ACADEMIA ROMÂNĂ

Revue Roumaine de Chimie

http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2018, *63*(5-6), 455-458

Dedicated to Dr. Maria Zaharescu
on the occasion of her 80th anniversary

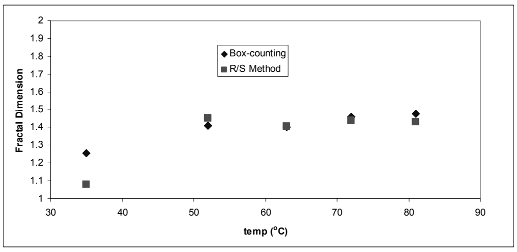
THE FRACTAL DIMENSION OF OSCILLATIONS ON A CO/Pd SUPPORTED CATALYST

Gianina DOBRESCU,* Veronica BRĂTAN and Niculae I. IONESCU

"Ilie Murgulescu" Institute of Physical Chemistry of the Roumanian Academy, 202 Spl. Independentei, 060021 - Bucharest, Romania, Phone/Fax (40-21) 312 1147

Received

The fractal dimension of oscillations in CO-Pd/TiO_2 system was determined using two methods: the box-counting and the R/S Analysis Interface one at different temperatures. The small differences in the obtained values can be assigned to experimental conditions.



INTRODUCTION

The interest in self oscillatory phenomena produced in heterogeneous catalytic reactions is caused by the fact that these 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.[1,2] In the same time, the interest in such oscillatory behaviours is caused by the possibility to perform a lot of processes more efficiently using unsteady-state operations.

Fractal has been applied also in catalysis,[3] using mostly the fractal dimension. The 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 that of a surface is 2, the fractal dimension of profiles may be any real number between 1 and 2. The existence of a fractal dimension means that the structure is self-similar *i.e.* if the oscillations are irregular they present self-similarity. This fractal dimension was also determined for other catalytic systems too.[3-5]

In the present paper we describe the fractal character of oscillations appeared during heating Pd/TiO2 catalyst in the presence of carbon monoxide/oxygen mixture contained in the gas flow.

THEORY

For the determination of the fractal dimension two methods have been used: the box-counting method and the range-surface interface method.

1) Box-counting Method

Self-similarity can be mathematical described as:

* Corresponding author: dobrescugianina@yahoo.com

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

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.

The box counting dimension is defined as the exponent D in the equation (1) for a constant R:

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

The box-counting dimension computing process implies minimizing the number of boxes needed to cover the set. This is accomplished by the computer code, rotating the grid for each box size through 90 degreed and plotting the minimum value of N(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 logarithm of r on the horizontal axis. The slope of straight line is –D.

2) R/S Analysis Method Interface

For an interval, or a window of length w, S(w) is the standard deviation of the differences dy(x):

$$dy(x)=y(x)-y(x-dx) \quad (3)$$

The rescaled range uses S(w) to standardize the range R(w) and allow comparisons of different data sets. The rescaled range R/S(w) is defined as:

$$R/S(w)=\langle R(w)/S(w)\rangle \quad (4)$$

where w is the window length and the angled brackets $\langle R(w)\rangle$ denote the average of a number of values of R(w). Self-affinity implies that the range taken by the values of y in a window of length w to be proportional to the window length to a power equal to the Hurst exponent H, i.e.,

$$R/S(w) = w^H \quad (5)$$

For a given window length w, the input series is subdivided in a number of intervals of length w, the range R(w) and the standard deviation S(w) for each interval are computed, and R/S(w), the average ratio of R(w)/S(w), as in eq. (4) is computed, also.

This process is repeated for a number of window lengths, and the logarithms of R/S(w) are plotted versus the logarithms of w. For a self-affine trace this plot should follow a straight line and the slope will be the Hurst exponent H. The fractal dimension is related to the Hurst exponent by the equation:

$$D_{rs}=2-H \quad (6)$$

where D_{rs} is the fractal dimension computed from the rescaled range method.

