Heterogeneous Reactions Over Fractal Surfaces: A Multifractal Scaling Analysis

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ABSTRACT

Monte Carlo simulations of Eley–Rideal (ER) mechanisms with fixed and varying sticking probabilities, \( p \), as well as a three-step catalytic reaction (TCR) over fractal surfaces were performed to examine the morphological effect on the above-mentioned reactions. The effect of decay and enhancing profiles on the reaction probability distribution (RPD) for the ER reaction as well as effects of a varying probability of reaction steps on the normalized selectivity distribution (NSD) for the three-step reaction were then analyzed by multifractal scaling techniques. For ER with a fixed sticking probability, a small \( p \) value tends to yield homogeneous RPD. For ER with a varying sticking probability, the RPD is revealed to be spatially uniform at fast decay and rather concentrated at a faster enhancing rate. For the three-step reaction, a large dimerization/isomerization ratio increases the position distinction among active sites as the adsorption probability equals 1. At a small adsorption probability, the dimerization/isomerization ratio causes no effect on the NSD. Heterogeneity of surfaces as reflected in the multifractal analysis will also be discussed. © 1997 John Wiley & Sons, Inc.

Introduction

Owing to the realization that many of the sophisticated geometrical structures are fractal-like, the fractal theory has provided an appropriate approach to the study of chemical and physical processes taking place in a complicated environment. On applying a fractal approach to the heterogeneous physical and chemical processes, some interesting phenomena were found to require not one but an infinite number of exponents for their descriptions. Such multifractal phenomena reflect the heterogeneity of the surface

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and materials and have recently become an extremely active area of investigation [1].

The main contribution of fractal and multifractal analysis to those heterogeneous phenomena is to provide an appropriate and convenient way for the quantitative treatment of the effects caused by the complex structure and morphologies on the chemical and physical processes in those environments. For catalysis, beyond extracting a few useful parameters from plentiful data, the fractal approach also allows the development of predictive theories for transport and reaction rates. Using fractal geometries to provide concepts for designing optimal catalytic structures has simply just begun.

The surface heterogeneity is a consequence of the multiplicity of exposed crystallographic faces, structural defects, and the presence of chemisorbed impurities [2]. In practice, most surfaces are both geometrical and chemical heterogeneities. Needless to say, both kinds of disorder can be related and the difference between them may be purely conceptual. However, the study of the effects of both complex geometries and chemical heterogeneities separately should provide insight into the physical and chemical behavior of these surfaces [3, 4]. On the other hand, computer simulation results indicated that it is a powerful and successful tool in this field and, indeed, could qualitatively identify the important trends, although it is difficult to mimic in full a real process.

In what follows, the analysis of the reaction probability distribution (RPD) and the normalized selectivity distribution (NSD) over fractal surfaces were taken as examples to illustrate how the multifractal analysis permits the characterization of complex phenomena in a fully quantitative fashion, from which the high sensitivity of reaction to structure may be manifested. It is noteworthy that the structures used here are geometrically heterogeneous but energetically homogeneous. This article is composed as follows: Methods of simulation and multifractal scaling analysis (MSA) are briefly stated in the second section. Results are presented and discussed in the third section. Conclusions are given in the fourth section.

### Methods and Models

**MULTIFRACTAL APPROACH TO REACTIONS**

Multifractal analysis is useful to study processes in environments of complex geometry and it may help to extract fractal characteristics from the RPD [5–10] or NSD [11] through the scaling function, \( \tau(q) \), and dispersion relation, \( f(\alpha) \). Here, we briefly state the essence of the multifractal formalism used in our analysis. MSA is composed of three governing equations [1, 6, 12, 13]:

\[
M_q = \sum_i P_i^q = \sum_P n(P) P^q \sim L^{-\tau(q)},
\]

\[
\tau(q) = q\alpha(q) - f(\alpha),
\]

\[
\frac{d}{dq} \ln \tau(q) = \alpha(q),
\]

in which \( M_q \) is the \( q \)-th order moment of the RPD or NSD; \( \tau(q) \), the scaling exponent; \( P_i \), the probability of site \( i \); \( n(P) \), the number of sites with probability \( P \), and \( L \), the linear size of the fractal object, i.e., the average radius of the cluster. Among these three equations, Eq. (2) is obtained by the following scaling assumptions used in the limiting case of large \( L \):

\[
P(q) \propto L^{-a},
\]

\[
n[P(q)] \propto L^{f(\alpha)},
\]

in which \( P(q) \) denotes the value of \( P \) that dominates the sum of Eq. (1) for the \( q \)-th order moment. Substitutions of Eqs. (4) and (5) into Eq. (1) and taking the logarithm of the maximum elements as an approximation of the logarithm of the sum yields Eq. (2). Finally, Eq. (3) represents the value of \( \alpha \) that dominates the summation term in Eq. (1); it can be transformed into the explicit form

\[
\frac{d}{dq} \ln \tau(q) = \frac{\sum_i P_i^q \ln(P_i)}{\sum_i P_i^q \ln(1/L)}.
\]

