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Monomer-dimer reaction model with asymmetric adsorption of monomer and dimer on the catalyst surface

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The irreversible kinetics of the Ziff-Gulari-Barshad model in the presence of inhomogeneity on a catalyst surface is investigated by means of Monte Carlo simulation. We assume that only part of catalyst surface sites are active for surface catalytic reaction and randomly distributed on the catalyst surface. The adsorption of a O_2 molecule is permitted if one site of a nearest-neighbor vacant pair is active. CO can adsorb on all vacant sites, but the adsorption probability is $p(p<1)$ if the site is not active. In our modified model, the O-passivated phase disappears and the continuous phase transition between the O passivated and the reactive state is eliminated. We also find that the transition between the CO passivated and the reactive state is continuous if the concentration of the active sites is small, and it becomes discontinuous with increasing concentrations of active sites. Furthermore, it is shown that a hysteresis loop exists whether the CO-passivated transition is continuous or discontinuous. Our simulation results are in good agreement with many relevant experimental results and may provide an alternative explanation for the experimental observations.

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Recently, the nonequilibrium phase transition exhibited by numerous lattice gas models of the surface catalytic reactions has attracted widespread interest in statistical physics [1–4] since Ziff, Gulari, and Barshad (ZGB) [5] introduced a model to describe the catalytic oxidation of CO. In that model, a gas composed of CO and O_2 molecules with fixed molecular concentrations y_{co} and $1-y_{co}$, respectively, is allowed to react with a square lattice surface. A CO molecule can occupy a vacant site, while O_2 molecule can dissociate and fill each site of any nearest-neighbor pair of vacancies. Adsorbed CO and O atoms at nearest-neighbor sites can react immediately to form CO_2 that leaves the surface at once. It is shown that this model exhibits two phase transitions between reactive and passivated states: for $y_{co}<y_1$, an O-passivated system is formed, while for $y_{co}>y_2$ the reaction system is passivated by CO. For $y_1<y_{co}<y_2$ the reaction on the surface can proceed. At y_1 the phase transition is continuous, whereas at y_2 the transition is discontinuous.

However, the continuous phase transition from reactive state to O-passivated state is unphysical. A large number of experimental studies of CO oxidation on many transition metal catalytic surfaces have shown that the O-passivated state is not present and the CO_2 production rate is proportional to y_{co} for small values of y_{co} [6–9]. On the other hand, according to experimental results, the nature of the CO-passivated irreversible transition changes from second to first order with increasing reactions temperature, and at some temperatures, a hysteresis loop is found [8,9]. Many modified models were proposed in order to give a more realistic treatment for the complex reaction systems including effects such as the interaction between the adsorbed species [3], the Eley-Rideal process [10,11], the nature of the surface state [12], the diffusion and desorption of one of the adsorbed species [13], the fractal substrate [14], the effect of the subsurface oxygen [15], and contaminated sites [16,17].

Although much effort has been devoted to experimental investigations of the CO oxidation on many transition metal surfaces, only part of the physical and chemical processes on the surfaces are really understood because the surface elementary steps are influenced by a whole variety of specific microscopic and mesoscopic details that are not very well-known in all cases. In this paper, we study the influence of surface inhomogeneity on the irreversible kinetic transition behavior. We take a two-dimensional square lattice with periodic boundary condition as the catalytic reaction surface and consider that only a fraction f of lattice sites are active for surface reactions and randomly distributed over the lattice surface. We propose that oxygen molecule can adsorb on two nearest-neighbor empty sites and dissociates to form two adsorbed O atoms if, at least, one site of the vacant pair is active, otherwise adsorption of O_2 is not permitted. Therefore, the oxygen cannot fill up all surface sites even in excess oxygen gas. On the other hand, for CO molecule, it can adsorb on an empty active site with probability 1, but with probability p if the blank site is not active. The surface reactions in our modified model follow the Langmuir-Hinshelwood mechanism [18],

$$\mathrm{CO}(g)+{*}\rightarrow \mathrm{CO}^{*},$$

$$\mathrm{O}_2(g)+2{*}\rightarrow 2\mathrm{O}^{*},$$

$$\mathrm{CO}^{*}+\mathrm{O}^{*}\rightarrow \mathrm{CO}_2(g)+2{*},$$

where * is the vacant site on the surface, O* means the adsorbed O atom, and CO* the adsorbed CO molecule.

