Multifractal scaling analysis of the selectivity behavior of a multi-step reaction over DLA surfaces

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Abstract

Monte Carlo simulations of a three-step catalytic reaction over surfaces of diffusion-limited aggregates (DLA) were performed to examine the morphological effect on catalyst selectivity. The effect of varying the probability of the reaction steps and DLA cluster sizes on the normalized selectivity distribution were then analyzed by multifractal scaling techniques. Increase of DLA size is found to lower the position sensitivity of normalized selectivity distribution. The increase of the dimerization to isomerization ratio increases the selectivity of active sites as the adsorption probability equals 1. The ratio of dimerization to isomerization caused no effect on the normalized selectivity distribution as the adsorption probability $\ll 1$.

1. Introduction

It is well known that in all heterogeneous chemical systems, the geometry of the environment plays a key role in determining the reaction rate and their performance [1–18]. An example of such a process is the geometrical structure of a catalyst which may have a vital effect on catalyst selectivity. The sensitivity of selectivity of catalytic reactions to catalyst structure may be accounted for via several approaches. One such example is viewing the catalyst as a fractal-like structure and using a direct stochastic simulation which takes into consideration the random walk and reaction probability [19,20]. In this Letter, we would like to report some of our recent findings concluded from simulations of a three-step surface reaction over a Witten–Sander DLA surface with the emphasis placed in particular on the multifractality of the normalized selectivity distribution.

The multi-step reaction considered for simulation here is given by

\[ A + S^{p1} A_a , \]  
\[ A_a^{k_{12}} B , \]  
\[ A + A_a^{p3} C , \]  

where A and A$_a$ are the reacting particles and its adsorbed state, S the surface sites of fractal objects, and B and C the products. Reaction (1) represents the adsorption of a reacting A molecule onto the surface of catalyst (S). Reactions (2) and (3) represent a unimolecular and a bimolecular process, respectively, and in a real catalytic system these might individually correspond to an isomerization reaction and a dimerization process. The selectivity is defined as the ratio of the number of C molecules to that of B molecules produced. This system has been investigated by Meakin [19] on DLA and percolating clusters with steps (1) and (3) occurring with probabil...
ity one and by Tambe et al. [20] on a DLA surface with the focus mainly concentrating on the analyses of relationships among macroscopic average selectivity behavior, varying probability of reaction steps, and rate constant. In the present work, multifractal scaling analyses were adopted to examine the behavior of the normalized selectivity distribution (NSD) under varying reaction probabilities.

This Letter is composed as follows. Methods of simulation and multifractal scaling analysis are briefly stated in Section 2. Results are presented and discussed in Section 3. Conclusions are given in Section 4.

2. Method

Firstly, a 2D DLA is generated on a square lattice using a modified version of the Witten–Sander model, in which the particles are released one at a time from an equal-event boundary, i.e. a diamond-shaped boundary [21,22]. A particle then undergoes a random walk until it either reaches the surface site of the fractal cluster or it goes out of the outer perimeter. As the DLA grows to a certain size, the releasing particle is changed to the reacting species. If this particle reaches an unoccupied site adjacent to the DLA then reaction (1) would occur with a probability of $p_1$ or continue to diffuse with probability $1 - p_1$. Once reaction (1) takes place, reaction (2) follows and the number of B molecules, $N_B$, is incremented by $k_1N_A$, in which $k_1$ represents the rate constant for reaction (2) and $N_A$ denotes the number of adsorbed A molecules. When the increment of $N_B$ exceeds the integer one, a randomly chosen adsorbed A site is converted into a B molecule.

If a randomly moving A particle visits an occupied surface site then it can either dimerize with probability $p_3$ or continue to walk with probability $1 - p_3$. If the reaction occurs, then a certain number of C molecules, $N_C$, is produced and also a randomly chosen adsorbed A surface site is vacated. Neither the B nor C molecules are allowed to occupy the surface site.

If this random walk results in any one of reactions (1) and (3) it is considered to be successful and the same procedure as outlined above is repeated. The selectivity is then determined for each of the surface sites where both the B and C molecules are produced. If a moving particle travels far away from the cluster, the trial is discarded and a new A particle is released. For the simulations that have been carried out, a large enough number of A particles were launched until a steady state was achieved, i.e. as a nearly constant selectivity value was obtained. $10^6$ successful random walk trajectories were used and the rate constant $k_1$ was assumed to have a value of $3 \times 10^{-4}$ in all simulations.

