Effect of inert species in gas phase on oscillatory dynamics of oxidation system of CO on Pt(100)

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We present a Monte Carlo simulation for the global oscillation of the CO catalytic oxidation system in the presence of inert species in gas phase, which can adsorb and desorb on the catalytic surface but cannot react with other species. It is found that the impurity has a dramatic effect on the oscillatory dynamics, although it does not involve in the reaction of CO oxidation. The simulation results show that with an increase in the fraction of impurity in gas phase, the periodic oscillation may change into an irregular oscillation and even can be inhibited completely. However, as the desorption rate of the impurity is increased, the regular oscillation will be recovered again.

The study of chemical oscillations in many heterogeneous catalytic reaction systems has developed into a very active field of research in recent years. In particular, the catalytic oxidation of carbon monoxide on platinum has attracted particular attention [1–19]. These reaction systems are far from thermodynamic equilibrium and can exhibit complicated rate oscillations, spatiotemporal patterns, and chaos as a result of the interplay between the reaction steps and the surface reconstructions [3,20,21]. A comprehensive overview is given in the review paper by Imbihl and Ertl [1].

However, the previous works have mainly focused on oscillatory phenomena in the reaction systems composed of pure reactants. Actually, the gas phase will inevitably be contaminated by some impurities. Although these impurities do not involve chemical reaction steps, they will always affect the adsorption of the reactants and diffusion of adsorbates by occupying the surface sites and, therefore, cause a significant effect on the dynamic or static behaviors of the reaction systems [22]. On the other hand, some authors have paid attention to the effect of the inert species in gas phase, and show that the oscillations can be induced through site blocking of adsorbed inert species [23–25].

In this paper, we study the effect of inert species in gas phase on oscillatory dynamics of oxidation system of CO on Pt(100). We find that the impurity has a dramatic effect on the oscillatory dynamics and may be an important factor that causes the irregularity of the oscillations in the CO catalytic oxidation system although it does not involve in the chemical reaction steps. This may explain some irregular oscillations observed experimentally, while only regular oscillations were reported in many previous theoretical models [12,13]. Furthermore, our simulation results show that the oscillation may be inhibited by the impurity as its fraction becomes high enough, therefore, it is always difficult to observe the oscillatory behavior in the presence of inert impurities. However, the regular oscillation will be recovered again as the desorption rate of the impurity is increased.

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The atoms on a single-crystal Pt(100) surface may be in a stable hexagonal (hex) phase or a metastable (1×1) phase. The clean Pt(100) surface is in the hex phase because of a 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-neighbor (NN) substrate atoms and the interaction of adsorbate-substrate, 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 energies: 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 taken to be ΔE and the energy of Pt atoms in the 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 favor 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}. Interactions between next-nearest-neighboring Pt atoms are neglected. Here, we only emphasize the physical differences of the surface phases while disregarding their geometrical differences. In fact, it seems remotely possible to give a full-scale simulation of the surface at present.

We assume that the adsorbed particles occupy hollow sites. The interactions between an adsorbed CO particle 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 $\varepsilon_{AM}(\varepsilon_{AM} = \varepsilon_{AM}^{(1 \times 1)} - \varepsilon_{AM}^{hex}$, where the subscript A refers to CO). Furthermore, we simply take ε_{AM}^{hex} as zero, and then

$\varepsilon_{AM} = \varepsilon_{AM}^{(1\times1)}$. 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 an adsorbed CO molecule, the adsorption and desorption of an inert impurity X, and the surface reconstructions.

Adsorption of a CO particle occurs on vacant adsorption sites and an O_2 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 CO_2 particle, 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 Metropolis (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 $W_{diff} = 1$ if $\Delta\mathcal{E}\leq0$ and $W_{diff}=\exp(-\Delta\mathcal{E}/k_BT)$ if $\Delta\mathcal{E}>0$. The adsorbed CO particles are also allowed to desorb. The metal surface will certainly have some effects on the desorption of CO particles. However, since almost all the CO molecules are on (1×1) phases as a result of rapid diffusions, we just consider the desorption of CO in a constant probability k_A for the sake of simplicity.