EXPERIMENTAL

The 1% wt Pd/TiO_2 catalyst was obtained by impregnating TiO_2 (Rhone Poulenc, S_{BET}-103 m^2/g) with $Pd(OAc)_2$ dissolved in acetone, at room temperature. The resulted material was treated at 500^{o}C for 4 hours, after it has been dried at 120^{o}C. The sample has a specific surface of 90 m^2/g.

The electrical conductance, G, was measured at 1592 Hz, in gas flow with a RLC bridge Hioki, using a reaction cell specially designed to allow the measurements in powder.[6] The catalyst (1.5 cm^3) powder (fraction between 0.25 and 0.5 mm) was filling the annular space between the electrodes and supported on a frit. In these conditions the measured conductivity is dominated by surface conduction.[7] The sample was flushed in $CO:O_2:He$ (4.75:4.75:91.5 molar ratio) mixture at different temperatures. The total flow rate was 72 mL/min.

RESULTS AND DISCUSSION

The obtained oscillations of the electrical conductance are presented in Figure 1. These oscillations are irregular having different shapes, amplitudes and frequencies but all present a fractal character.

The fractal dimensions calculated with the box-counting method and the R/S analysis method interface are summarized in Table 1.

The oscillations depend on the temperature. At the beginning, the fractal dimension is greater calculated with the box-counting method. In case of the other temperatures the values of D remain greater with this method, except being the temperature of 52^{o}C when the R/S method is greater. At 52^{o}C the oscillations have other frequencies as the others, but with greater amplitude. In this case the oscillations with greater amplitude as the others at this temperature are present quite regular. It seems that for the same oscillation there is regular and irregular type of oscillations. These oscillations produced at 52^{o}C could be produced by an other part of the catalyst with another degree of oxidation or reduction. In the other cases, the fractal dimension D increases with the increase of temperature. The fractal dimension seems to be sensible to the reaction parameters as in other cases too.[4,5] In this case the temperature was this parameter.

