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Fractal analysis of catalyst surface morphologies on hydrogenation in process of 2-((1-benzylpiperidin-4-yl)methyl)-5,6-dimethoxy-2, 3-dihydroinden-1-one hydrochloride synthesis



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ABSTRACT

Catalytic hydrogenation of 2-((1-benzyl-1,2,3,6-tetrahydropyridin-4-yl)methylene)-5,6-dimethoxy-2,3-dihydroinden-1-one hydrochloride (**1**) to 2-((1-benzylpiperidin-4-yl)methyl)-5,6-dimethoxy-2,3-dihydroinden-1-one hydrochloride (**2**) was investigated in batch-slurry reactor. The 5% Pt/C catalysts were chosen for optimizing the catalytic activity. The catalyst activity has been changed by using the differently morphologically structured fractal catalysts. The kinetic terms of hydrogenation for (**1**) change with the fractal dimensions of the 5% Pt/C catalysts. The kinetic terms of hydrogenation for (**1**) change with the fractal dimensions of the 5% Pt/C catalyst. The most active and selective (with the highest reaction rate for production of (**2**), and with the least impurities level) is the catalyst K3, and the worst te catalyst K4. This most active and selective catalyst has an intermediate fractal surface dimension, $D_{F,ads} = 2.77$, and the worst catalyst is represented by almost smooth surface with a high $D_{F,ads} = 2.82$. The interface D[BW] fractal indices (derived from the thresholded SEM images, at the magnifications in the range 600–2000×) are largest ones for the most suitable catalyst K3, and lowest for the catalyst K4.

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1. Introduction

2-((1-Benzylpiperidin-4-yl)methyl)-5,6-dimethoxy-2,3-dihydroinden-1-one hydrochloride (2 HCl, compound **2**) is an active pharmaceutical ingredient (API) available for the treatment of all kinds of senile dementia and (**2**) and its pharmaceutically acceptable salts can be produced by catalytic hydrogenation of 2-((1-benzyl-1,2,3,6-tetrahydropyridin-4-yl)methylene)-5,6dimethoxy-2,3-dihydroinden-1-one hydrochloride (compound **1**) as presented in Fig. 1 (see [1]).

Since catalytic hydrogenation is the last production step for the preparation of compound (2), there is a need for improving a hydrogenation step that minimizes or eliminates impurities generated as side products of the reaction. For this particular reaction, a wide variety of catalysts have been investigated [1]. Each catalyst appears to have at least some of advantages and, notably, significant disadvantages. The reaction conditions for hydrogenation of compound (1) can also significantly influence the yield of compound (2) and impurity profile. However, the aim of this work is the search

for the 5% Pt/C catalyst morphology which will meet requirements for high reaction selectivity toward main product, compound (2) (highest purity of the reaction mixture) and at the same time high activity, good stability and possibility of catalyst reuse (shorter reaction time). Ren et al. [2] have found a difference which indicated an effect of the Pt surface roughness. The reaction becomes slower on a highly rough Pt surface, *i.e.*, a surface with more defects, such as edges, kinks and step sites, than on a less rough surface. Beden et al. [3,4] have found that the structure of the Pt surface plays an important role in diminishing the phenomena of adsorption poisoning. Mikhaylova et al. [5] obtained the catalytic effect increases with increasing roughness factor of platinum. Umeda et al. [6] found the strong effect of the Pt surface textures. Tang et al. [7] found that the particle size and dispersion of Pt deposits are important factors determining the activity of a catalyst. Duarte et al. [8] explained the increase of activity with increasing mass specific surface area by the reduction of the particle size. Scheijan et al. [9] concluded that the platinum shape and the morphology played predominant role in the reaction kinetics. Characterization of catalysts in terms of fractal geometry has been found useful during the last decades [10]. Fractal analysis has been used in the study of heterogeneous catalysis to determine the structure sensitivity of a reaction [11]. Particularly, much of the research on reaction in porous catalysts with a fractal structure has focused on the derivation of general, qualitative scaling laws expressing the power law dependence of



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Fig. 1. Catalytic hydrogenation of compound (1) to compound (2).

certain properties on the observation scale [12]. All the experimental studies [13-17] of heterogeneous catalytic processes show that the fractal nature of the active phase may be responsible for the variation in reactivity. In the present communication we report results regarding a relation between fractal dimension of the 5% Pt/C powders catalyst and the rate constant. The fractal characteristics of 5% Pt/C powders were studied both by nitrogen adsorption and scanning electron microscopy (SEM). Results of catalytic tests for the hydrogenation show a good correspondence of rate constant and the fractal dimensions. The influence of catalyst texture characteristics defined by the fractality is examined and the optimal type of the Pt/C texture is defined in order to obtain product in high purity and yield. Porous catalysts and catalyst supports (Pt/C) have a rough internal surface. This surface is often fractal on molecular scales as derived from adsorption experiments. Reaction processes dependence on surface roughness can be quantified using fractal geometry. The influence of morphological properties of fractal surfaces on the selectivity between competing catalytic reactions have been already studied [18]. In an attempt to identify the appropriate properties of a real material that should be represented the previous work has been extended to consider fractal models, in order to correlate activity and selectivity with characteristics which may be related to input from experimental characterization data, such as that from SEM imaging. The correlation linear models have shown that both the porosity and the fractal dimension are important to accurately represent kinetic behavior of a real porous material.

2. Experimental

2.1. Materials

Compound (1) was produced by patent application WO/2007/015052 A1. The structure of compound (1) was confirmed by mass spectrum and NMR analysis (see [1]). Four types of commercially available (5% Pt/C) catalysts were used. All catalysts were used as received.

2.2. Experimental setup

The hydrogenation experimental setup and the reaction kinetic have been already described elsewhere [1].

2.2.1. Nitrogen adsorption

Nitrogen adsorption isotherms were measured at 77 K with a Gemini 2380 Surface Area Analyzer (Micromeritics). Samples were outgassed at 423 K for 1 h to remove adsorbed contaminants prior to the measurement. The BET specific surface area was calculated using the multipoint BET method [19] on five points of the adsorption isotherm near monolayer coverage. Surface fractal dimension (DS) was calculated using the Frenkel–Halsey–Hill (FHH) method [20] from adsorption data near monolayer coverage [21].

