decomposes forming donors in the presence of catalysts, especially transition metals ions.

Hydrogen peroxide decomposes with: OH^-, $HO_2^{\cdot}$ radicals and other active intermediates formation. The catalytic activity of perovskites was measured in the reaction of hydrogen peroxide decomposition in alkaline aqueous solution.

$$HO_2^-(aq) \rightarrow \frac{1}{2}O_2(g) + OH^-(aq) \qquad (4)$$
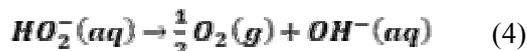
From equation (4) one obtains:

$$\frac{d[HO_2^-]}{dt} = K_{hom}[HO_2^-] \qquad (5)$$

After integration:

$$ln[HO_2^-] = -k_{hom}t + ln\,[HO_2^-]_0 \qquad (6)$$

$[HO_2^-]_0$ being the concentration of HO_2^- at $t=0$. Thus k_{hom} can be obtained from the slope of $ln[HO_2^-]$ vs time.

Because the heterogeneous reaction of hydrogen peroxide decomposition takes place in volume of solution which contains a mass of catalyst m_{cat}, the catalytic rate permit of catalyst in aqueous solutionis can be defined as :

$$k_{het} = \frac{V_{sol}}{m_{cat}} \cdot k_{hom} \qquad (7)$$

For each temperature, the rate constant, k_{hom}, was obtained from equation (6) and k_{het} was calculated with equation (7). Hydrogen peroxide decomposition kinetics was measured in order to characterize the catalytic activity of the $La_{1-x}Sr_xCoO_3$ perovskite. Evaluation of the rate constant implies two stages:

- in the first step, the results were obtained for the hydrogen peroxide decomposition in basic aqueus solution on lantanum cobaltite in an homogeneous mediumand k_{hom} is calculated.

- in the second step, k_{het}, was calculated through the normalization of k_{hom} per unit of catalyst.

From the k_{het} versus $1/T$ curve, the apparent activation energy has been obtained. For all catalysts, a linear corelation between the logarithm of hydrogene peroxide concentration *vs* time can be observed, with the correlation factor >0.9. This good linearity corresponds to first order reaction in accord with results reported in the literature for mixed oxides perovskite type.[13]

The catalytic activity of hydrogen peroxide decomposition reaction on the $La_{1-x}Sr_xCoO_3$ (x=0; 0.2; 0.3) varied in the following order: $LaCoO_3 < La_{0.9}Sr_{0.1}CoO_3 < La0_8Sr_{0.2}CoO_3 < La_{0.7}Sr_{0.3}CoO_3$. This correlation could be explained by that the catalytic activity increase with the number of oxygen vacancies created by the partial substitution of La with Sr [22]. Kinetic results of the $La_{1-x}Sr_xCoO_3$ (x=0-3) are presented in Table 3.

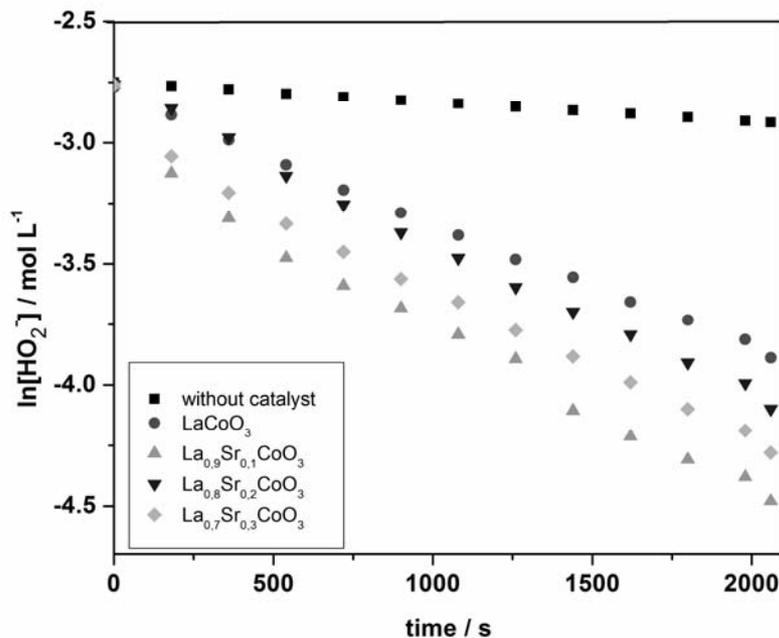Fig. 2 – Plot of $ln[HO_2^-]$ *vs.* time for $La_{1-x}Sr_xCoO_3$ catalysts, m_{Cat}=50 mg, 0.8 M H_2O_2.