As for impurity X, it adsorbs on a vacant site and its interaction with the surface atoms is neglected. The probability for desorption of X is k_X.

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

From the above description we can see that the probabilities of all these processes are either constants or are 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 parameters $\Delta E/T=2$, $\varepsilon_{MM}/T=0.5$, $\varepsilon_{AM}/T=2$, and $k_A=0.01$ during simulating the reaction process. In addition, we need to introduce several other parameters in simulation [18]: y_A, y_X, p_{rea}, and p_{res} ($p_{rea}+p_{res}<1$). y_A refers to the fraction of CO in the gas phase and y_X refers to the fraction of X in the gas phase (correspondingly, the fraction of O_2 is $1-y_A-y_X$). 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 $1-p_{rea}-p_{res}$.

We carry out our simulation on a square lattice $L\times L$ by sequential trials of reacting (adsorption and desorption processes are also included), surface restructuring, and CO diffusion according to their relative probabilities defined above. A random number $\rho_1(0<\rho_1<1)$ 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 in steps (a), (b), and (c) as follows.

(a) When executing an adsorption-reaction trial, we first choose an adsorption site randomly. If the site is already occupied by a CO (or X) particle, then a CO (or X)

-desorption trial is realized, using the rule described above. If the site is vacant, a new random number ρ_2 is generated, and a CO-adsorption, O_2-adsorption, or X-adsorption trial is carried out, depending on which of the three intervals $[0,y_A]$, $[y_A,y_A+y_X]$, and $[y_A+y_X,1]\rho_2$ belongs to. For the adsorption of O_2, another adsorption site is randomly chosen from the four NN adsorption sites of the first chosen site. If the pair adsorption sites are vacant and the six nearest-neighbor metal atoms of the pair adsorption sites are in the 1×1 state, O_2 adsorbs on the two vacant adsorption sites and dissociates. After each successful adsorption trial of CO or O_2, a reaction trial follows immediately. To do this, all the four NN adsorption sites of the present site are scanned, and the reaction occurs and two vacant sites are generated provided that any pair of these sites is occupied by a different kind of reactants.

(b) 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.

(c) 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 (a).

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 $L=128$ under periodic boundary conditions.

When impurities are not present, the coverage of CO will develop into regular, periodic oscillations, as shown in Fig. 1. We can describe the oscillatory process as follows. For the initial clean surface, the stick coefficient for O_2 is taken to be zero and the only possible process is CO adsorption. The increase in the CO coverage on the surface drives Pt atoms to change into the (1×1) phase. With the continuing of this process, most of the metal surface begins to be covered by CO patches, and, correspondingly, most of the Pt atoms are in the (1×1) phase, where the stick coefficient for O_2 adsorption becomes high. However, O_2 cannot still be adsorbed because the vacant sites required by O_2 adsorption are lacking on the (1×1) phase. Now, desorption of CO plays a main role; it provides neighboring vacant sites for O_2 adsorption. When O_2 molecules are adsorbed on these sites, they will react with neighboring CO and more vacant sites are produced. This process is similar to an autocatalytic reaction that prevents the balance between CO adsorption and desorption. Thus the CO coverage inside islands starts to decrease, which is accompanied by a decrease in the restructured patches. With the passage of time, the CO coverage becomes rather small, and then the CO adsorption becomes dominated again and a new cycle begins.

