Catalysis on a fractal lattice: A model for poisoning

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We investigate the problem of a reaction kinetics scheme on a catalytic surface poisoned by a foreign species. The reaction model we use is a monomer-monomer Langmuir-Hinshelwood scenario. First we present theoretical calculations and Monte Carlo simulations on geometrically disordered lattices such as percolation clusters in Euclidean dimension $d=2$ and in $d=3$. Then, we apply our findings to the problem of poisoning of a catalytic surface. We show that the structural changes on the surface strongly affect the reactivity of the catalysis though the poison is taken to remain inert to the reaction.

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INTRODUCTION AND BACKGROUND

Heterogeneous catalysis is a field of considerable interest for its practical application. In the industrial world, mass production of numerous chemical compounds is achieved using various forms of catalytic recipes. Though catalytically activated processes have been known for a very long time now, there still is a great wealth of phenomenology which is unexplained and remains a challenge for fundamental research. Recently, one of the most active development in the field has been the introduction of statistical physics concepts to describe collective phenomenon taking place on the catalytic substrate such as, wave formation in an excitable media [1] or stochastic processes showing departures from a mean-field description [2,3]. The vision stresses the importance of multiparticle effects, fluctuations, and self-organization effects as opposed to local energetic considerations. The aim of an efficient catalysis is to bring together on a same substrate and at the same place reactants and thus increase the reaction rate as compared to a gaseous phase. A fundamental notion is the existence of "active sites" that reactants can reach and where reaction may occur. It is known that this notion of active sites in a catalyst is not an easy one since real catalytic surfaces are not purely bidimensional and translationally invariant, most of the time they contain defects or preferential directions that can inhibit or on the contrary activate the reaction process [4]. In this paper, we study a model that shows the importance of poisoning by a foreign and inert species. We show on this model, that the concentration of poison does not only reduce in a simple way, the proportion of accessible sites but has a net effect on the reactivity of the remaining active sites. The origin of this effect is found in a topological transition taking place on a surface progressively covered by blocking sites. This is the so-called "percolation transition [5]." The poisoned sites are disconnecting the active sites into independent clusters each of them with a specific behavior depending on the cluster topology. The interpretation of this striking phenomenon is radically different from what has been proposed before to account for macroscopic changes in reactivity observed in nature, when a foreign species is adsorbing on the surface. The idea usually put forward is that an adsorbed foreign species affects the local electronic structure in such a way that a variation in reactivity comes as a consequence. Adsorption of an electropositive element is viewed generally as an activator [6] and an adsorbed electronegative element is currently viewed as an inhibitor [7]. Here, we surely do not claim that the "local" approach is not pertinent but we put emphasis on some simple topological effect that may have been overlooked and that could, in some cases, complete or modify the picture. The model we use here was first introduced by Fichthorn, Gulari, and Ziff [3] (FGZ) in order to demonstrate the influence of fluctuations on a simple bimolecular reaction scheme. The model is certainly simplistic as compared to a real-life catalytic process but is has the advantage to show clearly the possible importance of topological confinement on the active site reactivity. We use an exact solution of this model on an Euclidean lattice [8] in order to extend the solution to a fractal structures. We test the theoretical predictions using Monte Carlo simulations on two-dimensional (2D) and on 3D percolation clusters. These predictions are applied to the problem of the poisoning of a surface by a third species *immobile and inert* to the reaction. A theoretical prediction is given around the percolation concentration. Then, we span the whole poison concentration range and we show how the topological character of this surface percolation problem is reflected on the reaction rate.

THE FGZ MODEL

We have two different species A and B absorbed on the catalytic surface and the reaction scheme follows a Langmuir-Hinshelwood scenario that splits into three phases:

