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Dedicated to Professor Dr. ALEXANDRU T.
BALABAN, member of the Roumanian Academy
on the occasion of his 75th anniversary

THE FRACTAL DIMENSION OF OSCILLATIONS IN SnO_2/HUMID O_2 SYSTEM

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The fractal dimension of the oscillations in the SnO_2/humid O_2 system were determined using the variable scale method. The obtained values of the fractal dimensions are quite the same at the beginning of oscillations but decrease if the oscillations are observed for a longer time. These results are discussed.

INTRODUCTION

Approximation of natural objects (curves, surfaces, objects) with a fractal model is an important tool for research. Since their description in 1972 by Mandelbrot,[1] fractals have been used to describe and explain a multitude of natural phenomena in physical chemistry, biology or medicine.

Fractals have been applied also in catalysis[2] using mostly the fractal dimension. The dimension of a fractal curve is the number that characterizes the way in which the measured length between given points increases as the scale decreases. As the topological dimension of a line is 1 and that of a surface is 2, the fractal dimension of profiles may be any real number between 1 and 2.

The fractal dimension D is defined as:

$$D = \frac{\log(l_1 / l_2)}{\log(s_1 / s_2)} \tag{1}$$

where l_1 and l_2 are the measured lengths of two curves (in units) and s_1 and s_2 are the size of the units (*i.e.*, the scales) used in measurements. In this power law relationship, the exponent is the fractal dimension of a set of points. The existence of a fractal dimension means that the structure is self-similar, *i.e.*, these irregular oscillations present a self-similarity.

In the previous papers we have described the appearance of electrical conductance oscillations of the SnO_2 powder when heated at constant temperature up to 400ºC in humid gas flow.[3,4] In the present paper we describe the fractal character of some oscillations appeared during the heating of the SnO_2 powder in the presence of oxygen containing moist gas flow.

This approach will be demonstrated by analyzing the appeared oscillation in the system SnO_2/humid O_2 during temperature increase, the dynamic reactor-conductivity cell, the equipment and the experimental conditions being described earlier.[3-7]

THE MODEL

The variable scale method was used to evaluate the fractal dimension. The model was proposed by Chauvy *et al.*[8] and consists of several steps: (*i*) defining an interval of length ε (or a box of size ε x ε); (*ii*)

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performing a linear (or planar) least square fit on the data within the interval and calculating the roughness; (*iii*) moving the interval along the profile (surface) and repeating step (*ii*); (*iv*) computing the rms deviation for multiple intervals, and (*v*) repeating steps (*ii*)-(*iv*) for increasing lengths (box sizes). The smallest size for an interval corresponds to 10 data points (10 × 10 points for 3-dimensional embedded objects) and its maximum size is the total length of the profile (the characteristic size of the surface). Rms deviation $R_{q\varepsilon}$, averaged over n_ε, the number of intervals of length ε, is defined by:

$$R_{q\varepsilon} = \frac{1}{n_\varepsilon}\sum_{i=1}^{n_\varepsilon}\sqrt{\frac{1}{p_\varepsilon}\sum_{j=1}^{p_\varepsilon} z_j^{\,2}} \tag{2}$$

where z_j is the jth height variation from the best fit line within the interval i, and p_ε is the number of points in the interval ε.

The log-log plot of $R_{q\varepsilon}$ *versus* ε gives the Hurst or roughening exponent *H*, and the fractal dimension *D*, can be calculated as:

$$D=D_T-H \tag{3}$$

where D_T is the topological dimension of the embedding Euclidean space ($D_T = 2$ for profiles and $D_T = 3$ for surfaces).

RESULTS AND DISCUSSION

Keeping the SnO_2 sample at constant temperature up to 400 ºC, in an atmosphere containing mixtures of argon with humid oxygen, self-sustained oscillations usually occurred. These oscillations are either regular or irregular. The last type oscillations are presented in Figs. 1,2 .

The oscillations from Figs. 1,2 are irregular having different shapes, amplitudes and frequencies but all present a fractal character.

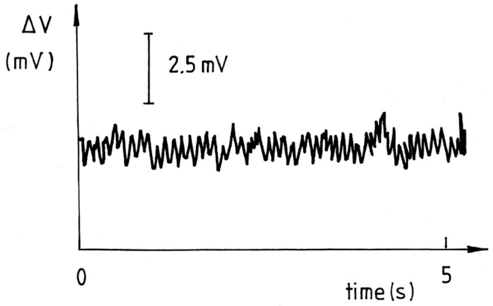

Fig. 1 – Oscillations of conductance for the SnO_2 sample in an Ar atmosphere containing 340 mg H_2O/Lgas and 1% O_2 at 140°C.