As the impurity X is introduced into the reaction system, it does not change the reaction network of the system but may block the adsorption of CO and O_2 by occupying the vacant sites. Such an effect becomes stronger for O_2, which needs two (neighboring) sites for adsorption. However, for a
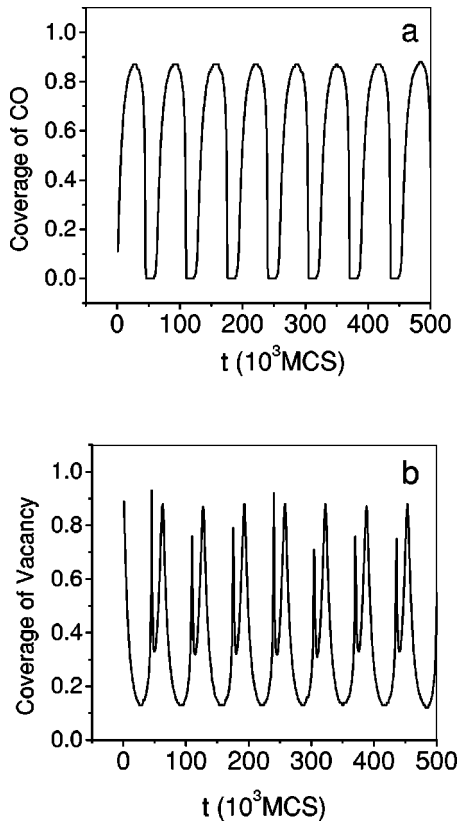
FIG. 1. The regular global oscillation of CO coverage on the surface under $y_A = 0.20$ when no impurity X is present ($y_X = 0$). $p_{rea} = 0.0007$, $p_{res} = 0.0003$.

fixed desorption probability of impurity k_X (here, $k_X = 0.01$), when the fraction of impurities in gas phase y_X (also representing the adsorption probability of X) is small, the effect of X will not be notable enough, and both the coverage of CO and the coverage of vacancy still display regular and periodic oscillation [Fig. 2(a)]. As the value of y_X is increased, the oscillatory behavior of the system will be dramatically changed as is illustrated in Fig. 2(b). We can see that irregular oscillation appears and the system jumps between the states with high CO coverage and low CO coverage randomly.

As is well known, when the coverage of CO has been very high on the surface, it will need the adsorption of O_2 to form a reaction front, then the reaction front propagates over the whole surface by an autocatalytic reaction. The adsorption of X will effectively affect the propagation of the reaction front by occupying the vacant sites. As the CO coverage is high, most of the Pt atoms at the subsurface are in the (1×1) phase and the stick coefficient for O_2 is high. As a result, O_2 can easily adsorb on the surface and form a reaction front. However, O_2 adsorption needs two neighboring vacant sites, but at the early stage of the formation of the reaction front, the blank region is still very small and just the adsorption of a few X particles may block the adsorption of O_2 and suppress the further propagation of the reaction front. If the reaction front is not blocked by the X adsorbate at the beginning of its formation, the propagation of the reaction front is a rapid process compared with the X adsorption and the blank areas become too large to be blocked by the X adsorbate, therefore, the propagation of the reaction front continues and the CO coverage decreases to nearly zero.

We believe that the occurrence of irregular oscillatory behavior is due to the introduction of impurity X. If the relative amount of O_2 with respect to CO remains the same as that in
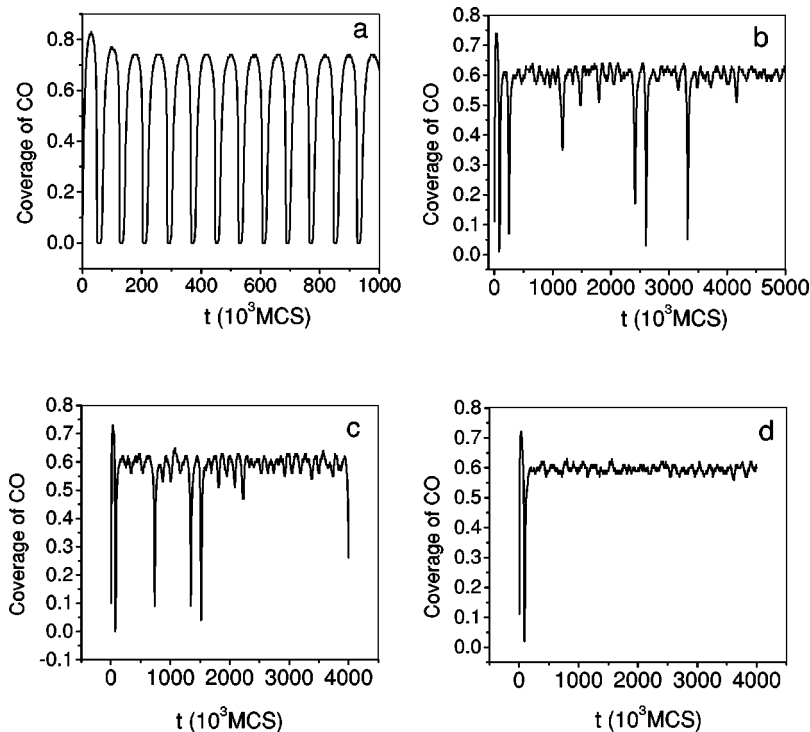