Adsorption

$$A^*+[\,]\rightarrow A\ ,$$

$$B^*+[\,]\rightarrow B\ .$$

Reaction

$$A+B\rightarrow[\,]+[\,]+AB^*\ .$$

Desorption

$$A\rightarrow[\,]+A^*\ ,$$

$$B\rightarrow[\,]+B^*\ .$$

Symbol "$_*$" means a species in the gaseous phase and symbol "[ ]" means a free site on the surface. A particularity of the FGZ model is that we are at such high pressures in A^* and B^*, that no empty site is allowed and each time a reaction takes place, the adsorption mechanism replaces the empty sites by either A or B with the same probability. Clearly, no diffusion of species is introduced in this model. The reaction is taking place between nearest neighbors. The microscopic time scale is the reaction time. The desorption mechanism is controlled by a desorption probability p, per unit time, equal for A and B. Fichthorn, Gulari, and Ziff [3] have shown on simulations that the kinetics of the model is controlled by fluctuations at low desorption rate and exhibits a bistability transition. Moreover, Clément, Leroux-Hugon, and Sander [8] have shown that this model leads to an evolution equation that can be exactly solved on an Euclidean space of dimension d, at steady state. A claim is that the critical dimension of the problem is $d_c=2$ and that above this dimension, one recovers the mean-field results of Redner and Takayatsu [9]. Note that Kapivski [10] and also Flament *et al.* [11] have solved the dynamical aspect. The central result of Ref. [8] is that the catalytic scheme, though reaction limited by construction, is the locus of an effective diffusion phenomenon as the result of a cooperative effects of reaction and adsorption. Therefore, the phenomenology bears strong resemblance with the situation of a bimolecular diffusion-limited reaction of the type $A+B\rightarrow 0$ that has been extensively studied in recent years in transient and/or in steady regime [for reviews on the problem see, for example, Refs. [12] and [13]]. Similarly to this case, the FGZ models exhibits in low Euclidean dimension a self-organization phenomenon called segregation that creates domains of mesoscopic scale containing identical species. This model was solved on finite-sized lattices and it has been shown that a transition, depending on size and space dimension, occurs at low enough desorption rate to a regime where the surface is mostly saturated by one or the other species. This regime is a low reactive regime and is characterized by long periods of complete calm separated by reaction bursts corresponding to the passage of one dominant species coverage to the other [8,14].

EXTENSION TO A FRACTAL LATTICE

Here we propose, as a first step towards the study of poisoning, to extend the result of Euclidean dimensions to fractal structures. The fractal model is a common approach of geometrical disorder. A monomer-monomer model of reaction on a percolation cluster was investigated by Albano [19] to study general scaling properties of an out of equilibrium second order transition. Also study of the Barshad-Gulari-Ziff model on fractals was undertaken by Casties, Mai, and Von Niessen [20] and Albano [21]. The scale invariance property of a fractal set is often attractive for a theorist since it may provide a powerful predictive tool. In the case of real catalysis, from the single crystal surface to the pulverulent metal, nonforgetting the porous structure of zeoliths and metal alloys with complex surface segregation properties (for a review see Ref. [4] and references therein), it is clear that the effective reactive substrate may take a great deal of different geometrical forms. A crucial question is to know whether or not the geometrical aspect has some direct influence on the kinetics. We present here a model for which geometry of the substrate is relevant. More precisely, we will show that the fundamental property to consider here is the *compactness* of a random walk on the reactive substrate. On a fractal structure, the number of distinct sites visited by a random walker is a compact subset of the structure and has some particular scaling properties with time which are controlled by the *spectral dimension.*

A central result of Ref. [8] is that on an Euclidean square lattice of dimension d and with $N=L^d$ sites, if z_i is the local state variable at a site with a vectorial index i, ($z_i=1$ means A and $z_i=-1$ means B) the evolution equation for the correlation function $m_k=\langle z_i z_{i+k}\rangle$ is

$$\frac{dm_k}{dt}=2D\Delta_k m_k-2pm_k-2DQ(p)\Sigma_\alpha\delta_{\alpha,k}+2[2Q(p)+p]\delta_{0,k}\ , \tag{1}$$

where $Q(p)$ is the macroscopic reaction rate, Δ_k is the discrete Laplacian operator, $D=1/2d$ is an effective diffusion constant, α means a nearest neighbor direction, and $\delta_{k,k'}$ is the Kronecker symbol. The closure of the problem is achieved with the reaction rate property:

$$2Q(p)=D\sum_\alpha(1-m_\alpha)\ . \tag{2}$$

The transition parameter for the saturation transition is naturally defined to be

$$\Delta_{AB}=\langle(N_A-N_B)^2\rangle/N^2\ . \tag{3}$$

We have $\Delta_{AB}=(1/N)\Sigma_k m_k$ and using Eq. (1) one shows that a general property at steady state, of Δ_{AB} is

$$N\Delta_{AB}=1+Q(p)/p\ . \tag{4}$$

This relation is obtained by summing the correlation function m_k over all **k** vectors and applying Eq. (1).