Tabel 3

Kinetic results for H_2O_2 decomposition on $La_{1-x}Sr_xCoO_3$ (x=0-3)

Sample	$K_{het}15^oC$ mL g^{-1}s^{-1}	$K_{het}25^oC$ mL g^{-1}s^{-1}	$K_{het}35^oC$ mL g^{-1}s^{-1}	$K_{het}50^oC$ mL g^{-1}s^{-1}	lnA	E_a Kjmol^{-1}
$LaCoO_3$	0.043	0.051	0.062	0.074	2.54	52.5
$La_{0.9}Sr_{0.1}CoO_3$	0.059	0.076	0.085	0.091	3.45	56
$La_{0.8}Sr_{0.2}CoO_3$	0.068	0.083	0.089	0.096	3.95	57.5
$La_{0.7}Sr_{0.3}CoO_3$	0.072	0.094	0.105	0.112	5.62	64.5
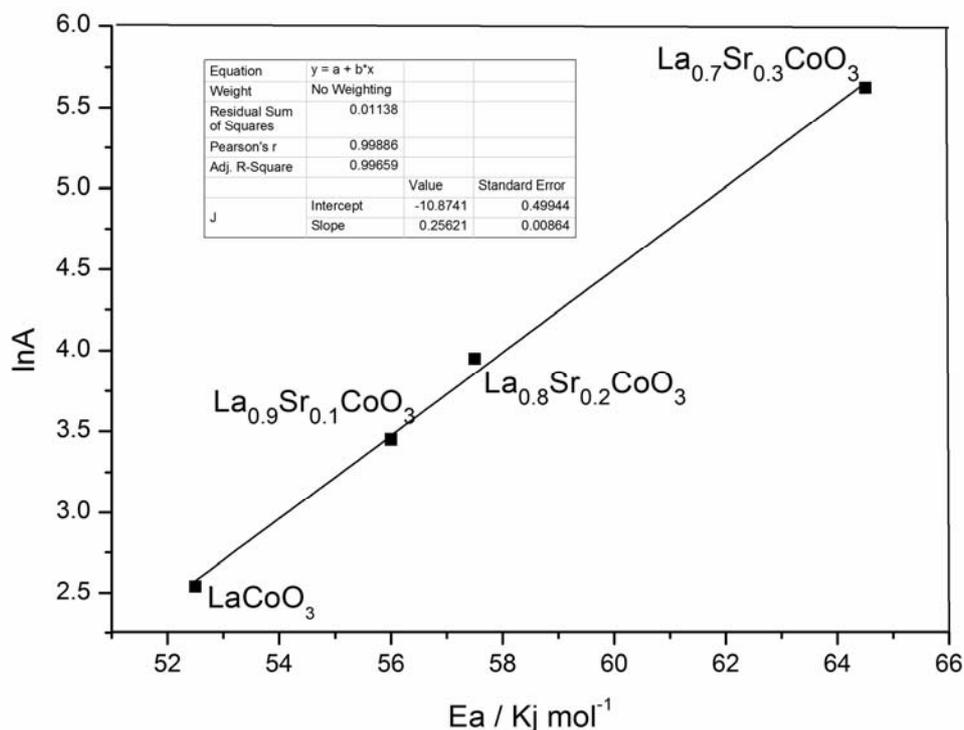
Fig. 3 – Compensation effect for H_2O_2 decomposition for the different Sr concentration on $LaCoO_3$.

In the same time, a linear relationship between the logarithm of the preexponential factor (*A*) and the apparent activation energy was observed (Figure 3) for the H_2O_2 decomposition, expressing a compensation effect that could be explained by an energetically non-uniform surface or the variation of the active sites number because of the Sr-presence.

Trypolskyi *et al.*[23] have found that the activation energy of heterogeneous process depends on the surface fractal dimension. The activation energy is higher when the fractal dimension has greater value if other physical and chemical parameters remain constant. So, the representation of activation energy versus the surface fractal dimension would be linear.

According the theoretical arguments.[21,23] the activation energy versus fractal dimension curve for the H_2O_2 decomposition has a linear behavior (Figure 5). Also, due to the compensation effect, a linear dependence between the pre-exponential factor and the fractal dimension, (Figure 4).