2.2.1.1. Physical adsorption on fractal solids. Fractal geometry [22] has been an appropriate tool to study problems related to structure and scale of various porous solids [23–30]. There is experimental evidence for the fractal roughness of the internal surface of many amorphous catalysts over a finite scaling range that includes the size of typical diffusing molecules [31,32]. The irregular

catalyst morphology and its influence on diffusion and reaction can therefore be modeled in a realistic way using fractal geometry. The different experimental and theoretical methods of determining the fractal dimension ($D_{F,ads}$) of solid adsorbents have been developed based on the results of a single adsorption isotherm measurement [33]. The fractal dimension of the surface $2 \le D_{F,ads} < 3$ accessible for adsorption is a global measure of surface irregularity, and for highly porous systems "fractal behavior does not reflect the structure of the basic objects (such as pores or clusters) but their distribution" [34,35]. The value of fractal dimension $D_{F,ads}$ is obtained directly from the linearization of adsorption data according to the equation that was developed by Avnir and Jaroniec [36,37].

$$\frac{N}{N_{\text{mono}}} = \kappa \left[\ln \left(\frac{p_0}{p} \right) \right]^{-(3-D_{F,\text{ads}})} \tag{1}$$

where p_0 and p are the saturation and equilibrium pressures, κ and N_{mono} are constant and monolayer capacity, respectively. The calculation of the fractal dimension is fast and simple, and $D_{F,\text{ads}}$ is a very convenient measure of the comparative analysis of surface irregularity of the catalysts.

2.2.2. Scanning electron microscopy (SEM)

Samples were fixed on an aluminum stub with conductive double sided adhesive tape and coated with gold by Edwards S150 sputter coater. The micrographs were acquired by the JEOL JSM-5800 scanning microscope coupled to an Oxford ISIS EDX detector for the elemental composition and mapping.

2.2.2.1. Image fractal analysis approaches. Fractal dimension values were computed for the microscopic fine-sized texture in the SEM images of catalysts particles by the mono- and the multi-fractal approaches.

Modified box counting method. The fractal analysis method uses pixel intensity height profiles, extracted from the SEM images and presented as z-heights in an x-y image plane. Counting black, white and partially black squares separately can modify this method. The three fractal dimensions D_{BW} (surface box dimension), D_{WBW} (coating box mass dimension), and a classical box dimension D_{BBW} (solid box mass dimension) (as defined by the HarFa [38]) are capable of describing morphological differences in lactose materials. The method is based on a simple principle where a square mesh of various sizes $1/\varepsilon$ is laid over the image object. Mesh boxes $N_{BBW}(\varepsilon)$ that contain any part of the boxes which cover the pore phase fractal are counted (e.g. squares which are completely filled up by the fractal N_B and squares which contain just part of fractal N_{BW} are added). The numbers are recorded. This is repeated for different sized boxes. For a fractal set, the number of boxes $N(1/\varepsilon)$ satisfies the relation, $N(1/\varepsilon) \sim (1/\varepsilon)^{-D}$, where *D* is the mass fractal dimension. A log-log plot of $N(\delta)$ against δ then yields a line of slope equal to -D. Dimension D[B+BW] is then referred to as a classical box dimension. Counting black, white and partially black squares separately can modify this method. Three new fractal dimensions D[B], D[W], D[BW] can be obtained. D[B] and D[W] characterize fractal properties of black and white plane, while D[BW] characterizes properties of black and white boundary. Therefore, five independent fractal dimensions can be computed: the most important: the interface D[BW], the "classical" box-counting D[B+BW], and coating fractal index D[W+BW] (arises by adding white squares N_W and remaining white and black squares N_{BW} that contain just boundary part of fractals). The interface or "surface" D[BW], and the "classical" box-counting D[B+BW] "mass" fractal index do not necessarily describe the same physical property of the objects, and thus may have different values. In particular, they diverge at the morphological extremes of space filling and tenuous objects. Fractal indices D[BW] characterizes the complexity of the pellets surface whereas the D[B+BW] represents the complexity of the general "mass" structure. The fractal dimension of image is established in the whole range of threshold conditions (Fractal Analysis-Range). The "fractal spectrum" represents the fractal dimension as a function of threshold condition (*e.g.* fractal dimension as a function of masked intensity (shade of gray) value, n) [39]. Intuitively, the larger the fractal dimension, the rougher the texture is. The SEM images are not deterministic but have a statistical variation. This makes the computation of fractal dimension more difficult.

Multifractal approach. The concept of multifractal scaling can be well applied in quantitatively characterizing complex geometric shapes or a singular distribution of physical parameters. A multifractal characterization is presented in one of two equivalent fractal dimension spectra [40]: (i) the Rényi fractal dimension spectrum, D(q), or (ii) the spectrum of scaling indices [41], $f(\alpha)$, which here is called the Mandelbrot fractal dimension spectrum. The Rényi fractal dimension spectrum is important because it has a geometric interpretation for positive integral q. Nice interpretations exist for subsets of the D(q), in particular for the capacity dimension q=0, also called the box-counting dimension, the information dimension q = 1, and the correlation dimension q = 2. The second spectrum, the Mandelbrot fractal dimension spectrum describes a multifractal as a union of interwoven monofractal sets, and therefore has a nicer interpretation, and also provides a functional form with compact support.

Rényi fractal dimension spectrum, D(q). The self-similarity of the pellets investigated here was not invariant in the whole range of scale. Thus multi-fractal approach appeared appropriate approach for these objects. Rényi dimensions, D(q), may be used, among other multifractal parameters, to characterize CSLM images. Rényi dimensions, also called generalized dimensions, may be computed through parameter q by:

$$D(q) = \lim_{\varepsilon \to 0} \left[\frac{1}{q-1} \right] \left[\frac{\ln \left[\sum_{i=1}^{N} p_i^q(\varepsilon) \right]}{\ln \varepsilon} \right]$$
(2)

where q is any real integer, p_i is probability, ε is size scale, where $\varepsilon = 2^{-k}L$, being L the length of interval, $N = 2^{k}$ number of cells, and k = 0, 1, 2 [42]. Parameter q acts as a scanning tool scrutinizing the denser and rarer regions of the measure μ . For $q \gg 1$, regions with a high degree of concentration are amplified, while regions with a small degree of concentration are magnified for $q \ll -1$. Most often used Rényi dimensions are D(0) and D(1). D(0) is called boxcounting dimension which gives account of the scaling properties of those cells that contain some amount of measure. It represents the dimension of the set of sizes with non-zero relative volume. Value D(1) is the entropy dimension of the measure and gauges the scaling in the concentration of the measure by taking into account the amount of measure in each cell. The higher the D(1) is the more even is the distribution. The values D(q) of 0, 1, or 2 a point, line, or twodimensional surface, respectively, independently of the parameter q. However, if the fractal becomes more complicated, then its dimension can be a fractal number, whose actual value varies with q. Rényi dimensions spectra are, in general, non-increasing functions with a characteristic sigmoid form (see Supplement). When studied distributions are close to monofractal measures (a uniform distribution of mass on a fractal set), Rényi dimensions spectra are closer to horizontal lines, so that $D(q) \approx D(0)$. Thus the multifractal dimension D(q) weights in a different manner the various density regions. In particular the limiting dimension $D(-\infty)$ and $D(+\infty)$ are related to the regions of the set in which the measure is most dilute and most dense respectively. $D(+\infty)$ corresponds to the region where the points are mostly concentrated, while $D(-\infty)$ is determined by the region where the points have the least probability to be found. If D(q) is a constant for all q, then the point density is uniform. Only in the very particular case of an object with

equal probabilities for all the cells, *i.e.* for a *monofractal*, we have D(q) = D(0) for all q. The q-moments accentuate different aspects of the image. For q > 0, the partition function emphasizes large fluctuations and strong singularities, whereas for q < 0, the partition function stresses the small fluctuations and the weak singularities. The negative moments deserve a cautionary note because they can easily become unstable, introducing artifacts into the calculation [43]. Thus, the interpretation of the generalized correlation dimensions must be judged with some caution for q < 0.

