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Oscillatory oxidation of CO on Pt(100): Monte Carlo simulations

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Abstract

We apply a comprehensive Monte Carlo simulation for the global oscillations in the CO catalytic oxidation system on the Pt(100) surface based on a well defined lattice gas model. The basic reactive steps of the present model follow the Langmuir–Hinshelwood mechanism incorporated with adsorbate-induced surface restructuring which follows the statistical theory of first-order phase transitions. It is shown that oscillation only exists in a certain range of CO fraction in gas and the production rate of CO₂ forms a double-periodic oscillation, while the coverages of CO and O₂ and fraction of (1 × 1) phase are in single-periodic oscillation. We give an explanation for these phenomena. Moreover, the simulation results clearly show that the diffusion of adsorbed CO works to synchronize local oscillators and the oscillation in the system will disappear with the decrease of the diffusion.

1. Introduction

The study of chemical oscillations in heterogeneous catalysis has developed into a very active field of research in recent years. These reaction systems are far from thermodynamic equilibrium and can exhibit complicated rate oscillations, spatiotemporal patterns and chaos. A comprehensive overview is given in the review article by Imbihl and Ertl [1].

Among all heterogeneous catalytic reaction systems, the catalytic oxidation of carbon monoxide on platinum is paid particular attention. Many experimental investigations have found that the metal atoms on the Pt single-crystal surface in the CO oxidation system may display two structures: the (1 × 1) phase and the quasihexagonal ('hex') phase [2]. The former is metastable compared with the latter one which is close compacted. Moreover, the reconstructions can be lifted (i.e., the (1 × 1) phase forms) by chemisorption of a number of CO in gas phase [3]. On the other hand, the experimental results show that the stick coefficient of O₂ on (1 × 1) phase is much larger than that on 'hex' phase ($s_{(1 \times 1)}/s_{hex} \sim 10^3$) [4]. The previous investigations have shown that the interplay of these factors plays an important role in the formation of temporal oscillation.

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Many experimental and theoretical works for the CO catalytic oxidation system are given in the literature [5–13]. On the other hand, cellular automation and Monte Carlo simulation have also been used to investigate the details of this reaction system [14–26] since the pioneering work done by Ziff, Gulari and Barshad (ZGB) [14]. The classical ZGB model is an idealized model which only includes the adsorption of CO and O₂ and the reaction between adsorbed CO and O particles. In order to display the oscillatory behaviour of such a reaction system, it is necessary that the desorption and diffusion of adsorbed CO molecules and the surface reconstructions are added to the ZGB model.

The theoretical treatment of the reconstructions occurring on the substrate surface was very difficult and many models were proposed as mentioned above. Based on a mesoscopic concept, some authors proposed an $n \times n$ matrix for the definition of the surface reconstruction [16, 20]. On the other hand, Kortlücke *et al* [25] introduced a so-called local definition of the surface restructuring process. In their model, all possible microscopic transitions take place only on one or two nearest lattice sites and all possible processes in surface restructuring are listed, including nucleation and phase propagation. Moreover, each process is given a fixed and physically meaningful transition probability. Recent studies [24, 27–29] also developed a model which treats the surface restructuring locally but introduces a quantitative Hamiltonian of the system to describe the complicated dynamical behaviour in heterogeneous catalytic reaction systems. In their model, the surface restructuring is considered as a first-order phase transition.

In the present paper, we systematically study the dynamical behaviour of the CO catalytic oxidation on an infinite single-crystal surface, based on the statistical theory of the first-order phase transition for the local surface restructuring. Instead of the classical ZGB model [14] we add the dynamics of CO desorption, CO diffusion and surface restructuring, which capture the essential features of the experiment such as oscillatory oxidation of CO on Pt(100). On the other hand, unlike Zhdanov's model [29] which considered infinite repulsive interactions between adsorbed neighbouring O atoms, our model does not include such an interaction and treats the O₂ adsorption in the same way as the ZGB model because the real interaction between adsorbed particles is still unclear at present. Additionally in the present model, the probability of the surface restructuring processes is calculated by the Metropolis (MP) rule instead of deterministic transition probability which was performed by Kortlücke and co-authors [25]. Using the present model, we for the first time determine the oscillatory region given by the governing parameter y_A (the fraction of CO in gas phase) by Monte Carlo simulations. Meanwhile, we find that the production rate of CO₂ forms a double-periodic oscillation, while the coverages of CO and O₂ and fraction of (1 × 1) phase are in single-periodic oscillation. We also give a reasonable explanation for these phenomena. In addition, we find that the rapid diffusion of CO synchronizes the local oscillators to form a well developed regular global oscillation distinct from the nm scale [29].

