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Effect of Surface Impurities on Oscillation in NO+CO/Pt(100) Reaction System

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A lattice gas model was proposed to explore the effect of inert surface impurities on the oscillation in the NO+CO reaction system on Pt(100). It was found that when the fraction of the impurities is small, the (1×1) phase resulting from the surface restructuring can form a connected phase and the system exhibits a global sustained oscillation. With the fraction of the impurities increasing, the (1×1) phase only can form many isolated patches and the spatial coherence between the local oscillators with a random phase relationship lost, and as a result, the sustained oscillation changes into a damped one. When the diffusion rate of adsorbed CO and NO increases, the synchronization between local oscillators is enhanced and the global sustained oscillation can appear again.

Key words: NO+CO/Pt(100) reaction system, Chemical oscillation, Heterogenous catalytic reaction, Monte Carlo method, Lattice gas model

I. INTRODUCTION

The NO+CO reaction on Pt(100) has received much attention in the past two decades because of the key role of NO_x emission in air pollution and the interesting dynamic behavior it displays [1-3]. The kinetic oscillations in the system were first reported by Singh-Boparai and King in single crystal studies [4]. This reaction system being far from thermodynamic equilibrium can exhibit complicated rate oscillations, spatiotemporal patterns and chaos [1,5-14]. Several theoretic models which are based on mean-field (MF) nonlinear differential equations have been established to reproduce most of the experimental facts [5,10,15].

The previous theoretical studies have mainly focused on the reaction behaviors on a perfect periodic substrate. Actually, the inhomogeneities in the catalytic surface can affect almost all kinds of kinetic processes on the surface in various subtle ways, such as the adsorption-reaction step, the surface diffusion and the surface restructuring process [16-26]. On the other hand, the NO+CO/Pt(100) reaction system in the high temperature regime exhibits a damped kinetic oscillation when there is no temperature modulation [5,25]. Some experimental results and theoretical studies have shown that the surface active defects can lead to a damped oscillation behavior [25-27]. In Ref.[5], the oscillation behavior integrated over the whole surface area damps much faster than that integrated over a small part of the surface area, which implies that a loss in spatial coherence may be responsible for the damped oscillation behavior. Obviously, the mechanism of the damped behavior in the reaction system is still an open question.

In this work, the authors proposed a lattice gas model to explore the effect of inert surface impurities on the oscillation in the CO+NO/Pt(100) reaction system incorporating the treatment of the CO- and NO-induced surface restructuring in terms of the first-order phase transition theory [12,16]. It was found that, with the fraction of the inert impurities increasing, the active restructuring (1×1) phase only can form small isolated patches and the sustained oscillation changes into a damped one. Moreover, the oscillation behavior over a large lattice size system damps faster than that over a small one. These simulation results show that the effect of the impurities results in a loss of the spatial coherence between local oscillators and then leads to a damped oscillatory behavior.

II. REACTION SCHEME AND MODEL

Many experimental phenomena indicate that the catalytic reaction of CO+NO on Pt(100) includes the following steps [5]:

$$\mathrm{CO_{gas}} + * \rightleftharpoons \mathrm{CO_{ads}} \quad (1)$$
$$\mathrm{NO_{gas}} + * \rightleftharpoons \mathrm{NO_{ads}} \quad (2)$$
$$\mathrm{NO_{ads}} + * \rightarrow \mathrm{N_{ads}} + \mathrm{O_{ads}} \quad (3)$$
$$\mathrm{CO_{ads}} + \mathrm{O_{ads}} \rightarrow (\mathrm{CO_2})_{\mathrm{gas}} + 2* \quad (4)$$
$$\mathrm{N_{ads}} + \mathrm{N_{ads}} \rightarrow (\mathrm{N_2})_{\mathrm{gas}} + 2* \quad (5)$$

where "*" means an empty lattice site, and the subscripts gas and ads denote the species in gas-phase and adsorbate on the surface, respectively.

In the current reaction system, an $L\times L$ square lattice is employed to model the Pt(100) surface. On the

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lattice surface, every site corresponds to a Pt atom and some sites are occupied by impurities. We assume that reaction particles can be adsorbed in a center hollow site around four lattice sites, which is called an adsorbate site. (The assumption is not important; when the adsorption is on the top of a site, the model can be described using the same formulas.) However, an adsorption is inhibited if all of four sites around a hollow site are occupied by impurities, in this case the hollow site is called an "impurity position".

