

Damped oscillation in the NO+CO/Pt(100) reaction system

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Considering the influence of the surface defects formed in the surface restructuring phase transition in the CO+NO/Pt(100) reaction system, we propose a lattice gas model to investigate the damped oscillation in the high-temperature oscillatory regime by means of a Monte Carlo simulation. The simulation results show that the persistent oscillation can change into a damped one when the fraction of the defects increases. The production rate of CO₂ is near to the maximum value when the oscillation is damped to the end. Furthermore, it is found, in the early stage of the oscillation, that the NO decomposition mainly occurs in the 1×1 phase and the hex phase is inactive for the reaction. However, as the reaction proceeds, defects are gradually formed in the 1×1⇌hex phase transition, the hex phase becomes active and dominative for the NO decomposition, and then the oscillation becomes damping. The simulation results give an explanation for some previous experimental phenomena.

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I. INTRODUCTION

Kinetic oscillations in the NO+CO/Pt(100) reaction system were reported by Singh-Boparai and King in single crystal studies [1]. Later on, many interesting dynamical behaviors, such as rate oscillations, spatiotemporal patterns, and chaos, were discovered [2–11]. Moreover, several theoretic models, which are based on mean-field (MF) nonlinear differential equations, have been established to describe the complicated dynamical behaviors in the systems [5,10,12].

Recently, the Monte Carlo method was employed to explore the detailed mechanism of the kinetic oscillation in the catalytic reaction system and many interesting results were obtained [13]. The understanding of the oscillation mechanism of the reaction system is of interest due to the nontrivial interplay of the chemistry reaction and the adsorbate-induced surface restructuring process. It has been observed that the rate oscillation is related to the 1×1⇌“hexagonal” (hex) surface phase transition [14,15] and that adsorbed CO, NO, and O species can stabilize the 1×1 phase of Pt atoms, which is in a metastable state on a clean surface compared to the hex phase. Kortluke *et al.* introduced a so-called local definition of the surface restructuring process [16]. On the other hand, Zhdanov proposed a model that treats the surface restructuring locally but introduces a quantitative Hamiltonian to describe the surface restructuring in terms of a first-order phase transition [17,18].

The previous simulation studies have focused on a defect-free substrate and have reproduced the sustained oscillation in the NO+CO/Pt(100) reaction system [16–18]. Actually, the defects or inhomogeneities in the catalytic surface could have an important influence on the dynamical behavior in various subtle ways [18–26]. On the other hand, it was found that the NO+CO/Pt(100) reaction system usually exhibits a damped oscillation behavior in two temperature regimes [5,12,27] and the production rate of CO₂ is increased to the

maximum as the oscillation is damped to the end in the high-temperature regime. In Ref. [5], the damped oscillation is ascribed to the absence of an efficient synchronization between the local oscillators. For this explanation, there needs to be more information about the detailed surface processes. Zhdanov has also aimed to reproduce the damped oscillation by assuming that the NO decomposition can occur only on the interface between the hex phase and the 1×1 patch formed due to the adsorbate-induced surface restructuring [28], but the experimental results show that the reaction can proceed when the surface remains in the 1×1 phase [5].

In this paper, we propose a model by introducing a kind of structural defect to understand the damped oscillation, incorporating the treatment of the adsorbate-induced surface restructuring in terms of the first-order phase transition theory [17,18]. According to some experimental phenomena, we assume that the defects are induced from the surface restructuring and can accelerate the decomposition of the adsorbed NO molecule. It is found that the damped oscillation in the NO+CO/Pt(100) reaction system in the high temperature oscillatory regime can be explained from the effect of the defects.

The paper is organized as follows: Sec. II is devoted to the description of the model and the simulation algorithm. In Sec. III, we discuss the simulation results. Finally, a brief summary is given in Sec. IV.