The paper is organized as follows. Section 2 is devoted to the description of the model. The simulation algorithm is given in section 3. In section 4, we show the simulation results and give some further discussions. Finally, a brief summary is given in section 5.

2. Model

The atoms on a single-crystal Pt(100) surface may be in a stable 'hex' phase or a metastable (1 × 1) phase. The clean Pt(100) surface is in the 'hex' phase because of the lower surface energy. However, the relative stability of the two surface phases may switch and a reconstruction occurs if an adsorbate of CO is more strongly bound on the (1 × 1) phase and a gain in adsorption energy overcompensates the loss in reconstruction energy. We employ a

lattice-gas model to describe this adsorbate-induced surface restructuring. For simplicity, we consider the interaction between the nearest-neighbour (NN) substrate atoms and the adsorbate–substrate interaction, but neglect the adsorbate–adsorbate interaction. The main ingredients of the model are described as follows.

The Pt atoms in the surface bear two kinds of energy: self-energy and interactive energy. Self-energy of Pt atoms is due to the relative stability of the ‘hex’ phase to the (1×1) phase. For simplicity, the self-energy of Pt atoms in (1×1) phase is considered to be ΔE and the energy of Pt atoms in ‘hex’ phase is assumed to be zero, i.e., the energy difference between the (1×1) and the clean ‘hex’ surface states is fixed to be ΔE . The interactive energy between Pt atoms is chosen to favour the congregation of Pt atoms which are in the same phase; that is, the two NN Pt atoms in the same phase have a negative interactive energy $-\varepsilon_{MM}$ and two NN Pt atoms in different phases have a positive interactive energy ε_{MM} . The interactions between next-nearest-neighbouring (NNN) Pt atoms are neglected. Here, we only emphasize the physical differences of the surface phases while disregarding their geometrical differences. In fact, it seems hardly possible to give a full-scale simulation of the surface at present.

We assume that the adsorbed particles occupy hollow sites. The interactions between adsorbed CO particles and the two structures of surface metals are different, but the interactions between adsorbed O particles and the two structures are almost the same. Therefore, for the sake of simplicity, only the interactions of adsorbed CO and substrate metal are considered, and we define the energy difference of interactions from the adsorbed CO and two surface states as ε_{AM} ($\varepsilon_{AM} = \varepsilon_{AM}^{(1 \times 1)} - \varepsilon_{AM}^{\text{‘hex’}}$, where the subscript A refers to CO). Furthermore, we simply take $\varepsilon_{AM}^{\text{‘hex’}}$ as zero, and then $\varepsilon_{AM} = \varepsilon_{AM}^{(1 \times 1)}$. In the following, we will see that these simplifications will not affect the simulation results at all.

Therefore, our model includes the adsorption–reaction process following the Langmuir–Hinshelwood mechanism, the desorption and diffusion of adsorbed CO molecules and the surface reconstructions.

Adsorption of a CO occurs on vacant adsorption sites and an O₂ adsorbs on two NN vacant sites and dissociates to form two adatoms only if all the nearest Pt atoms of the two NN vacant adsorption sites are in the (1×1) state. The nearest CO molecule and oxygen atom react to form a CO₂ which desorbs and leaves two vacant sites immediately. Adsorbed CO particles are allowed to jump to nearest vacant sites. The probability for CO diffusion follows the MP rule; that is, the difference of the adsorption energy $\Delta \mathcal{E}$ before and after the diffusion is calculated, and the accepted rate for the diffusion attempt $W_{dif} = 1$ if $\Delta \mathcal{E} \leq 0$ and $W_{dif} = \exp(-\Delta \mathcal{E}/k_B T)$ if $\Delta \mathcal{E} > 0$. In a realistic system, the CO diffusion process is very fast compared to other processes (e.g., the surface reconstruction and adsorption–reaction), and thus most adsorbed CO particles will congregate on the top of the patches of (1×1) phases due to a fast CO diffusion process. The adsorbed CO particles are also allowed to desorb. The metal surface certainly will have some effects on the desorption of CO particles. Since almost all the CO molecules are on (1×1) phase as a result of rapid diffusions, we will just consider the desorption of CO with a constant probability k_{des} for the sake of simplicity.

