Surface restructuring and kinetic oscillations in heterogeneous catalytic reactions

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We extend our earlier Monte Carlo simulations of isothermal kinetic oscillations in the NO-H$_2$/Pt(100) system [V. P. Zhdanov, Phys. Rev. E **59**, 6292 (1999)]. The analysis, based on a lattice-gas model describing surface restructuring in terms of the statistical theory of first-order phase transitions, is primarily focused on adsorbate-diffusion-mediated synchronization of oscillations. The conventional condition for synchronization, $(D\tau)^{1/2} > L$ (D is the diffusion coefficient, τ the oscillation period, and L the lattice size), is proved to considerably underestimate the role of surface diffusion. Due to the formation of mesoscopic islands, well developed oscillations are found to be possible in the cases when the left part of this condition is much lower than the right part. [S1063-651X(99)12611-4]

I. INTRODUCTION

Knowledge accumulated in surface science during the past two decades indicates that the phenomenon of adsorbate-induced surface restructuring is pervasive. It lies behind a variety of interesting processes including kinetic oscillations and chaos in such catalytic reactions as, e.g., CO+O$_2$, CO+NO, NO+H$_2$, and NO+NH$_3$ on Pt(100) [1]. Simulations of the peculiarities observed in the kinetics of these reactions are often based on the mean-field (MF) kinetic equations [2]. However, MF models cannot be used to analyze spatio-temporal distribution of adsorbed reactants on the nm scale because they operate only with average coverages of surface phases. Application of the Monte Carlo (MC) technique is more promising in this case. However, available MC models (see, e.g., Refs. [3,4]) suffer from the lack of a physical background. In particular, the rules employed to realize the elementary reaction steps related to surface restructuring are far from those prescribed by statistical mechanics. The latter is not surprising, because the understanding of microscopic details of adsorbate-induced surface restructuring is now far from complete. Nevertheless, the fact that surface restructuring should be analyzed in terms of theory of phase transitions is well established. Under such circumstances, it seems reasonable to formulate a simple well-defined lattice-gas model treating surface restructuring as a first-order phase transition, and to employ this model for analyzing oscillatory kinetics. This approach was recently realized in our studies [5–8], where we proposed such a model [5] and used it to simulate the kinetics of the first three reactions mentioned above.

The MC treatment [8] of the NO+H$_2$ reaction on Pt(100) was especially instructive because, in agreement with experiment, for this system the model predicts oscillations in a relatively wide range of the model parameters. On the nm scale, the model shows the formation of restructured islands with atomically sharp boundaries. The shape of islands was found to change dramatically with varying reaction conditions. Despite phase separation on the surface, the transition from almost harmonic oscillations (with relatively small separate islands) to chaos (with merging islands) was dem-

onstrated to occur via the standard Feigenbaum scenario. Taking into account the richness of the model behavior, we focused our simulations [8] on the dependence of the reaction kinetics on the reactant (NO) pressure. All the calculations were executed at fixed temperature. In the present report, we first briefly recall (Sec. II) the main ingredients of the model employed earlier [8], and then, using this model, show how oscillations disappear with increasing temperature (Sec. III) and discuss synchronization of oscillations via adsorbate diffusion (Sec. IV).

II. MODEL

The conventional mechanism of the NO-H$_2$ reaction occuring on Pt(100) at UHV conditions includes (i) NO adsorption, desorption, and decomposition; (ii) reversible dissociative adsorption of H$_2$; (iii) nitrogen desorption; and (iv) reactions between adsorbed H, O, N, and NO resulting in the formation and desorption of H$_2$O, NH$_3$, and N$_2$O. At the most interesting temperatures (above 430 K), steps (ii)–(iv) are rapid, and the surface coverages by H, O, and N are low. This makes it possible to use a reduced scheme of the reaction, involving only reversible NO adsorption and decomposition. The decomposition products (N and O) are removed from the surface immediately. Thus we have only one adsorbed species, NO.

To mimic the NO-induced restructuring of the Pt(100) surface [i.e., the transition from the quasi-hexagonal (''hex'') arrangement of Pt atoms, which is stable before NO adsorption, to the 1×1 arrangement stable after NO adsorption], we use the lattice-gas model.