Let us now consider a fractal structure of dimension d_f, which is a subset of an Euclidean lattice of dimension d. In Eq. (1), the site dependence is not explicitly shown. In fact, the site dependence of this equation was removed by the averaging procedure over space and realizations since the situation is taken to be translationally invariant. On a fractal substructure, the geometrical disorder of the lattice implies that the site dependence of this equation

should be manifest. Also, the α variable, indicating the nearest neighbor directions, is site dependent. Furthermore, the diffusion constant D should be replaced by a site dependent jumping rate which is the inverse of the number of jumping directions at site i. Therefore, instead of having N coupled equations we have $N(N-1)/2$ equations for the number of (i,j) pairs. At first, let us notice that it is easy to check that the important result of Eq. (4) is formally conserved if we sum twice $\langle z_i z_{i+k} \rangle$ over the sites belonging to the fractal. The only thing is that now we only consider quantities dealing with the fractal sites. Thus we have

$$N_s \Delta_{AB} = 1 + Q(p)/p \ , \tag{5}$$

where N_s is the number of sites belonging to the fractal substructure and $O(p)$ the reaction rate per site belonging to the fractal set. Now, we have this large set of equations on the $\langle z_i z_{i+k} \rangle$ we may expect to restore statistically the site invariance if an average over realizations and also over "fractal disorder," is performed. This is the procedure used by O'Shaugnessy and Procaccia (OP) [15] in the study of the propagator of the diffusion process on a fractal lattice. Thus, an equation for a function of a single *continuous* variable, namely, the *Euclidean distance* r should be obtained. Strictly speaking, the differential equation obtained in the continuum limit is valid only for the envelope of the correlation function. The correlation function $m(r)$ is defined on an effective Euclidean space which has the dimension d of the space embedding the fractal structure, but the elementary volume of reference has the weight of the fractal volume embedded in the Euclidean space, i.e., $d^f r \approx r^{d_f - 1} dr$. In other words, the densities involved here, are mean probabilities per site belonging to the fractal lattice. Following the OP method we generalize Eq. (1) for an infinite isotropic and averaged fractal structure. We obtain for the envelope of the correlation function, $m(r)$, for $r > a$ the following equation:

$$D \Delta_{\mathrm{OP}} m(r) - p m(r) = 0 \ , \tag{6}$$

where Δ_{OP} is the OP diffusion operator [15]

$$\Delta_{\mathrm{OP}} = \frac{1}{r^{d_f - 1}} \frac{\partial}{\partial r} \left[r^{d_f - 1} \left[\frac{r}{a} \right]^{-\theta} \frac{\partial m_r}{\partial r} \right] , \tag{7}$$

where a is the microscopic size (for us $a \equiv 1$). The exponent θ is the *anomalous diffusion* exponent which introduces the spectral dimension d_s, through the relation

$$\theta = 2(d_f/d_s - 1) \ . \tag{8}$$

D is the *local* diffusion constant, which means in our case, the inverse of the average number of nearest neighbors (a possible reaction site is chosen at random among the local available nearest neighbors). Σ_{d_f} is the local reaction surface $\Sigma_{d_f} \approx a^{d_f - 1}$ (in the lattice case, Σ_{d_f} identifies with the average number of nearest neighbor). Equation (6) was solved in Ref. [16] for $r > a$ and we obtain

$$m(r) = A \left[\frac{r}{a} \right]^{\beta u} \frac{K_u[(a/\beta\xi)(r/a)^{\beta}]}{K_u[(a/\beta\xi)]} \ , \tag{9}$$

where $K_u(z)$ is a modified Bessel function, $\beta = d_f/d_s$, $\xi = (D/p)^{1/2}$, and $u = 1 - d_s/2$. We have

$$A = m(a) = \frac{Q\xi}{D\Sigma_{d_f}} \frac{K_u(a/\beta\xi)}{K_{1-u}(a/\beta\xi)} \ . \tag{10}$$

The constant A is determined through the continuity condition $m(a+) \to 1$, which defines Q's value which is shown, in the limit $a/\xi \ll 1$, to be consistent with the continuum limit formulation of equation (2): $Q \approx \nabla m(r)|_{r=a}$. A scaling relation is extracted when the desorption probability verifies $p \ll \exp -[2/(2-d_s)]$. In this case we obtain

$$Q(p) \approx p^u . \tag{11}$$

Therefore, when $p \to 0$, a diverging segregation length shows up in the system with an organization up to the scale

$$\Lambda \approx 1/Q(p) \approx p^{-u} \ . \tag{12}$$

For a finite size lattice, with N_s sites, using Eq. (8) a cross over argument shows that we get to a saturated regime when $\Delta_{AB} \cong 1$, i.e., when