From the previous investigation [12,27], the complicated kinetic processes in the catalytic reaction system have important influences on the oscillatory dynamic behavior. Our model considers adsorption of CO and NO molecules, decomposition of the adsorbed NO, reaction process between an adsorbed CO and O atom from the decomposition of NO, desorption of CO and NO whose probability is determined by the interaction between the particle and surface atoms, surface diffusion of CO and NO, and surface restructuring process. We will discuss the details of every process.

The clean Pt(100) surface is in the hexagonal (hex) phase because of a lower surface energy. A surface reconstruction occurs to form the (1×1) phase if an adsorbate is more strongly bound on the (1×1) phase and a gain in adsorption energy overcompensates for the loss in reconstruction energy. The relative stability of the two surface phases may switch and it has been observed that the rate oscillation accompanies a periodic restructuring, which confirms the restructuring mechanism of the oscillation [28,29]. On the other hand, we assume that when the surface site is occupied by an inert impurity, it is more stable than in the hex phase and it can not restructure into the (1×1) state.

In the model, a self energy of Pt atom is defined to describe the relative stability of a surface atom in different surface phase where the difference of surface atom density is neglected. For simplicity, the self-energy of a surface atom is assumed to be zero when the site is occupied by an impurity. Therefore, we assume that the self-energies of Pt atoms in the hex phase and the (1×1) phase are taken to be δE and $2\delta E$, respectively.

Furthermore, two kinds of interactions should be considered including the interactions between the nearest-neighbor (NN) substrate atoms and between adsorbate-substrate. The adsorbate-adsorbate interaction is neglected in the model (although if necessary, this interaction can be easily included in the model). For the interactive energy between Pt atoms, the two NN Pt atoms in a same phase have a negative interactive energy $-\varepsilon_{\rm MM}$ ($\varepsilon_{\rm MM}>0$) and two NN Pt atoms in two different phases have a positive interactive energy $\varepsilon_{\rm MM}$. On the other hand, the interaction between the atom of an impurity and other atom is assumed to be negligible.

The interactions between an adsorbed particle and the surface atoms in different phases are different. We define that $\varepsilon_{\rm AM}$, $\varepsilon_{\rm BM}$, $\varepsilon_{\rm CM}$ and $2\varepsilon_{\rm AM}$, $2\varepsilon_{\rm BM}$, $2\varepsilon_{\rm CM}$ (A=CO, B=NO, C=O) are the adsorption energies between adsorbed particles and Pt atoms in the stable and metastable state, respectively. For the sake of simplicity, we neglect the interaction between adsorbed particle and the atom of an impurity.

The adsorbed CO or NO particles are allowed to desorb. The metal surface certainly has some effects on the desorption of adsorbate particles. The probability of desorption of a given particle is determined by $W_{\rm des}=\exp(-\sum_j \varepsilon_{\rm AM} n_j{}^{\rm M}/k_BT)$, where $n_j{}^{\rm M}$ is a variable to denote the state of metal atom j in the NN sites of the particle A. Values $n_j{}^{\rm M}=2$, 1 or 0 is assigned to the metastable state, the stable state and an impurity state, respectively.

An adsorbed CO (NO) particle is allowed to jump to a NN vacant adsorption site but an "impurity position" is excluded. In an approximation, the probability of the diffusion jump is calculated by the Metropolis (MP) rule [30]: $W=\min\{\exp(-\Delta E/k_BT),1\}$, where ΔE is the energy difference between the final and initial state, k_B is the Boltzmann constant and T is temperature. Oxygen atom diffusion is ignored because the process is very slow [12].

NO decomposition needs another NN vacant adsorption site and it occurs only if all nearest Pt atoms of the two NN adsorption sites are in the meta stable state and the NN vacant site is not in an "impurity position". (In the model, we neglect the effect of the active defects on NO decomposition [26,27].) Because the reaction rate of N_2 production is very rapid, we assume that O atom from NO decomposition process occupies the previous vacant site and N atom is removed from the surface [5,12].

CO and O in two NN sites can react to form a CO_2 particle, which desorbs and leaves two vacant sites immediately.

The metal surface can be restructured by changing the state of the Pt atom during the adsorption-reaction processes. The probability of the surface restructuring is determined according to the MP rule. The restructuring process for the surface sites occupied by impurities is excluded.

