Eley–Rideal reactions over rough surface: effect of sticking probability

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Abstract

Eley–Rideal reactions are analyzed over rough surface of random deposition model. Different sticking probabilities viz. 1, 0.7, 0.4 and 0.1 of the reacting particles are considered. Reaction probability distributions are transformed into a useful compact form through the multifractal scaling analysis. Range of reaction probability decreases with decrease in sticking probability. The non-linearity in the $q$–$r(q)$ multifractal plots and range of $x$ values in $x$–$f(x)$ multifractal plots increases with an increase in sticking probability indicating greater heterogeneity in the reaction probability distribution with an increase in sticking probability where $q$ is the moment order, $r(q)$ is the scaling exponent, $x$ and $f(x)$ are the characteristic scaling exponents for reaction probability distributions.

Keywords: Surface roughness; ER mechanism; Multifractal analysis

1. Introduction

Heterogeneous catalysis is of fundamental importance in the chemical industry and in other technologically relevant applications. Understanding of the complex behavior of atoms and molecules at surfaces e.g., adsorption/desorption, chemical reactions, etc., requires detailed knowledge of both macroscopic and microscopic processes that take place. Catalyst design, which is most crucial for the development of novel catalytic processes, is an extremely interdisciplinary endeavor. It requires some understanding of the mechanism of the catalytic reaction, and knowledge of the crucial properties, which determine the activity, selectivity and lifetime of the catalyst. Studies of the interrelationship between structural and chemical properties of solid materials and their catalytic properties are at the origin of catalyst design. These studies are frequently carried out using specially prepared model catalysts, which are amenable to analysis with modern surface analytical methods providing structural and chemical information on molecular scale [1–3].

Heterogeneous chemistry plays key role in a large variety of natural and man made chemical processes. Any heterogeneous catalytic reaction is governed by the elementary mechanism involved in the chemical kinetic scheme, by the external operating parameters, but also by the geometry of the surface on which the reaction occurs [4]. Eley–Rideal (ER) reaction mechanism [5] represents a physical situation where the molecules or ions approach from the bulk to the interface and react or adsorb when encounter [3]. This mechanism is a reaction of an important class in condensed phase, e.g., in solution [6] and surface catalytic reactions [7]. Therefore, it is important to investigate the influence of the geometrical structure of the reactive substrate on this key process. Many authors have tried to understand the sensitivity of this reaction in which surface site is one of the reactants, to structure [8–13]. Gutfraind
et al. [8] reported multifractal scaling analysis of the ER reaction over two mathematically made fractal surfaces, the Cantor set and Devil's staircase. Lee et al. [9,10] have used Monte Carlo random walk algorithm to simulate ER reaction mechanism over fractal surfaces of diffusion limited aggregation. Multifractal scaling analysis technique was then applied to analyze the reaction probability distribution. Recently, we have analyzed ER reaction over rough surface of random deposition model to study the surface heterogeneity effect on this reaction mechanism and obtained wide range of reaction probability distribution for rough surface than smooth surface [11]. In a comparative study of ER reactions over rough surface of random deposition and that of random deposition with surface diffusion, we have shown that the reaction probability distribution has wider range for the former than the latter [12]. Dynamic scaling theory is applied on ER reaction mechanism over the fractal surface of diffusion-limited aggregation to study the time dependence of ER reaction [13].

All the above studies of ER reaction over fractal/rough surface are with perfect sticking case i.e., sticking probability = 1. Sticking probability = 1 means zero activation energy. In real catalytic systems, the reactions occurring at active sites of surface having non-zero activation energy seem to be more reasonable. The aim of this work is to study ER reaction mechanism over two-dimensional rough surface with different sticking probability ($P_{\text{st}}$) viz 1, 0.7, 0.4 and 0.1 and to show how the sticking probability affects reaction probability distribution through multifractal scaling analysis. Our model for ER reaction mechanism is suitable for the catalytic reactions in which one of the reactant is the surface site [14]. The model is also suitable for the catalytic reactions consisting of single adsorption and reaction step of the type [15–17].

$$A^+ \rightarrow A_{\text{ad}},$$

$$A_{\text{ad}} \rightarrow P^+*,$$

where $*$, $P$ and subscript $\text{ad}$ represent vacant surface site, product and adsorbed species, respectively. We have shown in this study that how the sticking probability affects the range of reaction probability distribution for the rough surface.

This paper is organized as follows: In the following section, method of rough surface generation is outlined. In Section 3, the details of multifractal scaling are given. Results are discussed Section 4. Finally, the conclusions are inferred in Section 5.

2. Simulation procedure

The rough surface is generated by depositing $5 \times 10^5$ particle over a square lattice of linear dimension $L = 300$ lattice units, using random deposition (RD) model [18]. In random deposition, the particles are deposited at the top of the column selected randomly. Here, the column means height of $(x,y)$ position of a lattice which is initially zero and increases with increase in number of deposited particles. The particles simply rain down onto a smooth surface. Particles move along straight-line trajectories until they reach the top of the column in which they are dropped, at which point they stick to the deposit and become part of the aggregate. As there is no horizontal correlation between neighboring columns, the surface is extremely rough. The rough surface generated is shown in Fig. 1. We defined the surface roughness as

$$S_r = h_{\text{max}} - h_{\text{min}},$$

where $h_{\text{max}}$ and $h_{\text{min}}$ are the maximal and minimal height among the columns, respectively.