II. MODEL AND SIMULATION ALGORITHM

Many experimental phenomena indicate that the catalytic reaction of the CO+NO/Pt(100) system includes the following steps [5]: $\text{CO}_{gas} + * \rightleftharpoons \text{CO}_{ads}$, $\text{NO}_{gas} + * \rightleftharpoons \text{NO}_{ads}$, $\text{NO}_{ads} + * \rightarrow \text{N}_{ads} + \text{O}_{ads}$, $\text{CO}_{ads} + \text{O}_{ads} \rightarrow (\text{CO}_2)_{gas} + 2*$, $\text{N}_{ads} + \text{N}_{ads} \rightarrow (\text{N}_2)_{gas} + 2*$, where * means an empty lattice site, and the subscripts *gas* and *ads* denote the species in the gas phase and adsorbate on the surface, respectively.

A full-scale simulation for the surface restructuring process is very difficult at present [17]. For simplicity, the density difference of the two phases is neglected, therefore, we

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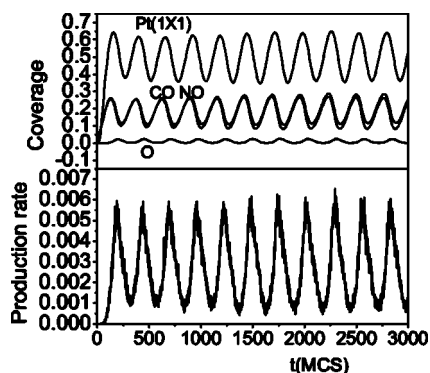


FIG. 1. Regular oscillation of CO, NO, O, and Pt atoms in the 1×1 phase coverage in surface when no defect is present. The simulation parameters are $P_{CO}=P_{NO}=0.005$, $\delta E/T=2$, $\epsilon_{MM}/T=0.5$, $\epsilon_{AM}/T=\epsilon_{BM}/T=\epsilon_{CM}/T=0.5$, $P_{CO}^{des}=P_{NO}^{des}=0.05$, $P_{dec}+P_{NO}^{des}=0.2$, $P_{res}/(P_{rea}+P_{res})=0.1$, and $N_{dif}=100$. The unit of production rate is CO_2 molecule per site per Monte Carlo steps (MCS). One MCS is defined as a Monte Carlo attempt of the adsorption-reaction-surface restructuring events per site.

can employ a $L \times L$ square lattice to model the catalytic surface [16–18]. In the lattice surface, every site corresponds to a Pt atom. We assume that the reaction adsorbate particles can be adsorbed in the center hollow site around four lattice sites, which is called an adsorbate site. The regular Pt atoms in the surface bear two kinds of energies: self-energy and interactive energy. The relative stability of the hex phase to the 1×1 phase is due to the self-energy of Pt atoms. The self-energy of the atom in the stability of the hex phase is assumed to be zero. Therefore, the self-energy of the Pt atom in the 1×1 phase is taken to be δE , i.e., the energy difference between the different surface states is fixed to be δE .

The interaction between the nearest-neighbor (NN) substrate atoms and the interaction of adsorbate substrate are included, but the adsorbate-adsorbate interaction is neglected. For the interactive energy between Pt atoms, the two NN Pt atoms in the same phase have a negative interactive energy $-\epsilon_{MM}$ ($\epsilon_{MM} > 0$) and two NN Pt atoms in the different phases have a positive interactive energy ϵ_{MM} .

The interactions between an adsorbed particle and the different structures of surface metals are different. We take that ϵ_{AM} , ϵ_{BM} , ϵ_{CM} , and $2\epsilon_{AM}$, $2\epsilon_{BM}$, $2\epsilon_{CM}$ ($A=\text{CO}$, $B=\text{NO}$, $C=\text{O}$) are the adsorption energies between adsorbed particles and Pt atoms in the hex phase and the 1×1 phase, respectively.

On the other hand, the model includes the desorption and diffusion of adsorbed particles, the NO decomposition, the adsorption-reaction process following the Langmuir-Hinshelwood (LH) mechanism, and the surface restructuring [17]. They are described as follows.