III. ALGORITHM OF SIMULATIONS

Before describing the simulation algorithm, we define several parameters in the simulation. For simplicity, we use $k_B=1$ and fix parameters $\delta E/T=2$, $\varepsilon_{\rm MM}/T=0.5$, $\varepsilon_{\rm AM}/T=\varepsilon_{\rm BM}/T=\varepsilon_{\rm CM}/T=2.0$ during the simulation. $P_{\rm rea}$ and $P_{\rm res}$ ($P_{\rm rea}+P_{\rm res}<1$) are used to characterize the relative rates of the adsorption-reaction steps and the surface restructuring, respectively, and the diffusion rate of particles will be proportional to $1-P_{\rm rea}-P_{\rm res}$. In order to discuss the effect of the diffusion, a parameter $N_{\rm dif}$ is introduced to denote the relative rate of the diffusion to other processes. $N_{\rm dif}$ is defined as $N_{\rm dif}=(1-P_{\rm rea}-P_{\rm res})/(P_{\rm rea}+P_{\rm res})$. $P_{\rm CO}$ and $P_{\rm NO}$ refer to the fraction of CO and NO in gas phase.

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The adsorption-reaction step includes CO and NO adsorption and desorption, NO decomposition, and LH reaction between CO and O, their relative rates are considered to be proportional to $P_{\rm CO}$, $P_{\rm NO}$, $P_{\rm CO}^{\rm des}$, $P_{\rm NO}^{\rm des}$, $P_{\rm dec}$ and $1-P_{\rm CO}^{\rm des}$, respectively. In the simulation, $P_{\rm CO}=P_{\rm NO}=0.005$, $P_{\rm CO}^{\rm des}=P_{\rm NO}^{\rm des}=0.05$, $P_{\rm dec}+P_{\rm NO}^{\rm des}=0.2$ and $P_{\rm res}/(P_{\rm rea}+P_{\rm res})=0.1$.

The simulation is carried out by sequential trials of the adsorption reaction step, the surface restructuring process, and the diffusion process according to their relative probabilities defined above.

A random number ρ_1 ($0<\rho_1<1$) is first generated. If $\rho_1<P_{\rm rea}$, an adsorption-reaction trial is selected; if $P_{\rm rea}<\rho_1<P_{\rm rea}+P_{\rm res}$, a surface restructuring process attempt is selected, and if $\rho_1>P_{\rm rea}+P_{\rm res}$, a diffusion trial is selected. The corresponding steps are carried out by the following items.

(i) When executing an adsorption-reaction trial, a new random number ρ_2 is generated and an adsorption site is chosen randomly. If the site is already occupied by a CO (or NO) particle, CO (or NO) desorption or LH reaction (NO decomposition) is performed for $\rho_2<P_{\rm CO}^{\rm des}$(or $\rho_2<P_{\rm NO}^{\rm des}$) and $\rho_2>P_{\rm CO}^{\rm des}$(or $P_{NO}^{\rm des}<\rho_2<P_{\rm NO}^{\rm des}+P_{\rm dec}$), respectively. For CO (or NO) desorption, a new random number ρ_3 is generated and the trial is executed if $\rho_3<W_{\rm des}$. For CO reaction, one of the NN sites is selected randomly. If the latter site is occupied by O, the trial is executed. When NO decomposes, one of the NN adsorption sites is selected randomly and the trial is executed if the latter site is vacant but not an "impurity position" and the two sites are located on the (1×1) phase.

If the site is vacant, a CO-adsorption or NO-adsorption trial is carried out provided that $\rho_2<P_{\rm CO}$ and $P_{\rm CO}<\rho_2<P_{\rm CO}+P_{\rm NO}$, respectively.

(ii) For the surface restructuring trial, a Pt atom is selected randomly and its state is changed following the probability given by the MP rule. If the selected site is occupied by an impurity, the trial ends.

(iii) To simulate the CO or NO diffusion, an adsorption site is selected randomly. When the site is occupied by a CO or NO molecule, an adjacent adsorption site is selected randomly, and if the latter site is vacant but not an "impurity position", the CO or NO particle jumps to it according to the MP rule. Otherwise the trial ends.

At the beginning of a simulation, some sites are occupied by impurities distributed randomly according to a fraction p, the other Pt atoms are in the hex phase. The simulations are carried out on a (200×200) lattice with periodic boundary conditions.

IV. RESULTS OF SIMULATIONS

Using the algorithm defined above, the reaction system can evolve into different dynamical stationary states under different extensive conditions.

