Fractal Analysis of Mixed Oxides Type Cu-Cr Catalysts Supported on γ-Al_2O_3 and γ-Al_2O_3 + SiO_2

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Supported mixed metal oxide systems, Cu-Cr on γ-Al_2O_3 and γ-Al_2O_3 + SiO_2 were prepared and studied using fractal theory. The catalysts exhibit fractal properties. Fractal dimensions were computed analyzing the SEM images using the correlation function method and the variable length scale method. The influences of the support and of the preparation procedures on fractal properties are emphasized.

Keywords : fractal dimension, Cu-Cr, mixed-oxides

The idea of analysing the fractal properties of catalysts was related to the particle size influences on catalytic properties of supported metals [1,2]. The necessity of highly performant techniques able to describe, even only in a geometric way, the complexity of the nature is the reason of utilizing the fractal theory. Several experiments confirmed that the surfaces and the internal structure of many solid materials are fractal at molecular level [2-6]. Catalysts always have surfaces with high specific surfaces, meaning that fractal theory is an useful tool to characterize such irregular surfaces [5,6]. Many papers were published on the effect of fractal properties of catalytic surfaces on catalytic reactions [5-8].

In a geometric way, a perfect catalyst must be an object with a high surface to volume ratio, in other words a fractal object, because for these kind of objects the ratio surface to volume is maximum. If an object has a fractal behaviour it is possible to compute a quantity named "the fractal dimension" able to describe its irregular geometry.

There are a lot of methods to compute fractal dimension. The direct methods ussually analyse microscopic images (AFM, SEM, STM, TEM micrographs), using different algorithms, such as: the "box-counting" method, the mass-radius relation, the correlation function method, the variable length scale method. Our goal is to compute fractal dimension of different catalysts using SEM micrographs and two different methods: the correlation function method and the variable length scale method.

Experimental parts

Methods

Catalysts preparation

The complex precursors were obtained by precipitation at *p*H=7 of a mixture of aqueous solution of Cu:Cr nitrates mixed with tartaric acid, in solution of ethanol and ammonium hydroxide in the ratio 1:1. After precipitation the resulted compound was dried in vacuum at 90° C [9]. They were subsequently submitted to chemical analysis, IR Spectrometry, magnetic measurements and thermal analysis [9]. All the obtained results gave the following formula for the precursor:

$$[\ Cr\ Cu_4\ Ta_6\ ]\ .5H_2O \qquad (1)$$

In order to prepare the supported catalysts two procedures have been used:

- the first procedure consists in the synthesis of the precursor directly on the support by successive impregnations of the solution of tartaric acid and of the nitrates mixture (samples C_1 and C_2);
- the second procedure consists in the synthesis of the precursor, its dissolution in water and deposition on the support by evaporation (samples C_5 and C_6).

Two supports were used for impregnation or deposition: pellets of γ- Al_2O_3 (ϕ = 6 mm) and a mixture of γ- Al_2O_3 +20% SiO_2 grains (Φ = 3-5 mm). The supported catalysts prepared by the two above mentioned procedures, have been dried for 8h at 90°C and calcined at 650°C for 6h. The samples prepared by the first procedure gave egg-shell type catalysts (thickness 0.7 - 1 mm) after calcinations.

Table 1
PREPARATION PROCEDURES AND SUPPORTS USED FOR THE Cu-Cr CATALYSTS

Sample	BET specific surface area (m^2/g)	Support	Preparation procedure
C1	167	γ - Al_2O_3	First procedure
C2	155	γ - Al_2O_3 + SiO_2	First procedure
C5	152	γ - Al_2O_3	Second procedure
C6	143	γ - Al_2O_3 + SiO_2	Second procedure

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The optimal calcination temperature was established from thermogravimmetric (T.G.A.) data. Therefore, the complex precursors are totally decomposed before the temperature reaches 400°C-450°C. For oxide phases stabilization, the samples were calcined at temperature higher than 450°C ; when the temperature reaches 650° C, a maximum content of $CuCr_2O_4$ (the active spinelic phase in total oxidation of volatile organic compounds) is obtained. At temperatures higher than 750°C, $CuCr_2O_4$ is totally transformed in $Cu_2Cr_2O_4$ – the inactive phase for the total oxidation [9].