The metal surface can be restructured during the adsorption–reaction processes. The probability of surface restructuring also obeys the MP rule.

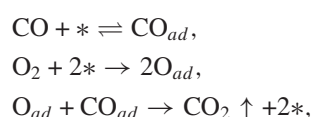
From the above description we can see that the probabilities of all these processes are either constants or determined by the MP rule in which the probability is only dependent on the difference of energy due to the changes of states.

We will fix the parameters $\Delta E/T = 2$, $\varepsilon_{MM}/T = 0.5$, $\varepsilon_{AM}/T = 2$ and $k_{des} = 0.01$ during simulation of the reaction process. In addition, we need to introduce several other parameters in the simulation [24]: y_A , p_{res} and p_{rea} ($p_{res} + p_{rea} < 1$). y_A refers to the fraction of CO in the gas phase (correspondingly, the fraction of O₂ is $1 - y_A$). p_{res} and p_{rea} are

used to characterize the relative rates of surface restructuring and adsorption–reaction steps, respectively, and the diffusion rate of CO particles will be $1 - p_{res} - p_{rea}$.

3. Algorithm of MC simulation

We carry out our simulation by sequential trials of reacting, surface restructuring and CO diffusion according to their relative probabilities defined above. Here, the dynamic processes of CO and O₂ adsorption, CO desorption and the reaction process between CO and O are chosen to meet the requirement of the well established Langmuir–Hinshelwood scheme, which can be described in the following three reaction equations:



where CO_{ad} and O_{ad} are the adsorbed states of the CO molecule and oxygen atom on the surface respectively, and * is an empty site. On the other hand, in the CO diffusion and surface restructuring processes, the Kawasaki exchange dynamics between CO and vacancies and Glauber flipping dynamics due to the change of the state of a metal site in surface restructuring are applied respectively. Compared with the real reaction system in which only part of the actual physical surface processes is really understood, our application of these dynamics is reasonable. Importantly, we emphasize that the interplay between different dynamic processes plays a much more important role than each process itself. We now give a brief description of our simulation algorithm as follows. A random number ρ_1 ($0 < \rho_1 < 1$) is first generated. If $\rho_1 < p_{rea}$, an adsorption–reaction trial is selected, if $p_{rea} \leq \rho_1 < p_{rea} + p_{res}$, an attempt of surface restructuring is selected, and else if $\rho_1 \geq p_{rea} + p_{res}$, a CO diffusion trial is selected. The corresponding steps are carried out by the following items (1)–(3), respectively.

- (1) When executing an adsorption–reaction trial, we first choose an adsorption site randomly. If the site is already occupied by a CO particle, then a CO-desorption trial is realized, using the rule described in section 2. If the site is vacant, a new random number ρ_2 is generated, and a CO-adsorption or O₂-adsorption trial is carried out, depending on whether ρ is less than y_A or not. After each successful adsorption trial, a reaction trial follows immediately. To do this, all four NN adsorption sites of the present site are scanned, and the reaction occurs and two vacant sites are generated provided that any of these sites is occupied by a different kind of particle.
- (2) The surface restructuring is realized according to Glauber dynamics, that is, one tries to ‘flip’ the state of a Pt atom by the MP rule.
- (3) For CO diffusion, an adsorption site is chosen at random. The trial continues only when the site is occupied by a CO molecule. In this case, the CO particle located in this site tries to diffuse. Then, an adjacent site is randomly selected, and if the latter site is vacant, the CO particle jumps to it with the probability prescribed by the MP rule. If the diffusion succeeds, a reaction trial will also follow it in the same way as stated in item (1).