The quantities \( \tau(q) \), \( \alpha(q) \), and \( f(\alpha) \) are computed as follows: The probability distribution is first determined from the simulations. Then, for each \( L \), \( \tau(q) \) is obtained from Eq. (1) by first calculating the proportional constant with the condition of \( \tau(0) = D \), where \( D \) is the fractal dimension of the fractal object. \( \alpha(q) \) is then computed from Eq. (6). Having \( \tau \) and \( \alpha \) in hand, one can compute \( f(\alpha) \) from Eq. (2). The distribution of measure \( P_i \) is called multifractal if all moments [Eq. (1)] scale as power laws, with an infinite set of independent exponents \( \tau(q) \).

The multifractal formalism has been successful in describing many phenomena of current interest to physicists and chemists [1]. However, some
warnings have been suggested concerning its applicability to real systems [14]. One problem is concerned with the difficult to accurately obtain the negative moments of the measures, which are dominated by the small probabilities. Since these rare measures are often missed in the counting process, large fluctuations are frequently observed for \( q < 0 \). On the other hand, it is often obtained by averaging over many fractals; thus, a numerical simulation may yield different results depending on the average used. Moreover, the assumption, used in multifractal formalism, that all the probabilities scale as powers of the size may be wrong for the very small probabilities. Therefore, the behavior of \( f(\alpha) \) for large \( \alpha \) and \( \tau(q) \) for \( q < 0 \), which relies critically on the size dependence of these rare events, should be interpreted with great care.

### THE FRACTAL OBJECTS

The fractal objects used in this study were generated on a square lattice by a modified version of the Witten–Sander model in which the particles were released one at a time from an equal-event boundary, i.e., a diamond-shaped boundary [15, 16]. The movement of the released particle on the grid was monitored by Monte Carlo techniques under the influence of a certain drift. In this work, clusters with fractal dimensionality equal to \( D = 1.72 \) (see Fig. 1) were used and cluster sizes were chosen to be \( 3 \times 10^3, 6 \times 10^3 \), and \( 10^4 \). Note that the cluster with \( D = 1.72 \) is the so-called diffusion-limited aggregate (DLA) [17].

### RPD GENERATION

Reaction probabilities, \( P_i \), for all surface sites were determined by Monte Carlo simulations of the motion of the random walkers released from an equal-event boundary. Particles are released one at a time and it them undergoes a random walk until it either reaches the surface site of the fractal cluster or it moves out of the outer perimeter. When this random-walking particle comes onto a site occupied by the fractal, it gets adsorbed with probability \( p_i \), which is given by various forms and will be defined later. The acceptance/reject check can be achieved by generating a random number when the particle visits the fractal site and checking whether it is less than \( p_i \). If it is less than \( p_i \), then the reaction counts on that surface site are added by one or the particle continues its random walk (with probability \( 1 - p_i \)).

In this presentation, the effects of fixed and varying sticking probability on the RPD were probed. For the former, two values, \( p_i = 1.0 \) and \( p_i = 0.01 \) were used, while for the latter, a decay function, defined as \( P(n_i) = P_{ini} \exp(-n_i/m) \), and an enhancing function,

\[
P(n_i) = P_{ini} + \frac{n_i b}{1 + n_i b'},
\]

were adopted, where \( P_{ini} \) is the initial sticking probability for every site, \( n_i \) represents reaction counts over active sites \( i \), and both \( m \) and \( b \) are tuning factors to adjust the rate of decaying and enhancing, respectively. According to the definition of an enhancing function, one further comment should be added: The enhancing function \( P(n_i) \) might reach 1 at a finite value of \( n_i \), and in simulation, once exceeding 1, it would be regarded as 1.

Recall that in the multifractal formalism a scaling assumption is made for the moments of the distribution [Eq. (1)], namely, at the limit of large \( L \) values, the \( \tau(q) \) curve should converge to a unique \( L \)-dependent curve. To test the scaling assumption, three different cluster sizes, \( 3 \times 10^3 \), \( 6 \times 10^3 \), and \( 10^4 \) sites individually were used. Finally, a noise reduction algorithm (i.e., reaction counts over a certain site are added by one only
after a certain number of reactive collisions are counted on that site) under a fixed sticking probability was used to check the changes of the RPD. For the case of the fixed sticking probability, the results were obtained averaging over 20 runs and every run contains $10^5$ reaction events.