Spectrum of scaling indices or the Mandelbrot fractal dimension spectrum, $f(\alpha)$. With multifractal analysis it is common practice to evaluate the singularity $f(\alpha)$ spectrum [44,45]. The number of boxes $N(\alpha) = L^{-f(\alpha)}$ is given by the probability P_i of finding a white pixel within a given region *i* scales as $P_i = L_i^{\alpha}$, and $f(\alpha)$ may be understood as the fractal dimension of the union of regions with singularity strengths between α and $\alpha + (\alpha + d\alpha)$. The relationship between the D(q) spectrum and the $f(\alpha)$ spectrum is made *via* the Legendre transform:

$$f(a(q)) = q \times \alpha(q) - \tau(q) \tag{3}$$

where $\alpha(q) = d\tau(q)/dt$ and $q\tau(q) = (q-1)D(q)$ is the mass correlation exponent of the *q*th order. For a simple fractal, the fractal dimension is independent of *q* and therefore represented by a single point $f(\alpha) = \alpha = D$ on the $f(\alpha)$ spectrum.

Lacunarity. The lacunarity (λ) is referred in morphological analysis as gappiness, visual texture, in-homogeneity/heterogeneity, translational and rotational invariance, *etc.* Lacunarity reported here represent measures of λ based on data gathered during overlapping scans (sliding box lacunarity) [40]. Lacunarity λ is generally based on the pixel distribution for an image, which we get from scans at different box sizes at different grid orientations, so that because $\lambda \sim \varepsilon$, there are many lacunarity values λ .

$$\lambda_{\varepsilon,g} = \left[\frac{\sigma}{\mu}\right]_{\varepsilon,g}^2 \tag{4}$$

where σ is the standard deviation and μ is the mean for pixels per box at this size, ε , in a box count at this orientation, g. A completely homogeneous image will not vary in the pixels per box, so that the standard deviation, σ , for a box count at some ε will be 0. This means that $\lambda = 1 + (\sigma/\mu)^2 = 1$. A completely homogeneous image has a slope of 1, corresponding intuitively to the idea of no rotational or translational invariance and no gaps. The slope can be determined from the ln–ln regression line of λ over all ε , $[\ln(\lambda)/\ln(\varepsilon)]$. Also, in this approach a mass fractal dimension $D_{\rm MF}$ is calculated as: $D_{\rm MF} = 3 - (s/2)$, where $s = {\rm slope}[\ln \sum I/\ln \varepsilon]$ and for intensity I at (ij) position for $\varepsilon = (\max - \min) \times {\rm size}^2$.

3. Results and discussion

The reaction was found to proceed through complex consecutive/parallel reaction network. The reaction pathway, as presented in Fig. 2, involves the formation of compound (**2**) (with selectivity nearly 94%) and two impurities (A, B) as result of further hydrogenation of product compound (**2**).

Typical concentration-time plots showing the course of hydrogenation of compound (1) over investigated supported noble metals are previously presented [1]. Catalyst activity and selectivity were two main criteria in the catalyst selection for the compound (2) production. Selectivity of various catalysts for hydrogenation of (1) was expressed as content of compound (2) and content of impurities A and B in reaction mixture in the moment when reaction was completed. Impurity B is most difficult to eliminate by crystallization and re-crystallization processes. At the end of reaction, it should not be present in reaction mixture in content above 2.8×10^{-4} mol dm⁻³. Also, the content of impurity A should



Fig. 2. Reaction pathway scheme.

Table 1Nitrogen adsorption isotherm parameters of the 5% Pt/C catalysts.

Catalyst	Single point surface area $(m^2/g)^a$	BET surface area (m ² /g)	Langmuir surface area (m²/g)	Pore volume (cm ³ /g) ^b	Pore size (nm) ^c
K1	758	753 ± 30	1127 ± 19	0.385	2.044
K2	763	757 ± 30	1132 ± 20	0.387	2.047
K3	764	761 ± 24	1148 ± 31	0.388	2.039
K4	803	796 ± 31	1190 ± 21	0.407	2.048

^a Single point surface area at $p/p_0 = 0.3$.

^b Single point adsorption total pore volume of pores less than 2.72 nm diameter at $p/p_0 = 0.3$.

^c Adsorption average pore width (4 V/A by BET).

be below 1.0×10^{-3} mol dm⁻³. The rate of a catalytic reaction is modeled by fitting empirical equations, such as power laws, to experimental data to describe its dependence on concentration and time and to determine rate constants [46]. The chemical kinetics at catalyst is not spatially homogeneous as it occurs on fractallike surfaces [47]. Under these conditions, the conventional rate law exhibits a characteristic reduction of the rate constant with time. The rate coefficient k is time dependent and is related to the classical rate constant k_1 , by $k = k_1 \times t^{-n}$, where *n* is fractal kinetics exponent. In 3D homogeneous space, n = 0, and thus k is a constant. For a typical fractal system n has a value near one third [47]. The geometry of the environment on which the catalytic reaction takes place is a crucial parameter in determining the reaction rate. The heterogeneous catalytic reaction rate and selectivity are inseparably determined by the details of the chemical nature involved and by the geometry of the environment in which the catalytic process takes place [48]. The catalytic surface is usually irregular, convoluted and fractured and there are considerable effects, especially when the kinetic order is fractional [49]. The effect of the interface fractality on catalytic reactions has been investigated by Avnir [24]. Fractals have been used to describe the morphology of the pore network of certain porous catalysts [50,51] and also the distribution of metal particles deposited on an inert surface that resulted in superior catalytic properties [52] (Table 1).