We consider that initially ($t = 0$) the surface is clean and all the Pt atoms are in the ‘hex’ state. The simulations are carried out for ($L \times L$) Pt lattices with $L = 200$ under period boundary conditions.

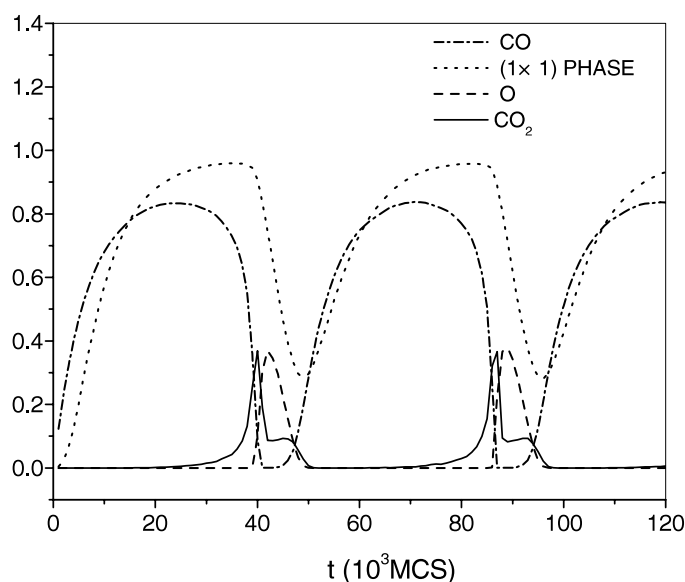


Figure 1. The temporal evolution of the well developed regular global oscillation of the reaction system under $y_A = 0.20$, $p_{res} = 0.0003$ and $p_{rea} = 0.0007$.

4. Results and discussion

With the parameters given in section 2, well developed regular global oscillations are found for $0 < y_A < 0.36$. From figure 1, we can see that both the coverage of CO and O and the fraction of Pt atoms in (1×1) phase display single-periodic oscillations. However, the oscillation of the production rate of CO_2 is apparently double periodic. In the following subsection, we will discuss it in detail.

4.1. The detailed dynamic process of the global oscillation

From figure 1, we can clearly understand the complicated process of oscillations. At the beginning of chemical reaction, the surface is in a 'hex' phase; only CO molecules can be adsorbed. With the increase of CO molecules on the surface, some patches of 'hex' phase begin to transit to the (1×1) phase (figure 1), but most of them are still occupied by CO molecules. Therefore, until the maximum coverage of the CO, the production rate of CO_2 is very small and the coverage of oxygen is almost zero. However, with the increase of CO desorption, a number of sites in (1×1) phase become vacant and the O_2 adsorption increases. The adsorbed O atoms react with neighbouring CO and more vacant sites are produced, which is similar to an autocatalytic reaction. As a result, the CO coverage decreases rapidly (figure 1) and the coverage of oxygen and production rate of CO_2 increases rapidly. Due to the rapid diffusion of CO, it reacts with oxygen adatoms and its coverage tends to decrease to zero; therefore, the fraction of (1×1) phase decreases slowly and then the adsorption of oxygen and its coverage both decrease rapidly. With the continuing adsorption of CO, the coverage of CO and fraction of (1×1) phase increase again and the oscillation occurs.

The production rate of CO_2 is determined by both CO coverage and O coverage, and will not reach its maximal value when the CO (or O) coverage is too high or too low. Therefore, an extreme value of the production rate of CO_2 can be seen in a certain time before the O

coverage reaches its peak point (figure 1). When it passes this time, the production rate begins to drop, until the CO coverage decreases nearly to zero. At this time, the adsorption of CO particles becomes dominant again and the CO coverage begins to increase again. Because of the rapid diffusion rate of CO, the probability of the collision between CO and O is still increased although the O coverage is decreasing, compared to the case with nearly zero CO coverage. Therefore, the production rate of CO₂ is lifted (though only a little), and the second extreme value of the production rate of CO₂ appears (figure 1), and thus the production rate of CO₂ shows a double-periodic oscillation.