The simulation process for our model begins with a random collision of a gas molecule on a square lattice. The colliding molecule is chosen to be monomer (CO) with a given probability y_{co} and dimer (O_2) with probability $1-y_{co}$.

If a monomer CO is chosen, then (1) a site on the lattice is chosen randomly; (2) if the site is occupied, the trial ends;

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(3) otherwise, the site is checked to be active or not. If the site is active, the monomer CO is adsorbed, but if the site is not active, the monomer is adsorbed with a probability *p*; (4) the four nearest-neighbor sites are checked in random order. If an O atom is found, then the two sites are vacated and a CO_2 is produced.

If a dimer O_2 is selected, then (1) two adjacent sites are chosen randomly; (2) if either site is occupied, the trial ends; (3) if both sites are vacant, then the two sites are checked to be active or not. If two sites are inactive, the trial ends. Otherwise the dimer O_2 is adsorbed and dissociates to form two O atoms; (4) the six nearest-neighbor sites of the two O atoms are checked in random order. If a monomer CO is found, then it reacts with the adjacent O atom to form a CO_2, and then both sites are emptied.

The simulations are performed for different values of the concentration *f* of active sites and the adsorption probability *p* of CO on the inactive sites. The simulation starts with all sites vacated, and then distribute the chosen fraction *f* of active sites over the lattice surface randomly. Generally, we take 3000 Monte Carlo steps for a system (100×100) to reach the stationary states.

We first discuss the behavior of catalytic reactions when *f* is small, i.e., the active region is poor. Figure 1 shows the simulation results with $f=0.1$ and different values of the adsorption probability *p*. We see from Fig. 1(a) that the O-passivated phase disappears and the continuous phase transition between the O passivated and the reactive state is eliminated. On the other hand, it is exhibited from Fig. 1(b) that the transition from the reactive state to the CO-passivated phase is continuous. These simulation results are in consistence with the experimental results where the O-passivated state does not exist and the CO-passivated transition is continuous when the reaction temperature is low [8,9]. Furthermore, Fig. 1(c) shows that the maximum production rate of CO_2 increases with increasing the adsorption probability *p*. In the present model, we can find from Figs. 1(a)–1(c) that with the increase of the adsorption probability *p*, the CO-passivated phase transition point will move towards the direction of the smaller value of y_{co}, i.e., CO-passivated region is enlarged.

Generally speaking, due to the active center theory of heterogeneous catalytic reaction, the concentration *f* of the active center of the catalytic surface plays an important role on controlling the effectiveness of a kind of catalyst, and it may violently change with reaction conditions such as the reaction temperature. As a result of most experimental observations, the catalytic activity of a catalyst (or equivalently, the concentration *f* of active sites) can increase with increasing temperature under suitable conditions. Here we discuss the influence of the concentration *f* of active sites. When $f=1$, our model reduces to the classical ZGB model. For a given value $p=0.6$ and different values of *f*, the simulation results are shown in Fig. 2. It is shown that the O-passivated phase is not present at different values of the concentration *f*. On the other hand, we find that the phase transition between the CO passivated and the reactive state becomes continuous for small values of *f* and it becomes discontinuous as *f* is increased. According to some experimental results, the CO-passivated transition can be seen as a continuous one if the reaction temperature is low and it becomes discontinuous with increasing the reaction temperature [8,9]. Moreover, the maximum value of the CO_2 production rate increases as the reaction temperature increases [8,9]. From Fig. 2(c), it is shown that our simulation results are in good agreement with the experimental observations. In some literatures [16,17], the change of the CO-passivated transition has also been observed.