$$p^{d_s/2} N_s = O(1) \ . \tag{13}$$

This way to go from an Euclidean structure to a fractal structure was already applied in a diffusion-limited problem analogous to this one [16]. But at this point an important question arises on the validity of this generalization procedure. It is not proven that the OP procedure is valid for any kind of fractals. It was developed mostly to deal with highly connected ones like Sierpinski gaskets or percolation clusters. A careful analysis was made by Klafter, Zumofen, and Blumen [17] on the validity of the O'Shaugnessy and Procaccia approach. A clear conclusion was drawn stating that this operator describes correctly the diffusion on a fractal structure as long as the distances implied are smaller or equal to the diffusion length. In Ref. [16] Clément, Kopelman, and Sander discuss the relevance of the method to the diffusion limited problem $A + B \to 0$. Using a scaling argument they come to the conclusion that it should be a matter of typical lifetime τ of a particle in the system. This lifetime τ has a natural upper bound in our problem as the inverse of the desorption probability p. The argument is the following: the typical diffusion length is τ^{1/d_w} and the scale of segregation is $\Lambda \approx \tau^{(1-d_s/2)}$. Therefore, when this time is becoming large we have a possible crossover between those scales if the condition $d_f(2/d_s - 1) > 1$ is met. Note that this condition is never fulfilled for a $d = 2$ percolation cluster. But for a $d = 3$ percolation cluster, it is possible and thus a deviation from the predictions could show up. The exact value of τ for the occurrence of this crossover is not predicted and could be very large and not accessible in practice, to computer simulations. Note that in the case of this catalytic process, it is not possible to directly transfer this argument since diffusion is only an effective term in the equation. Nevertheless, we have some confidence in the OP method since that outcome was in good predictive agreements with simulations of

various diffusion limited problems on fractal structures such as percolation clusters [16,18]. Here, we test the theory with the outcome of computer Monte Carlo simulations.

In conclusion, for intermediate desorption rate, a simple scaling behavior dependent on the *spectral dimension* d_s is expected; at much lower desorption rate there is a transition towards saturation. Equation (13) shows that the general behavior depends on the reduced parameter $X = N_s p^{d_s/2}$. Thus, we obtain the following result.

If $X = N_s p^{d_s/2} \gg 1$, we have a *segregated* regime with a reaction rate per site $Q(p)$ independent of N_s:

$$Q(p) \approx p^{1-d_s/2} . \tag{14}$$

If $X = N_s p^{d_s/2} \ll 1$, we have *saturation* of the finite cluster and a fluctuation dominated regime with a size dependent reaction rate per site:

$$Q(p) = N_s p . \tag{15}$$

This prediction is tested numerically on two fractal lattices, i.e., the 2D and the 3D incipient percolation clusters obtained at the critical concentration but with a "cut" at a finite size L, and where cyclic boundary conditions were applied. The interest of 3D, though academic, is that we should test the range of validity of the O'Shaughnessy and Procaccia approximation. In Figs. 1 and 2 we display all the results on an universal plot: $Q(p)N_s p$ is plotted as a function of $X = N_s p^{d_s/2}$. If the theoretical prediction is correct, we should obtain on a log-log scale, a straight line for $X \ll 1$, and a slope -1 for $X \gg 1$. We use in $d = 2$ and 3 the value $d_s = \frac{4}{3}$. We see clearly on the graphs that the two regimes predicted in Eqs. (14) and (15) indeed show up and the slope of the segregated regime is best fitted to the value -1. For the $d = 3$ case, let us remark that we cannot see any significant deviation from the scaling laws predicted by the OP approximation. Going to lower p without getting saturation would have required a tremendous computer power out of the scale of our actual computer means.

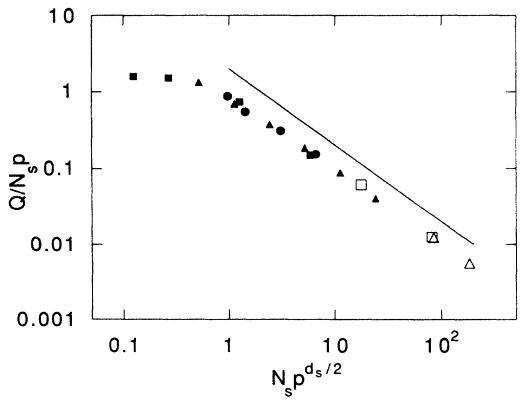

FIG. 1. Scaled reaction rate $Q/N_s p$ versus scaled variable $N_s p^{d_s/2}$ for a 2D incipient percolation cluster: solid squares, $L = 33$; solid triangles, $L = 46$; empty squares, $L = 132$; empty triangles, $L = 20$; solid line, slope -1.

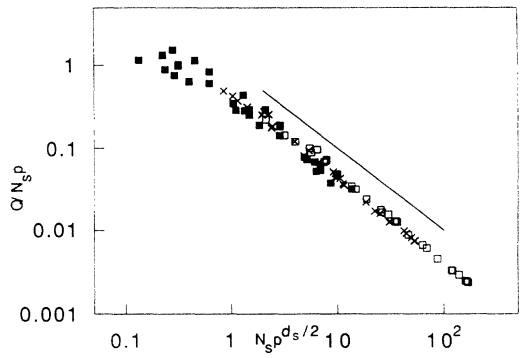

FIG. 2. Scaled reaction rate $Q/N_s p$ versus scaled variable $N_s p^{d_s/2}$ for a 3D-incipient percolation cluster: solid squares $L = 10$, $XL = 20$; empty squares $L = 30$; solid line, slope -1.