When there is no impurity, the coverage of CO, NO, O, and Pt atom in the (1×1) phase will develop into regular oscillations as shown in Fig.1. The simulation results are consistent with previous work [12]. We can describe the oscillatory process to understand the feedback in the oscillation system. For the initial clean surface, the decomposition for NO is taken to be zero and the only possible process is CO and NO adsorption. The increase of CO and NO coverage on surface drives Pt atoms to be restructured into the (1×1) phase. With the adsorption and restructuring process continuing, most of the metal surface is covered by CO and NO patches and most of Pt atoms are in the (1×1) phase, where NO decomposition is in a high probability. However, NO cannot be decomposed yet because the vacant sites required are lacking on the (1×1) phase. Now the desorption of CO and NO plays an important role. It provides neighboring vacant sites for NO decomposition. When NO molecules are decomposed on these sites and O atoms are left, they will react with neighboring CO and more vacant sites are produced. This process is called "surface explosion" [25] and it is similar to an autocatalytic reaction which prevents a balance between CO and NO adsorption and desorption. Thus CO and NO coverage inside islands start to decrease, which is accompanied by a decrease of the restructured patches. With the passage of time, CO and NO coverage becomes rather small, and then the adsorption of CO and NO dominates again and a new cycle begins.

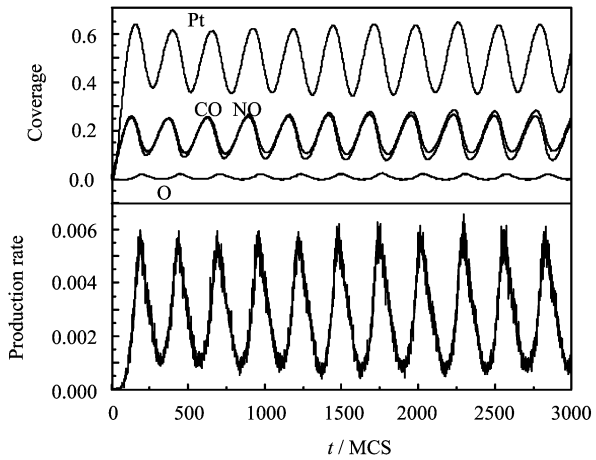

FIG. 1 The regular oscillation of CO, NO, O, and Pt atoms in the (1×1) phase on the surface when no impurity is present. p=0.0, $N_{\rm dif}$=100.

When there are impurities on the metal surface, they cannot change the reaction mechanism, but can block the adsorption of CO and NO and inhibit the restructuring process of surface atoms. When the impurity fraction is small, the simulation results are shown in Fig.2 (a) and (b). The coverage of CO, NO, O and the fraction of Pt atoms in the (1×1) phase show regular oscillations. It is obvious that the impurities can not have a determinative effect on the oscillation behavior.

With the fraction of the impurities increasing, as il-

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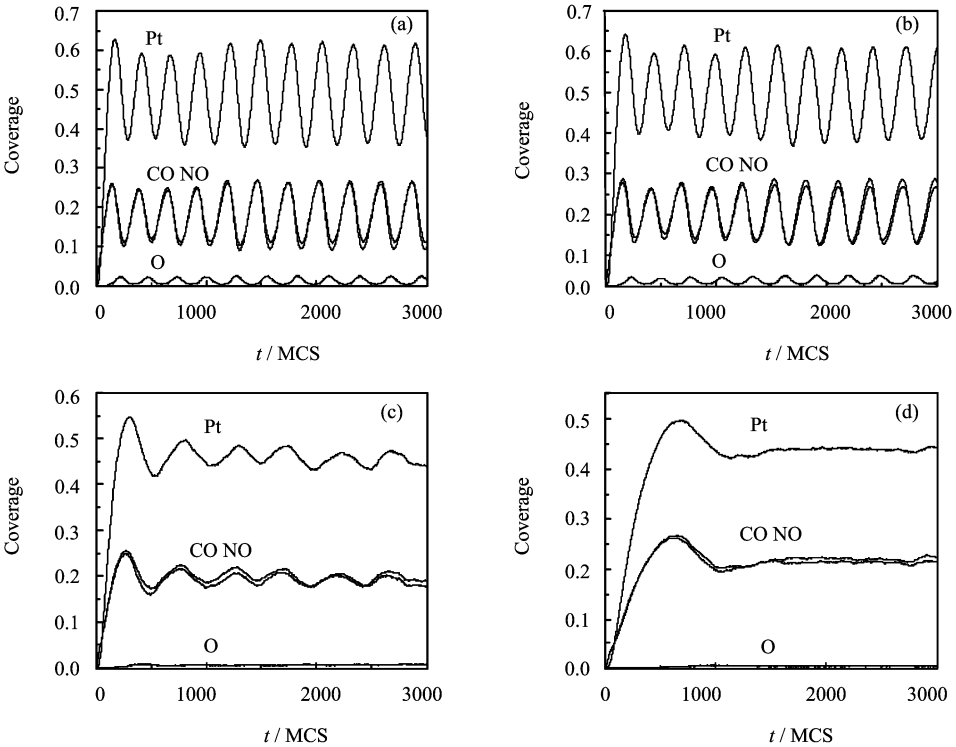