The adsorbed CO or NO particles are allowed to desorb. The metal surface will certainly have some effects on the desorption of the adsorbate particles. The probability of desorption of a given particle is determined following $W_{des} = \exp(-\sum_j \epsilon_{AM} n_j^M / k_B T)$.

The adsorbed CO and NO particles are allowed to jump to the NN vacant adsorption sites. According to the local approximation, the probability of diffusion can employ the Me-

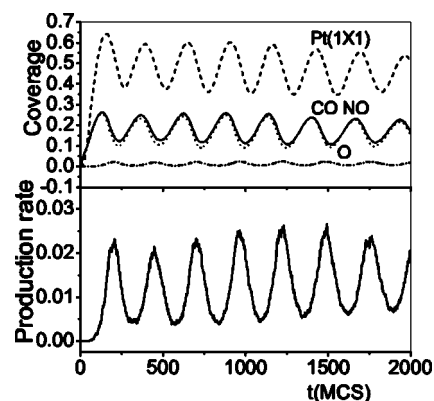


FIG. 2. Regular oscillation of CO, NO, O, and Pt atoms in the 1×1 phase coverage in surface for $p=0.0001$. The unit of production rate is CO_2 molecule per site per MCS.

tropolis (MP) rule [29]: $W = \min\{\exp(-\Delta E/k_B T), 1\}$ where ΔE is the energy difference between the new and old positions, k_B is the Boltzmann constant, and T is the temperature. That is, the difference of the adsorption energy ΔE before and after the diffusion is calculated, and the accepted rate for the diffusion attempt $W_{dif}=1$ if $\Delta E < 0$ and $W_{dif} = \exp(-\Delta E/k_B T)$ if $\Delta E > 0$. Oxygen atom diffusion is ignored because this process is very slow [17].

The NO decomposition is very complicated and takes an important role in the reaction system. In previous works [5,16–18], it is considered that the NO decomposition can occur only on the 1×1 phase and the hex surface is inactive. Most recently, Miners and Gardner have shown that the high-reaction-rate branch of the oscillatory cycle coincides with the maximum area of the surface in the hex phase [27]. Therefore, we assume that, in both the 1×1 and hex phase, the NO molecule can decompose. For the 1×1 surface, the NO decomposition needs another NN vacant adsorption site and this occurs only when all the nearest Pt atoms of the two NN vacant adsorption sites are in the 1×1 state. For the hex surface, the NO decomposition is ascribed to a kind of structural defect formed in the $1 \times 1 \rightleftharpoons$ hex phase transition. Since there is a slight difference between the surface densities of Pt atoms in the hex and the 1×1 phases, the surface phase

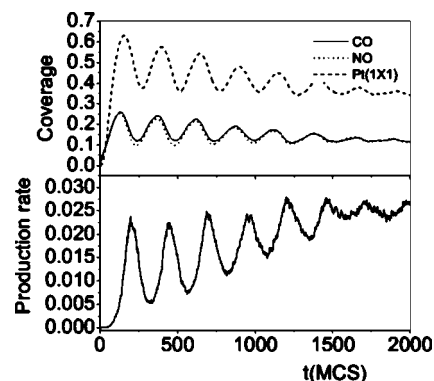


FIG. 3. Regular oscillation of CO, NO, O, and Pt atoms in the 1×1 phase coverage in surface for $p=0.0005$. The unit of production rate is CO_2 molecule per site per MCS.