Another interesting results is that we keep all the previous result and the universal plot of Figs. 1 and 2 if we formally replace p by $1/t$ (t is time), as long as $\exp[2/(2-d_s)] \ll t \ll 1/p$. This interesting property is a generalization of a property that was proven exact in Ref. [11], for an Euclidean lattice.

Thus, we see that in the steady state and also in the transient regime, results proven to be valid on an Euclidean spaces can be extended on a fractal structures. The Euclidean dimension in then replaced by the spectral dimensional. In another words, fractal structures are interpolating between the two-dimensional case and the one-dimensional case. Note that the spectral dimension is the exponent controlling the number of *distinct* sites visited on a lattice and, therefore, reveals the compactness of the random walk [24]. Anomalies in the reaction rate due to the compactness of random walk in low dimension are now currently identified for most diffusion-limited system [12,13].

POISONING BY AN INERT SPECIES

Now we consider that the catalytic surface was *prepared* by the irreversible random adsorption of an inert and immobile species P. The first effect of poisoning is to reduce the number of active nearest-neighbors an active site may react with. Thus, it reduces the overall reaction rate. The second effect of poisoning is to confine the reacting species on clusters for which the typical linear extension may be smaller than the length of the sample. This introduces the so-called percolation problem (see, for example, Refs. [5,23] for a review). If we denote c to be the concentration of *active* sites, when c in increased we obtain clusters of connected active sites having a larger and larger sizes. In the limit of very large lattice sizes and above a certain concentration c_0, an infinite cluster that connects the edges of the lattice is showing up. This is analogous with a second order phase transition where the order parameter is a connectivity parameter of the network, namely, the probability to belong to this "infinite cluster." Here, we are interested by the consequences of this topological transition on the catalysis. Note that the idea of obtaining an anomalous re-

action kinetics through a percolation confinement is an original idea that was found to be fruitful by Kopelman and his co-workers, but it was worked out in a completely different context (isotopic mixture of naphthalene molecular crystals) [13].

On Fig. 3, $Q_a(c,p)$ the reaction rate *per active site* is plotted as a function of the concentration c and this for a set of four different desorption probabilities. Note that in a mean-field approach, we would get a linear dependence in c for $Q_a(c,p)$ but here we evidence at low p, a sharp drop in the reactivity of the sites when the active site concentration is varied from $c=1$ to 0 and the lower is the probability p, the sharper is the drop. The idea of the following theoretical approach is not to provide exact calculations of the reaction rates but rather to give an intuitive insight in this *a priori* difficult problem using concepts already defined in the previous chapters.

For a lattice occupied by a fraction c of active sites, we can write in general the total reaction rate per site $Q_T(c,p)$ by splitting the lattice into a set of independent clusters. We have

$$Q_T(c,p)=\sum_s n(c,s)Q(p,s)s+P_\infty(c)Q(p,\infty)\ , \tag{16}$$

where, for a concentration c, $n(s,c)$ is the number per site of cluster of size s (s is the number of sites in the cluster), $Q(p,s)$ is the reaction rate per site for a cluster of size s, $P_\infty(c)$ is the probability per site to be on the infinite cluster. An important quantity is the reaction rate per *active* site $Q_a(c,p)$. We have, in general,

$$Q_a(c,p)=\frac{Q_T(c,p)}{c}\ . \tag{17}$$

We remind you that in a classical mean-field approach, the reaction rate per site is the product of concentrations in A and B and, thus, $Q_a(c,p)$ should be independent of p and proportional to c.

Situation at the percolation transition. Now, we consider the *critical percolation concentration* c_0. For an infinite surface, we have a collection of fractal clusters of size s with a distribution $n(c_0,s)$ such that

$$n(c_0,s)\approx s^{-\tau}\ . \tag{18}$$

In the 2D-percolation problem, we have $\tau=2.055\ldots$ and in the 3D-percolation problem we have $\tau=2.1+/-0.1\ldots$. The probability to be on the infinite cluster vanishes at the critical concentration. Now, the sum over cluster sizes is split into two contributions. The small sizes which are saturated and the large sizes which are segregated. An estimate of both contribution is done by considering a cross over size $s^*(p)$ such that

$$s^*(p)p^{d_s/2}=1\ , \tag{19}$$

therefore, the sum of Eq. (16) is split into two parts and we obtain

$$Q_T(c_0,p)=\sum_{s<s^*} n(c_0,s)Q(p,s)s + \sum_{s>s^*} n(c_0,s)Q(p,s)s\ , \tag{20}$$

$$Q_T(c_0,p)\approx \sum_{s<s^*} s^{-\tau}s^2p+\sum_{s>s^*} s^{-\tau}sp^{1-d_s/2}\ . \tag{21}$$

Interestingly, computing these sums shows that both contributions have the *same* weight and we obtain

$$Q_T(c_0,p)\approx p^{1-d_s(3-\tau)/2}\ . \tag{22}$$

The reaction rate shows an exponent modified by the cluster distribution as compared to the infinite cluster. Note that in 2D the value is almost the one of Eq. (14) since $3-\tau\cong 1$. The case of 3D is, of course, academic but is useful as a test for the validity of the theory.