**NSD GENERATION**

A typical three-step reaction considered here is given by

$$A + S \xrightarrow{p_1} A_a,$$  \hspace{1cm} (7)

$$A_a \xrightarrow{k_1} B,$$  \hspace{1cm} (8)

$$A + A_a \xrightarrow{p_2} C,$$  \hspace{1cm} (9)

in which $A$ and $A_a$ are reacting particles and its adsorbed state; $S$, the surface sites of fractal objects; and $B$ and $C$, products. Reaction (7) represents the adsorption of reacting molecule $A$ onto the surface of catalyst $S$ with adsorption probability $p_1$. Reactions (8) and (9) represent a unimolecular and a bimolecular process, respectively, and in a real catalytic system, these might correspond individually to isomerization and dimerization. $k_1$ and $p_2$ are the rate coefficient and reaction probability, respectively. The selectivity is defined as the ratio of the number of $C$ molecules to that of $B$ molecules produced. This system was investigated by Meakin [18] on the DLA and percolating clusters with both $p_1$ and $p_2$ equal to 1.0 and by Tambe et al. [19] on the DLA surface focusing mainly on the relationship among macroscopic average selectivity, probability of reaction steps, and rate coefficient.

For applying the multifractal analysis to study the behavior of catalytic selectivity, the spatial distributions of selectivity, $P_i$, are defined as the normalized selectivity:

$$\frac{S_i}{\sum_i S_i'},$$  \hspace{1cm} (10)

in which $S_i$ is the selectivity of surface site $i$. The value of $S_i$ was determined by Monte Carlo simulations in which the particle ($A$ molecule) was released from outside the region occupied by the fractal and followed a random walk trajectory on the lattice. If this particle reached on unoccupied site adjacent to the cluster, then reaction (7) would occur with a probability $p_1$ or continue to diffuse with probability $1 - p_1$. Once reaction (7) took place, reaction (8) followed and the number of $B$ molecules, $N_B$, was incremented by $k_1 N_A$, in which $k_1$ represents the rate coefficient for reaction (8) and $N_A$ denotes the number of adsorbed $A$ molecules. When the increment $N_B$ exceeded integer one, a randomly chosen adsorbed $A$ site was converted into a $B$ molecule.

If a randomly moving $A$ particle visited an already occupied surface site, then it either dimerized with probability $p_3$ or continued to walk with probability $1 - p_3$. If the reaction occurred, then $C$ molecules, $N_C$, were produced and a randomly chosen adsorbed $A$ surface site was vacated. Neither $B$ nor $C$ molecules are allowed to occupy a surface site.

If this random walk resulted in any reaction (7) and (9), it is considered successful and the same procedure as outlined above is repeated. The selectivity is then determined for each surface site at which both $B$ and $C$ molecules are produced. If a moving particle traveled far from the cluster, the trial is discarded and a new $A$ particle is released. In our simulations, the reacting $A$ particles were launched in a sufficient number that the steady state was achieved, i.e., as a nearly constant selectivity value was obtained, $10^6$ successful random walk trajectories were used for further analysis.

**Results and Discussion**

**MSA OF THE RPD FOR THE ELEY-RIDEAL (ER) MECHANISM**

In a steady-state regime, the reaction rate at each active site is proportional to the active site reaction probability. This property is measured in our case by two-dimensional random walk simulations of particles diffusing to the surface. In what follows, discussions were divided into two parts involving cases with a fixed and varying sticking probability, respectively.

**ER DLR with Sticking Probability $P = 1.0$ and .01**

When the probability of reaction of a fractal set with diffusing particles is measured, RPD curves for the fractal object are obtained. A typical result shown in Figure 2 was taken as an example from the simulation of the ER diffusion-limited reaction mechanism on a DLA with $D = 1.72$. It can be seen in Figure 2 that the number of low reaction probability sites gradually increases as the size of the DLA increases. The RPD pictures may be
transferred into a useful compact form through the multifractal formalism, namely, through the \( \tau(q) \) and \( f(\alpha) \) plots. In Figure 2(d), \( \tau(q) \) is plotted against \( q \) for the above RPD profiles. As can be seen in Figure 2(d), deviation from linearity indicates multifractality, representing that simple single-valued fractal scaling does not apply in this condition. The difference among three different sizes can also be observed in the parts of high negative \( q \) values and it shows a bigger deviation from a full superposition of the \( \tau(q) \) curve as the radius increases. This result can be interpreted by the fact that the number of active sites with lowest reacting probability, which dominates the sum in Eq. (1) at the large negative \( q \) region, are quite different for the DLA of different sizes.