According to the transition state theory for a surface reaction, the pre-exponential factor depends on the concentration of active sites and the number of possible locations of the activation complex. In our studies, the pre-exponential factor increased when the fractal dimension was higher, meaning that the concentration of the active sites on surface increases too. Based on this we could explain the compensation effect by the variation of active sites number as result of Sr-dopant presence.
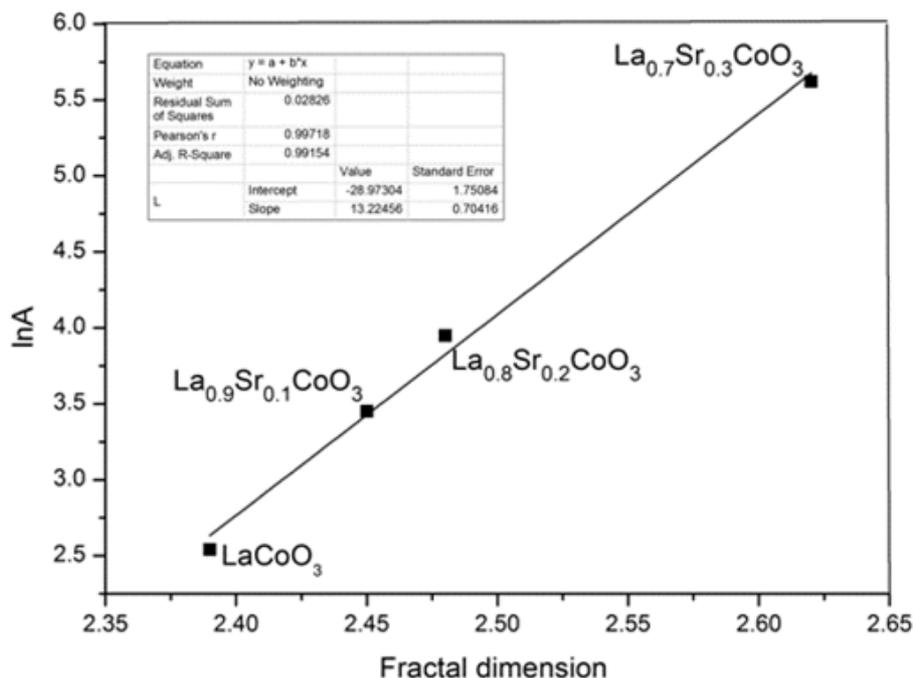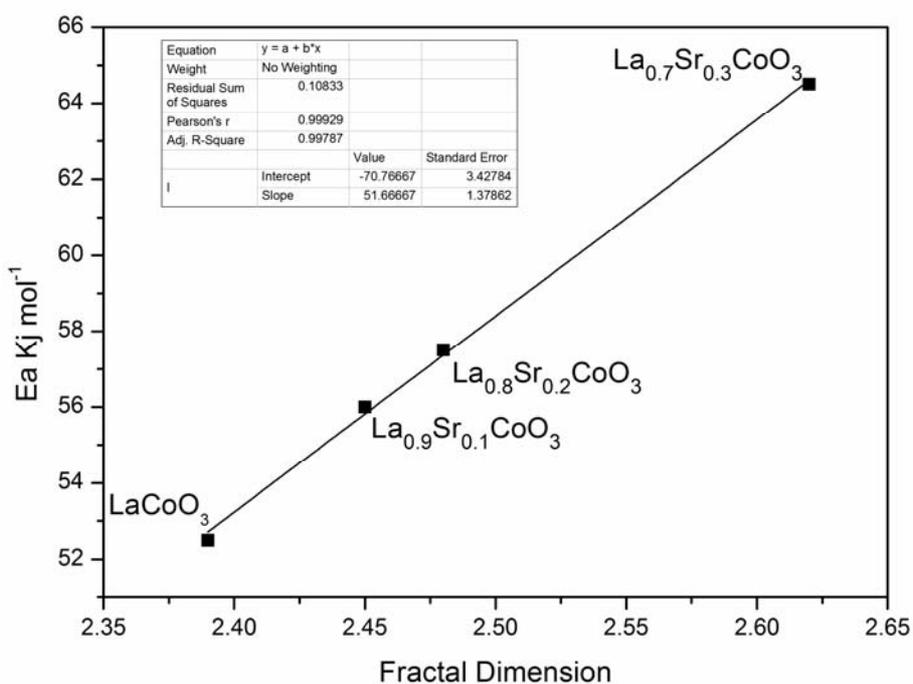
Fig. 4 – Pre-exponential factor *vs.* fractal dimension.

Fig. 5 – Activation energy *vs.* fractal dimension of the $La_{1-x}Sr_xCoO_3$.

CONCLUSIONS

Our study was focused on the influence of surface chemical composition and fractal properties of $La_{1-x}Sr_xCoO_3$ catalysts on the hydrogen peroxide decomposition. The lanthanum substitution with strontium ions determined an increase of specific surface area values. The substitution of lanthanum by strontium ions resulted a higher specific surface area and fractal dimension values. As the fractal dimension measures the roughness and the self-similarity of the exposed surface to adsorption, the increase of the fractal dimension when Sr concentration is higher supported partial segregation of strontium ions on the catalyst surface, increasing the surface roughness.

The catalytic activity of hydrogen peroxide decomposition on the $La_{1-x}Sr_xCoO_3$ (x=0; 0.2; 0.3) increases in the following order: $LaCoO_3 <$ $< La_{0.9}Sr_{0.1}CoO_3 < La0_{.8}Sr_{0.2}CoO_3 < La_{0.7}Sr_{0.3}CoO_3$. A linear relationship between the logarithm of preexponential factor (A) and the apparent activation energy was observed, expressing the compensation effect. The activation energy and the pre-exponential factor increased with the fractal dimension increase, the same trend having the active sites concentration.

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