To test Eq. (22), Monte Carlo simulations were performed in two and three Euclidean dimensions. In $d=2$ (respectively, $d=3$), the concentration threshold $c_0\cong 0.59$ (respectively, $c_0\cong 0.313$). To be aware of possible finite size effects leading to saturation, we plot the results using the same universal representation we used before for the percolation clusters. In this case, the scaled variable X is

$$X=N_a p^{d_s(3-\tau)/2}\ , \tag{23}$$

where N_a is that total number of active sites ($N_a=Nc$). On a log-log scale, $Q_a(c_0,p)/N_a$ is plotted as a function of X. Results are presented on Fig. 4 for $d=2$ and on Fig. 5 for $d=3$. In $d=2$, we use the value $\tau=2.055$ and get on a log-log scale a slope equal $-1.0+/-0.02$. In $d=3$ the results for a slope $-1.0+/-0.01$, are best fitted using the value $\tau=2.1$, which is in accordance with the value we found in the literature of $\tau=2.2+/-0.1$ [5]. Thus, Monte Carlo simulations corroborate the theoretical estimation.

Situation above the percolation threshold. For $c>c_0=0.59$, the contribution to the reaction rate $Q_T(c,p)$ from the infinite cluster increases rapidly with c. On Fig. 3, the infinite cluster contribution to the reaction rate is plotted in dashed lines in the case of $p=3.16\times 10^{-04}$.

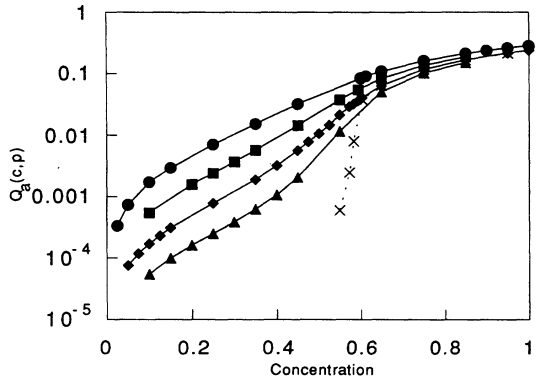

FIG. 3. Reaction rate Q_a versus concentration for a poisoned 2D lattice, $L=500$; solid circles, $p=3.16\times 10^{-3}$; solid squares, $p=10^{-3}$; solid diamonds, $p=3.16\times 10^{-4}$; solid triangles $p=10^{-4}$; crosses, reaction rate per active site of the infinite cluster, $p=3.16\times 10^{-4}$. Full lines and dotted lines are guides to the eyes.

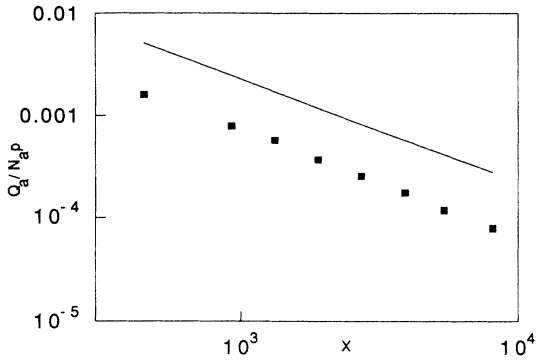

FIG. 4. Scaled reaction rate Q_a/N_ap versus scaled variable $X=N_ap^{d_s(3-\tau)/2}$ for a poisoned 2D lattice at the critical concentration $c_0=0.593$: solid square, $L=500$; solid line, slope -1.