3.1. The surface fractal dimension

The surface fractal dimension *D* was calculated from the plots of the nitrogen quantity adsorbed (cm³/g STP) (ordinate) *vs.* relative pressure (p_0/p) using the fractal isotherm equations derived from the Frenkel–Halsay–Hill (FHH) theory (Table 2). It has been found that for K1, K2 and K4 catalyst samples, the $D_{F,ads}$ values evaluated using fractal FHH equation were nearly constant (2.8) despite large differences of the BET surface area and pore volume. The most active and selective (with the highest reaction rate for production of compound (**2**), and with the least impurities level) is the catalyst K3, and the worst case is the catalyst K4. This most active and selective catalyst has an intermediate fractal surface dimension, $D_{F,ads} = 2.77$, and the worst catalyst is represented by almost smooth surface with a high D_{Frads} = 2.82. However, it must be realized that different methods can lead to quiet different fractal dimensions. The fractal dimensions *D* obtained from pore-size distribution (gas adsorption) analysis is not the same as the surface fractal dimension (SEM images). Different types of the fractal dimension can be used to describe very diverse objects according to the property of interest (*i.e.* mass, pore, surface, and edge).

3.2. Morphology

The Pt/C catalyst consists of particles exhibiting the shape of the carbon precursor. Platinum catalyst is incorporated in a porous surface (Figs. 3 and 4, Table 3). Higher magnifications reveal that the larger-scaled particles are made up of smaller platinum structures with sizes of about 10–80 nm. The Pt/C catalysts consist of platinum catalytic centers integrated into a carbon matrix.

3.3. Fractal analysis approaches

Fractal dimension values were computed for the microscopic fine-sized texture in the SEM images of catalysts particles by the mono- and the multi-fractal approaches. Additional results can be found in the Supplement.

3.3.1. Modified box counting method

The terms of the fractal analysis by the modified box counting method show a gradual increase (D[B+BW]) or decrease (D[W+BW]) or bell-like shape D[BW] in the fractal dimension of the surface with changing the threshold, reflecting the disappearance of small features. This behavior is known and can be described

Table 2
Fractal adsorption dimensions D _{F,ads} of the 5%Pt/C catalysts estimated from the plot
of the nitrogen quantity adsorbed (cm ³ /g STP) (ordinate) vs. relative pressure (p_0/p

Catalyst	Fractal dimension D _F , _{ads}	Constant, κ (cm ³ /g STP)	R^2
K1	2.812 ± 0.01	259 ± 2	0.992
K2	2.820 ± 0.006	260 ± 1	0.997
К3	2.769 ± 0.003	262 ± 1	0.999
K4	2.825 ± 0.006	273 ± 1	0.997



Fig. 3. Overlay of the SEM image and the Pt and map (magnification $1500\times$, image sizes $88 \mu m \times 66 \mu m$); (a) K1, (b) K2, (c) K3, (d) K4.



Fig. 4. Overlay of the SEM image and the added Pt and carbon (C) maps (magnification 1500×, image sizes 88 μ m × 66 μ m); (a) K1, (b) K2, (c) K3, (d) K4.



Table 3

Optical microscopy, silicon oil (at magnification $10\times$) and SEM images (at magnification $2000\times$).



in more general terms as fractal coarsening of the surface. The descriptive statistics relating to the distribution of fractal indices are shown in Table 4, and Tables S1–S4. The most active and selective (with the highest reaction rate for production of compound (**2**), and with the least impurities level) is the catalyst K3 has the largest value of the "interface" $D[BW]_{n=128}$ and the lowest value of the "classical" box-counting $D[B+BW]_{n=128}$ fractal indices (derived from the SEM images, $1000-2000 \times$ magnification) of the 5% Pt/C catalysts. The worst catalyst K4 is represented by the largest values of the "interface" $D[BW]_{n=128}$ fractal indices (derived from the

Table 4

The "classical" box-counting $D[B+BW]_{n=128}$, the interface $D[BW]_{n=128}$ and the "void" $D[W+BW]_{n=128}$ fractal indices (derived from the SEM images, 2000× magnification) of the 5% Pt/C catalysts.

Catalyst	$D[BW]_{n=128}$	$D[B+BW]_{n=128}$	$D[W+BW]_{n=128}$
K1	1.538 ± 0.02	1.965 ± 0.03	1.664 ± 0.02
K2	1.499 ± 0.01	1.972 ± 0.04	1.627 ± 0.01
К3	1.598 ± 0.03	1.950 ± 0.03	1.737 ± 0.04
K4	1.562 ± 0.02	1.962 ± 0.04	1.683 ± 0.02

SEM images, in the $50-600 \times$ magnification range) of the 5% Pt/C catalysts (Figs. 5–7).

3.3.2. The multifractal formalism

The reaction probability distribution pictures may be transferred into a useful compact form through the multifractal formalism, namely through the generalized dimensions D(q) vs. q (Fig. S1), mass exponent $\tau(q)$ vs. q (Fig. S2) and singularity spectrum $f(\alpha)$ vs. α plots. Figs. 8 and 9 show the multifractal plots $f(\alpha)$ vs. α plots for the Pt/C catalyst surfaces. The effect caused by surface roughness on reaction probability distribution can also be analyzed clearly through the $f(\alpha)$ dispersion of the reaction probability distribution profiles which allows a quantitative evaluation of the degree of reaction probability distribution in-homogeneity (Figs. 8-9, Figs. S3–S9). The $f(\alpha)$ profiles show that the reaction probability distribution is characterized by a wide range of α values, indicating the existence of multi-fractality. The range of α values decreases with decrease in surface roughness. This can be connected to the reaction probability distribution. The surface with higher roughness is found to have much higher position sensitivity than that with less



Fig. 5. Fractal index *D*[*BW*] spectrum *vs.* threshold level, *n* (magnification: 2000×): (●) K1, (△) K2, (●) K3, (■) K4.

roughness. For the surface with less roughness, the greater number of low reaction probability sites would level out the distribution and lower the position distinction. The $f(\alpha)$ figures are asymmetric with respect to α . The key feature is that the curves contract upwardly at high α values indicating that the number of lowest reaction probability sites and the number of large reaction probability sites are not even. The image showing homogeneity is characterized by a symmetrical $f(\alpha)$ spectrum with data points distributed equally around the point f=2. For the case of heterogeneity, strong asymmetry is observed with the curve skewed toward the lower end of the α axis.

The width of the $f(\alpha)$ curve is representative of the state of homogeneity. Namely, the narrower the $f(\alpha)$ curve width, the better the



Fig. 6. Fractal index *D*[*BW*] spectrum *vs.* threshold level, *n* (magnification: 2000×): (●) K1, (△) K2, (●) K3, (■) K4.



Fig. 7. Fractal index D[BW] spectrum vs. threshold level, n (magnification: 2000×): () K_1 , () K_2 , () K_3 , () K_4 .



