FRACTAL ANALYSIS OF MICROGRAPHS AND ADSORPTION ISOTHERMS OF La$_{1-x}$Sr$_x$CoO$_3$ SAMPLES

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Fractal dimensions of different samples of pure and strontium doped lanthanum cobaltite, La$_{1-x}$Sr$_x$CoO$_3$ (x=0-0.2), were computed using both single adsorption isotherm method and scanning electron (SEM) micrograph analysis. Fractal isotherms were used to fit directly the experimental nitrogen adsorption data. SEM micrographs were analyzed using correlation function method. Lanthanum cobaltite samples have good fractal properties. Both methods lead to the same fractal dimension.

1. Introduction

Since 1984, there are a lot of studies concerning structural heterogeneity of solid surfaces related to fractal geometry [1-5]. At molecular-size range, surfaces of most materials are fractals, in other words, geometric irregularities and defects are self-similar at different scales. Fractal dimensions, that describes such fractal materials, were found to be in the complete range $2 \leq D < 3$: low D=2.0 values, indicate regularity and smoothness, intermediate D values indicate irregular surfaces and D values close to 3 indicate highly irregular surface. Fractal dimension can be computed using direct methods such as micrograph analysis, or using methods related to chemical and physical properties behaviour when fractal characteristics are involved.

In the following we shall use both methods to compute fractal dimensions: scanning electron micrographs (SEM) analysis and the single adsorption isotherm method. In the first method, correlation function is used to compute fractal dimension and in the second one, experimental data will be fitted with the appropriate fractal isotherm.

Oxides with perovskite structure, with general formula ABO$_3$, where A represents a big cation with +3 oxidation state and B a transition metal ion with the same valence state, have been studied for their interesting physical and chemical properties [6,7]. Pure and doped lanthanum cobaltites have potential application as a catalyst for light hydrocarbon oxidation [8-10], for the control of automobile emissions [11,12], as a cathode material for SOFCs [13] and sealed CO$_2$ laser [14], as well as gas detection sensor [15].

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2. Theory

2.1 Image analysis

A fractal is an object of which observed volume depends on the resolution (length scale) over several orders of magnitude and follows a power law behavior with a nontrivial exponent. The most important property of fractals is the self-similarity, which is the property for a part to look like the whole. Isotropic fractals are self-similar: they are invariant under isotropic scale transformation. When object scales different on different space directions, we call it a self-affine fractal. From this point of view, rough surfaces are usually self-affine fractals [16].
Fractal dimension of a self-affine surface can be computed from the height correlation function [17]-[19]:

$$G(r) \equiv < C(\vec{x}, r) >_x \qquad (1)$$

where the symbol $<...>$ denotes an average over x, and C(x,r) is defined as:

$$C(\vec{x}, r) = [h(\vec{x}) - h(\vec{x} + \vec{r})]^2 \qquad (2)$$

and surface is described by the function h(**x**) which gives the maximum height of the interface at a position given by x .
Thus the height correlation function G(r) obeys the following scaling relation [20]:

$$G(r) \sim r^{2\alpha}, r << L, \qquad (3)$$

where, for a surface embedded in a 3-dimensional euclidean space:

$$\alpha = 3 - D, \text{ with } D \text{ - the fractal dimension.} \qquad (4)$$

The scaling range in which equation (3) is obeyed is called the "cut-off" limits and it indicates the range of self-affinity, in other words, the range where there are correlations between surface points.
In the following, in order to compute fractal dimension of scanning electron micrographs, we shall use equations (1)-(4).

2.2 Single adsorption isotherm method

The Dubinin approach [21] for adsorption on heterogeneous microporous solids lead to the following isotherm:

$$\theta = \int_{x_{min}}^{x_{max}} \exp(-mx^2 A^2) J(x) dx \qquad (5)$$

where A=RTln(p_0/p), the adsorption potential, T is temperature, θ is the monolayer coverage, p_0 and p are the saturation and equilibrium pressures, m is a constant, x is the pore size , J(x) is the pore size distribution function and exp(-m$x^2$$A^2$) is the Dubinin-Radushkevich (DR) isotherm for uniform micropores of size x. Considering a fractal object Avnir and Jaroniec [22] replaced the Gaussian distribution with the pore size distribution of a fractal object [1,23-26]. Avnir and Jaroniec showed [22] that for microporous solids in the region of p/p_o=0.05 to the micropore filling pressures, equation (5) becomes:

$$\theta = K[\ln(p_o / p)]^{-(3-D)} \qquad (6)$$

where D is the fractal dimension (2<D<3) and K is a constant.
The fractal isotherm from equation (6) shows highly dependence on D values of monolayer coverage at low p/p_0 values. This means that using this form, even at low pressures, one can compute fractal dimension. In the following we shall use equation (6) to fit experimental data for our samples.

