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2A + B_2 →2AB catalytic reaction over rough surface: the effect of Eley-Rideal mechanism

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Abstract

Monte Carlo simulations have been used to explore the effect of surface roughness and the Eley-Rideal (ER) mechanism on the simple Langmuir–Hinshelwood (LH) model for the 2A + B_2 →2AB monomer–dimer reaction. The rough surface is generated by a random deposition with surface diffusion model. It is found that the steady-state reactive window for the rough surface is narrower than that for the smooth surface. It has been seen that introduction of the ER process in the LH model changes the production rate significantly.

1. Introduction

Surface heterogeneity influences not only adsorption processes but also surface chemical reactions. This heterogeneity of the catalyst for heterogeneous reactions poses a serious challenge to experimental and theoretical approaches for catalyst design, since it can obscure the bridge between the structure of the catalyst and the observed reactivity. Ever since the introduction of the Ziff-Gulari-Barshad (ZGB) lattice model [1] for the heterogeneously catalyzed gas monomer–dimer reactions, the study of reactive processes using Monte Carlo simulation has undergone rapid growth. Several investigations of the surface heterogeneity effect on catalytic reactions have been reported [2–8].

Monomer–dimer (MD) reactions have been thoroughly studied by many authors [9–14], including various studies of the effect of surface heterogeneity [5,15–18]. Zhdanov and Kasemo [5] have studied this reaction via the restricted solid-on-solid model. Zhdanov [15] have used multifractal surfaces to study the effect of catalyst surface morphology on the catalytic activity and kinetic phase transition of the MD reaction. The effect of steps and kinks on the MD model reaction have been reported by Sholl and Skodje [16]. Furthermore, MD reactions have been studied on the Sierpinski carpet fractal lattice by Bustos et al. [17] and on percolation clusters by Khan and Ahmed [18].

In order to understand the influence of surface heterogeneity, we have studied the monomer–dimer catalytic reaction based on the Langmuir–Hinshelwood mechanism over a model rough surface generated by random deposition with surface diffusion. We have also studied here the effects of the Eley-Rideal (ER) mechanism on the coverage of the reactants and the production rate of MD reaction over rough surfaces. In the ER mechanism, gas phase reactants collide and react with reactants adsorbed on the surface. Several earlier attempts have been made to study the effect of the ER mechanism in catalytic reactions, including, monomer–monomer reactions [15], momomer–dimer reactions [14], NO–CO catalytic reactions on a rhodium surface [17], and on a square lattice [18], and gas phase hydrogen exchange with chemisorbed hydrogen on a silicon surface [19].

2. Rough surface generation

The rough surface is generated by a model comprising random deposition with surface diffusion [20]. In this 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. After reaching the surface, the particle is then allowed to diffuse on the surface. The diffusion continues until the particle finds the column of

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minimum height inside a domain of finite size around the initial contact. The morphology of the surface is specified by the set of column heights, i.e. the number of unit cells in the columns (i, j) over the reference plane. This model is used in chemical vapor deposition methods [21], and now a days chemical vapor deposition methods are widely used for the preparation of supported catalytic materials [22].

The rough surfaces in this study are generated by depositing 10^8 particles on a square lattice of linear dimension L = 75 lattice units. A measure of the surface irregularity can be obtained from the width of the surface [20] defined as

$$W = \left[\frac{\sum_i (H_i - H_{\mathrm{Avg}})^2}{N}\right]^{1/2} \quad (1)$$

where H_i is the height of the i^{th} column; $H_{\mathrm{Avg}} = \sum_i H_i/N$, the mean deposition height and; N, the number of surface sites. Here, the width of the surface obtained by Eq. (1) for the surface of $L = 75$ is 0.83. The rough surface generated by depositing 10^8 particles on a 75×75 lattice is shown in Fig. 1.

3. Model and simulation

First we considered the MD surface reaction by LH mechanism only according to the following three steps:

$$A_g + {}_* \rightarrow A_s \quad (2)$$

$$B_{2g} + 2_* \rightarrow 2B_s \quad (3)$$

$$A_s + B_s \rightarrow AB_g + {}_* \quad (4)$$

where subscripts *, s and g refer to the empty surface site, adsorbed molecule and gas phase molecule, respectively.