Fig. 8. The Mandelbrot fractal dimension spectrum $f(\alpha)$ of the K4 5%Pt/C catalyst; SEM images, magnification: $50 \times (\blacksquare, \land), 300 \times (\diamondsuit), 600 \times (\bigcirc), 1000 \times (\divideontimes), 2000 \times (\bigcirc).$

homogeneity. If curve width is described in terms of $\alpha_{max} - \alpha_{min}$ for the range of q exponents investigated, then the results are in the range of 1 (Table 5). In relation to a visual rating of homogeneity, the use of curve width measurements appears to be justified. Examination of the images similarly indicates that heterogeneity may be associated with higher values of the measure, $\alpha_{max} - \alpha_{min}$ and the presence of extreme spectral asymmetry. Again, good agreement between a visual rating of homogeneity and the width of the multifractal spectrum is demonstrated.

3.4. Catalyst activity

3.4.1. The chemical kinetic equation

The general chemical kinetic equations in a complex system can be formally followed by the fractional formation reaction equation or the power-law model, and by the so-called "Weibull function". A simple, integrated version first-order kinetic model (see Supplement) may be used as:

$$C = C_{\max} \times [1 - \exp(-kt)] \tag{5}$$

where C_{max} is the concentration as $t \to \infty$ and k is the rate constant (*i.e.* as defined by the classical Arrhenius equation). Note that k has units of (time)⁻¹ for a first-order rate law; also, k incorporates into it the term DAC_s/LV , where D the diffusion coefficient of the molecule, L the diffusion layer thickness, A the surface area of the solid, V the volume of the medium, C the concentration in the medium and C_s is the concentration of the dissolved solid in the diffusion layer surrounding the solid. This first-order model



Fig. 9. The Mandelbrot fractal dimension spectrum $f(\alpha)$ of the 5%Pt/C catalyst; SEM images, magnification $2000 \times$: K1 (\square), K3 (\land), K2 (\diamondsuit), K4 (\bigcirc).

Magnification (×)	K1		K2		К3		K4	
	$\Delta \alpha$	$\Delta f(\alpha)$	Δα	$\Delta f(\alpha)$	Δα	$\Delta f(\alpha)$	Δα	$\Delta f(\alpha)$
50	1.20 ± 0.12	-1.24 ± 0.46	1.26 ± 0.00	-1.73 ± 0.21	1.17 ± 0.12	-1.08 ± 0.43	1.15 ± 0.17	-1.73 ± 0.39
300	1.02	-0.21	1.51	-1.03	1.75	-0.75	0.93	-1.92
600	1.66	-0.25	1.61	-1.34	1.66	-0.48	1.06	-1.65
1000	1.140	-0.42	1.15	-0.84	1.68	-1.11	1.10	-1.09
2000	1.80	0.29	1.83	0.11	1.37	0.833	1.34	1.02

Table 5 The Mandelbrot fractal dimension spectrum differences $\Delta f(\alpha)$ and $\Delta \alpha$ of the 5%Pt/C catalysts.

adequately explains logarithmically increasing 'conversion–time' (C–t, or C/C_{max}–t) kinetic profiles.

The most challenging feature of common C/C_{max} – t kinetic curves is their asymmetric, sigmoid shape, which is not properly explained by these equations. This sigmoid behavior has been (qualitatively) attributed to various macroscopic events, and is believed to define the initial "induction period".

The general functional form of the power-law model is given by:

$$C = C_{\max} \times [kt^n] \tag{6}$$

where *n* is a parameter whose value can be obtained from curvefitting of the $C/C_{max}-t$ kinetic data. A key drawback of this model is that *n* is often empirical; *i.e.* it has a value which does not satisfy any particular model that has been mathematically derived to-date [53].

The so-called "Weibull function" has a mathematical form which appears to combine first-order kinetic model and power-law model:

$$C = C_{\max} \times [1 - \exp(-kt^n)] \tag{7}$$

However, the use of this model has received criticism because it also employs the 'non-physical' (*i.e.* empirical) fit parameter, *n*. On the other hand, Weibull function, with n=2, 3 or 4, are often referred to as the Avrami–Erofe'ev models in the thermal analysis literature. Weibull function has been called the Johnson–Mehl–Avrami (JMA) model, for instance when it is applied to the crystallizations of pharmaceutical compounds [54]. From the dispersive kinetics literature, it has recently been found that the Weibull function can be obtained from the Kohlrausch–Williams–Watts (KWW) relaxation function or 'stretched exponential', utilizing the concept of "fractal time" [55,56].

3.4.2. The fractional formation reaction equation

The hydrogenation reaction $A \xrightarrow{k} B$ has been described by the formation equation:

$$y = a - [a^{1-n} + kt(n-1)]^{\frac{1}{1-n}}$$
(8)

where *n* is reaction order, *a* the maximum concentration and *k* the rate constant. This equation corresponds to the fractional order rate equation:

$$\frac{dC}{dt} = -kC^n \tag{9}$$

where the half-conversion time is given by the equation:

$$x_{50} = \frac{(a/2)^{1-n} - a^{1-n}}{k(n-1)}$$
(10)

The hydrogenization of compound (1) is a heterogeneous reaction. Before the reaction, the compound (1) must be adsorbed on the catalysts surfaces and then diffuse on the surfaces to a reactive site. Thus the diffusion conditions strongly affect the reaction kinetics. Fractal kinetic analysis has been applied for the kinetics of hydrogenization of (2) precursor. Based on the first-order kinetic, a fractional kinetic model with two parameters (rate coefficient and exponent, reaction order n) has been used. The model fits very well with the experimental data of hydrogenization of (2)precursor under different catalyst morphology. The model exhibits that the morphological change increases the rate coefficient and decreases the fractal exponent at the same time. The fractal surface morphology $D_{F,ads}$ is related to the effective reaction rate. The hydrogenation fractional order formation rate constant is fairly, and the reaction order, n, is strongly related to the fractal indices $D[BW]_{n=128}$, $D[B+BW]_{n=128}$ (Fig. 10) and $D[B+BW]_{n=128}$ of the Pt/C catalysts.



Fig. 10. Effect of the fractal index $D[B+BW]_{n=128}$ of the Pt/C catalysts (magnification 2000×) on the hydrogenation fractional order reaction order, n (a) ($R^2 = 0.994$), and the reaction rate (b) ($R^2 = 0.917$).