Multifractal analysis has been proven to be useful in the study of processes in environments of complex geometry. In fact, Avnir and co-workers [12,14] have made some efforts along this line. They reported the multifractal scaling analyses of a diffusion-limited reaction over two mathematician-made fractal surfaces, the Cantor set (CS) and the DS, and indicated that multifractalsities exist for both surfaces. In our previous investigation [15,16], multifractal analyses were carried out on the reaction probability distribution to study the effect of fractal environment of DLA surfaces on Eley–Rideal DLR. Here, the method was used to extract the fractal characters from the spatial distributions of selectivity with distribution of the measure, $P_n$, defined as the normalized selectivity

$$S_i = \frac{S_i}{\sum_j S_j},$$

where $S_i$ is the selectivity of surface site $i$ and is determined from the simulations.

For our analysis, the sizes of the DLA were chosen to be $3 \times 10^3$, $6 \times 10^3$ and $10^4$, whose average radii were equal to 85, 124, and 169 lattice units, respectively. The fractal dimension of these three DLAs is $1.72 \pm 0.02$.

3. Results and discussion

In the present study, the effects of different $p_1$, $p_3$ values and DLA cluster sizes on the normalized selectivity distribution were examined by multifractal scaling analysis. To study the effect of cluster sizes on NSD, simulations were run over $3 \times 10^3$-particle, $6 \times 10^3$-particle, and $10^4$-particle DLA clusters with $p_1$ and $p_3$ equal to one. In order to understand the position sensitivity of the selectivity distribution, the normalized selectivity probability was plotted as a
Fig. 1. The normalized selectivity as a function of active site position for simulations over (a) $3 \times 10^3$-particle (b) $6 \times 10^3$-particle (c) $10^4$-particle DLA ($D_t = 1.72 \pm 0.02$) with both $p_1$ and $p_3$ equal to 1.0. The active sites are numbered from the inner part of the fractal object outwardly. For active sites of the same radius, they are numbered clockwise.

function of active site position for the three DLAs as shown in Fig. 1, where the active sites are numbered from the inner part of the DLA outwardly. For active sites of the same radius, they are numbered clockwise. Note that the inactive sites and the screened active sites are not included in this plot. As the DLA size decreases, the range of the selectivity probability has a wider distribution showing a higher position sensitivity. It can be seen in Fig. 1 that the number of low normalized selectivity sites gradually increases as the DLA size increases. Bear in mind that the outermost sites of the fractal object have a much higher selectivity because the most exposed tips produce more bimolecular products than the inner surface sites which are more deeply buried, as displayed by the spike-shaped distribution in Fig. 1.

Multifractal characteristics are demonstrated in Fig. 2. Also shown are the multifractal characteristics of the reaction probability distribution (RPD) of the Eley–Rideal (ER) reaction mechanism with fixed sticking probabilities equal to 1.0. As can be seen in Fig. 2, the $\tau - q$ relation is not linear, indicating that the simple single-valued fractal scaling does not apply in this condition. The nonlinearity is decreased as the cluster size increases implying that the NSD becomes more homogeneous as the cluster size increases. This behavior is a direct consequence of the distribution of the probabilities for surface sites to be

![Diagram](image)

Fig. 2. Dependence of multifractal characteristics on the sizes of three different DLAs, also shown are the multifractal characteristics of the RPD of the Eley–Rideal reaction with sticking probability equal to 1.0: (a) $\tau(q) - q$ curves and (b) $f(\alpha) - \alpha$ curves. (-- --) 3000; (--- ) 6000; (...) 10000; (-----) sticking probability = 1.0.
found by random walkers in step (1) which, in fact, can be viewed as RPD in the ER diffusion limited reaction over the DLA [15,16]. The NSD is expected to be comparatively homogeneous relative to the RPD. As can be seen in Fig. 2a, the nonlinearity of the NSD is lower than that of the RPD. This fact is also reflected by the wider range of \( \alpha \) for the RPD than for the NSD in Fig. 2b. The reason can be explored from the view point of the noise reduction effects on the RPD; it can be seen that under noise reduction, the RPD becomes more homogeneous or uniform because it clears out some low reaction probability sites and shows no effect on the high reaction probability parts. Since a site possesses selectivity implying that site must be visited often by reacting particles (note both B and C molecules must be produced), 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 as presented in Fig. 2b.