Another important feature in Figure 2(d) is the curve curvature, which implies the degree of heterogeneity and is also quite different for three sizes. The trend is for the smaller DLA cluster used to have a greater curvature in the \( \tau(q) \) curve. These results agreed with RPD profiles for different sizes, i.e., inhogeneity in the RPD increases as the DLA size decreases, and can also be analyzed through the \( f(\alpha) \) dispersion of the RPD profiles, which allows a quantitative evaluation of the degree of the RPD inhomogeneity: High nonlinearity of the \( \tau(q) \) curves is translated into wider distribution in the \( f(\alpha) \) plots, i.e., the range of the \( \alpha \) value decreases as the cluster radius increases, as shown in Figure 2(e). As demonstrated in Figure 2, the smaller size of the DLA leads to a much
higher position sensitivity than that of the bigger one. For a larger DLA, a great number of low reaction probability sites would level out the distribution and thus lower the position distinction. This result may also be explained by the relation between the \( f(\alpha) \) values at extremes of \( \alpha \) and cluster sizes; as the cluster size becomes larger, the right extreme \( f(\alpha) \) value becomes larger and the left smaller. This implies that as cluster size increases the low reaction probability part is associated with larger sets (with larger fractal dimension) but the higher reaction probability part is connected to very small sets, and as a result, it produces a relatively homogeneous RPD pattern. Owing to anisotropic screening of the DLAs studied, the RPD profiles observed appear to be asymmetric and the \( f(\alpha) \) figures are also asymmetric with respect to \( \alpha \), in contrast to the symmetric \( f(\alpha) \) profiles of Cantor sets and the Devil’s staircases obtained by Gutfraind et al. [5, 6]. The key feature is that the curve contracts upwardly at a high \( \alpha \) value and the number of lowest reaction probability sites and the number of large reaction probability sites are not even.

Finally, one may observe that the left part of the \( f - \alpha \) plot (\( q > 0 \)) coincides remarkably. This is consistent with the \( \tau - q \) curves, but the \( f - \alpha \) curves seem to scale up the difference. Note that the scaling of the moments of the distribution [Eq. (1)] does not imply the scaling of the singularities of the probability distribution [Eq. (4)] and the scaling behavior of the sets associated with each singularity [Eq. (5)].

According to the multifractal scaling theory, in the limit of infinite large size, the measure can be well characterized by size-independent multifractal functions. But from Figure 2(d) and (e), the multifractal scaling assumption at the limit of high \( L \) values was not achieved and, indeed, one can see that the convergence of multifractal scaling with respect to size is relatively slow compared to the rather fast convergence of the fractal dimension of the object that supports the probability measure.

The ER diffusion-limited reaction mechanism (\( p = 1.0 \)) is a limiting case with zero activation energy, while in real catalytic systems, reactions occurring at active sites of the surface used to have nonzero activation energy. For comparison, another limiting case, \( p = .01 \), was used to check the effects of activation energy on the RPD pictures. Owing to high activation energy, every active site possesses nearly the same adhesive opportunity and, hence, screening effects are almost smoothed out. Finally, a more homogeneous RPD is obtained and is shown in Figure 3(a) and (b).

Similar to the \( p = 1.0 \) case, the above-discussed RPD profiles can also be mapped into the MSA, i.e., the \( \tau - q \) and \( f - \alpha \) plots. As can be seen in Figure 3(c) and (d), even at the low sticking probability, the distribution is still multifractal and implies that the screen effects always exist. Because the RPD for the \( p = .01 \) case is more homogeneous than that for \( p = 1.0 \), the \( \tau - q \) curve is closer to linearity than that for \( p = 1.0 \) and the \( \alpha \) range in \( f(\alpha) \) plot is narrower than that for \( p = 1.0 \).

From the above result, one can conclude that as \( p \) approaches a higher value, the RPD profile should be closely related to multifractal structure and the distinction caused by screening effect among active sites is remarkably evident.

### Autopoisoning Reactions

In this section, we deal with a more general case where an event-dependent sticking probability at each active site was considered. Here, we define sticking probabilities of two types: the decay and enhancing probability for each active site to mimic autopoisoned and autocatalytic reactions that occurred in real systems individually.

For an autopoisoned system, a decay function defined \( P(i) = P_{ini} \exp(-n_i/m) \) for each surface site is used to describe the variation of the sticking probability as the reaction proceeds, in which \( P_{ini} \) is the initial sticking probability, \( n_i \) is the reaction event occurring at active site \( i \), and \( m \) is a parameter used to regulate the decay rate. Accordingly, the two parameters \( P_{ini} \) and \( m \) control the properties of the decay function and, thus, the reaction dynamics. In principle, factors that can accelerate the rate of decay would lead to a more homogeneous RPD profile. The reason is that after some reaction events the sticking probability is decreased quickly to a minute value and the RPD is similar to that of the case of fixed small sticking probability, namely, a nearly uniform RPD. According to the decay function, both lower \( P_{ini} \) and \( m \) values can influence the decay rate and lead to more uniform RPD pictures.