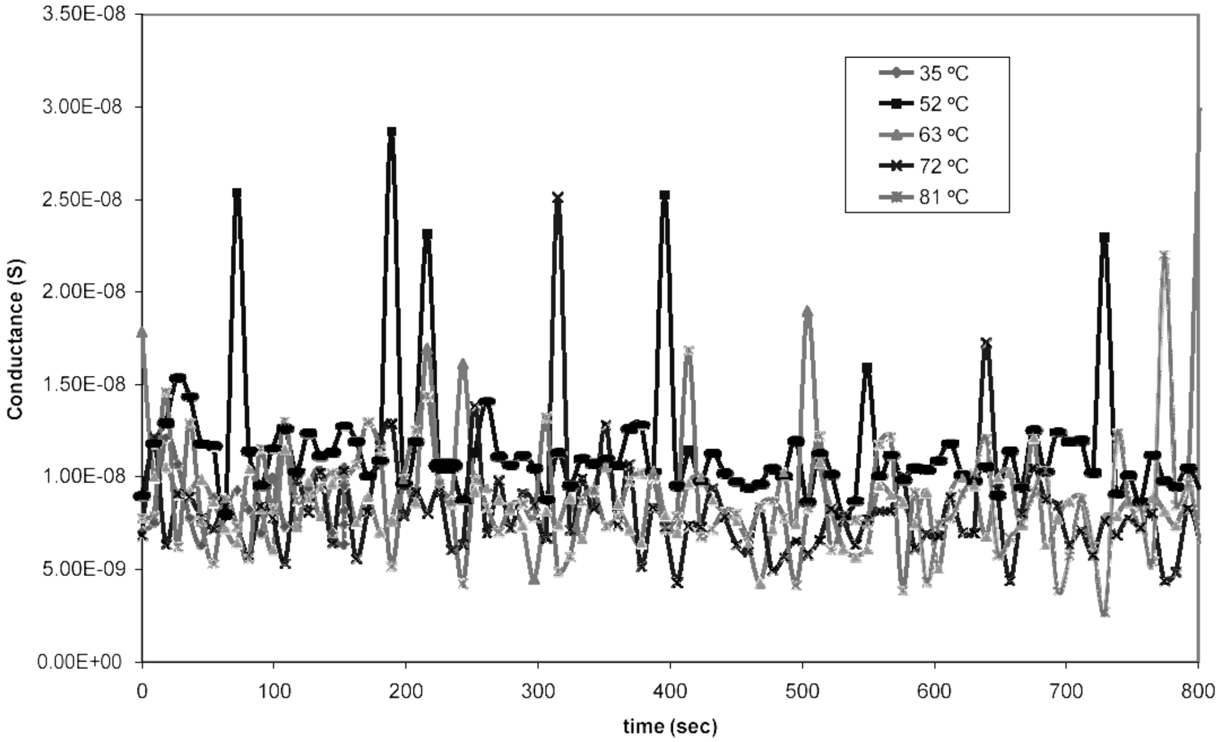


Fig. 1 – The oscillations of electrical conductance of the sample flushed in $CO:O_2$:He mixture at different temperatures.

Table 1

The fractal dimensions calculated with two methods

Temperature of reaction (°C)	Method	Fractal Dimension
35	Box-counting	1.2570±0.0072
	R/S Method	1.0800±0.0035
52	Box-counting	1.4122±0.0126
	R/S Method	1.4500±0.3070
63	Box-counting	1.4009±0.0067
	R/S Method	1.4070±0.2270
72	Box-counting	1.4605±0.0046
	R/S Method	1.4380±0.2210
81	Box-counting	1.4761±0.0050
	R/S Method	1.4310±0.2299

Oscillations observed in heterogeneous catalytic systems under atmospheric pressure have some unique features: their local activity and transport properties are inherently non-uniform and the boundary conditions affect them because by the long range impact of the enthalpy balance.[8] Moreover, the interaction between the solid and fluid phases can create and stabilize states which would not exists in its absence.[9,10] This fact can explain the appearance of irregular oscillations which in some cases can be transformed in regular one.

CONCLUSIONS

The oxidation of carbon monoxide on a Pd supported catalyst presents a fractal behavior. An overall kinetic model and the corresponding mathematical one was presented for the explanation of the irregular oscillations appeared in this system. The fractal dimension seems to be sensible to the temperature of the reaction.

Acknowledgements: The authors are gratefully acknowledged the support of the EU (ERDF) and Roumanian Government which approved acquisition of the research infrastructure under POS-CCE O 2.2.1 project INFRANANOCHEM - No. 19/01.03.2009.

REFERENCES

1. G. Ertl, *Adv. Catal.*, **1990**, *37*, 213.
2. N. I. Ionescu and C. Hornoiu, in “Form and Patterns” C. Vasilescu, M.-L. Flonta and I. Craciun (Eds.), Roumanian Academy Printing House, 2015, p. 166.

3. G. Dobrescu, D. Berger, F. Papa and N. I. Ionescu, *Appl. Surf. Sci.,* **2003**, *207*, 154.
4. G. Dobrescu, N. I. Ionescu and M. Caldararu, *Rev. Roum. Chim.*, **2006**, *51*, 521.
5. G. Dobrescu and N. I. Ionescu, *Rev. Roum. Chim.*, **2016**, *61*, 307.
6. M. Caldararu, D. Sprînceana, V. T. Popa and N. I. Ionescu, *Sens. Actuators B: Chemical*, **1996**, *30*, 35.
7. M. Caldararu, M. Scurtu, C. Hornoiu, C. Munteanu, T. Blasco and J. M. López Nieto, *Catal. Today*, **2010**, *155*, 311.
8. D. Luss and M. Sheintuch, *Catal. Today*, **2005**, *105*, 254.
9. N. I. Ionescu, *Rev. Roum. Chim.,* **2012**, *57*, 629.
10. V. Bratan and N. I. Ionescu, *Rev. Roum. Chim.,* **2017**, *62*, 619.