FIG. 2. The temporal evolution of CO coverage on the surface under $k_X = 0.01$. (a) $y_A = 0.20$, $y_X = 0.01$; (b) $y_A = 0.20$, $y_X = 0.04$; (c) $y_X = 0.04$, $y_A = 0.192$; and (d) $y_A = 0.20$, $y_X = 0.05$. Other parameters are the same as in Fig. 1.
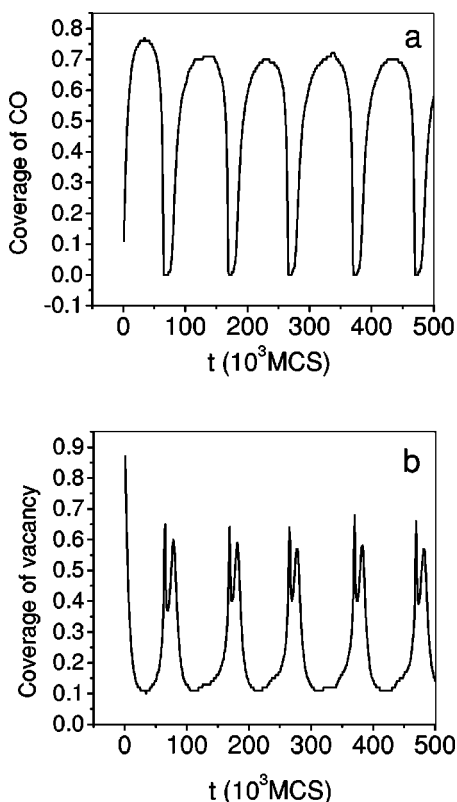
FIG. 3. The oscillation behavior under $y_A = 0.20$, $y_X = 0.04$, and $k_X = 0.04$. (a) The evolution of CO coverage, and (b) the evolution of vacancy fraction on the surface. Other parameters are the same as in Fig. 1.

Fig. 1 and the fraction y_X of the impurity X is the same as in Fig. 2(b), we find from Fig. 2(c) that the temporal series is in analogy with the simulation result in Fig. 2(b). This means that the change of oscillation in Fig. 2(b) is mainly from the effect of impurity X.

If the fraction of impurities is further increased, the adsorption probability of impurity X increases and its effect becomes more serious. As y_X is high enough, the reaction front will inevitably be blocked at the beginning of its formation. Therefore, the autocatalytic reaction cannot occur at all. According to the simulation results, when y_X is increased to 0.05, the oscillatory behavior can be inhibited completely by the impurity and the system is trapped in a high CO coverage state as is shown in Fig. 2(d). The present result clearly indicates that as impurity X is introduced, the oscillatory behavior may be suppressed.

Furthermore, the desorption probability of X plays an important role on the oscillatory dynamics of the system. In Fig. 3, we show the temporal evolution of CO coverage and vacancy fraction on the surface by increasing k_X to 0.04 for a fixed value $y_X = 0.04$. Compared with Fig. 2(b), we can clearly see that as k_X is increased to 0.04, the effect of X particles on the surface may be weakened and the oscillation turns back to a period 1.

According to the investigation of some authors [26,27], the size effect of the lattices may play an important role on the oscillation behavior of the system. In Fig. 4, we present the simulation results as the size of lattice is changed. It is shown that the irregular oscillation behavior remains unchanged although the quantitative behavior exhibits some small differences as the lattice size is increased.