There are various procedures for preparing the heterogeneous catalyst. Chemical vapor deposition is one of them and is widely used now a days for preparing heterogeneous catalyst [19]. Family [18] suggested a model for growing surfaces by chemical vapor deposition method. According to this model, the active sites are situated at different heights. Thus, such surfaces can be considered as rough surfaces with active sites situated at different heights. Hence, this model is the appropriate choice to study the effect of surface roughness on catalytic reactions.

For many industrial chemical reactions, noble metals like Pt, Pd or Rh are used as catalytically active materials. As the price of these metals is very high, it is virtually impossible to use pure metal catalyst. In order to avoid this problem, the noble materials are usually dispersed at atomic or few atoms of cluster level on the top of low cost catalytically active inert rough support [2,20]. Thus the active sites are located at different height and there is no correlation between the heights of the columns. For preparing such catalyst chemical vapor deposition (CVD) method is widely used [19]. Thus, random deposition model suggested by Family [18] for
CVD process is the appropriate choice for such catalyst surface. Our study is also applicable to the unimolecular gas phase reactions in CVD reactor [21].

Second important parameter in catalytic reaction is sticking probability. In the reaction considered here, very first step is the adsorption of the reacting species $A$ on the surface. The probability that adsorption of $A$ will occur generally depend on temperature of the catalyst surface. Adsorption (sticking) probability = $f \exp(-\Delta E/kT)$, where $f$ is preexponential factor, $\Delta E$ is binding energy, $k$ is Boltzmann’s constant and $T$ is temperature of the surface.

But in terms of Monte Carlo simulation, the term $f \exp(-\Delta E/kT)$ is best represented by some fixed value called sticking probability.

The third important parameter in surface reaction is the rate of the reaction. It is not possible to study the rate of reaction in the reaction of the type studied here for the following reason. Here, the rate of reaction = $k \cdot \theta_{A}$, where $\theta_{A}$ is coverage of $A$. As the products leaves the surface immediately after adsorption takes place, no species remain adsorbed on the surface. So, it is not possible to calculate the coverage of $A$ here. Therefore, we have studied here the reaction probability distribution i.e., fluctuation in reaction probability instead of rate of the reaction. We are trying to find the relation between the reaction probability distribution and the rate of the reaction. The properties of the model required to study reaction probability distribution is the number of reacting species visited (number of products formed) at each surface site. It is calculated using Monte Carlo simulation as follows.

After generating the rough surface of $5 \times 10^5$ particles, the releasing particles are considered as reacting species. The columns are selected randomly. The reacting species are allowed to react at the top of the column having maximal height among the four nearest neighboring columns and with sticking probability $P_{\text{ini}}$. The probability of reaction can be achieved by generating a random number when the particle visits the surface site and checking whether it is less than or equal to the given fixed sticking probability $P_{\text{ini}}$. If it is less than $P_{\text{ini}}$ the reaction count on that surface site are added by one and if it is greater than $P_{\text{ini}}$ then a new reacting particle is considered. After $10^6$ reacting particles are launched, the reaction probabilities of different surface sites are recorded and analyzed. The results were obtained after averaging 25 runs each with $10^6$ reaction events.

3. Multifractal scaling analysis

Multifractal scaling is useful in the study of processes in the environment of complex geometry and it helps to extract the fractal characters from the reaction probability distribution picture through $f(x)$ spectrum. We apply the multifractal scaling which relates the analysis of the distribution of the reaction probabilities over the length of the rough surface. The multifractal formalism [22] has been used for geometrical description of other physical and chemical phenomenon such as fractons on a percolation cluster, [23] scaling of molecular spectra [24], distribution of solvent accessibilities in proteins [25], distribution of reaction probabilities in diffusion limited reactions [8–12]. The steps in the multifractal scaling analysis are given below. For details one can refer to the article by Halsey et al. [22].

The three basic equations in the multifractal scaling analysis are

$$M_q = \sum_i P_i^q = \sum_P n(P)P^q \propto L^{-\tau(q)},$$

$$\tau(q) = q\alpha(q) - f(x),$$

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

where $M_q$ is the $q$th order moment of reaction probability distribution, $\tau(q)$ is the scaling exponent, $P_i$ is the reaction probability of site $i$, $n(P)$ is the number of sites with reaction probability $P$ and $L$ is the length of the surface. The exponents $\alpha$ and $f(x)$ are the characteristics scaling exponents for reaction probability distributions. Among these three equations, Eq. (2) is obtained by the following scaling assumptions used in the limiting case of large $L$.