We first verify the effects of \( m \) on the RPD. Basically, a smaller value of \( m \) corresponds to more rapid decay. Simulations were performed with \( P_{ini} = 1.0 \) and \( m = 5, 30, 150, \) and \( 300 \), respectively, after \( 10^5 \) reaction events. The RPD pro-
files were demonstrated in Figure 4(a)–(d) and the corresponding multifractal characteristics were shown in Figure 4(e) and (f). According to Figure 4(e), the $\tau - q$ curves for different $m$ coincide in the range $q < 0$ (lower parts in $\tau - q$ curves), which implies that the number of active sites with a small reaction probability are nearly equal for different $m$, and as $m$ decreases, the curvature of the $\tau - q$ curve also decreases gradually, indicating a relatively homogeneous RPD. The $\tau - q$ curve in Figure 4(e) for $m = 5$ exhibits a nearly linear relationship, representing a homogeneous RPD, and the slope almost equals $D$, implying that the homogeneity was distributed over almost every active site. The effect of more rapid decay on RPD is also reflected from the narrower dispersion and relatively symmetric pattern in $f(\alpha)$ as shown in Figure 4(f).

All results obtained above were analyzed after $10^5$ reaction counts. If the simulations were extended to infinite times, the sticking probability of every active site would approach the same minute value, leading to a homogeneous RPD, and the decay function would become ineffectual. RPD curves obtained for increasing reaction events showed an increased number of active sites and increased homogeneity in the RPD. The rate for a system to reach homogeneous RPD is clearly de-
FIGURE 4. Dependence of the RPD: (a) \( m = 300 \), (b) \( m = 150 \), (c) \( m = 30 \), and (d) \( m = 5 \), and the corresponding multifractal characteristics: (e) \( \tau(q) - q \) curves and (f) \( f(\alpha) - \alpha \) curves on \( m \) parameters for decay-type ER reactions over a \( D = 1.72 \) and \( 3 \times 10^3 \) particle cluster with \( P_{ini} = 1.0 \). The analyses were done after \( 10^5 \) total reaction events.

determined by the ratio of the cluster size to the total reaction events; a smaller cluster size and more numerous reaction events could increase the rate.

**Autocatalytic Reactions**

In simulating autocatalytic systems, an enhancing function defined as 
\[
P(n_i) = P_{ini} + n_i \cdot b/(1 + n_i \cdot b)
\]
is used to follow the variation of attaching probability, in which \( P_{ini} \) and \( n_i \) are defined as above, and \( b \) is used to modulate the enhancement rate. The enhancing function is controlled by two parameters: \( P_{ini} \) and \( b \). While the decay function induces an “averaged” effect, the enhancing function gives in contrast a “biased” effect on the RPD.

The effect of \( b \) values on the RPD was examined by analysis of the RPD profiles obtained from simulations over \( D = 1.72 \) and \( 6 \times 10^3 \) particles in
a cluster with \( P_{\text{ini}} = 0.0 \) and \( b \) equals .0005, .01, and .1 after \( 10^5 \) reaction events. The RPD profiles are presented in Figure 5(a) and multifractal characteristics are presented in Figure 5(b) and (c). In the limiting case \( (P_{\text{ini}} = 0.0) \), the initial choice of sites at which reaction events occur is completely random. However, once a certain active site is selected, the succeeding reaction events are strongly biased to concentrate on those specific sites. According to Figure 5(a), the active sites concentrate at specific points, and as \( b \) increases, the number of active sites decreases due to the more strongly biased effect. Another feature of Figure 5(a) is that no matter how small is the enhancing rate of sticking probability the enhancing effects invariably exist. Although the reaction events are congregated at a few specific points, the RPD is not necessarily homogeneous. However, on closer inspection, the nearly linear \( \tau - q \) curves in Figure 5(b) and in Figure 4(e) are distinct. The slope of the nearly linear curve in Figure 5(b) is much smaller than that in Figure 4(e). Hence, the homogeneity revealed in the case of enhancement [Fig. 5(b)] spans only a few active sites but the homogeneity of the decaying case [Fig. 4(e)] covers a large portion of the fractal surface.

**FIGURE 5.** The reaction probability as a function of the active site position for enhanced type ER reactions over a \( 6 \times 10^3 \) particle and \( D = 1.72 \) cluster with \( P_{\text{ini}} = 0.0 \) and different \( b \) after \( 10^5 \) total reaction events (a), and the corresponding multifractal characteristics: (b) \( \tau(q) - q \) curves, (c) \( f(\alpha) - \alpha \) curves.
As for the relationship between homogeneity and $b$ values, there seems no regularity as shown in Figure 5(b) and (c). Due to the minute initial sticking probability, the choice of active sites for first few reaction events is totally random. If those selected sites are all distributed over the outer region or in the inner region, the RPD profile has more opportunity to become homogeneous; otherwise, it is likely to become heterogeneous.

