Dynamic Scaling for Eley-Rideal Reactions Over Rough Surface

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ABSTRACT: Eley-Rideal reaction mechanism is studied over rough surface of random deposition model. Two types of rough surface are considered: (1) different rough surface with same surface density and (2) different rough surface with different surface density. Dynamic scaling theory, which is generally applied to the growing surface, is applied for this reaction mechanism to obtain the temporal and spatial scaling parameters $\alpha$ and $\beta$. The scaling parameters are found to be negative in contrast to the positive scaling parameters in surface growth model. The values of $\beta$ are the same for both types of surface whereas the values of $\alpha$ are different.


INTRODUCTION

Heterogeneous chemistry plays a key role in a large variety of natural and man-made processes. The problem of heterogeneous reaction is of major importance in the chemical industry. Diffusion controlled reactions play an important role in various branches of biology, chemistry, and physics. In heterogeneous catalysis, reaction performance depends strongly on the structure and geometry of the environment in which the catalytic process takes place. The importance of heterogeneity of solid surface in catalysis is more and more recognized. The structure of a real catalyst is never a perfect crystalline one. The heterogeneity can result from surface defects, partial poisoning and in case of supported catalyst their surface are intrinsically heterogeneous. Geometric structure of catalyst surface as well as its energetic heterogeneity not only may lead to the catalyst deactivation but also frequently change kinetics of catalytic reactions. The surface nonuniformity is a well-known factor playing crucial role in heterogeneous catalysis. The structure and activity of the adsorbing catalyst surface are the major parameters that influence reaction yield, selectivity, and determine path of reaction [1,2].

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. On the molecular level, diffusion limited reactions correspond to a process where almost every collision of a reactive molecule on the interface leads to a reaction (i.e. activation energy is small) [3]. Eley-Rideal (ER) reaction mechanism [4,5] is an elementary step in many complex interfacial processes and has received much attention in the past decade. Numerous experimental studies of ER reactions on metal [6–11], semiconductor [12,13], carbon [14], and even liquid [15] have appeared primarily in the past decade and so. Many authors [16–20] have analyzed these reactions theoretically. Gutfraind et al. [17] have studied ER reactions over two fractal surfaces of Cantor set and Devil’s staircase using multifractal scaling analysis. Lee et al. [18,19] have analyzed ER reactions...
over the fractal surface of diffusion limited aggregation using multifractal analysis. In both the studies, the authors found a wider range of reaction probability distribution.

But the catalyst surfaces are neither totally irregular (fractal) nor perfectly regular (geometrically and energetically homogeneous) [21]. Real catalyst surfaces represent an intermediate case, which can be viewed as rough surfaces. Then a question arises whether and how the rough surface influences the kinetics. In our previous study [20], we have shown how the surface roughness affects the ER reaction mechanism through multifractal scaling analysis. We obtained a wider range of reaction probability distribution than the smooth surface. In all the above studies, the authors have not considered the time parameters in their study. The aim of this paper is to study the time dependence of ER reactions over rough surface.

In this study, the rough surfaces are generated by deposition of \( N \) number of particles over lattice size \( L \), using random deposition model [22]. Two types of rough surfaces are considered here: (1) different rough surface with same surface density and (2) different rough surface with different surface density, where surface density is defined as, surface density = \( N/L \).

To study the time dependence of ER reactions over rough surface, dynamic scaling theory [23] is applied. Dynamic scaling theory has been applied earlier in various surface growth models [23–28]. Botelho and Reis [24] have studied the deposition model of two types of particles and applied dynamic scaling theory. Kinetic roughening and phase ordering during growth of binary systems has been studied by Kotrla et al. [25] using solid-on-solid model with Ising-like interaction between the two components. Horowitz et al. [26,27] have proposed a deposition model, which is a mixture of random deposition and random deposition with surface relaxation model, and obtained three exponents rather than the two exponents obtained in the original random deposition model by Family [22]. Wang and Cerdeira [28] have applied dynamic scaling to randomlike and ballisticlike deposition models. In almost all the deposition models, the study concentrated on the width of the growing surface and the scaling exponents are found to be positive in these studies.