As pointed out in our previous study [15,16] there is a broad distribution in the probabilities that particular sites are visited by random walkers which are launched from outside and the reaction probability distribution becomes more heterogeneous as the DLA cluster size decreases. This revealed the fact that the adsorption probability distribution must behave in the same manner. Accordingly, the NSD could also possess multifractal characteristics and the \( \alpha \) range in \( f(\alpha) \) plots should shift to larger values as DLA radii decrease as shown in Fig. 2b. Therefore, the smaller the DLA is, the higher the position sensitivity in the selectivity distribution. These results might be attributed to screen effects, i.e. sites on the outer region have greater opportunity to be found by random walkers and the rate of production of C via the bimolecular reaction is higher; on the contrary, in the inner part the probability for dimerization is smaller and an adsorbed A molecule could have a relatively high probability of being converted into a B molecule before it is found by another A molecule. This would lead to a large variation in the selectivity among active sites.

To study the effects caused by different \( p_1 \) and \( p_3 \) values on the selectivity distribution, several sets of \( p_1 \) and \( p_3 \) values were used in our simulations. Results of the multifractal scaling analysis including \( \tau(q) \) and \( f(\alpha) \) curves are presented in Fig. 3. Also shown are the multifractal characteristics of the RPD of the ER reaction mechanism with fixed sticking probabilities equal to 0.01.

We first check the effects of varying \( p_3 \) with \( p_1 \) equal to 1.0 on normalized selectivity distribution. As can be seen in Fig. 3b, by varying \( p_3 \) values from 1.0 to 0.01, the \( \alpha \) ranges are almost the same and the dispersion curves \( f(\alpha) \) are separated by some distance. This indicates that the difference between the lowest and the highest selectivity for these two cases is nearly equal, and the populations possessing low and high selectivity are quite different for these two cases. Thus, it is concluded that the increase of the dimerization reaction probability increases the position

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**Fig. 3.** Dependence of multifractal characteristics on \( p_1 \) and \( p_3 \). Also shown are the multifractal characteristics of RPD of the Eley–Rideal reaction with sticking probability equal to 0.01: (a) \( \tau(q) \) curves and (b) \( f(\alpha) \) curves.

*---* \( p_1 = 1.0; p_3 = 1.0; \) *---* \( p_1 = 1.0; p_3 = 0.01; \) *---* \( p_1 = 0.01; p_3 = 1.0; \) *---* \( p_1 = 0.01; p_3 = 0.01; \) *---* sticking probability = 0.01.
sensitivity in the NSD as the adsorption probability equals 1.0.

This effect could be diminished if we let \( p_1 = 0.01 \). As can be seen in Fig. 3, the \( \tau-q \) and \( f(\alpha) \) curves for different \( p_1 \) values almost collapse into one curve. Note that the selectivities for \( p_1 = 1.0 \) and for \( p_1 = 0.01 \) are distinct (the former is 50.6 and the latter is 1.5). Thus, as \( p_1 \) becomes low, the \( p_3 \) value becomes ineffective on the normalized selectivity distribution although the selectivity over each active site is quite different.

Additional features can be obtained from Fig. 3 by fixing the value of \( p_3 \). As can be seen in Fig. 3, increasing \( p_1 \) values under fixed \( p_3 \) increases the \( \alpha \) range no matter how small a value for \( p_3 \) is used and the normalized selectivity distribution becomes more heterogeneous. Basically, a lower \( p_1 \) value smooths out the screen effects because the surface sites possess nearly the same adhesive opportunity and the normalized selectivity distribution becomes more homogeneous.

From the above analyses, the adsorption probability \( p_1 \) is found to have a stronger effect on the selectivity distribution than does \( p_3 \). This observation may be attributed to the intrinsic properties of the three-step reaction system, namely, C molecules are produced by a series reaction in which A molecules must first adsorb. Thus \( p_1 \) would play a key role in determining the final normalized selectivity distribution. A lower \( p_1 \) value could smooth out the screen effects caused by the structure of fractal objects and a more uniform NSD is generated.

4. Conclusions

Multifractal scaling analyses of the NSD were performed for a three-step reaction over DLA surfaces. The adsorption process in the three-step reaction is found to play a key role in determining the homogeneity of normalized selectivity distribution. 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 0.01 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