FIG. 2 The temporal evolution of the fraction of Pt(1×1) and the coverage of CO, NO, and O on the surface. $N_{\rm dif}$=100. (a) p=0.01, (b) p=0.02, (c) p=0.10, (d) p=0.20.

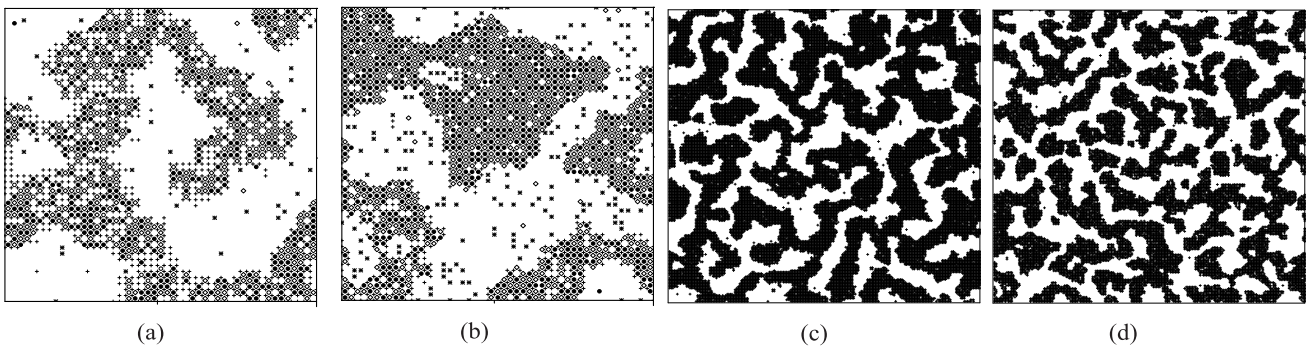

FIG. 3 Snapshots during the simulations at t=3000 MCS. (a) p=0.02, (50×50), (b) p=0.10, (50×50), (c) p=0.02, (200×200), and (d) p=0.10, (200×200). Plus signs represent Pt atoms in the state corresponding to the (1×1) phase. Stars signify impurities. Pt atoms in the state mimicking the "hex" phase are not shown. Filled circles, open circles, and diamonds correspond to CO, O, and NO species, respectively. In (c) and (d), only the (1×1) phase is shown.

lustrated in Fig.2(c), the oscillatory behavior of the system changes into a damped oscillation. As shown in the snapshot of Fig.3 (a) and (b), it is found that the impurities have an important influence on the restructuring process. The surface atoms in the adjacencies of some places where the impurities are concentrated are almost in the hex phase. On the other hand, the adsorbed CO and NO are mainly concentrated in the (1×1) phase.

Furthermore, when the impurity fraction is small, as shown in Fig.3(c), it is found that the (1×1) phase can almost form a connected phase under a periodic boundary condition, so an efficient synchronization of the local oscillators can be developed to form a sustained oscillation. However, in Fig.3(d), the fraction of the impurity increases and the (1×1) phase is divided into many small isolated patches, and so the "surface explosion" can not spread over the whole (1×1) phase. As a result, the synchronization between local oscillators is lost. Moreover, the simulation results under different lattice sizes are shown in Fig.4, it is found that the oscillation behavior is damped more quickly when the lattice size is increased. It is obvious that, with the lattice size increasing, many more patches of the (1×1) phase appear to form more local oscillators with a ran-