3.4.3. The half-order formation equation reaction path fit

The hydrogenation reaction $A \xrightarrow{k} B$ has been described by the formation equation:

$$y = a - \left[\sqrt{akt} - \left[\frac{kt}{2}\right]^2\right]$$
(11)

where the reaction is of half-order, *a* the maximum concentration and *k* the rate constant. This equation corresponds to the half-order rate equation:

$$\frac{dC}{dt} = -k\sqrt{C} \tag{12}$$

where the half-conversion time is given by the equation:

$$x_{50} = \frac{2k\sqrt{a} - k\sqrt{2a}}{k^2}$$
(13)

3.4.4. The Weibull reaction equation

The power law time dependence of the reaction rate which describes adequately the experimental data of many complex systems can appear quite naturally if we introduce in a Weibull function [57]:

$$c_{n,\alpha}(t) = c(0) \exp_{n} \left[-\left(\frac{t}{\tau_{n,\alpha}}\right)^{\alpha} \right] = c(0) \left[1 + (n-1) \left(\frac{t}{\tau_{n,\alpha}}\right)^{\alpha} \right]^{\frac{n}{n-1}}$$
(14)

or, as alternative the cumulative Weibull probability distribution function:

$$y = a \times \left(1 - \exp\left(-\left(\frac{x-b}{c} + (\ln 2)^{1/d}\right)^d \right) \right)$$
(15)

where *a* is the maximum concentration, *b* the reaction center (or 50% conversion), *d* is the kinetic shape, and the reaction window is:

$$y = 2^{1/d} \times c \times (\ln 2 - 2\ln 2 + \ln 3)^{1/d}$$
(16)

The hydrogenation reaction $A \xrightarrow{k} B$ has been described by the Weibull equation, which indicates a first-order process with a time dependent rate coefficient:

$$y = a - \left[1 - \exp\left[\left(-\frac{(t + c(\ln 2)^{1/d}) - x_{50}}{c}\right)^d\right]\right]$$
(17)

where *a* is the maximum concentration, x_{50} is the half-conversion time, and the reaction time window width *W* is given by the Weibull equation constants *c* and *d*:

$$W = 2^{1/d} c (\ln 2)^{1/d} - c (2 \ln 2 - \ln 3)^{1/d}$$
(18)

The "interface" fractal indices $D[BW]_{n=128}$ are related to the Weibull equation reaction time window width $W(R^2 = 0.836)$ and the half-conversion time x_{50} ($R^2 = 0.917$) (Fig. 11). The "classical" box-counting fractal indices $D[B+BW]_{n=128}$ are related to the Weibull equation maximum concentration ($R^2 = 0.833$) and the half-conversion time x_{50} ($R^2 = 0.808$) (Fig. 12). The "void" fractal indices $D[W+BW]_{n=128}$ are related to the Weibull equation maximum concentration ($R^2 = 0.832$) and the half-conversion time x_{50} ($R^2 = 0.785$) and the half-conversion time x_{50} ($R^2 = 0.785$) and the half-conversion time x_{50} ($R^2 = 0.852$) (Fig. 13).

3.4.5. Selectivity and activity of the catalyst

The activity of a catalyst is its ability to increase the rate of a particular reaction. The ability of the catalyst to direct a reaction to yield a particular product is referred to as the selectivity of the catalyst. In order to investigate an optimal condition of activation, the activity and selectivity of four catalysts on compound (1) transformation were tested and the results are summarized in Tables 6–11. Results are discussed using the initial reaction rate (r_0). Remarkable



Fig. 11. Correlation of the interface fractal indices $D[BW]_{n=128}$ (derived from the SEM images, 2000× magnification) and the Weibull equation reaction time window width (\blacksquare) and the half-conversion time x_{50} (\blacklozenge).



Fig. 12. Correlation of the "classical" box-counting fractal indices $D[B+BW]_{n=128}$ (derived from the SEM images, 2000× magnification) and the maximum concentration (\blacksquare) and the half-conversion time x_{50} (\diamondsuit).

reduction in reaction time, improved isolated yields of products and sometimes effects on selectivity. The hydrogenation of compound (1) can be presented by a simplified reaction pathway as shown in Fig. 1. In this study the main by-products before complete conversion of compound (1) were impurities A and B. First of all, from



Fig. 13. Correlation of the "void" fractal indices $D[W+BW]_{n=128}$ (derived from the SEM images, 2000× magnification) and the maximum concentration (\blacksquare) and the half-conversion time x_{50} (\blacklozenge).

Table 6

The fractional formation reaction equation terms on the 5% Pt/C catalyst.

Catalyst	Maximum concentration, $a (mol/m^3)$	Rate constant, k ((mol/m ³)/min)	Reaction order, n	<i>x</i> ₅₀ (min)	R^2
K1	136 ± 7	0.078 ± 0.058	0.618 ± 0.173	51 ± 38	0.989
K2	128 ± 2	0.025 ± 0.004	0.715 ± 0.039	102 ± 29	0.999
K3	132 ± 11	0.440 ± 0.163	0.363 ± 0.134	28 ± 26	0.995
K4	135 ± 7	0.105 ± 0.072	0.578 ± 0.159	46 ± 32	0.992

Table 7

The half-order formation reaction equation terms (±standard error) on the 5% Pt/C catalyst.

Catalyst	Maximum concentration, $a (mol/m^3)$	Rate constant, <i>k</i> ((mol/m ³)/min)	<i>x</i> ₅₀ (min)	R^2
K1	134 ± 5	0.130 ± 0.009	52 ± 2	0.991
K2	121 ± 2	0.063 ± 0.002	103 ± 2	0.996
K3	142 ± 16	0.227 ± 0.040	31 ± 3	0.992
K4	133 ± 5	0.146 ± 0.009	46 ± 2	0.990

Table 8

The reaction Weibull equation terms (\pm standard error) on the 5% Pt/C catalyst.

Catalyst	Maximum concentration, $a (mol/m^3)$	<i>x</i> ₅₀ (min)	Reaction time window width, W(min)	R^2
K1	129 ± 2	57 ± 2	55 ± 1	0.982
K2	129 ± 1	105 ± 2	138 ± 1	0.998
КЗ	136 ± 2	31 ± 2	31 ± 2	0.986
K4	129 ± 1	50 ± 4	49 ± 4	0.996

these graphs the large difference in hydrogenation activity between Pt/C K3 catalyst and other Pt/C catalysts is striking. Using other Pt/C catalysts, after 300 min, only 80% conversion is obtained, while compound (1) is completely converted, within less than 60 min, by using Pt/C K3. The activity of the catalysts was found to decrease in the order: K3>K1 \approx K4>K2. This could be related to the catalyst morphological characteristics. Selectivity can be defined as the amount of desired product obtained per amount of consumed reactant. Selectivity values are only useful if the conversion is also reported. The selectivity is calculated by the following equation:

selectivity(%) =
$$100 \times \frac{C_d}{\sum C_{d+i}}$$
 (19)

where C_d is the molar concentration of compound (2), and $\Sigma C_{d+i} = C_d + C_{impurities}$. The selectivity of the catalyst increased in the

opposite direction, in accordance with the rule, lower activity led to higher selectivity: $K1 > K3 \approx K4 > K2$.