Calcination temperature effect on catalytical properties of different systems (Fe-Cr) was studied in literature [10].

In figures 1 and 2 SEM/EDX results show Cu, Cr and Al mapping together with energy dispersive using X-ray spectrum for samples C1 and C5.

Theoretical methods for computing fractal dimension

Fractal dimension can be computed using more elaborated methods, such as the "height correlation function" [11]:

$$G(r) \equiv < C(\vec{x}, r) >_x \quad (2)$$

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

$$C(\vec{x}, r) = [h(\vec{x}) - h(\vec{x}, + \vec{r})]^2 \quad (3)$$

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 [11]:

$$G(r) \sim r^{2\alpha}, r << L, \quad (4)$$

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

$\alpha = 3 - D$, and D is the fractal dimension. (5)

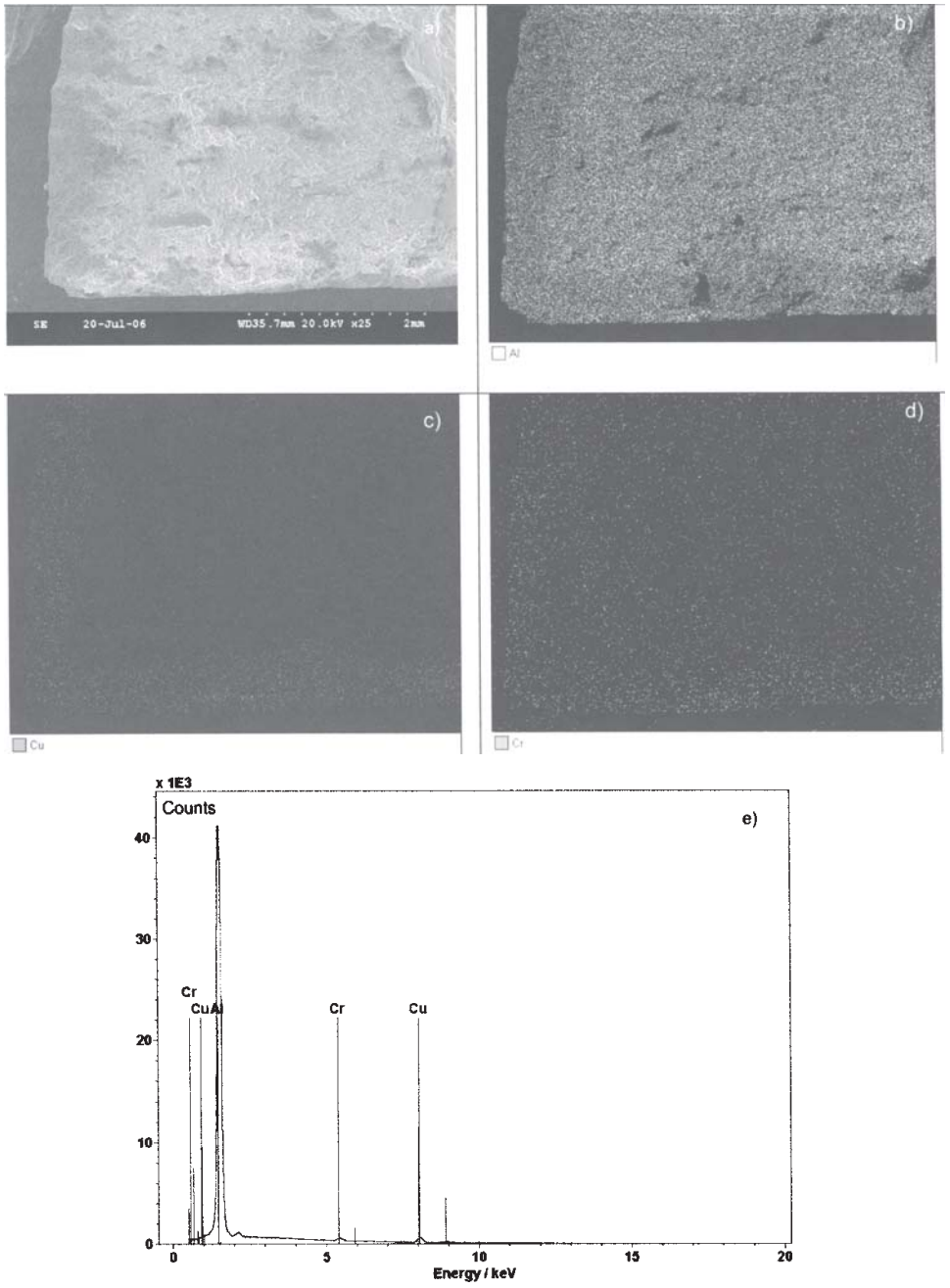

Fig. 1 SEM/EDX result measured for sample C1; a) SEM image of sample C1 used in EDX mapping; b) EDX mapping of Al; c) EDX mapping of Cu; d) EDX mapping of Cr; e) EDX spectrum of C1 sample.

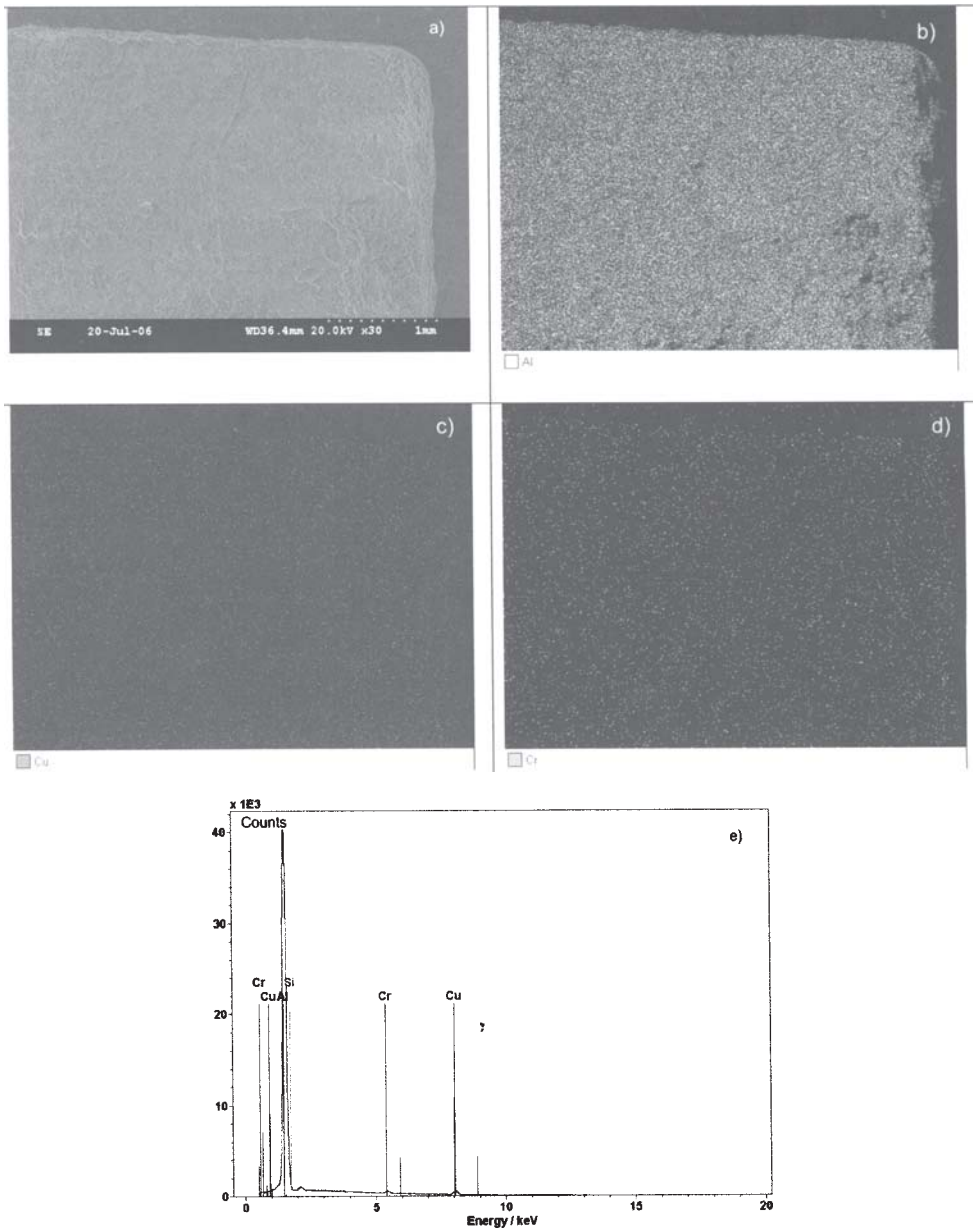

Fig. 2 SEM/EDX result measured for sample C5; a) SEM image of sample C5 used in EDX mapping; b) EDX mapping of Al; c) EDX mapping of Cu; d) EDX mapping of Cr; e) EDX spectrum of C5 sample

The scaling range where equation (4) 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 columns.

