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Dedicated to Professor Alexandru T. Balaban
on the occasion of his 85th anniversary

THE FRACTAL DIMENSION OF OSCILLATIONS IN METHANOL-OXYGEN SYSTEM

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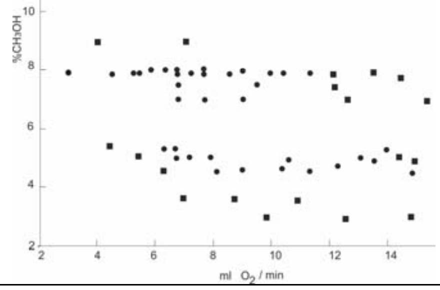
The fractal dimension and the information fractal dimension have been determined in case of the oxidation of methanol on supported Pd in oscillatory and non-oscillatory regime. The small differences in the obtained values in these cases can be assigned to experimental conditions.



INTRODUCTION

Heterogeneous catalytic reactions are non-linear multilevel chemical reaction systems far from thermodynamical equilibrium which exhibit complex temporal behavior such as instabilities, oscillations, chemical waves or chaos.[1] The observed temporal behavior depends not only upon the properties of oscillators, but also upon the strength and nature of the coupling between them.[2-5]

The oscillations cycles of different products may have different forms and surface phases with respect to each other. This can produce valuable information on the mechanism of such reactions. The interest in oscillatory phenomena in catalytic reactions is caused by the possibility to perform such processes more efficiently using unsteady-state operations.

The goal of this paper is to study the fractal behavior of thermochemical oscillations obtained during the oxidation of methanol on a $Pd/LiAl_5O_8$ catalyst (Bayer), the installation and the experimental methods used being described earlier.[6]

THEORY

Approximation of natural objects (curves, surfaces, objects) with a fractal model is an important tool for research. Since their description in 1972 by Mandelbrot,[7] fractals have been used to describe and explain a multitude of natural phenomena in physics, chemistry, biology or medicine.

Fractals have been applied also in catalysis[8] using mostly the fractal dimension. The fractal dimension of a fractal curve is the number that characterized the way in which the measured length between given points increases as the scale decreases. Because the topological dimension of a line is 1 and of a surface is

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2, the fractal dimension of profiles may be any real number between 1 and 2.

(i) The "box-counting" dimension

One of the most useful methods to measure the fractal dimension is the "box-counting" method.

The method uses the self-similarity property of the fractal object. Self-similarity has a mathematical description:[7,9]

$$N(r,R) \sim (r,R)^{-D} \quad (1)$$

where D is the fractal dimension and $N(r, R)$ is the number of boxes of size r which cover the object of linear size R; in other words, self-similarity is the property of an object to look the same when zooming it.

Keeping constant the maximum size of the object R, the box dimension is defined as the exponent D in the relation:

$$N(r) = Ar^{-D} \quad (2)$$

where $N(r)$ is the number of boxes of linear size r necessary to cover the object in a two-dimensional plane. For Euclidean objects, one needs a number of boxes proportional to r^{-D}, so the exponent D is the Euclidean dimension of the plane, 2. The prefactor A, sometimes named lacunarity, is a measure of how the space is filled, a measure of the gap or of the object texture.[10]

To define a box dimension, boxes are placed at the position and orientation that minimizes the number of boxes needed to cover the set. It is obviously a very difficult computational problem to find the configuration that minimizes $N(r)$, among all the possible ways to cover the set with boxes of size r.

In practice, to measure the box-counting fractal dimension, one counts the number of boxes of linear size r necessary to cover the set for a range of values of r and plots the logarithm of $N(r)$ on the vertical axis *versus* the logarithm of r on the horizontal axis. The slope of the straight line is $-D$. In theory, for each box size, the grid should be overlaid in such a way that the minimum number of boxes is occupied. This is accomplished by the computer code rotating the grid for each box size through 90 degrees and plotting the minimum value of $N(r)$.

(ii) The information dimension

This fractal dimension is often used in literature, and is generally different from the box dimension.

The information dimension assigns weights to the boxes in such a way that boxes containing a greater number of points count more than boxes with less points.

The information entropy $I(r)$ for a set of $N(r)$ boxes of linear size r is defined as:

$$I(r) = -\sum_{i=1}^{N(r)} m_i \log(m_i) \quad (3)$$

where $m_i = M_i/M$, M_i is the number of points in the *i-th* box and M is the total number of points in the set.

Therefore, the information dimension is defined as:

$$I(r) \approx -D_i \log(r) \quad (4)$$

In practice, to measure D_i, one covers the set with boxes of linear size r, computes m_i for each box and calculates the information entropy $I(r)$ from the summation in Eq.(3). If the set is fractal, a plot of $I(r)$ *versus* the logarithm of r will follow a straight line with the slope equal to $-D_i$.