As mentioned earlier, the total reaction events would affect the RPD. The RPD profiles for $P_{ini} = 0.0$ and $b = 0.01$ have been collected after total reaction events $= 10^5, 2 \times 10^5,$ and $3 \times 10^5$. As the total reaction events increased, there exists a chance to activate more sites in the process and to increase the number of active sites. This number increases only slightly because of the strongly biased effects induced by the enhancing function. The MSA show no clear relation between total reaction events and homogeneity of the RPD.

THE SELECTIVITY BEHAVIOR OF TCR

The results obtained from Monte Carlo simulations involve the initial transient behavior and final steady state. Here, the analyses and discussions focus mainly on the steady-state characteristics of the reaction system involving macroscopic average selectivity behavior and the MSA of the NSD, respectively.

Macroscopic Average Characteristics

In the present study, the effects of varying $p_1$, $p_3$, $k_1$, and the cluster size on the selectivity of reaction products were analyzed. Typical results are presented in Figure 6 for simulation carried out on DLA clusters with different sizes. Also shown are simulation results over a diamond-shaped smooth surface with radii equal to 100 lattice units. According to Figure 6(a), as the probability for reaction (9) increases for a given $p_1$ and $k_1$, there is an enhancement in the selectivity for both smooth and DLA surfaces. It is obvious that higher values of $p_3$ result in the enhanced production of C molecules and increase the selectivity. However, fractal catalysts behave differently from the smooth surface. For the smooth surface, the selectivity is slightly dependent on values of $p_3$, but results of fractal catalysts are consistent with a $p_3$-dependent selectivity of the form $S \propto p_3^g$, and the exponent $g$ has a value of about 0.64 (note the linear degree increases as the cluster size increase). The implication of the above result is that the screening effect induced by the fractal catalyst, enhancing the dependence of selectivity on $p_3$.

![FIGURE 6. Dependence on selectivity on reaction system parameters: (a) selectivity as a function of $p_3$ with $p_1 = 1.0$ and $k_1 = 3 \times 10^{-4}$; (b) selectivity as a function of the rate constant $k_1$ with $p_1 = 1.0$ and $p_3 = 1.0$; (c) selectivity as a function of $p_1$ with $p_3 = 1.0$ and $k_1 = 3 \times 10^{-4}$.](image)
Figure 6(b) shows how the catalyst selectivity depends on the first-order rate-constant \( k_1 \) for simulations over three DLA surfaces with \( p_1 = 1.0 \) and \( p_3 = 1.0 \). It can be easily understood that as the rate constant increases the selectivity drops. The curves in Figure 6(b) might be represented by a straight line, implying that \( S \propto k_1^{-\beta} \), where \( S \) is the selectivity. Exponent \( \beta \) has a value of about 0.89 for fractal catalysts. Note that from a simple mean field analysis [18] the selectivity for a smooth surface should be proportional to \( k_1^{-1} \). The dependence of catalyst selectivity on the rate constant exhibits nonclassical power law behavior that is a direct consequence of the broad distribution of the probabilities that the surface sites in the cluster will be found by random walkers. The screen effect causes the outer regions of the cluster to have a greater opportunity to produce \( C \) molecules than have the inner parts.

Figure 6(c) shows how the mean selectivity depends on the \( p_1 \) values. The mean selectivities were obtained by averaging over simulations on 20 DLA clusters (generated using different sets of random numbers, keeping the same total number of fractal sites). It can be easily seen that as the \( p_1 \) increases the selectivity drops. The decrease is, however, sharp in the initial range and approaches flat gradually. The explanation for the occurrence of such a situation can be given as follows: By an increase in the probability for the first step, the number of sites containing adsorbed \( A \) molecules is increased. However, the first-order and second-order reactions would compete on those adsorbed \( A \) molecules. Because the rate of formation of \( C \) molecules depends both on adsorbed \( A \) and the free particles of \( A \) on the fractal surface and the \( A_s \) increase would decline the free \( A \) molecules concentration, the rate of formation of \( C \) molecules would decrease gradually as \( p_1 \) increase. Contrary to the formation of \( C \) particles, the formation of \( B \) depends solely on the amount of \( A_s \) and an increase in \( p_1 \) enhances the production of \( B \). It is noticed from Figure 6(c) that due to the dependence of \( C \) formation on \( p_1 \), giving a monotonous decrease, the final selectivity plot does not go through a minimum as shown by Tambe et al. [19].