In this study we have applied dynamic scaling theory to the ER mechanism to obtain the scaling exponents for the time dependence of the ER mechanism. The present paper is organized as follows. In the next section, the method of generation of rough surfaces is given. This is followed by a section that gives the details of the dynamic scaling theory. In the last two sections we present the results and the conclusions.

**ROUGH SURFACE GENERATION**

The random deposition model has been used for generating the rough surfaces. It is the simplest deposition model. In random deposition model, 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.

Rough surfaces with different surface density are generated by the deposition of \( 10^4 \) particles on lattice size \( L = 100, 200, 300, 400, \) and 500. The surface density for these five surfaces is 100, 50, 33.3, 25, and 20 respectively. Rough surface with same surface density are generated by deposition of different number of particles on different \( L \). The number of particles deposited on lattice size 100, 200, 300, 400, and 500 is 2000, 4000, 6000, 8000, and 10000 respectively and the surface density for these five surfaces is 20.

**DYNAMIC SCALING THEORY**

After generating the rough surface by depositing proper number of particles as explained above, the releasing particle is changed to reacting species. The columns are selected randomly. The reacting particles are allowed to react at the top of the column having maximum height among the neighboring columns. When the reacting particle reaches to top of the column, the reaction count on that surface site is added by one. Total reacting species used in our simulation are \( 10^5 \). We considered total reaction event as a time parameter in our simulation.

The number of reacting particles visited at each site at time \( t \) is counted.

\[
P(x, y, h; t) = \frac{r(x, y, h; t)}{r_{\Sigma}(t)}
\]

where \( r(x, y, h; t) \) is the reaction event occurring at \((x, y, h)\) at particular time \( t \). \( r_{\Sigma}(t) \) is the total reaction event amount all over the surface in time interval \( t \).

The average probability \( P_x(t) \) on each surface site is

\[
P_x(t) = \frac{\sum P(x, y, h; t)}{N_f} = \frac{1}{N_f}
\]

where \( N_f \) is the number of free sites available for reaction particles. Free site means the site where there is possibility of the particle to visit. The remaining sites are the inactive sites where the reacting particle can’t reach due to the surrounding four nearest neighbors.
Because of the surface roughness, the reacting particle has greater probability to react at the surface sites which are at the top. This causes heterogeneity in the reaction probability distribution. This heterogeneity can be estimated by standard deviation of $P(x, y, h; t)$ as

$$\sigma(t) = \left[ \frac{\sum (P(x, y, h; t) - P_0)^2}{N_f} \right]^{1/2}$$  \hspace{1cm} (3)

We have obtained the scaling behavior of $\sigma(t)$, i.e., correlation between $\sigma(t)$ and time and also the surface roughness. The total reaction events (i.e. time) used for dynamic scaling are $10^5$.

RESULTS

Figure 1 shows one sample rough surface generated by depositing $10^4$ particles onto a lattice size $L = 200$. Figures 2 and 3 show a log-log plot of the fluctuation of reaction probability $\sigma(t)$ on $t$, for different rough surfaces with different surface density, and that with same surface density, respectively. It can be seen from these figures that for all the rough surfaces whether with same surface density or with different surface density, $\sigma(t)$ first decreases quickly and finally becomes constant (independent of $t$) after experiencing a slowing down. Initially $\sigma$ depends on $r_\Sigma$ and the scaling relation between $\sigma$ and $t$ is

$$\sigma = t^\beta$$  \hspace{1cm} (4)

The values of $\beta$ obtained for different rough surfaces with same surface density and with different surface density, are given in Table I. It should be noted that the value of $\beta$ is negative and is different from the positive value obtained by Family [22]. For both type of surfaces, $\beta$ values decrease with increase in $L$ and
Figure 3  Dependence of the probability standard deviation $\sigma$ on time for different rough surfaces with same surface density.

Figure 4  Dependence of the probability standard deviation $\sigma$ on length of the lattice $L$ as $t \to \infty$ for different rough surface with different surface density.