3. Experimental

Fine particles of La$_{1-x}$Sr$_x$CoO$_3$ (x = 0 – 0.2) were obtained by thermal decomposition of the complex precursors prepared in the following system, La(NO$_3$)$_3$ - Sr(NO$_3$)$_2$ - Co(NO$_3$)$_2$ – maleic acid – NH$_3$ at molar ratio, La : Sr : Co : maleic acid, 1-x : x : 1 : 8.6, at *p*H = 7. High purity metal nitrates (Merck) were dissolved in a minimum volume of deionized water. Then, 10% maleic acid solution was added as a chelating agent. By adding 10% ammonia solution to this mixture, to keep the *p*H above 7, a light – violet solution was formed. The solution was then heated at ~110°C on a hot plate to evaporate the water and a light-violet precipitate was obtained. The La$_{1-x}$Sr$_x$CoO$_3$ (x=0–0.2) powders were prepared by calcining the isolated complex precursors at 800°C, 3h for LaCoO$_3$, 1000 °C, 4-6h for La$_{1-x}$Sr$_x$CoO$_3$ (x=0.1-0.2).

X-ray diffraction data were collected using a Bruker AXS D8 Advance diffractometer with Cu*K*α radiation at a step of 0.02°/s in the range 2θ=10 to 90°. The *XRD data* for La$_{1-x}$Sr$_x$CoO$_3$ (x = 0 – 0.2) obtained by thermal treatment of complex precursors show that all the samples are single phases with rhombohedral distorted perovskite structure, space group $R\bar{3}m$.

Scanning electron micrographs of the La$_{1-x}$Sr$_x$CoO$_3$ (x=0–0.2) powders were obtained using a JEOL JSM-5800 scanning electron microscope. Nitrogen adsorption isotherms were obtained at liquid nitrogen temperature.

4. Results and discussion

Scanning electron micrographs for La$_{1-x}$Sr$_x$CoO$_3$ (x = 0 – 0.2) are presented in Fig.s 1-3.
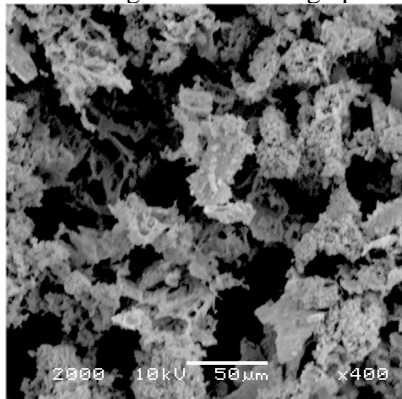
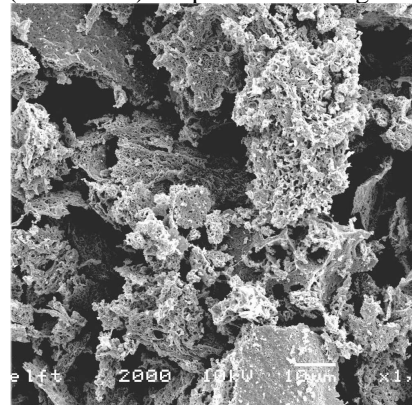

Fig. 1. Scanning electron micrograph of LaCoO$_3$ sample.

Fig. 2. SEM image of La$_{0.9}$Sr$_{0.1}$CoO$_3$ sample
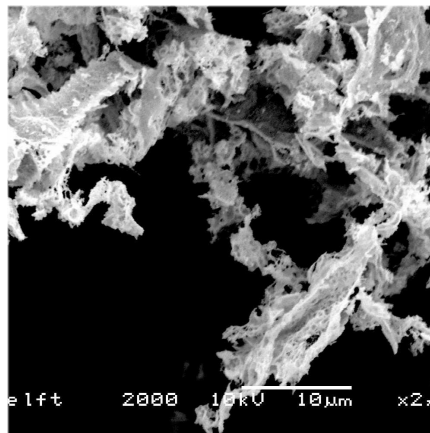

Fig. 3. SEM image of La$_{0.8}$Sr$_{0.2}$CoO$_3$ sample.