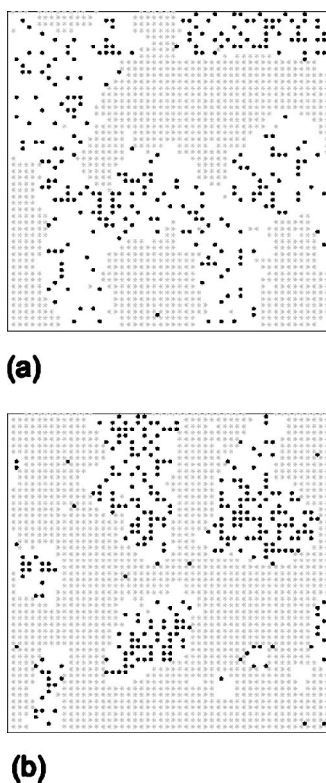


FIG. 4. Snapshots of 50×50 at $t=2000$ MCS. The gray area is the hex phase, the 1×1 phase is in the light areas, and the black particles are NO. (a) $p=0.0001$ and (b) $p=0.0005$.

transition may cause structural imperfections, such as a surface vacancy. For simplicity, we consider the structural defect as a regular Pt atom in the hex state combining with an additional NN vacancy; therefore, the influence of the structural imperfections can be shifted to the effect of the Pt atom in the defect state. The effect of the defect is assumed to be that the adsorbed NO molecule can decompose very rapidly if one of its NN Pt atoms is in the defect state. Because the reaction rate to produce N_2 is very rapid, we assume that the O atom released from the NO decomposition occupies the previous vacant site and the N atom is removed from the surface.

The nearest CO molecule and O atom react to form a CO_2 particle, which desorbs and leaves two sites vacant immediately.

The metal surface can be restructured by changing the state of Pt atom. According to the local approximation, the probability of surface restructuring can be determined according to the MP rule. The Pt atom in the hex phase that has performed a turnover of the surface restructuring may be in the defect state with a probability p .

In addition, we have to introduce several parameters for the model described above. For simplicity, we use $k_B=1$. P_{res} and P_{rea} are used to characterize the relative rates of surface restructuring and adsorption-reaction steps, respectively, and then the diffusion rate of particles will be $1-P_{rea}-P_{res}$. P_{CO} and P_{NO} refer to the fraction of CO and NO in the gas phase. The CO and NO desorption operations are proportional to P_{CO}^{des} and P_{NO}^{des} , respectively. The NO decomposition in the

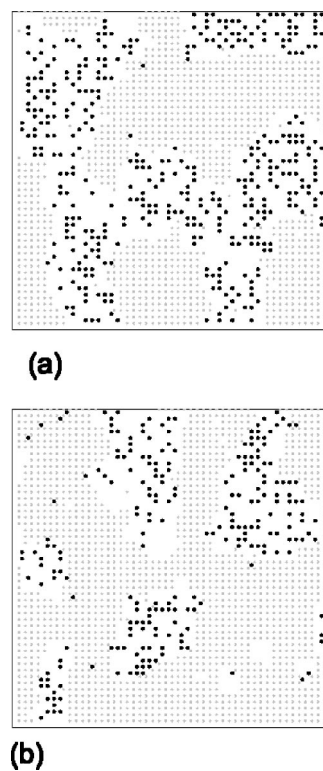


FIG. 5. Snapshots of 50×50 at $t=2000$ MCS. The gray area is the hex phase, the 1×1 phase is in the light areas, and the black particles are CO. (a) $p=0.0001$ and (b) $p=0.0005$.

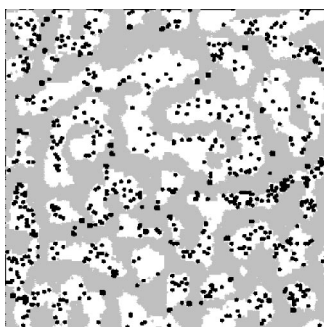
1×1 phase and the LH reaction between CO and O are proportional to P_{dec} and $1-P_{CO}^{des}$. For the surface diffusion, a parameter N_{dif} is introduced to denote the relative ratio of the diffusion to other processes. N_{dif} is defined as $N_{dif} = (1-P_{rea}-P_{res})/(P_{rea}+P_{res})$.

We carry out our simulation by sequential trials of reacting (adsorption and desorption processes are also included), surface restructuring, and diffusion according to their relative probabilities.