The method is applied for a narrow scale range and cannot be extended on a larger one because of the great amount of computations needed. To extend the scale ranges to higher values, in order to investigate the fractal behaviour, a second method was used: the variable length scale method [12].

This method was proposed by Chauvy et al [12] and consists of computing the root mean square (rms) deviation of the surface. The algorithm is the following: (i) an interval of length ε, in case of a profile, (or a box of size ε x ε, in case of a surface) is defined; (ii) a linear (or planar) least square fit on the data within the interval is performed and the roughness is calculated; (iii) the interval (box) is moved along the profile (surface) and step (ii) is repeated ; (iv) the rms deviation for multiple intervals is computed, and (v) steps (ii)-(iv) are repeated for increasing lengths (box sizes).

The smallest size for an interval corresponds to 10 data points (10 x 10 points for 3-dimensional embedded objects) and its maximum size is the total length of the profile (size of the surface). Rms deviation $R_{q\varepsilon}$, averaged over n_ε, the number of intervals of length ε, is defined by:

$$R_{q\varepsilon} = \frac{1}{n_\varepsilon}\sum_{i=1}^{n_\varepsilon}\sqrt{\frac{1}{p_\varepsilon}\sum_{j=1}^{p_\varepsilon} z_j^{\,2}} \qquad (6)$$

where z_j is the j^{th} 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:

$$D = D_T - H \qquad (7)$$

where D_T is the topological dimension of the embedding Euclidean space (D_T=2 for profiles and D_T=3 for surfaces). The variable length scale method is more suitable for higher

scaling range than the correlation function method because of the necessity to have enough points in an interval ε x ε to compute rms deviation $R_{\alpha\varepsilon}$, averaged over n_ε, meaning that ε must be high enough for a good statistic.

Results and discussions

SEM images of samples C_1-C_2, C_5-C_6 are presented in figures 3-10.