In figure 2, we plot the time evolution of the surface pattern within a complete period. We start from the nearly empty surface (figure 2(a)). At this time the adsorption of CO molecules is dominant, thus the surface coverage of CO molecules is increasing (figure 2(b)) until it reaches its maximal value (figure 2(c)). In figure 2(c), the small blank dots inside the CO patches will become reaction fronts caused by the desorption of CO molecules. In figure 2(d), these reaction fronts begin to propagate over the surface and the CO patches decrease. The coverage of CO molecules becomes very small again in figure 2(e) and a new oscillation period will be followed.

From the description above, we show that the desorption of adsorbed CO molecules is a pre-requisite condition in triggering the oscillation. From figure 3, it is found that the system will be rapidly passivated by adsorbed CO molecules without the desorption of CO.

4.2. Dependence of oscillation dynamics on y_A

Many experimental results have found that the oscillatory dynamical behaviour is dependent on the fraction of CO in gas phase. In figure 4, we show the amplitude of oscillation as a function of y_A . It is exhibited that the well developed oscillation exists only in the interval $0 < y_A < 0.36$. For $y_A > 0.36$, the system traps into a CO-poisoned state and no oscillation occurs. It is easy to understand this result.

For the homogeneous (1×1) phase where the reconstruction of the surface is not considered, we can reduce the system by neglecting the desorption and diffusion of adsorbed CO molecules to the ZGB model [14] in which there is a reactive window between $0.375 < y_A < 0.525$. As the desorption and diffusion of CO molecules are added to the ZGB model, the simulation result is shown in figure 5. We can find that the reactive window is between 0.36 and 0.62, and when $y_A < 0.36 (> 0.62)$, the surface is almost covered by oxygen adatoms (CO molecules), where the reactive rate is very low. On the other hand, for the homogeneous 'hex' phase where the surface reconstruction is neglected, the only possible state is the CO-poisoned state because the adsorption of O₂ is inhibited on this phase.

From the above description, we can find that the oscillatory region in our model corresponds roughly to the region of the O-poisoned state on homogeneous (1×1) phase without the inclusion of the surface reconstructions. When the metal surface is empty ('hex' phase), CO molecules are easily adsorbed and the coverage of CO will increase, inevitably leading to the formation of the (1×1) islands. On the other hand, as is well known, the regime $0 < y_A < 0.36$ is within the domain of O poisoning where the O coverage increases and the CO coverage decreases on these (1×1) islands, which further disturbs the growth of the (1×1) phase and then leads to the decline of the (1×1) phase. When the (1×1) islands become small enough, the CO coverage will increase again. Therefore oscillations become possible in this range. When y_A becomes larger, the poisoning process of O adatoms does not exist on the (1×1) phase, so the coverage of O adatoms may not be high enough to suppress the further growth of (1×1) islands. Therefore, the oscillation may not occur and the system is finally poisoned by CO molecules. Interestingly, from the above results,