Log-log plot of height correlation function computed from equations (1)-(4) from SEM image versus squared distances curve is presented in Fig. 4 (sample $La_{0.8}Sr_{0.2}CoO_3$, x=0.2). Similar curves can be computed for the other samples. Computing slopes of log-log plot of height correlation functions versus squared distances curves with a least square method one can obtained fractal dimensions in Table I. Good determination coefficients (0.98-0.99) were found meaning that for correlation distances of 0.25-1.11 µm (x=0), 0.1-0.44µm (x=0.1) and 0.03-0.33 µm (x=0.2) samples have shown very good fractal properties.
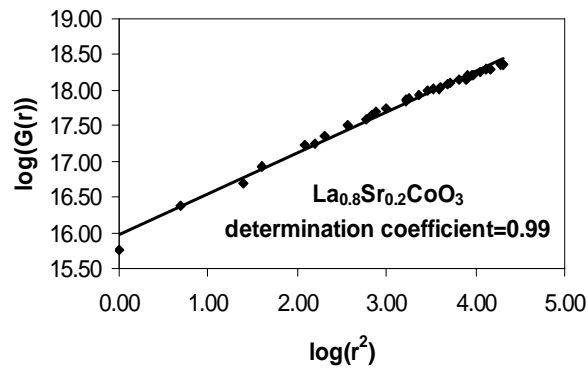

Fig. 4. Log-log curve of height correlation function versus squared distance for x=0.2

Fig. 5 show log-log plot of experimental adsorption isotherm and the fitting adsorption isotherm from equation (6), for x=0.2. Similar curves can be computed for x=0 and x= 0.1. Again, good determination coefficients (0.98-0.99) are found showing very good fractal properties. The least square method used to fit experimental data indicates fractal dimensions in Table 1.
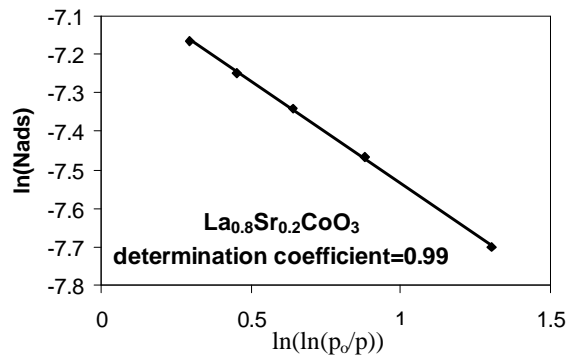

Fig. 5. The relationship between logarithm of the adsorbed amount N_{ads} and logarithm of $ln(p_o/p)$ for x=0.2

Table 1. Fractal dimensions computed from the two methods.

x	SEM analysis	Single Adsorption Isotherm Method
0	2.32±0.01	2.34±0.06
0.1	2.51±0.02	2.58±0.02
0.2	2.43±0.01	2.48±0.01

Results presented in Table I show good fractal properties of the samples and good agreement between fractal dimensions computed from the two methods. The intermediate fractal dimensions obtained (D≈2.3-2.6), show that the pore size distribution J(x) from equation (5) is not so steep, that

means that there are more and more the wider pores of the microporosity regime when fractal dimension decreases. In such case, the multilayer micropore filling requires higher p/p$_o$ values for the same coverage when compared with high fractal dimension materials. This behavior leads to type II isotherms.

Another remark is that fractal dimension increases when Sr is added, but a maximum for fractal dimension is obtained for x = 0.1.

5. Conclusions

There are three major conclusions to be drawn:
- all samples, La$_{1-x}$Sr$_x$CoO$_3$ (x=0-0.2), have fractal properties at molecular scale.
- fractal dimension increases when Sr is added, but a maximum for fractal dimension is obtained for x=0.1.
- there was found a good agreement between fractal dimensions computed by two different methods, SEM analysis and nitrogen adsorption isotherm,.

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