$$P(q) \propto L^{-\tau(q)},$$

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

where $P(q)$ denotes the value of $P$ that dominates the sum in Eq. (1) for the $q$th order moment. Substitution 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) and it can be transferred into a more explicit form

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

In practice, the quantities $\tau(q)$, $\alpha(q)$ and $f(x)$ can be computed as follows. The probability distribution is first determined from the simulation. Then for each $L$, $\tau(q)$ is calculated from Eq. (1). $\alpha(q)$ is then computed from Eq. (6). By knowing $\tau$ and $\alpha$, one can compute $f(x)$ from Eq. (2). The distribution of the measure $P_i$ is called multifractal if all of these moments (Eq. (1)) scale as power
laws with an infinite set of independent exponents $\tau(q)$. The calculated values of $\tau$, $x(q)$ and $f(x)$ are presented through two types of plots $\tau$ vs. $q$ and $f(x)$ vs. $x$.

4. Results and discussion

The rough surface generated by depositing $5 \times 10^5$ particles over the square lattice of linear dimension $L = 300$ is shown in Fig. 1. The surface roughness, defined as the difference between the maximal height and minimal height among the columns, is 18 lattice units for this surface. The reaction events occurring at each site on the surface are recorded by counting the number of visits by the reacting particle and the reaction probability is calculated at each site. The plot of reaction probability as a function of active site position gives the position sensitivity of the reaction probability. Here, the active site position means the numbering or position of the active site on the surface. Fig. 2 shows the plot of reaction probability vs. active site position for different sticking probability. The active sites are numbered from negative to positive in $y$ direction and finally in upward direction. From Fig. 2, it can be seen that the range of reaction probability decreases with decreasing sticking probability. Higher the sticking probability, wider is the distribution of the reaction probability, indicating higher position sensitivity. Valleys among the spikes in reaction probability distribution profile arise mainly from a screening effect, i.e., the inner surface sites are screened by the outer ones showing that the inner sites are rarely visited. The inner and outer surface are the active sites which are at lower height and greater height than the neighboring sites, respectively.

The reaction probability distribution pictures may be transferred into a useful compact form through the multifractal formalism namely, through the $q-\tau(q)$ and $x-f(x)$ plots. Fig. 3 shows the multifractal plots for different sticking probability. The deviation from linearity for $q-\tau(q)$ plots indicates multifractality, i.e., simple single-valued fractal scaling does not apply in this condition. The difference among the four different sticking probabilities can also be observed. From Fig. 3(a), higher the sticking probability, bigger is the deviation of the $q-\tau(q)$ curve from linearity. The curve curvature also implies the degree of heterogeneity in reaction probability distribution. These results agree with the reaction probability distribution profiles for the different sticking probability. As the sticking probability decreases, the non-linearity in the $q-\tau(q)$ curve decreases representing a homogeneous reaction probability distribution.

The effect caused by sticking probability on reaction probability distribution can also be analyzed through the $f(x)$ dispersion of the reaction probability distribution profiles which allows a quantitative evaluation of the degree of reaction probability distribution inhomogeneity: high non-linearity of the $q-\tau(q)$ curves is translated into wider distribution in the $f(x)$ plots. Higher the sticking probability, greater is the deviation in the $q-\tau(q)$ curve results in wider range of $x$ values representing greater heterogeneity in the reaction probability distribution. Also, $f(x)$ figures are asymmetric with respect to $x$ for all the sticking probabilities. The difference in the $f(x)$ spectrum for these four sticking probabilities can also be seen at the low and high $x$ values. As the sticking probability decreases, the right extreme $f(x)$ value becomes larger and left are smaller. This implies that as the sticking probability decreases, the low reaction probability part is associated with larger sets but the higher reaction probability part is connected to very small sets and as a result it produces a relatively homogeneous reaction probability distribution pattern.

In Fig. 4, the reaction probability is plotted as a function of height to further analyze the position sensitivity, for different sticking probability. The simulation results show that the active region is not the topmost height of the rough surface. The reaction probability increases

![Fig. 2. Reaction probability as a function of active site position, for different sticking probability.](image)

![Fig. 3. Multifractal plots for different sticking probability: (a) $q-\tau(q)$ plot; (b) $x-f(x)$ plot.](image)
with increasing height, gets a maximum value and decreases thereafter and finally gets zero, for all the sticking probabilities. A maximum reaction probability (RP_{\text{max}}) is obtained for each sticking probability at a particular height. The RP_{\text{max}} increases with increasing sticking probability. The linear increase of RP_{\text{max}} with sticking probability is shown in Fig. 5. The increase shows the linear behavior of the type RP_{\text{max}} = -0.00011 + 0.2216^*P_{\text{ini}}. The fits of data are also shown in Fig. 5.

5. Conclusions

Eley–Rideal reactions with different sticking probability are analyzed over the rough surface of random deposition model. Multifractal scaling is applied to study the heterogeneity in reaction probability distribution. The range of reaction probability decreases with decreasing sticking probability. The maximum reaction probability is obtained at a particular height, which decreases linearly with decrease in sticking probability.

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References