With the introduction of the ER mechanism, one has to add the following step to the LH mechanism.

$$A_g + B_s \rightarrow AB_g + {}_* \quad (5)$$

The following steps are involved in the simulation of the LH mechanism:

a. A surface site (top of the column) is picked randomly.
b. If the site is occupied, the molecule is backscattered and the trial ends. In case the site is vacant, the colliding molecule is chosen to be A with a given probability y_A and B with probability $(1-y_A)$.
c. If the colliding molecule is A, then it adsorbs on the single vacant site. If the colliding molecule is B_2 and the selected surface site is vacant then one more vacant site is scanned from the four nearest neighbors. If this site is also vacant and has a similar height then the dimer B_2 is adsorbed in atomic form on these sites.
d. After the adsorption event, all the nearest neighbor sites are checked. The reaction on the surface between A_s and B_s proceeds immediately when these species appear in the nearest neighborhood and at the same height leaving two empty surface sites on the surface. If the adsorbed species appear in the nearest neighbor but at different heights then no reaction occurs in this case, and the species remain adsorbed at that position.

In order to introduce the ER mechanism, simulation step (b) is modified for the case of the site not being vacant. If the colliding molecule is A and the site is also occupied by A, then the trial ends, i.e. the molecule is backscattered. If the colliding molecule is A and the site is occupied by B, then A directly reacts with B_s to complete the ER process (step 5) leaving one vacant site. The other steps are similar to the LH case.

We are interested in the coverage and the production rate, i.e. how the surface roughness and the ER process affect the coverage and the production rate of MD reactions over rough surfaces. The coverage of the molecules A (θ_A), B(θ_B) and the production rate P (number of AB molecules produced

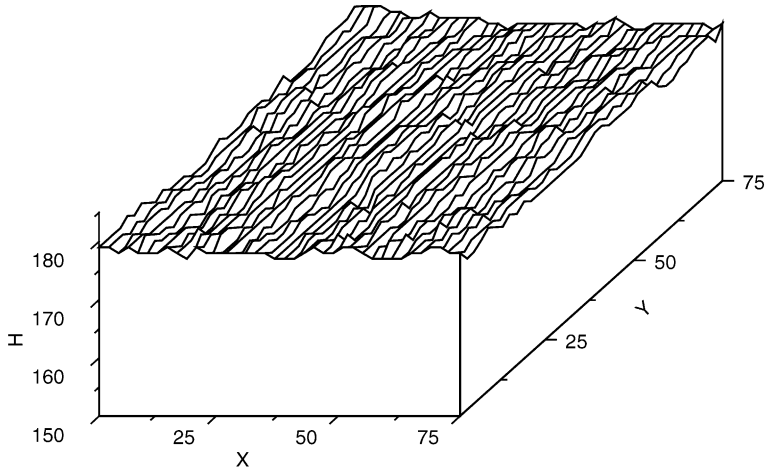

Fig. 1. Rough surface generated by random deposition with surface diffusion model.

per collision) are measured as a function of y_A. One hundred independent runs, each of 10^{10} MC cycles, are carried out so that the final coverage and production rate are the average of 100 runs.

4. Results

The rough surface generated by random deposition with surface diffusion is shown in Fig. 1. Fig. 2 shows the coverage and the production rate for the monomer–dimer reaction for the rough as well as the smooth surface by ZGB model. As shown earlier, the ZGB model on smooth surface exhibits two phase transitions between reactive and passivated states—for $y_A < y_1$, a B-passivated system is formed, while for $y_A > y_2$ the reaction system is passivated by A. For $y_1 < y_A < y_2$ the reaction on the surface can proceed. At y_1, the phase transition is continuous whereas at y_2 the transition is discontinuous.

A difference between the coverage and the production rate for the ZGB model over a rough surface and a smooth surface can be seen from Fig. 2. For smooth surface for $y_A < y_1$, the surface is completely covered by B. In contrast for rough surface at this concentration region, a few sites are also occupied by A. This happens because even though the two vacant sites are found by B_2 for adsorption, the two sites may be at different heights. So B_2 could not adsorb on the surface. As a single vacant site is required for A to be adsorbed, it occupies some sites even in the low concentration region of A.

For $y_A > y_2$ the surface is completely covered by A for smooth as well as rough surfaces since it requires only one vacant site for adsorption. So it makes no difference in this region whether the surface is a rough surface or smooth. The y_1 and y_2 shift to lower values for the rough surface versus in the case for the smooth surface thereby decreasing the width of the reaction window.

The coverage and the production rate for the ZGB model with inclusion of the ER mechanism for smooth and rough surfaces are shown in Fig. 3. It can be seen that introduction of the ER mechanism significantly changes the coverage and the production rate for the ZGB model. By adding the ER process to the ZGB model, the poisoning of the surface via complete occupation by B molecules is no longer possible. Consequently, the B poisoning regime in the ZGB model disappears completely. The maximum coverage $y_A = 0$ is 0.908. The production of AB starts at a very low concentration of A and the surface is not poisoned by B molecules at 0 or very low concentrations of A. The surface is completely covered by A at y_A = 0.4975.