We see that the infinite cluster contribution is already dominant for $c>0.62$. Obviously, on an infinite lattice the distribution of reactants on the infinite percolation cluster is segregated. On Fig. 6 the reaction rate per active site is plotted as a function of the desorption probability p for different active sites concentrations. We see a strong dependence in p, which is a nonclassical feature and an effective slope that decreases with the increasing concentration. We understand this, as the passage from a reaction on a geometrically disordered structure (for larger p and c values which are the closest to the percolation threshold) to an effective bidimensional structure (when the concentration c is the closest to one and p is small enough). In the following we give a tentative interpretation of these raw data using a geometrical picture of the infinite cluster. We assume that the infinite cluster is a fractal structure up to a scale defined by the correlation length ξ, with all scaling behaviors identical to the infinite percolation cluster. The correlation length ξ decreases when c goes to one and we take $\xi\approx(c-c_0)^{-\nu}$. As we have seen before, the reaction kinetics implies a segregation length scale $\Lambda\approx p^{d_s/2-1}$ in the fractal regime and $\Lambda\approx 1/\ln(1/p)$ in a 2D Euclidean regime. We propose to consider a crossover for $\Lambda\equiv\xi$, between a fractal environment and an effective 2D structure when the reaction probability is decreased. This provides a crossover value p^* such that

$$p^*\approx(c-c_0)^{2\nu/(2-d_s)}. \tag{24}$$

Moreover, we propose that for $p\ll p^*$ the reaction kinetics has all the characteristics of a 2D medium with an effective diffusion D_{eff}. This effective diffusion corresponds to the effective diffusion constant of a random walker on an infinite percolation cluster with a finite correlation length, in the long time limit. From Ref. [23] we know that

$$D_{\text{eff}}\approx(c-c_0)^{2\nu/(d_f/d_s-1)}. \tag{25}$$

Thus, we plot the raw data of Fig. 6(a) on a rescaled form in Fig. 6(b). The x axis is the reduced variable p/p^* and the y axis if the reduced reaction rate Q_a/D_{eff}. We observe indeed a data collapse for $p/p^*\leq 0(1)$ indicating that our vision may have some rational. Nevertheless, we are aware of the limits of this tentative reasoning, and to

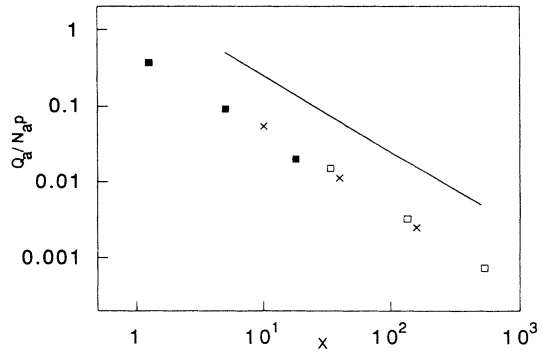

FIG. 5. Scaled reaction rate Q_a/N_ap versus scaled variable $X=N_ap^{d_s(3-\tau)/2}$ for a poisoned 3D lattice at the critical concentration $c_0=0.313$: solid squares, $L=10$, $XL=20$; empty squares, $L=30$; solid line, slope -1.

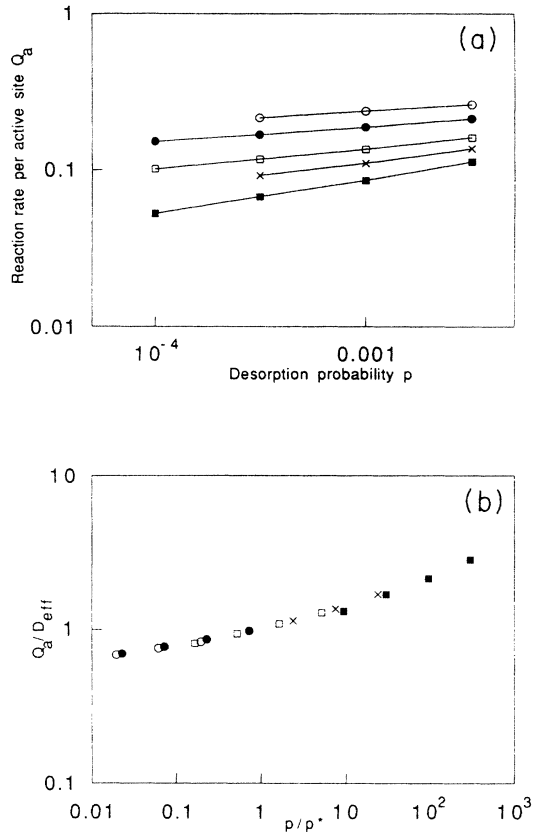

FIG. 6. Reaction rate Q_a for a poisoned 2D lattice at concentrations higher than c_0: empty circles, $c=0.95$; solid circles, $c=0.85$; empty squares, $c=0.75$, $Xc=0.70$; solid circles, $c=0.65$. (a) Reaction rate versus desorption probability. Full lines are guides to the eyes. (b) Scaled reaction rate versus scaled desorption probability.

really prove it valid, we would need more computer testing and maybe more work on other model structures.