The effects of the catalyst roughness on conversions and product distributions can be determined by the fractal geometry approach. Reactions of the molecules on active sites on the catalyst surface are mediated by the fractal roughness of the catalyst particles. Fractal effects prove to be significant. This is illustrated for the production of (**2**) at various 5%Pt/C catalysts that have similar chemical composition. Fractal geometry can therefore be a useful tool to optimize heterogeneously catalyzed processes. The fractal surface morphology of porous catalysts has an influence on the higher conversions and selectivities for desirable products. The catalyst "interface" fractal index $D[BW]_{n=128}$ (derived from the SEM images, 2000× magnification) has effect on the impurity A (R^2 = 0.719) and impurity B (R^2 = 0.932) rate constants (Fig. 14). The catalyst

Table 9

The reaction zero-order equation terms (±standard error) for impurity A formation at the 5% Pt/C catalysts.

Catalyst	Zero-time concentration (mol/m ³)	Rate constant, k (mol/m ³)/min	Inhibition time (min)	R^2
K1	-0.009 ± 0.008	0.0013 ± 0.0001	7 ± 6	0.985
K2	0.101 ± 0.019	0.0017 ± 0.0001	-60 ± 14	0.972
К3	-0.012 ± 0.027	0.0036 ± 0.0005	3 ± 8	0.975
K4	0.026 ± 0.009	0.0026 ± 0.0001	-10 ± 4	0.990

Table 10

The reaction zero-order equation terms (±standard error) for impurity B formation at the 5% Pt/C Catalysts.

Catalyst	Zero-time concentration (mol/m ³)	Rate constant, k (mol/m ³)/min	Inhibition time (min)	R^2
K1	-0.072 ± 0.013	0.0015 ± 0.0001	48 ± 6	0.965
K2	-0.024 ± 0.002	0.0003 ± 0.0000	80 ± 6	0.990
K3	-0.0047 ± 0.011	0.0022 ± 0.0002	21 ± 3	0.982
K4	-0.039 ± 0.008	0.0017 ± 0.0001	23 ± 4	0.988

Table 11

The lacunarity Λ of the 5%Pt/C catalysts.

Magnification (×)	K1	K2	К3	K4
50	0.12 ± 0.0107	0.08 ± 0.04	0.11 ± 0.01	0.0369 ± 0.01
300	0.46	0.20	0.10	0.03
600	0.20	0.07	0.13	0.05
1000	0.43	0.12	0.09	0.10
2000	0.25	0.18	0.28	0.48



Fig. 14. The catalyst fractal index $D[BW]_{n=128}$ (derived from the SEM images, 2000× magnification) effect on the impurities A (\blacklozenge) and B (\blacksquare) rate constants.



Fig. 15. The catalyst fractal index $D[B+BW]_{n=128}$ (derived from the SEM images, $2000 \times$ magnification) effect on the impurities A (\blacklozenge) and B (\Box) rate constants.

"classical" box-counting fractal index $D[B+BW]_{n=128}$ has effect on the impurity A ($R^2 = 0.786$) and impurity B ($R^2 = 0.828$) rate constants (Fig. 15). The catalyst "void" fractal index $D[W+BW]_{n=128}$ has also effect on the impurity A ($R^2 = 0.764$) and impurity B ($R^2 = 0.870$) rate constants (Fig. 16).

Decrease in the catalytically active surface area results in an equivalent decrease in the reaction yield and efficiency. This is indeed observed for the compound (**2**) formation. Correlation of the adsorption fractal dimension $D_{F,ads}$ (derived from the nitrogen adsorption) and the Weibull kinetic term, the maximum



Fig. 16. The catalyst fractal index $D[W+BW]_{n=128}$ (derived from the SEM images, 2000× magnification) effect on the impurities A (\blacklozenge) and B (\Box) rate constants.



Fig. 17. The catalyst fractal adsorption dimension $D_{F,ads}$ effect on the impurities A (\blacklozenge) and B (\blacksquare) rate constants.

concentration is fair ($R^2 = 0.919$), and with the half-conversion time x_{50} is rather weak. The correlation of the Weibull kinetic terms with the pore size is weaker than with the adsorption fractal dimension $D_{F,ads}$. However, the correlation of impurity rate constants and the adsorption fractal dimensions $D_{F,ads}$ is not strong enough to be significant (Fig. 17). Our findings counter the intuitive expectation for the impurities formation by showing that the conversion rate essentially changed by using fractals for spatial distribution of the catalyst load the active surface and hence the catalyst active surface loading is not related to the conversion rate in the diffusion-limited heterogeneous reaction systems.

3.5. The multifractal formalism

The zero-order reaction rate constants of the impurities A and B formation at the 5% Pt/C catalysts are fairly related to the Mandelbrot fractal dimension spectrum $\Delta f(\alpha)$ terms ($R^2 \approx 0.6$, Fig. 18). The zero-order reaction inhibition time of the impurity A formation at the 5%Pt/C catalysts does not depend on the Mandelbrot fractal dimension spectrum $\Delta f(\alpha)$ term. However, the zero-order reaction inhibition time of the impurity B formation at the 5%Pt/C catalysts strongly depends on the Mandelbrot fractal dimension spectrum $\Delta f(\alpha)$ term ($R^2 = 0.869$, Fig. 19).

The Mandelbrot fractal dimension spectrum difference term $\Delta f(\alpha)$ of the 5%Pt/C catalysts (SEM images, magnification 2000×) can be related to the formation (order 0.5) kinetic equation terms: x 50% formation term (R^2 = 0.719) and to the rate constant (R^2 = 0.817,



Fig. 18. The zero-order reaction rate constants the impurities A (\blacklozenge) and B (\square) formation at the 5%Pt/C catalysts *vs.* the Mandelbrot fractal dimension spectrum $\Delta f(\alpha)$ terms.



Fig. 19. The zero-order reaction inhibition time of the impurities A (\blacklozenge) and B (\Box) formation at the 5%Pt/C catalysts *vs.* the Mandelbrot fractal dimension spectrum $\Delta f(\alpha)$ terms.

Fig. 20). The compound (**2**) maximum concentrations (for the formation (order 0.5) kinetic equation) can also be described by the linear equation (SEM images magnification $2000 \times$, $R^2 = 0.705$):

maximum concentration = $16.758 \times \Delta f(\alpha) + 122.88$ (20)

The Mandelbrot fractal dimension spectrum difference term $\Delta f(\alpha)$ of the 5%Pt/C catalysts (SEM images, magnification 2000×) has effect on the formation (order *n*) kinetic equation rate constant ($R^2 = 0.649$) and reaction order n ($R^2 = 0.790$, Fig. 21).

The compound (**2**) reaction rate constant (for the order *n* formation kinetic equation) can also be described by the linear equation of the Mandelbrot fractal dimension spectrum difference term $\Delta f(\alpha)$ even for the SEM images at 50× magnification (R^2 = 0.853):

rate constant =
$$0.361 \times \Delta f(\alpha) + 0.654$$
 (21)

Also, the half-conversion x_{50} for the order *n* formation kinetic equation is related to the Mandelbrot fractal dimension spectrum difference term $\Delta f(\alpha) (R^2 = 0.726)$.