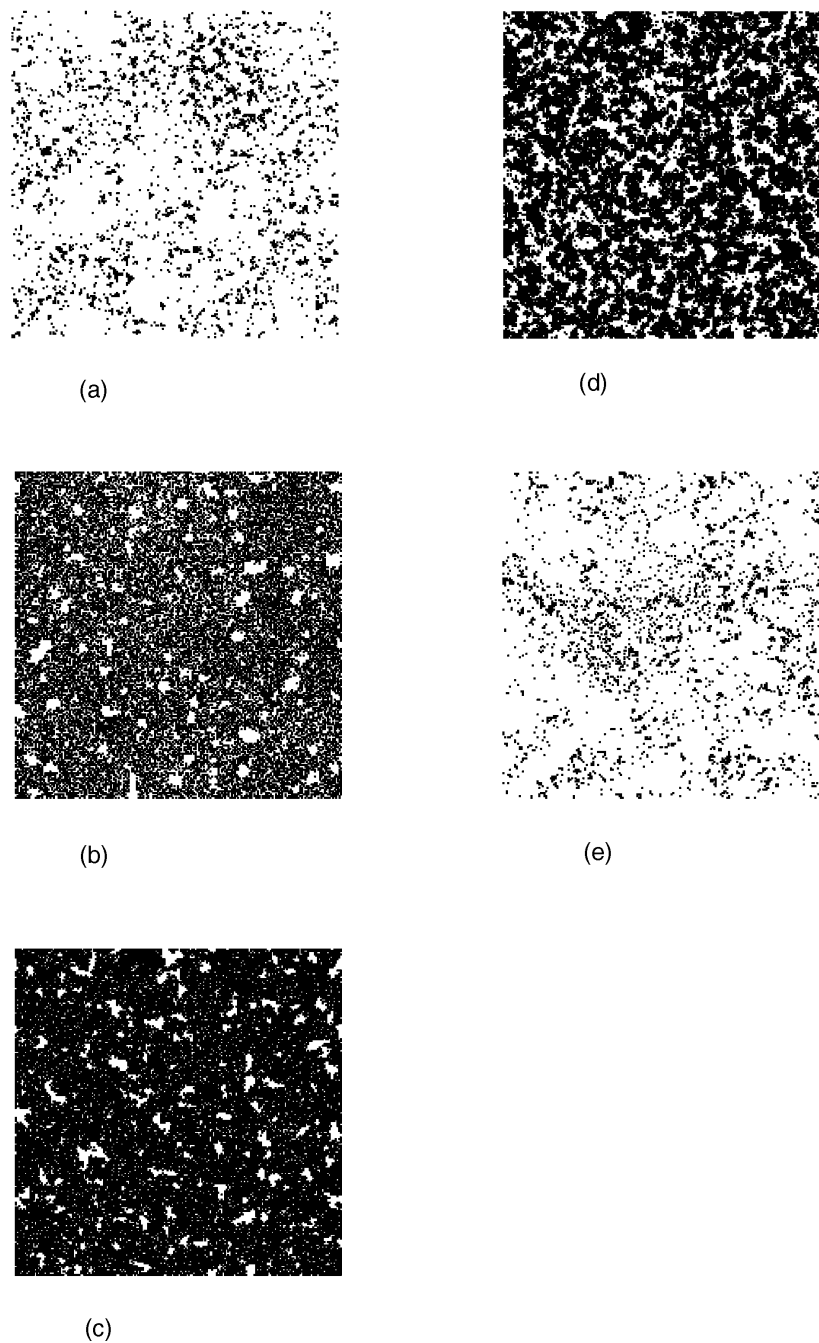


Figure 2. Snapshots of CO on metal surface during the oscillation for $y_A = 0.20$. CO particles are represented by black colour, and O particles are left blank. (a) $t = 235\,000$ MCS; (b) $t = 245\,000$ MCS; (c) $t = 265\,000$ MCS; (d) $t = 280\,000$ MCS; (e) $t = 285\,000$ MCS.

we also indicate that within the present framework of the statistical theory of the first-order phase transition for the local surface restructuring [24, 27, 28], the dynamical behaviour of

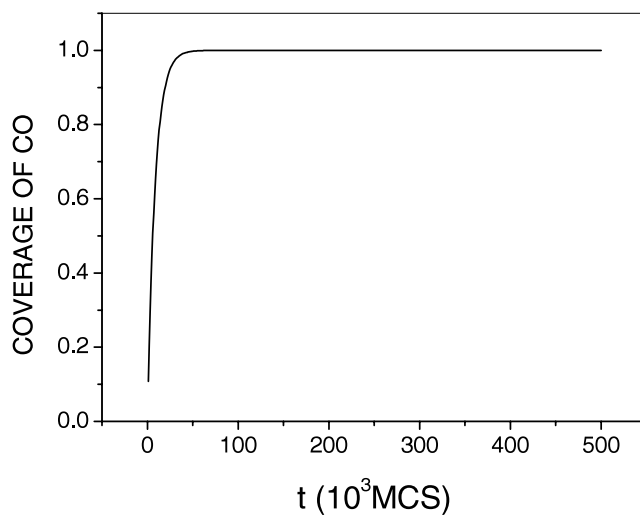


Figure 3. Time evolution of surface coverage of CO particles neglecting the desorption of CO molecules for $y_A = 0.20$, $p_{res} = 0.0003$ and $p_{rea} = 0.0007$.