RESULTS AND DISCUSSION

The appearance of oscillations in the system depends on the oxygen flow rate. The oscillations have been detected in an approximate area. This area is presented in Fig.1. All the points inside this area are oscillatory ones and all the points outside the area are non-oscillatory. Between them, there exist damped oscillations which represent transitions between steady-state and the oscillatory behavior of this reaction.

For the points inside the area, the box-counting fractal dimensions are:

$$D_1=1.412\pm0.021 \quad (5)$$

$$D_2=0.905\pm0.016 \quad (6)$$

The fractal behavior is a bi-modal one, characterized by D_1 which describes the short-range correlations and by D_2 describing the long-range correlations.

For the same points, the information fractal dimensions are:

$$D_{i_1}=1.525\pm0.025 \quad (7)$$

$$D_{i_2}=0.802\pm0.052 \quad (8)$$

As above, D_1 describes the short-range correlations and D_2 the long-range correlations.

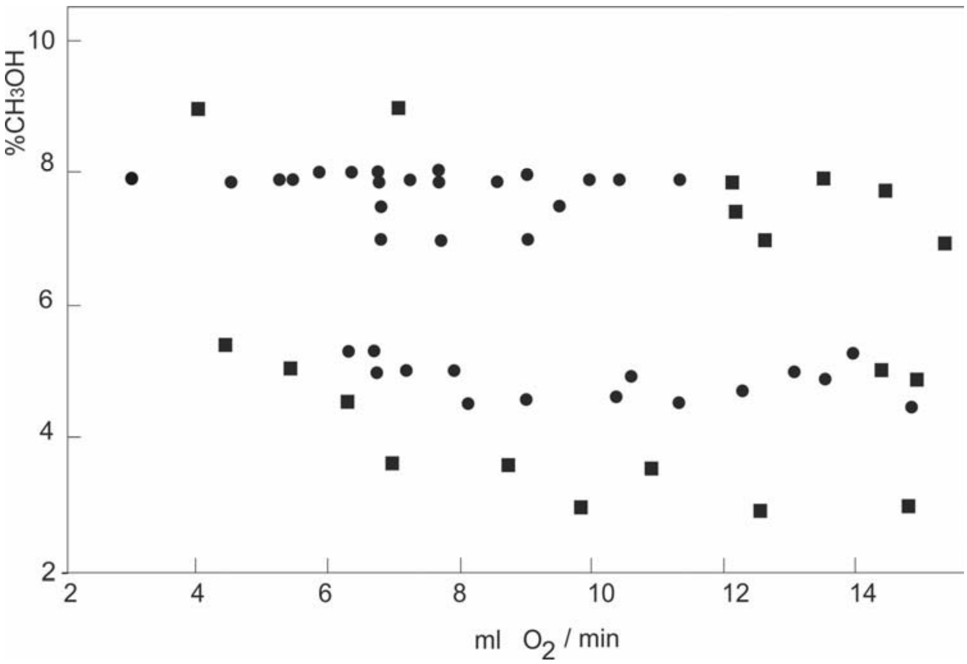

Fig. 1 – Experimental area for methanol concentration and oxygen flow rate, where thermal oscillations may be detected during methanol oxidation at 80 C on 20 mg palladium catalyst (● oscillatory regime; ■ non-oscillatory regime).

For the points outside the area, the box-counting fractal dimensions are:

$$D_1=1.295\pm0.037 \quad (9)$$

$$D_2=0.555\pm0.030 \quad (10)$$

and the information fractal dimensions:

$$D_{i_1}=1.476\pm0.118 \quad (11)$$

$$D_{i_2}=0.476\pm0.047 \quad (12)$$

The differences between box-counting dimensions and information fractal dimensions in the two cases, oscillatory state (points inside the area from Fig.1) and non-oscillatory state (points outside of the area) could be explained by the sensitivity of the methanol oxidation reaction on palladium to experimental parameters. The short-range fractal dimension seems to be very sensible to reaction parameters, as there is a high difference between oscillatory and non-oscillatory points. The oxygen flow rate, the methanol concentration, the temperature of the reaction cell, the size of the catalyst-samples and the catalyst powder disposal on the support in the differential dynamic calorimeter are the principal parameters of this reaction. Small changes in the values of these parameters are responsible for the transition from a steady-state to an oscillatory one.[11,12]

The methanol oxidation on Pd takes place in the manner known for the C_1-C_4 alcohols on platinum metals. The molecule contains one carbon atom and can be split in several bonds, depending on the type of interaction with the catalyst and the reaction conditions. On palladium the first step is the dissociative adsorption.[6,13] Modification in the nature and local relative distribution of the surface-adsorbed species due to experimental conditions could produce the observed different values in the fractal parameters.

CONCLUSIONS

The oxidation of methanol on a supported catalyst presents a fractal behavior. The fractal dimension and the information fractal dimension have been determined for the surface points when the surface reaction oscillates or is in steady-state. The small differences of these values between the oscillatory state and the steady-state can be assigned to experimental conditions.

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