The Mandelbrot fractal dimension spectrum difference term $\Delta f(\alpha)$ of the 5%Pt/C catalysts (SEM images, magnification 2000×) has an effect on the Weibull reaction kinetic transition center ($R^2 = 0.754$) and width ($R^2 = 0.576$) (Fig. 22). The Mandelbrot fractal dimension spectrum difference term $\Delta f(\alpha)$ has also some effect on the Weibull transition terms c ($R^2 = 0.76$) and no effect on the terms d.



Fig. 20. The Mandelbrot fractal dimension spectrum difference term $\Delta f(\alpha)$ effect on the formation (order 0.5) kinetic equation rate constant of the 5% Pt/C catalysts (SEM images, magnification 2000×).



Fig. 21. The Mandelbrot fractal dimension spectrum difference term $\Delta f(\alpha)$ of the 5%Pt/C catalysts (SEM images, magnification 2000×) effect on the formation (order n) kinetic equation reaction order n.



Fig. 22. The Mandelbrot fractal dimension spectrum difference term $\Delta f(\alpha)$ of the 5%Pt/C catalysts (SEM images, magnification 2000×) effect on the Weibull reaction kinetic transition terms: transition center (\blacksquare) and width (\blacklozenge).

The Mandelbrot fractal dimension spectrum lacunarity term Λ has *just* slight effect on the Weibull function transition *d* term of the 5%Pt/C catalysts (SEM images at magnification 2000×, R^2 = 0.612):

Weibulld term =
$$1.8843 \times \Lambda + 1.1463$$
 (22)



Fig. 23. The catalyst fractal index $D[B+BW]_{n=128}$ (derived from the Pt(La) elemental maps, $1500 \times$ magnification) effect on the Weibull kinetic equation term, the maximum concentration.



Fig. 24. The catalyst fractal index $D[BW]_{n=128}$ (derived from the topographic SEM images, 1500× magnification) effect on the Weibull rate constants, transition center or x_{50} conversion (\blacklozenge) and the c term (\blacksquare).

3.6. Elemental mapping

The Pt/C catalysts consist of platinum catalytic centers integrated into a carbon matrix. The surface of supported metal Pt/C catalysts consists of active metal particles placed on a carbon support. The metal particles are active in a surface reaction whereas the reaction cannot occur on the C support. The spacing between active metal particles strongly influence the kinetics of the reactions proceeding on supported metal catalysts [58]. The fractal dimension D_F carries information about the geometric irregularity of an object, whereas the platinum structural dimension D_{FPt} reflects the relative distribution of the catalytic sites on the surface. Reactions of the molecules on active sites on the catalyst surface are mediated by the fractal roughness of the catalyst particles. For this reason, it is questionable whether a better relative distribution of catalytic centers within the carbon support or the change of the fractal dimension is responsible for the observed structure sensitivity of the reaction kinetics. The latter case would also include optimization effects of the diffusion kinetics within the pores of the pyrolyzed carbon material.

The catalyst "classical" box-counting fractal index $D[B+BW]_{n=128}$ (derived from the platinum elemental maps by the EDS-SEM) has effect on the Weibull function maximum concentration term (R^2 = 0.936) (Fig. 23). The catalyst "interface" fractal index $D[BW]_{n=128}$ (derived from the topographic SEM)



Fig. 25. The catalyst fractal index $D[B+BW]_{n=128}$ (derived from the topographic SEM images, $1500 \times$ magnification) effect on the Weibull rate constants, transition center or x_{50} conversion (\blacklozenge) and the reaction time window width (\blacksquare).

images) has effect on the Weibull rate constants (Fig. 24), transition center or x_{50} conversion ($R^2 = 0.966$), the reaction time window width ($R^2 = 0.909$) and the c terms ($R^2 = 0.983$). The catalyst "classical" box-counting fractal index $D[B+BW]_{n=128}$ (derived from the topographic SEM images) has a strong effect on the Weibull rate constants (Fig. 25), transition center or x_{50} conversion ($R^2 = 0.896$) and the reaction time window width ($R^2 = 0.916$).

4. Conclusions

Exploratory studies were conducted to determine the reaction kinetic for the hydrogenation of compound (1) in the presence of Pt/C catalysts. The progress of the reaction was monitored. Factors affecting the hydrogenation rate of compound (1) in the presence of Pt/C catalysts were studied using reaction kinetic models. A mathematical model to describe the kinetics of the reaction was established and a limited predictive model for the rate constant of the hydrogenation was developed using regression methodology approach. Initially a first order kinetic model was used to describe the hydrogenation of compound (1) and estimate the reaction rate constant. Closer examination of the fit of the first order model indicated the need for a more accurate and kinetic model. Therefore, the data were re-analyzed using the *n*-order kinetic and the Weibull model to describe the hydrogenation of compound (1) by Pt/C catalysts. Results demonstrated that morphology of Pt/C catalysts, derived by the fractal indices significantly (p < 0.05) affected the hydrogenation *n*th-order and rate of the compound (**2**) formation. The dependency of the Weibull model terms on fractal indices was determined. The maximum concentration had a linear dependence on fractal indices D[B+BW] ($R^2 = 0.83$, p < 0.1). The half-conversion time x_{50} by the Weibull model was also morphology dependent, by the interface fractal indices D[BW] ($R^2 = 0.92$, p < 0.05). The reaction time window width W was also morphology dependent, by the interface fractal indices D[BW] ($R^2 = 0.92$, p < 0.05). Thus, a Weibull model produced consistently good fit. However, the maximum concentration and the half-conversion time x_{50} by the Weibull model was weakly morphology dependent, by the multifractal spectrum difference term $\Delta f(\alpha)$. The hydrogenation *n*th-order and rate of the compound (2) formation is just slightly influenced by the multifractal spectrum difference term $\Delta f(\alpha)$.

Several hydrogenation impurity products of compound (2) were determined and the reduction of impurities levels in compound (2) by morphologically different Pt/C catalysts was evident. A (linear) regression model was used to determine the effects of the morphological fractal indices of Pt/C catalysts on the formation rate of the hydrogenation impurities. The interface fractal indices D[BW] have the significant effect on the formation rate of the hydrogenation impurity B ($R^2 = 0.93$, p < 0.05). However, poor regression of the impurity A formation reaction rate constants are observed to the fractal dimensions derived from the porosimetry and SEM images.

In spite of the small differences between the values of the fractal dimension for the 5% Pt/C catalyst samples, all of them show the same trend of the changes in the fractal dimension effect on the reaction kinetic terms. The increase of the values of the fractal dimension of the catalyst samples indicates the roughness enhancement of their surfaces. This has an effect on the reaction kinetic terms. Nevertheless, the results show that optimization of the structure sensitivity by changing the catalyst morphology will provide new interpretations of the structure and function of catalyst centers.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.02.011.

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