Finally, we would like to discuss the hysteresis curves in the CO catalytic oxide system. We begin our simulation from an initial state where the lattice is almost covered by

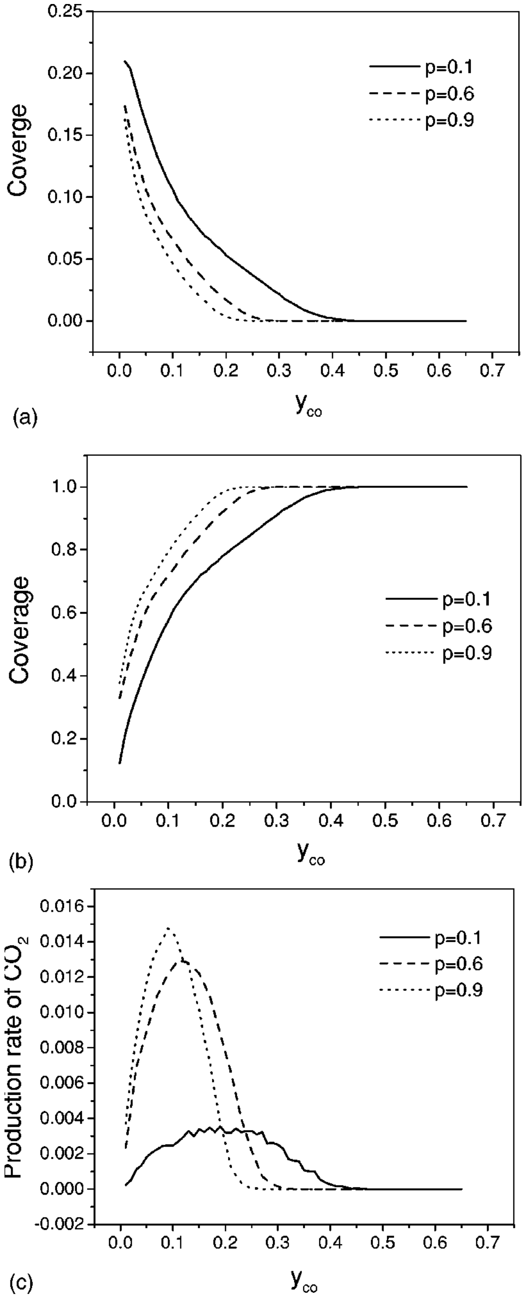

FIG. 1. The phase diagram with $f=0.1$ for different values of *p*. (a) The coverage of O atom versus the fraction y_{co}; (b) the coverage of CO versus y_{co}; (c) the production rate of CO_2 versus y_{co}.