Another interesting feature in Figure 6 is the effect of cluster sizes on selectivity. As can be seen in Figure 6, the smaller is the cluster the higher is the selectivity. The reason might be again attributed to the very broad distribution in the probabilities that particular sites being visited by random walkers launched from the releasing boundary. According to our previous investigation, the position sensitivity of those probabilities become higher as cluster sizes decrease and this leads to the higher rate of production of \( C \) via the bimolecular reaction. It can be concluded that the selectivity increases as the cluster size decreases.

According to above analyses, it was found that the geometry of fractal surfaces plays a key role in the determination of the selectivity behavior. One implication of those results is that the effective order of reactions catalyzed by fractal catalysts may not be integers or a simple rational fraction. To further analyze the sensitivity of selectivity of the multistep catalytic reactions to the catalyst structure, the MSA were carried out on the NSD as described in what follows.

**MSA of the NSD for the TCR**

In the present work, the effects of \( p_1 \) and \( p_3 \) and of cluster sizes on the NSD were examined by MSA. For the effect of cluster sizes on the NSD, simulations were run for \( D = 1.72 \) clusters having \( 3 \times 10^3, 6 \times 10^3, \) and \( 10^4 \) particles with \( p_1 \) and \( p_3 \) equal to 1. To understand the position sensitivity of the selectivity distribution, we first plotted the NSD as a function of the position of active site for three clusters, as shown in Figure 7(a)–(c). Note that even after \( 10^6 \) successful random walk trajectories most surface sites did not produce both \( B \) and \( C \) molecules and selectivity was not defined in these sites as seen by Meakin [18]. This figure demonstrates that the outermost sites of the fractal object have a much greater selectivity because the most exposed tips produce many more bimolecular products than do the inner surface sites which are relatively deeply buried, as indicated by the spike-shaped distribution (for a smooth surface, it should be emphasized that all surface sites possess the same intrinsic selectivity). As the cluster size decreases, the range of normalized selectivity has a wider distribution, showing increases position sensitivity. According to Figure 7(a)–(c), the number of small normalized selectivity sites gradually increases as the cluster size increases.

The NSD pictures may be further analyzed via the multifractal formalism, yielding the \( \tau(q) \) and \( f(\alpha) \) plots. In Figure 7(d) and (e), \( \tau(q) - q \) and \( f(\alpha) - \alpha \) are plotted for the above NSD profiles. Also shown are the multifractal characteristics of the RPD of the ER reaction over a 3000 particle
FIGURE 7. Normalized selectivity as a function of active site position for simulations over a $D = 1.72$ cluster containing (a) $3 \times 10^3$, (b) $6 \times 10^3$, and (c) $10^4$ particles with both $p_1$ and $p_3$ equal to 1.0 and $k_1 = 3 \times 10^{-4}$, and the corresponding multifractal characteristics: (d) $\tau(q) - q$ curves; (e) $f(\alpha) - \alpha$ curves. Also shown are the multifractal characteristics of the RPD of the ER reaction over a $D = 1.72$ and $3 \times 10^3$ particle cluster with and without noise reduction; both cases possess a sticking probability equal to 1.0.

Since this figure is similar to Figure 2, the conclusion can be easily drawn. According to the analysis of cluster-size effects on the RPD, we know that the NSD becomes more homogeneous as the cluster size increases. This behavior is a direct consequence of the distribution of probabilities for surface sites to be found by random walkers in step 1 which can be viewed as an RPD in the ER diffusion-limited reaction over the same cluster. The NSD is expected to be more homogeneous than is the RPD as displayed in Figure 7(d) in which the NSD is less nonlinear than is the RPD. This fact can also be reflected from the wider range of $\alpha$ for the RPD than that of the NSD in Figure 7(e). The reason can be explored following our understanding of the noise-reduction effects on the RPD; with noise reduction, the RPD becomes more homogeneous or uniform because surface sites with a small reaction probability are eliminated and there is no effect on the highly reactive probability parts. As a site possessing distinct selectivity must be visited frequently by the reacting particles (both $B$ and $C$ molecules must be produced), the NSD for a TSC is similar to the RPD of the ER reaction under a white noise and it
may have a narrower $\alpha$ range than has the RPD [Fig. 7(e)].

As pointed out earlier, there is a broad distribution of probabilities for surface sites visited by random walkers and the RPD becomes more heterogeneous as cluster size decreases. Hence, the adsorption probability distribution must behave similarly. Accordingly, the NSD can also possess multifractal characteristics and the $\alpha$ range in $f(\alpha)$ plots can shift to larger values as the cluster radii decrease [Fig. 7(e)]. Therefore, the smaller is the cluster, the greater is the position sensitivity of the selectivity distribution. These results might be attributed to screening effects, i.e., sites in the outer region have greater opportunity to be found by random walkers and the rate of production of $C$ via a bimolecular reaction is greater; on the contrary, in the inner part, the probability of dimerization is smaller and an adsorbed $A$ molecule has a relatively large probability to be converted into a $B$ molecule before it is found by another $A$ molecule. This effect would lead to a large variation in selectivity among active sites.