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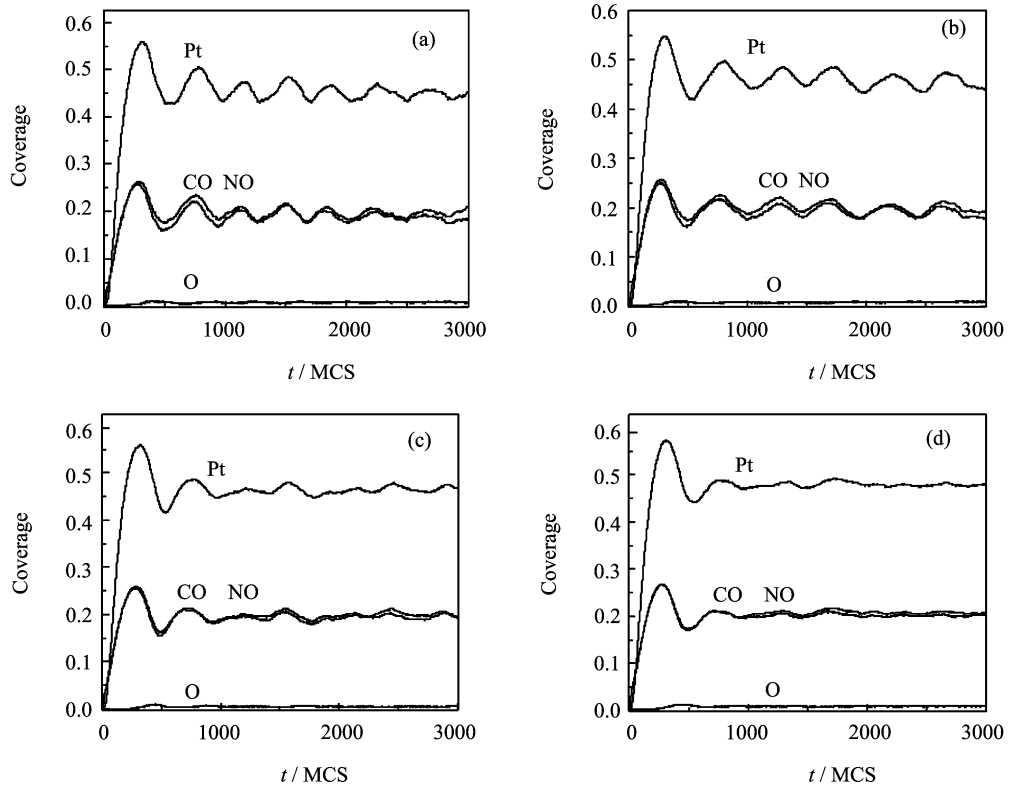

FIG. 4 The temporal evolution of the fraction of Pt(1×1) and the coverage of CO, NO for different lattice sizes. p=0.10, $N_{\rm dif}$=100. (a) (150×150), (b)(200×200), (c)(250×250), (d)(300×300).

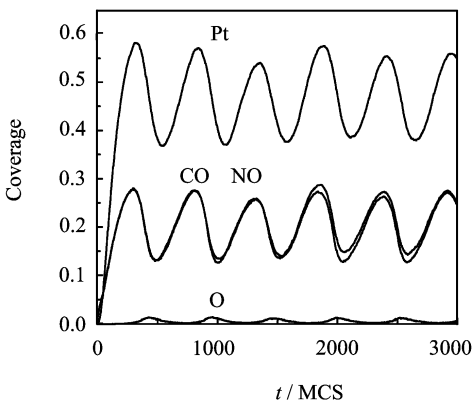

FIG. 5 The temporal evolution of the fraction of Pt(1×1) and the coverage of CO, NO for $N_{\rm dif}$=1000 and p=0.10.

dom phase relationship, after which the whole system loses the spatial coherence more quickly to reach the stationary state.

On the other hand, with increasing the diffusion rate, the synchronization between local oscillators can be enhanced again. When the rate of diffusion $N_{\rm dif}$ increases from 100 to 1000, the damped oscillation in Fig.2(c) changes into a sustained one again as shown in Fig.5. These simulation results are very consistent with previous experimental results [5].

When the fraction of the impurities is high enough, the oscillation will be inhibited completely as shown in Fig.2(d).

V. CONCLUSION

A model is proposed to investigate the oscillatory behaviors of the CO+NO/Pt(100) reaction system by introduction of the inert surface impurities on the catalytic surface. It is found that, when the impurity fraction is small, the (1×1) phase resulting from the surface restructuring can form a connected phase and the system exhibits a sustained oscillation. With the increasing of the impurity fraction, the (1×1) phase can only form many isolated patches, meaning that the spatial coherence between the local oscillators is broken and the spatial synchronization is lost. As a result, the sustained oscillation changes to a damped one. When the diffusion rate of adsorbed CO and NO increases, the synchronization between local oscillators is enhanced and the sustained oscillation appears again.

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