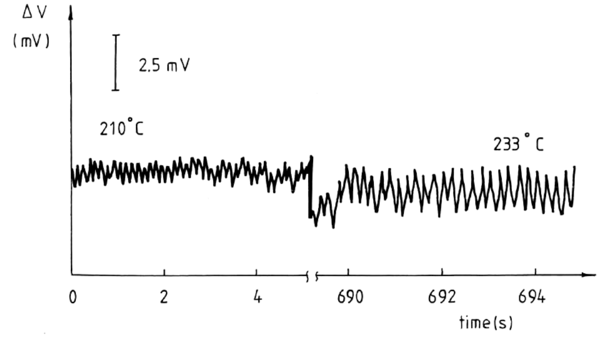

Fig. 2 – Oscillations of conductance for the SnO_2 sample in an Ar atmosphere containing 340 mg H_2O/Lgas and 1% O_2 at 210 and 233°C, respectively.

The fractal dimension was calculated with relationship (3). This fractal dimension is 1.68 ± 0.02 for the oscillations from Fig. 1. These dimensions are 1.72 ± 0.02 and 1.23 ± 0.04 for the first and the last oscillations, respectively, presented in Fig. 2. In the case of Fig. 2, the beginning of oscillations was at 210°C and the end at 233°C after 12 minutes. Increasing the temperature more, in the same conditions, the oscillations become regular[4] without a fractal character, the topological dimension being 1. The fractal dimension is quite the same at the begining of the oscillations, independently of temperature but is different if the oscillations last for a longer time at a higher temperature.

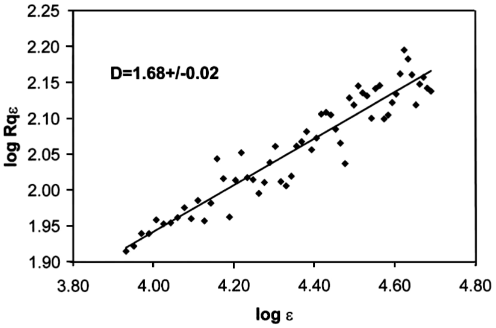

Fig. 3 – Determination of the roughening exponent H for the oscillations from Fig. 1 (correlation coefficient 0.822, scaling range 0.19 s–0.42 s).

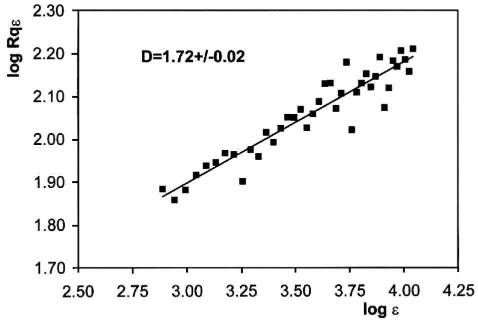

Fig. 4 – Determination of the roughening exponent H for the first oscillations at 210°C, from Fig. 2 (correlation coefficient 0.891, scaling range 0.15 s–0.47 s).

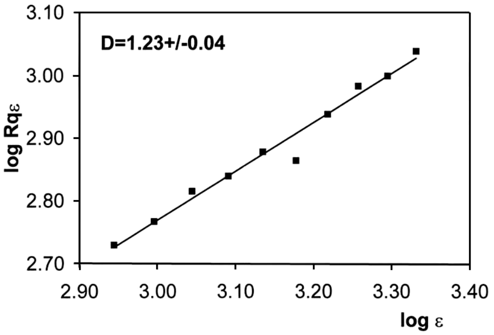

Fig. 5 – Determination of the roughening exponent H for the last oscillations, at 233°C from Fig. 2 (correlation coefficient 0.970, scaling range 0.15s–0.24 s).

In identical conditions, but using carefully dried gases, no oscillations were observed; this suggests that the oscillations are generated by the interaction of water with the SnO_2 surface.[6-7] The simultaneously presence of anion vacancies, OH protons and adsorbed oxygen species in the presence of moisture favors a dynamic synchronization of various adsorption-desorbtion processes on the surface. As the measured conductivity of the powder is controlled by the height of the intergrain Schottky barrier in the low frequency range, as in our case, we can suggest that the oscillating behavior must be related with variations in the occupancy of the donor levels in the band gap. The high water content facilitates a much higher contribution of the protonic conduction up to higher temperature. Modifications in the nature and local relative distribution of the surface-adsorbed species and lattice defects due to experimental conditions could produce the observed different values in the fractal dimension.

CONCLUSIONS

In conclusion, the irregular oscillations observed in the SnO_2/O_2 humid system present a fractal character. The fractal dimension is quite the same at the beginning of oscillations, but diminishes if the oscillations are observed for a longer time at higher temperature.

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