Effects on the NSD caused by varied $p_1$ and $p_3$ values were also examined. Several sets of $p_1$ and $p_3$ values were used in simulations over the $D = 1.72$ cluster having $10^4$ particles. Multifractal characteristics, $\tau(q) - q$ and $f(\alpha) - \alpha$ curves, are presented in Figure 8. Also shown are the multifractal characteristics of the RPD for the ER with a noise reduction of 10 and under fixed sticking probability equal to .01.

We first examined the effects of varying $p_3$ on the NSD for a TSC with $p_1 = 1.0$. In Figure 8(b), with $p_3$ values equal to 1.0 and .01, the $\alpha$ ranges are almost the same and the dispersion curves $f(\alpha)$ are separated by some distance. Hence, the difference between the smallest and the largest selectivity for these two cases is nearly equal, and populations possessing small and large selectivity are distinct for these two cases. Hence, the increased dimerization reaction probability increases the position sensitivity in the NSD for an adsorption probability equal to 1.0.

This effect was diminished when $p_1 = .01$. In Figure 8, the $\tau - q$ and $f(\alpha)$ curves for varied $p_3$ almost collapse into one curve. The selectivities for $p_3 = 1.0$ and for $p_3 = .01$ are distinct (the former is 50.6 and the latter is 1.5). Thus, as $p_1$ becomes small, the $p_3$ value becomes ineffectual on the NSD although the selectivity over each active site is distinct. Note that the $\tau - q$ curve for the NSD of these two cases is relatively linear than that for the RPD of the ER without noise reduction, and after noise reduction is applied, the difference between the NSD and the RPD becomes small. This again reflects a similarity between an NSD for a TSC and an RPD for an ER mechanism on which a noise reduction technique was taken.

Additional features were obtained from Figure 8 for cases with fixed $p_3$. Increasing $p_1$ values under fixed $p_3$ increases the range of $\alpha$ no matter how small a value for $p_3$ is used, and the NSD becomes more heterogeneous. Basically, a smaller

**FIGURE 8.** Dependence of multifractal characteristics on $p_1$ and $p_3$: (a) $\tau(q) - q$ curves; (b) $f(\alpha) - \alpha$ curves. Also shown are the multifractal characteristics of the RPD of the ER reaction with and without noise reduction; both cases possess a sticking probability equal to .01.
value of $p_1$ smooths the screening effects because surface sites possess nearly the same adhesive opportunity and the NSD becomes more homogeneous. Accordingly, the adsorption probability $p_1$ has a stronger effect on selectivity distribution than does $p_2$. This observation is attributed to the intrinsic properties of the three-step reaction system, namely, $C$ molecules are produced in a series of reactions in which $A$ molecules must first be adsorbed. Thus, $p_1$ plays a key role in determining the final NSD. A smaller value of $p_1$ smooths the screening effects caused by the structure of fractal objects and leads to a more uniform NSD.

**Conclusions**

The MSA of the RPD were performed for the ER mechanism and is modified versions, including a low fixed sticking probability and an event-dependent sticking probability over a fractal surface. By adopting different conditions, a variety of RPD patterns can be generated. The underlying trends were analyzed through the $\tau(q)$ and $f(\alpha)$ plots, which allow a quantitative estimation of the degree of RPD heterogeneity and a high nonlinearity of $\tau(q)$ curves can be mapped into wider distribution in the $f(\alpha)$ plots. Our analyses manifest the high sensitivity of catalysis to structure even in a basic reaction like the ER mechanism.

On the other hand, Monte Carlo simulations of competing first- and second-order catalytic reactions over fractal surfaces were performed to examine the morphological effect on catalyst selectivity. We have demonstrated that the geometry of the surface of a catalyst plays a crucial role on its performance. In particular, the dependence of catalyst selectivity on the rate constant shows nonclassical power law behavior (i.e., $S \propto k^{\delta}$, in which $\delta \neq -1$). To further examine the effect of the geometry of the catalyst on selectivity distribution, the MSA of the NSD were performed. The NSD is similar to the RPD on which a noise reduction technique has been taken and it may have a narrower $\alpha$ range than the RPD without noise reduction. The adsorption process in the three-step reaction is found to play a key role in determining the homogeneity of the NSD. In the limiting case of purely random adsorption in step 1, the position sensitivity in the NSD is increased as the dimerization rate constant is tuned from 0.1 to 1.0. Such an effect is found to be diminished as the adsorption probability in step 1 is lowered.

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**References**