By introducing surface roughness, the difference can be seen in Fig. 3(a). The nature of the coverage and the production rate slightly changes. It can be seen that for the smooth surface, for $y_A < 0.2675$, the coverage of A is 0 as all the A molecules are consumed in the LH process. In contrast, for rough surfaces it can be seen that the coverage of A at low values of y_A is not 0. Even at very low concentration, the coverage of A is 0.076. This is because, even in the high concentration region of B, due to surface roughness (non availability of two sites at similar heights), B_2 molecules could not adsorb and a few sites are vacant which are occupied by A. It can also be seen from maximum coverage of B at $y_A = 0$. Maximum coverage at $y_A = 0$ is 0.755 for the rough surface and is 0.908 for the smooth surface. Similar to the smooth surface, the product AB starts at very low concentration of A for the rough surface. The surface here is completely covered by A at

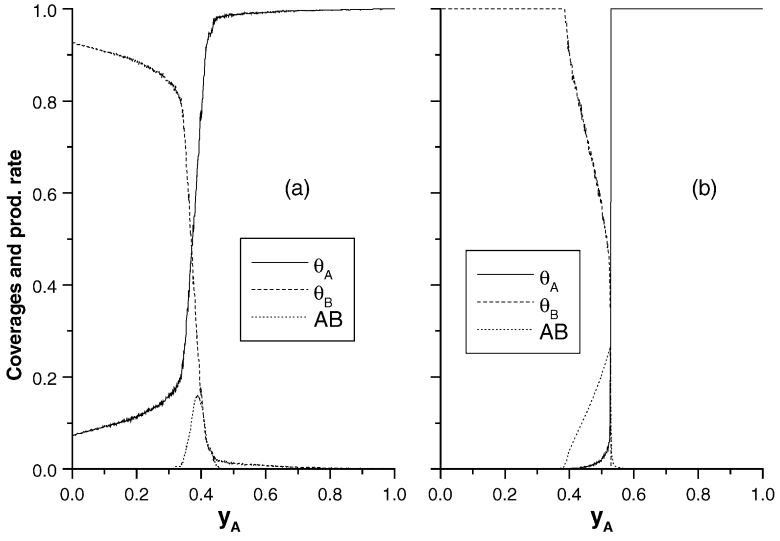

Fig. 2. Coverage and production rate for monomer–dimer reaction by LH mechanism for: (a) rough surface and; (b) smooth surface (ZGB model).

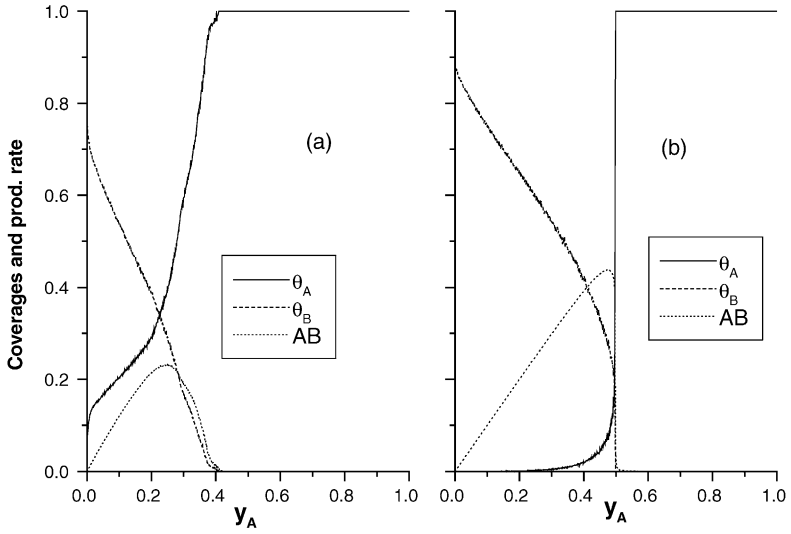

Fig. 3. Coverage and production rate for monomer–dimer reaction by LH and ER mechanism for: (a) rough surface; (b) smooth surface.

y_A=0.4090. The maximum production rate for the rough surface is >0.2 at y_A=0.2460 versus 0.438 for smooth surface at y_A=0.4740.

5. Conclusions

Monomer–dimer reactions have been studied by LH and ER mechanisms over rough surfaces generated by random deposition with surface diffusion. It is found that the surface roughness affects the coverage and the production rate of this reaction. The reaction window decreases for the rough surface versus the case of the smooth surface. By introduction of the ER mechanism to the ZGB model, the reaction window for rough surface increases, but remains less than that of the smooth surface.

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