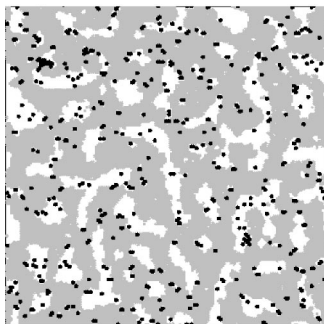
A random number ρ_1 ($0 < \rho_1 < 1$) is first generated. If $\rho_1 < P_{rea}$, an adsorption-reaction trial is selected; if $P_{rea} < \rho_1 < P_{rea}+P_{res}$, an attempt of surface restructuring is selected, and if $\rho_1 > P_{rea}+P_{res}$, a diffusion trial is selected. The corresponding steps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

(a) When executing an adsorption-reaction trial, an adsorption site is chosen randomly. If the site is already occupied by a CO (NO) particle, a new random number ρ_2 is generated, the CO (NO) desorption process is performed for $\rho_2 < P_{CO}^{des}$ ($\rho_2 < P_{NO}^{des}$) or CO surface reaction (NO decomposition) is executed for $\rho_2 > P_{CO}^{des}$ (or $P_{NO}^{des} < \rho_2 < P_{NO}^{des}+P_{dec}$), respectively.

For CO (or NO) desorption, a new random number ρ_3 is generated and the trial is executed if $\rho_3 < W_{des}$. For the CO reaction, one of the NN sites is selected randomly; if the latter site is occupied by O, the trial is executed. When an adsorbed NO molecule decomposes on the 1×1 phase, one of the NN adsorption sites is selected randomly, and the trial is executed if the latter site is vacant and the six NN metal atoms of two adsorption sites are in the 1×1 state.



(a)



(b)

FIG. 6. Snapshots for 200×200 at $t=2000$ MCS. The gray area is the hex phase, the 1×1 phase is in the light areas, and the black particles are O atoms. (a) $p=0.0001$ and (b) $p=0.0005$.

If the site is vacant, a CO-adsorption or NO-adsorption trial is carried out, provided that $\rho_2 < P_{CO}$ and $P_{CO} < \rho_2 < P_{CO} + P_{NO}$, respectively. Moreover, when a NO molecule is adsorbed successfully and if one of the NN Pt atoms is in the defect state, the NO molecule decomposes at once.

(b) 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 a restructuring attempt to the hex state is accepted, the Pt atom is in the regular hex state with a probability $1-p$ or the defect state with a probability p .

If the restructuring trial to the 1×1 state is not accepted, the selected Pt atom can change into the defect state with a probability p when its NN Pt atoms are in the hex state and it has executed a turnover of the restructuring phase transition. On the other hand, the selected Pt atom recovers into the regular hex state with a probability $1-p$ when it is in the defect state. After a Pt atom transforms into the defect state successfully, the NO molecules located in its NN adsorption sites decompose at once.

(c) To stimulate the CO or NO diffusion, an adsorption site is selected randomly. When the site is occupied by a CO or NO molecule, an adjacent site is selected randomly, and if the latter site is vacant, the CO or NO particle jumps to it according to the MP rule; otherwise the trial ends. When a NO molecule diffuses successfully and if one of the four NN Pt atoms is in the defect state, the adsorbed NO molecule decomposes at once.

In the beginning of the simulation, all of the Pt atoms are in the hex state and the simulations are carried out on the 200×200 lattice with periodic boundary conditions.

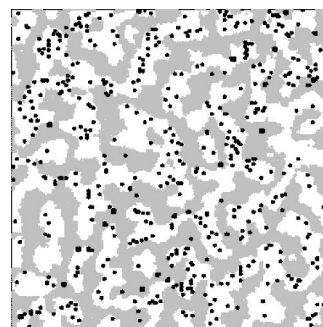


FIG. 7. Snapshots for 200×200 at $t=400$ MCS when $p=0.0005$. The gray area is the hex phase, the 1×1 phase is in the light areas, and the black particles are O atoms.