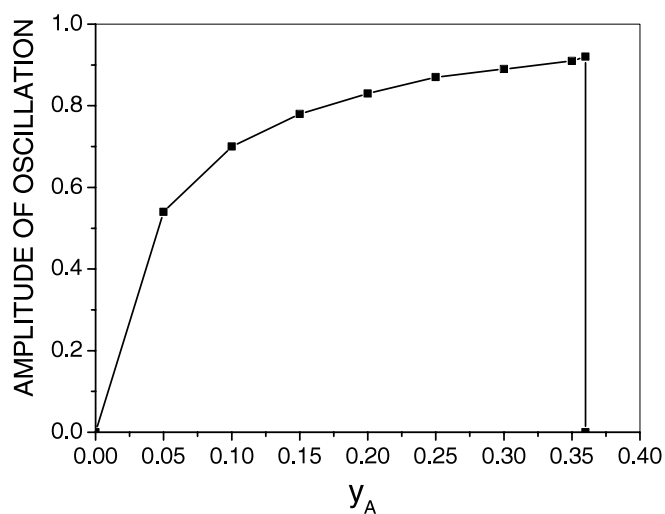


Figure 4. The amplitude of oscillation versus the fraction of CO in the gas phase.

the CO catalytic oxidation on an infinite single-crystal surface is similar to that obtained by Kuzovkov and his co-workers [22] based on a different mechanism in surface restructuring. In fact, from the above discussion about the detailed oscillatory kinetic processes, we can find that the interplay among the adsorption–reaction, the diffusion and desorption of adsorbed species and the surface restructuring plays a more important role in the oscillatory dynamics rather than the microscopic details of a special process. Therefore, the present study presents a possible route for building a universal oscillation mechanism caused by surface restructuring, and further studies will be highly desirable.

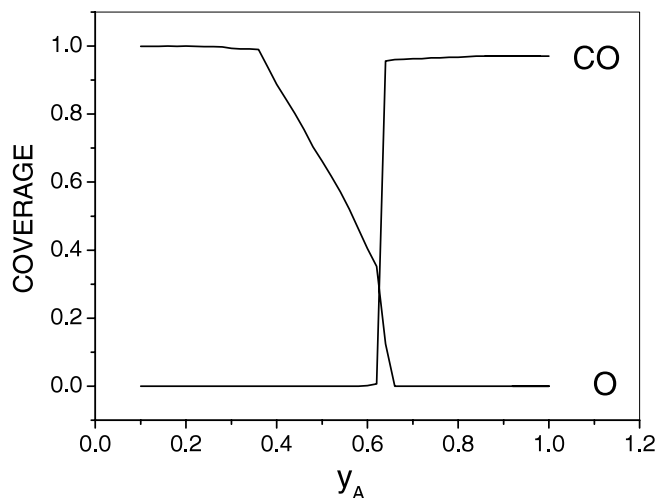


Figure 5. The coverage of CO and O on the pure (1×1) surface without considering surface restructuring. A reactive window is shown between 0.36 and 0.62 approximately.

4.3. Role of diffusion of adsorbed CO molecule

In the catalytic oxidation system of CO, the diffusion of the adsorbed CO molecule is usually fast compared to other steps and it plays an important role in oscillatory dynamics. To investigate the effect of CO diffusion, we introduce a parameter N_{dif} denoting the relative ratio of the CO diffusion to other processes. N_{dif} is defined as

$$N_{dif} = \frac{1 - p_{rea} - p_{res}}{p_{rea} + p_{res}}.$$

In figure 6, we show the temporal evolution of the CO coverage on the metal surface with $N_{dif} = 0, 10, 100$ and 1000 , respectively, where all other parameters remain unchanged. If the CO diffusion is not considered ($N_{dif} = 0$), CO coverage fluctuates randomly with time and no apparent oscillation is found (figure 6(a)). As the ratio of CO diffusion N_{dif} increases, when $N_{dif} = 10$, the evolution of CO coverage shows a damped oscillation (figure 6(b)). From the simulation results shown in figures 6(c) and (d), sustained oscillations are obtained, but for $N_{dif} = 100$ (figure 6(c)) the amplitude of the oscillation is not a constant. As $N_{dif} = 1000$, it is almost kept constant (figure 6(d)). In fact, from figure 2(c), we can see that there are many reaction fronts on the surface and each reaction front forms a local oscillator. In the case of low CO diffusive ratio, these local oscillators are nearly independent and uncorrelated, leading to the disappearance of cooperative oscillation behaviour. Thus, sustained global oscillation cannot occur. Only when N_{dif} is large enough can the local oscillators be efficiently synchronized so that global oscillations can happen.