Actually, the surface diffusion process of adsorbed CO directly affects the propagation of reaction front. In our
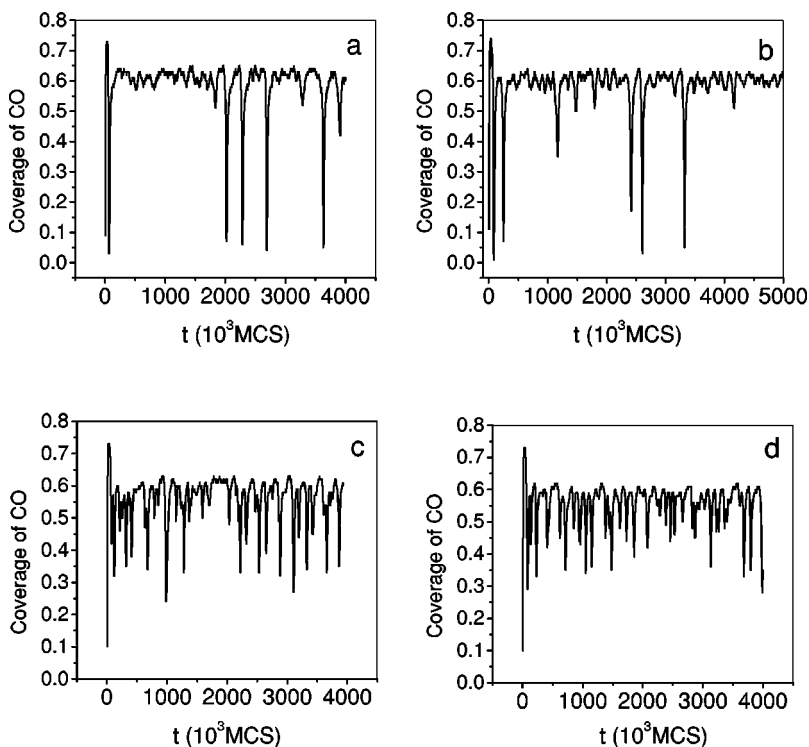

FIG. 4. The temporal evolution of CO coverage on the surface for different sizes of lattice. (a) $L = 100 \times 100$, (b) $L = 128 \times 128$, (c) $L = 200 \times 200$, and (d) $L = 256 \times 256$. Other parameters are the same as in Fig. 2(b).
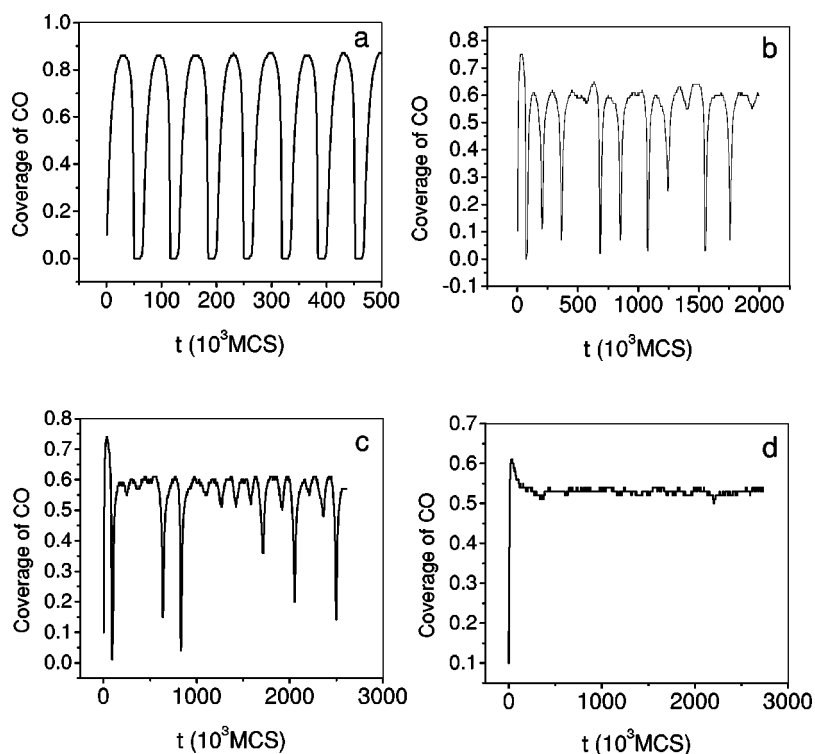
FIG. 5. The temporal evolution of CO coverage on the surface for $p_{rea} = 0.0005$. (a) $y_X = 0.0$, (b) $y_X = 0.04$, (c) $y_X = 0.05$, (d) $y_X = 0.10$. Other parameters are the same as in Fig. 2(b).