III. RESULTS OF SIMULATIONS

According to our algorithm described above, the reaction system can evolve into different dynamical stationary states under different extensive conditions. When defects are not present, the coverage of CO, NO, O, and Pt atoms in the 1×1 phase will develop into regular oscillations shown in Fig. 1. The simulation results are consistent with many previous works [5,9,17]. We can describe the oscillatory process as follows: for the initial clean surface, the only possible process is adsorption of CO and NO. The increase of the CO and NO coverage on the surface drives Pt atoms to change into the 1×1 phase. However, the 1×1 phase surface is occupied by the CO and NO molecular-lacking O atoms that are needed to form CO_2 . The desorption of CO leaves some vacant sites in the 1×1 phase. Then the NO molecules decompose to give O atoms. The O atom reacts with CO and leaves more vacant sites. The process is similar to an autocatalytic reaction. Thus the coverage of adsorbate particles starts to decrease, which is accompanied by a decrease of the restructured 1×1 phase. Therefore, the adsorption becomes dominative again and a new cycle begins.

As defects are formed in the surface, the NO decomposition can occur in the hex phase. When $p=0.0001$, the system still exhibits a persistent oscillation as shown in Fig. 2; this means that the defects have little influence on the dynamical behavior when its fraction is small. However, as shown in Fig. 3, with p increasing to 0.0005, the persistent oscillation changes into a damped one. When the oscillation is damped to the end, the production rate of CO_2 is very rapid and near to the maximum rate. However, a fraction of the 1×1 phase is damped to the minimum value. The simulated oscillation of the CO_2 production rate in Fig. 3 reproduces the damped behavior in the CO+NO/Pt(100) reaction system in the high temperature oscillation range [5,27].

From the simulation results in Figs. 1 and 3, it is obvious that, with the increase of defects in the surface, the NO decomposition is accelerated to release more O atoms to react with the adsorbed CO. As a result, the production rate of CO_2 increases, but the accumulation of NO and CO becomes more difficult and leads to the damping of the 1×1 phase. Thus, it is shown that the formation of the defects in the phase transition can result in the damped oscillation behavior.

When $p=0.0001$ and 0.0005 , both the NO and CO molecules almost locate in the 1×1 phase as shown in the snapshots of Figs. 4 and 5. Moreover, when the system exhibits a persistent oscillation for $p=0.0001$, the oxygen atoms that result from the NO decomposition mainly locate in the 1×1 phase as shown in Fig. 6(a); it is obvious that the reaction mainly occurs in the 1×1 phase. However, when the system exhibits a damped oscillation for $p=0.0005$, it is found that, from the snapshot in the end of the oscillation as shown in Fig. 6(b), many of the oxygen atoms locate in the hex phase; it is obvious that the hex phase becomes active for the reaction due to the defects. On the other hand, from the snapshot in Fig. 7, we find that, in the early stage of the oscillation for $p=0.0005$, the oxygen atoms mainly locate in the 1×1 phase. It means that the reaction mainly occurs in the 1×1 phase in the early stage of the damped oscillation. But with the reaction proceeding, the defects increase gradually in the hex surface due to the surface restructuring phase transition. The NO decomposition in the hex phase becomes rapid and dominative, and the adsorbed CO can react with the oxygen atom quickly in the hex phase; as a result, the surface reconstruction to the 1×1 phase is inhibited gradually and the hex phase becomes active also.

IV. CONCLUSION

We present a lattice gas model including the influence of the surface defects formed in the surface restructuring phase transition for the CO+NO/Pt(100) reaction system. The simulation results reproduce the damped oscillation in the system when the fraction of surface defects increases. The production rate of CO₂ is near to the maximum value when the oscillation is damped to the end; these simulation results are very consistent with the time series of rate oscillation in an UHV experiment [5,27]. Moreover, the simulation results show that, in the early stage of the oscillation, the NO decomposition mainly occurs in the 1×1 phase and the hex phase is inactive for the reaction. When the reaction proceeds, the surface defects are gradually formed in the $1 \times 1 \rightleftharpoons$ hex phase transition and the hex phase also becomes active and dominative for the NO decomposition and then the oscillation becomes a damped behavior.