Figure 5  Dependence of the probability standard deviation $\sigma$ on length of the lattice $L$ as $t \to \infty$ for different rough surface with same surface density.
Table I  Scaling Exponents in Dynamic Scaling Theory for ER Reactions Over Different Rough Surface with Same Surface Density and Different Rough Surface with Different Surface Density

<table>
<thead>
<tr>
<th>$L$ (Lattice Units)</th>
<th>Rough Surfaces with Same Surface Density</th>
<th>Rough Surfaces with Different Surface Density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\beta$</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>100</td>
<td>$-0.481$ ($\pm$0.003)</td>
<td>$-0.491$ ($\pm$0.002)</td>
</tr>
<tr>
<td>200</td>
<td>$-0.485$ ($\pm$0.003)</td>
<td>$-0.485$ ($\pm$0.004)</td>
</tr>
<tr>
<td>300</td>
<td>$-0.491$ ($\pm$0.002)</td>
<td>$-0.83$ (0.002)</td>
</tr>
<tr>
<td>400</td>
<td>$-0.491$ ($\pm$0.002)</td>
<td>$-0.491$ ($\pm$0.001)</td>
</tr>
<tr>
<td>500</td>
<td>$-0.491$ ($\pm$0.001)</td>
<td>$-0.491$ ($\pm$0.002)</td>
</tr>
</tbody>
</table>

converge to $-0.491 \pm 0.001$. The variation in $\beta$ values for different rough surface is due to the random fluctuation in the Monte Carlo algorithm. For different rough surface with different surface density as well as for different rough surface with same surface density, the value of the scaling exponent $\beta$ is same. Therefore we can conclude that the surface roughness does not affect the scaling exponent ($\beta$) value without bothering whether we are considering the rough surfaces with same surface density or with different surface density.

At $t \to \infty$, $\sigma$ becomes independent of $t$ but depends on surface roughness, for both types of surface. It can be seen from Figs. 4 and 5 that the scaling relation between $\sigma$ and $L$ is

$$\sigma = L^\alpha \quad \text{as } t \to \infty$$

with $\alpha = -0.83 \pm 0.002$ for different rough surface with same surface density and $\alpha = -1.0 \pm 0.001$ for different rough surface with different surface density.

The dependence of $\sigma$ on $t$ and $L$ given by Eqs. (4) and (5), respectively, can be combined into a single expression representing a dynamic scaling which has been argued to be universal [23,29] as

$$\sigma(t, L) = L^{\alpha} f(t/L^\gamma)$$

where $\gamma = \alpha/\beta$.

The scaling function $f(x)$ behaves as $f(x) = x^\beta$ for $x \ll 1$ and $f(x) = \text{constant}$ for $x \gg 1$. Figures 6 and 7 show plots of $\sigma(L, t) L^{-\alpha}$ versus $t/L^\gamma$ for different rough surfaces with different surface density and that with same surface density, respectively, using respective values of $\alpha$ and $\gamma$. It can be noted that the curves for different rough surfaces, for both types of surface, all collapse into a single curve indicating excellent agreement with the scaling form [Eq. (6)].
Recently, we have applied dynamic scaling theory to the diffusion-limited reactions over fractal surface of diffusion-limited aggregation [30]. We have considered two different cases of ER mechanism: first, with perfect sticking case (sticking probability 1) and second, with lower sticking probability (0.1) of the reacting particle and obtained the negative scaling exponents $\alpha$ and $\beta$. For the former $\alpha = -0.74$ and $\beta = -0.48$ whereas for the latter $\alpha = -0.72$ and $\beta = -0.5$. We have also shown by considering surface with different fractal dimension that the fractal dimension does not affect the scaling exponent $\beta$. Our results in this study agree with our earlier finding. We have shown here that surface roughness also does not affect the scaling exponent $\beta$. We can, therefore, conclude that, surface heterogeneity either in the form of fractal dimension or surface roughness does not affect the scaling exponent $\beta$.

CONCLUSIONS

Eley–Rideal reaction mechanism is performed over different rough surfaces with different surface density and with same surface density. The rough surfaces are generated by random deposition model. On applying dynamic scaling theory to Eley–Rideal reaction mechanism, the scaling exponent $\alpha$ and $\beta$ are both found to be negative. The surface roughness does not affect the scaling exponent $\beta$.

BIBLIOGRAPHY