simulation, we decrease p_{rea}, then the diffusion of adsorbed CO increases. In Fig. 5, we give the simulation results as p_{rea} is changed from 0.0007 to 0.0005. The reaction system exhibits an oscillation before the impurity is introduced and
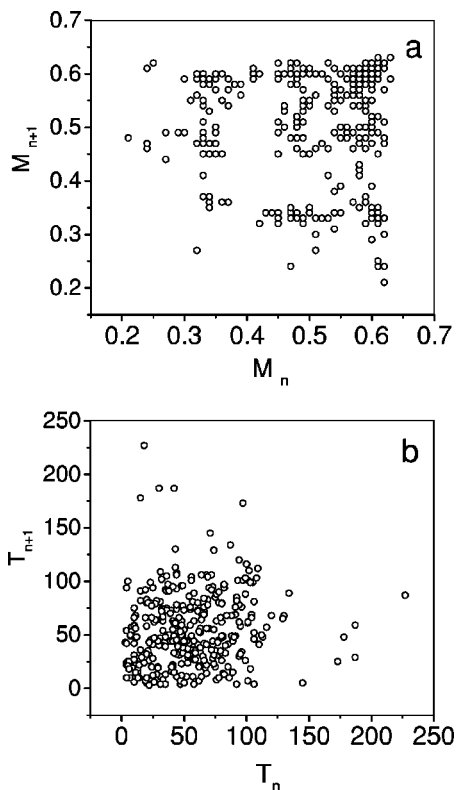

FIG. 6. The 1D map of the series minimum values M_n of CO coverage (a) and the series time interval T_n between two near minimum of CO coverage (b) from the simulation result in Fig. 4(c).

the effect of impurity X on the oscillation behavior is in analogy with that in Fig. 2. But with the increasing of the diffusion of adsorbed CO, the propagation of reaction front becomes more rapid. Therefore, compared to Fig. 2(d), the oscillation behavior cannot be inhibited completely, but exhibits an irregular oscillation even when $y_X = 0.05$. In this case, we find that until $y_X = 0.10$, oscillation can be inhibited completely. The result shows that with the decreasing of p_{rea}, the diffusion of adsorbed CO and propagation of reaction front increases, therefore, more inert species are needed to annihilate the oscillation completely.

Finally, in order to explore the feature of the irregular oscillations above, we discuss respectively, the time correlations of the series minimum values $M_n (n = 1, 2, \ldots)$ of CO coverage and the series time interval $T_n (n = 1, 2, \ldots)$ between two near minimum values of CO coverage, in which the first value M_1 (or T_1) of the object series is regarded as x and the second value M_2 (or T_2) is regards as y and then the second value M_2 (or T_2) is input as x and the third value M_3 (or T_3) is regarded as y and so on. In Fig. 6, we show the one dimensional (1D) map of series M_n and T_n according to the simulation results in Fig. 4(c). We find that the points in Figs. 6(a) and 6(b) are randomly distributed. This means that the minimum value series M_n and time interval series T_n are random, indicating that the irregular oscillation in Fig. 4(c) is not a chaotic oscillation but a random behavior.

In summary, we have conducted a Monte Carlo simulation for the oscillatory oxidation of CO on Pt(100) when there exists an inert impurity in the gas phase. It is found that it has a dramatic effect on the oscillatory dynamics by blocking the adsorption sites for the reactants. Its effects on the adsorption of CO and O_2 are asymmetric, since the adsorption of O_2 needs two neighboring sites. When the fraction of impurity is

high but its desorption rate remains low, the system exhibits an irregular oscillatory dynamics instead of periodic oscillation. Further increase in the impurity fraction may completely suppress the oscillation phenomena. Moreover, the simulation results show that the effect of the inert impurity bears an analogy with the increasing of the size of lattice and diffusion of adsorbed CO. During many experimental processes, it is very difficult to avoid impurity completely, and

we believe that further experimental investigation will be highly desirable.

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