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- [1] S. P. Singh-Boparai and D. A. King, *Suppl. Le Vide* **201**, 403 (1980) [ECOSS-3, Cannes, 1980].
- [2] R. Imbihl and G. Ertl, *Chem. Rev. (Washington, D.C.)* **95**, 697 (1995).
- [3] H. Bosh and F. Janssen, *Catal. Today* **2**, 369 (1988).
- [4] W. F. Egelhoff, *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, edited by D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1982), p. 401.
- [5] T. Fink, J. P. Dath, R. Imbihl, and G. Ertl, *J. Chem. Phys.* **95**, 2109 (1991).
- [6] R. Imbihl, Th. Fink, and K. Krischer, *J. Chem. Phys.* **96**, 6236 (1991).
- [7] G. Vesper and R. Imbihl, *J. Chem. Phys.* **100**, 8492 (1994).
- [8] G. Vesper and R. Imbihl, *J. Chem. Phys.* **96**, 7155 (1992).
- [9] G. Vesper and R. Imbihl, *J. Chem. Phys.* **100**, 8483 (1994).
- [10] N. Khrustova, G. Vesper, A. Mikhailov, and R. Imbihl, *Phys. Rev. Lett.* **75**, 3564 (1995).
- [11] O. Kortluke and W. von Niessen, *J. Chem. Phys.* **105**, 4764 (1996).
- [12] A. Hopkinson and D. A. King, *Chem. Phys.* **177**, 433 (1993).
- [13] V. P. Zhdanov, *Surf. Sci. Rep.* **45**, 231 (2002).
- [14] R. J. Behm, P. A. Thiel, P. R. Norton, and G. Ertl, *J. Chem. Phys.* **92**, 7437 (1990).
- [15] R. J. Behm, P. A. Thiel, P. R. Norton, and G. Ertl, *J. Chem. Phys.* **92**, 7448 (1990).
- [16] O. Kortluke, V. N. Kuzovkov, and W. von Niessen, *Phys. Rev. Lett.* **81**, 2164 (1998).
- [17] V. P. Zhdanov, *J. Chem. Phys.* **110**, 8748 (1999).
- [18] V. P. Zhdanov, *Surf. Sci.* **426**, 345 (1999).
- [19] R. C. Rose, R. Imbihl, B. Rausenberger, C. S. Rastomjee, W. Engel, and A. M. Bradshaw, *Surf. Sci.* **352–354**, 258 (1996).
- [20] M. D. Graham, M. Bar, and I. G. Kevrekidis, *Phys. Rev. E* **52**, 76 (1995).
- [21] M. Bar and I. G. Kevrekidis, *J. Phys. Chem.* **100**, 19106 (1996).
- [22] J. Mai and W. V. Niessen, *J. Chem. Phys.* **98**, 2032 (1993).
- [23] H. R. Siddiqui, P. J. Chen, X. Guo, and J. T. Yates, *J. Chem. Phys.* **92**, 7690 (1990).
- [24] H. Hopster and H. Ibach, *Surf. Sci.* **77**, 109 (1978).
- [25] M. Berdau, G. G. Yelenin, A. Karpowicz, M. Ehsasi, K. Christmann, and J. H. Block, *J. Chem. Phys.* **110**, 11551 (1999).
- [26] D. Hua and Y. Ma, *Phys. Rev. E* **66**, 066103 (2002).
- [27] J. H. Miners and P. Gardner, *J. Phys. Chem. B* **104**, 10265 (2000).
- [28] V. P. Zhdanov, *Catal. Lett.* **84**, 147 (2002).
- [29] K. Binder and D. W. Heermann, *Monte Carlo Simulation in Statistical Physics*, 2nd ed. (Springer, Berlin, 1992), p. 4107.