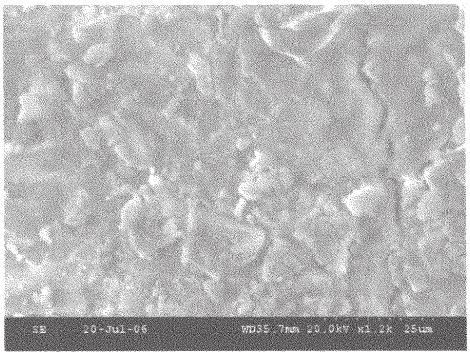

Fig. 3 SEM image of C1 sample

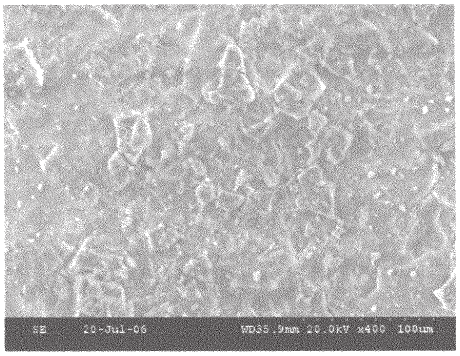

Fig. 4 SEM image of C1 sample

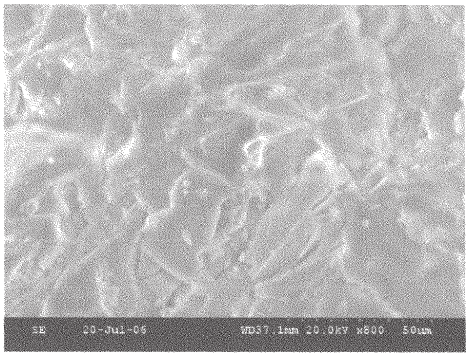

Fig. 5 SEM image of C1 sample

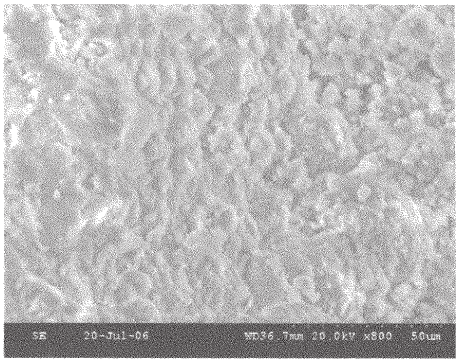

Fig. 6 SEM image of C2 sample

Using the correlation function method described (equations 4 and 5) and the variable length scale method (equations 6 and 7) the fractal dimensions of the SEM images were computed. The algorithm assigns for every pixel a height according to its grey-level. The surface is after that analysed using the equations described above. Results are presented in table 2.

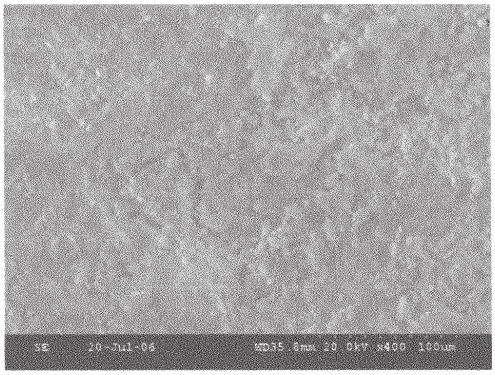

Fig. 7 SEM image of C5 sample

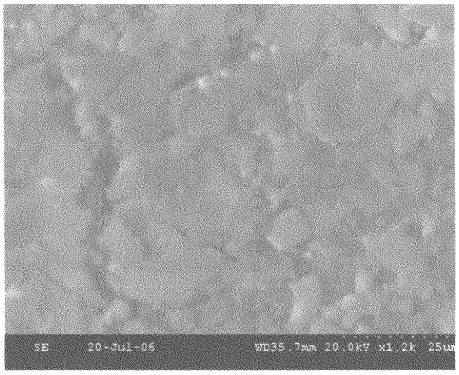

Fig. 8 SEM image of C5 sample

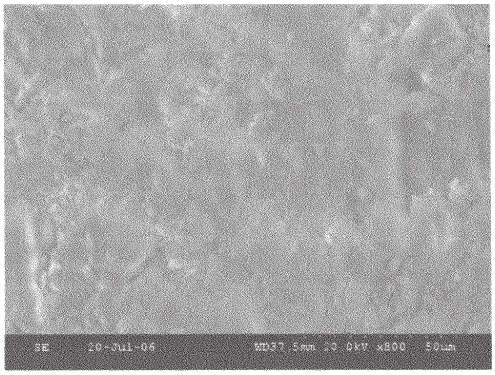

Fig. 9 SEM image of C5 sample

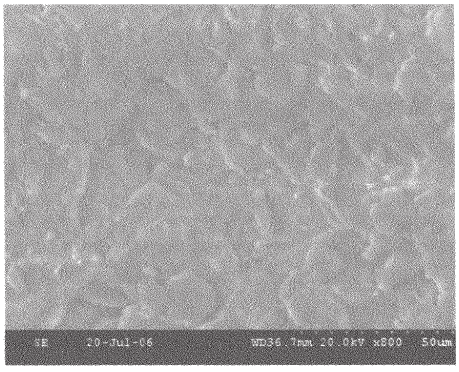

Fig. 10 SEM image of C6 sample

For the sample C6 the variable length scale method gives no self-similarity for higher domain.

The major conclusion of table 2 is that all samples exhibit fractal behaviour on a wide domain. This is a very important fact, as we already know that from a geometrical point of view an "ideal" catalyst has a fractal structure [4].