5. Conclusion

We have performed comprehensive Monte Carlo simulations of kinetic oscillations in the reaction of CO oxidation on the Pt(100) surface in the framework of the lattice-gas model explicitly describing adsorbate-induced surface restructuring in terms of first-order phase transitions. It is found that oscillation only exists in a certain range of CO fraction in gas and the production rate of CO_2 forms a regular double-periodic oscillation while the coverages

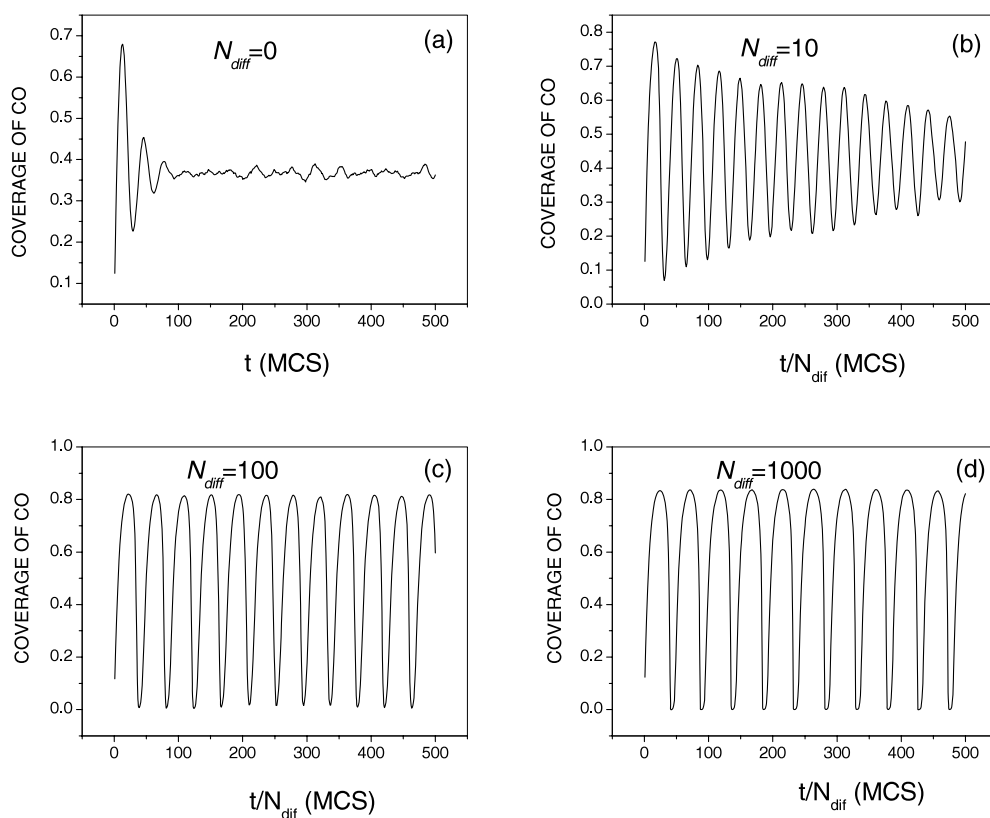


Figure 6. Time evolution of surface coverage of CO particles for $y_A = 0.20$ and $N_{diff} = 0, 10, 100$ and 1000 , respectively.

of CO and O₂ and fraction of (1×1) phase are in single-periodic oscillations. We discuss the dynamical behaviour of the double-periodic oscillation of the production rate of CO₂ and the necessity of the desorption of adsorbed CO molecules in detail. Moreover, the simulation results clearly show that the diffusion of adsorbed CO works to synchronize local oscillators and the oscillation in the system will disappear with the decrease of the diffusion.

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