Situation below the percolation threshold. For concentrations below the percolation concentration, the infinite cluster contribution is absent. The total reaction rate per site is the sum over the finite size clusters which are self similar up to a correlation length ξ which corresponds to the size of the largest clusters. The total reaction rate is then

$$Q_T(c,p)=\sum_{s=2}^{s_{\max}} n(c,s)sQ(s,p) . \tag{26}$$

The sum in Eq. (26) runs from $s=2$ because isolated sites do not react, $s_{\max}(c)$ is the largest cluster size. Using the results of the previous sections, we know that for a given value of p, the smallest clusters are in the saturated regime and show low reactivity while the largest clusters show segregation and are more reactive. In the saturated regime we have $Q(p,s)=ps$. At first, let us consider the limiting case where all clusters are saturated, i.e., at the smallest concentrations. In this case, the reaction rate per active site is

$$Q_a(c,p)=\frac{p}{c}\sum_{s=2}^{s_{\max}} s^2 n(c,s) . \tag{27}$$

In this limit, the distribution of cluster sizes can be evaluated exactly using the so-called "lattice animal expansion [5–22]." This calculation was performed by different authors for a square lattice. Using the polynomial tabulation of $n(c,s)$ given by Sykes and Glen [22] and letting it run the sum up to a large cluster size ($s_{\max}=15$), we evaluate the concentration dependence of the reaction rate. We fit the results and we obtained a limiting behavior for the reaction rate per active site:

$$Q_a(c,p)\approx pc^{\phi} , \tag{28}$$

with $\phi\cong 1.06$. On Fig. 7 we display $Q_a(c,p)/pc$ as a function of c on a log-log scale in order to evidence clearly the behavior below the percolation concentration. We see that for different values of p, all curves tend to collapse on the same curve when c goes to zero. Using a dashed line, we plotted the limiting theoretical estimation of Eq. (27) using the Sykes and Glen [22] polynomial calculation.

When c is increased, there are more and more clusters which size becomes larger than a crossover value $s^*(c,p)$ defining the passage from a saturated regime to a segregated regime. Equation (19) defines this crossover in the critical region, i.e., in a region where the percolation critical scaling behavior can be observed. As seen previously, the critical region corresponds to the region where the reactive weight of the saturated clusters is the same as the segregated clusters and thus a region defining a passage from a saturated reaction kinetics to a segregated reaction kinetics.

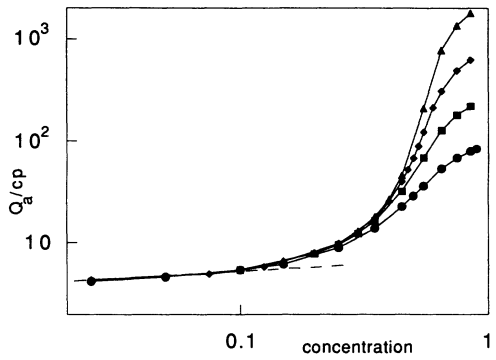

FIG. 7. Reduced reaction rate Q_a/cp versus concentration for a poisoned 2D lattice $L=500$: solid circles, $p=3.16\times10^{-3}$; solid squares, $p=10^{-3}$; solid diamonds, $p=3.16\times10^{-4}$; solid triangles, $p=10^{-4}$; solid line, "lattice animal" formula (5) extracted from Ref. [22]. Full lines are guides to the eyes and the dashed line is the lattice animal expansion.

CONCLUSION

In this paper, we extended the FGZ kinetic model to fractal structures like percolation clusters using the O'Shaugnessy-Procaccia prescription. We present a scaling argument validating the use of this approach for 2D percolation clusters. Furthermore, the theoretical predictions were tested by Monte Carlo simulations in 2D and 3D and the use of the prescription was validated *a posteriori* (at least in the limit of the numerical check). We show that a transition from a segregated state to a saturated state is present when the desorption probability is decreased just like in Euclidean dimensions $d=2$ and 1. The segregated state kinetics is controlled by the spectral dimension of the reactive substrate and thus a fractal structure interpolates between one and two Euclidean dimensions. As an application to a catalytic problem, we show on this simple kinetic model, that an inert poison distribution on a surface strongly influences the reaction rate. When the concentration of remaining active sites is spanned from zero to one on an infinite lattice, simulations show a transition from a saturated to a segregated regime with a reaction rate, in any case, much lower than what is predicted by a mean-field classical approach. The critical percolation corresponds to the onset of this transition. In the critical percolation region the reaction rate scaling is estimated and compares rather well with the result of 2D and 3D Monte Carlo simulations. From this very simple catalytic scheme, we suggest that in real catalysis such a reactive transition due to the topology of the connected active sites, could be observed or at least could lead to some reinterpretations of experimental measurements.

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