Table 2
FRACTAL DIMENSIONS OBTAINED BY SEM IMAGES ANALYSIS

Sample	Figure	Method	Fractal dimension	Self-similarity domain (nm)	Linear correlation coefficient
C1	3	Correlation function	2.59±0.01 2.78±0.01	600-1572 1572-3073	0.993 0.980
		Variable length scale	2.75±0.01	5000-13333	0.985
	4	Correlation function	2.78±0.01	2000-4609	0.976
		Variable length scale	2.77±0.01	10000-15000	0.999
	5	Correlation function	2.54±0.01 2.72±0.01	1060-1820 1820-4472	0.995 0.988
		Variable length scale	2.54±0.01 2.72±0.02	5000-10000 10000-18750	0.998 0.973
C2	6	Correlation function	2.59±0.01 2.77±0.01	790-1767 1767-2828	0.993 0.983
		Variable length scale	2.79±0.01	6250-12500	0.995
C5	7	Correlation function	2.65±0.01 2.81±0.01	1500-3041 3041-5220	0.990 0.936
		Variable length scale	2.63±0.02 2.85±0.01	5000-12500 12500-37500	0.989 0.983
	8	Correlation function	2.51±0.01 2.67±0.01	666-1536 1536-2505	0.996 0.979
		Variable length scale	2.42±0.02 2.69±0.01	1666-5833 5833-14166	0.994 0.983
	9	Correlation function	2.62±0.01 2.78±0.01	750-1802 1802-4069	0.992 0.986
		Variable length scale	2.56±0.02 2.74±0.01	2500-6250 6250-18750	0.997 0.993
C6	10	Correlation function	2.57±0.01 2.75±0.01	750-1767 1767-3162	0.991 0.951

Comparing the fractal dimensions obtained for the samples C1 and C5, (catalysts obtained using different preparation procedures, but the same support) one can notice that the sample C1 is characterized by two fractal dimensions, it has a bi-modal behavior, that is not affected by image resolution. The two fractal dimensions are situated around the value of 2.75±0.04 for the self-similarity domain of 1820nm-18750nm and 2.56±0.03 (600nm-10000nm). The two self-similarity domains are superposed, indicating the existence of a global fractal structure of high fractal dimension that characterizes the support (γ-Al_2O_3) and of another fractal structure, with a lower fractal dimension (2.56) that can be assigned to the Cu-Cr catalyst itself.

The sample C5 (prepared using the second preparation method) has a different behaviour. The images have bi-modal fractal behaviour, but the fractal dimensions decrease as image resolution increases. For figure 7, the average fractal dimensions are: 2.64± 0.03 (1500nm-12500nm) and 2.83±0.02 (3000nm-37500nm); for figure 9 the fractal dimensions are lower: 2.59±0.04 (750nm-6250nm) and 2.76±0.03 (1800nm-18750nm); for figure 8, the fractal dimensions are even lower: 2.46±0.07 (666nm-5833nm) and 2.68±0.02 (1536nm-14166nm). This behaviour indicates a non-homogeneous structure due to the preparation method. The precursor synthesis, its dissolution in water and deposition on the support by evaporation are complex processes, each of them characterized by a fractal dimension, and the result will be a self-similar structure characterized by a set of fractal dimensions.

We conclude that the second preparation procedure will lead to non-homogeneous fractal structures, with lower fractal dimensions than in the case of the first preparation method.

The support influence cannot be evidenced for the first preparation procedure (sample C1 and C2); for the second preparation procedure, using the support γ - Al_2O_3 + SiO_2 we obtained a structure with a narrow self-similarity domain and two specific fractal dimensions.

Conclusions

Mixed oxides type Cu-Cr catalysts supported on γ - Al_2O_3 and γ - Al_2O_3 + SiO_2 and prepared using different procedures were investigated using fractal theory. Catalysts exhibit fractal properties in a broad self-similarity domain. The catalysts prepared by synthesis of the precursor, its dissolution in water and deposition on the support by evaporation are un-homogeneous fractal structures, with low fractal dimensions. Also, this preparation method will lead to structures with narrow self-similarity domains if γ - Al_2O_3 + SiO_2 support is used.

Other works [8] have proved that both catalyst and substrate geometry have a very important influence on reaction. When the reaction occurs over fractal substrates, both the rate constant and the reaction order can change due to the fractal substrates. From this point of view, describing the catalysts geometry in terms of fractal theory will lead to a better understanding of the reaction kinetic.

On the other hand, attaching a number (the fractal dimension) to a SEM-image will describe quantitatively the surface of such an irregular object as the supported catalyst is.

We shall focus in the future on the analysis of other systems, such as Co-Cr catalysts, correlating the fractal properties with their physical and chemical properties, especially with their catalytic activity in the total oxidation of benzene.

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