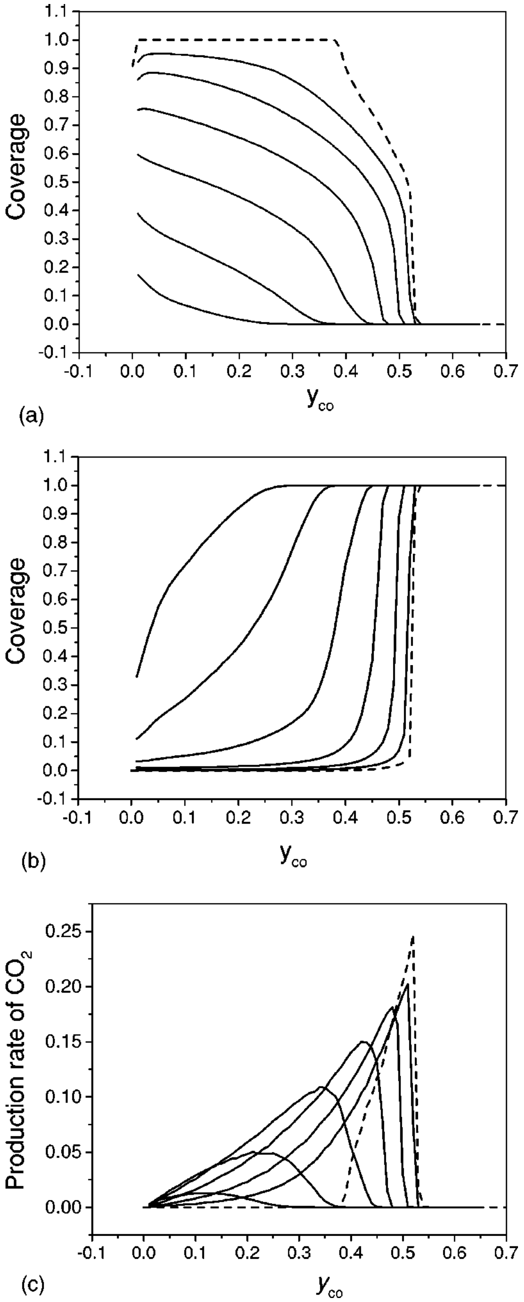

FIG. 2. The phase diagram for $p=0.6$ with different values of f. From left to right, $f=0.1$, 0.2, 0.3, 0.4, 0.5, and 0.6. The dash line is the simulation result for the standard ZGB model. (a) The coverage of the O atom versus the fraction y_{co}; (b) the coverage of CO versus y_{co}; (c) the production rate of CO$_2$ versus y_{co}.

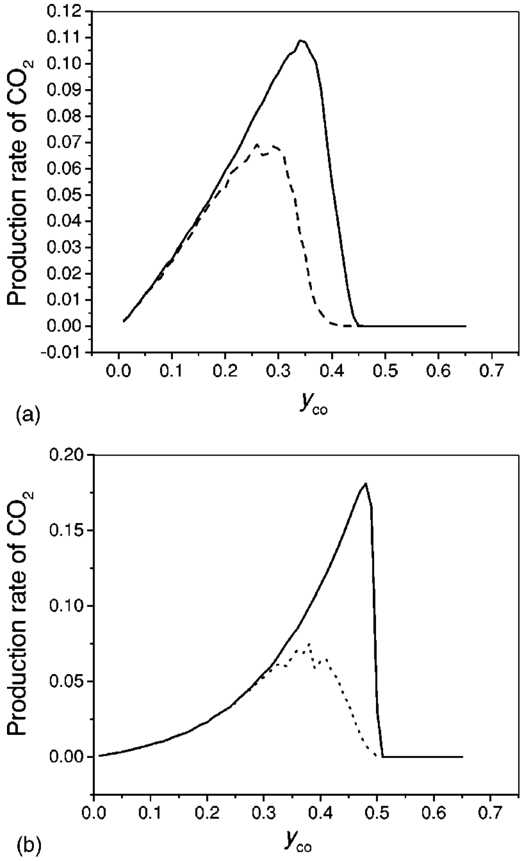

FIG. 3. The hysteresis loops for the production rate of CO$_2$. (a) $f=0.3$, $p=0.6$; (b) $f=0.5$, $p=0.6$. The dash lines are obtained from the initial condition in which a fraction of 5% of lattice sites are empty and others are occupied by the CO molecule.

CO, and only a fraction 5% of the lattice sites are empty and they are randomly distributed on the lattice surface. The simulation results are given in Fig. 3. We can clearly observe a hysteresis loop at different values of the active center concentration f. On the one hand, in Fig. 3(b), there exists a hysteresis loop when the CO-passivated transition is discontinuous; on the other hand, in Fig. 3(a) we still observe a hysteresis loop even if the CO-passivated transition becomes continuous. Hoenicke and Figueiredo [16] observed the hysteresis behavior in their model, and they, as a result of this phenomenon, obtained the critical concentration of inactive sites at which the CO-passivated transition becomes continuous. However, in our model, the hysteresis loop still exists for different values of f whether the CO-passivated transition is discontinuous or continuous, as is shown in Fig. 3. Our model may provide an alternative explanation for the experimental observations [8,9].

In conclusion, we have studied the effects of the asymmetric adsorption of CO and O$_2$ due to the presence of inhomogeneity on the catalyst surface. The O-passivated phase and the continuous phase transition of the classic ZGB model, which are never observed in experimental results, are eliminated based on our model. Moreover, it is shown that the CO-passivated transition is continuous when the concentration f of active sites is small, and its nature can become discontinuous with increasing concentration f. We find that there exists a hysteresis loop, irrespective of the nature of the CO-passivated transition.

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