(i) Metal atoms, M ($M=$Pt), form a square lattice. Every M atom may be in the stable or metastable state (the terms ''stable'' and ''metastable'' refer to the states which are stable and metastable on the *clean* surface). The energy difference of these states is ΔE. The nearest-neighbor (nn) M-M interaction is considered to be attractive, $-\epsilon_{MM}$ ($\epsilon_{MM}>0$), if the atoms are in the same states, and repulsive, ϵ_{MM}, if the states are different. The next-nearest-neighbor (nnn) interactions are ignored.

(ii) Adsorbed particles, A ($A=$NO) occupy hollow sites (this assumption is not essential, because for adsorption on

top sites the structure of the formal equations is the same). The adsorption energy of a given particle is considered to increase linearly with the number of nn substrate atoms in the metastable state (this is a driving force for the phase transition). In particular, the increase of the adsorption energy of an A particle after the transition of one nn substrate atom from the stable to the metastable state is ϵ_{AM} ($\epsilon_{AM} > 0$). The adsorbate-adsorbate interaction are for simplicity ignored.

The way to introduce the rate constants for all the relevant elementary rate processes in accordance with the model outlined was described in detail earlier [8]. Here we recall only that the decomposition of A (i.e., of NO) is considered to occur provided that (i) at least one nn site is vacant and (ii) all the M atoms adjacent to A and to a vacant site are in the metastable state. The latter condition takes into account that NO decomposition occurs primarily on the 1×1 phase.

To simulate the reaction kinetics, we used [8] the set of parameters, $\Delta E/T = 2$, $\epsilon_{MM}/T = 0.5$, and $\epsilon_{AM}/T = 2$ (with $k_B = 1$), corresponding to fixed temperature, $T \simeq 0.40 T_c$ (T_c is the critical temperature). In addition, we employed the dimensionless parameters p_{res} and p_{rea} ($p_{res} + p_{rea} \leqslant 1$), characterizing the relative rates of surface restructuring, adsorption-reaction steps, and diffusion of A particles. The rates of these processes were considered to be proportional to p_{res}, p_{rea}, and $1 - p_{res} - p_{rea}$, respectively. In reality, the rate of surface restructuring is lower than that of the adsorption-reaction steps (i.e., $p_{res} < p_{rea}$) which are in turn much slower compared to A diffusion (i.e., $p_{res} + p_{rea} \leqslant 1$). In our simulations, we employed $p_{res}/(p_{res} + p_{rea}) = 0.3$. In the framework of this scheme, the ratio of the rates of A diffusion and the other processes is $N_{dif} \equiv (1 - p_{res} - p_{rea})/(p_{res} + p_{rea})$. The results were presented for $N_{dif} = 1000$.

To simulate the catalytic cycle, we introduced the dimensionless parameters p_{NO} for A adsorption and p_{des} for A desorption (p_{NO} was the governing parameter). The rates of these processes are assumed to be proportional to p_{NO} and p_{des}, respectively. The A decomposition rate is considered to be proportional to $1 - p_{des}$. The simulations were executed for $p_{des} = 0.3$.

Initially (at $t = 0$), the surface was considered to be clean and all the M atoms to be in the stable state. The results were obtained for a ($L \times L$) M lattice with $L = 200$ and periodic boundary conditions. To measure time, we used the so-called MC step (MCS) defined as $L \times L$ attempts of the adsorption-reaction-surface-restructuring events.

The set of parameters introduced is below considered to be ''standard.'' Keeping the bulk of these parameters, we will change one or two parameters in order to illustrate the effect of such changes on oscillations. The algorithm of our present simulations is identical to that used earlier [8].

III. EFFECT OF TEMPERATURE

Our earlier results [8] were obtained at $T/T_c = 0.40$. With increasing this ratio, the driving force for adsorbate-induced phase separation on the surface and accordingly for oscillations will decrease. It is not clear, however, when and how oscillations will disappear. Taking into account that strong correlations in the arrangement of A (NO) molecules and metal atoms are possible even if temperature is slightly
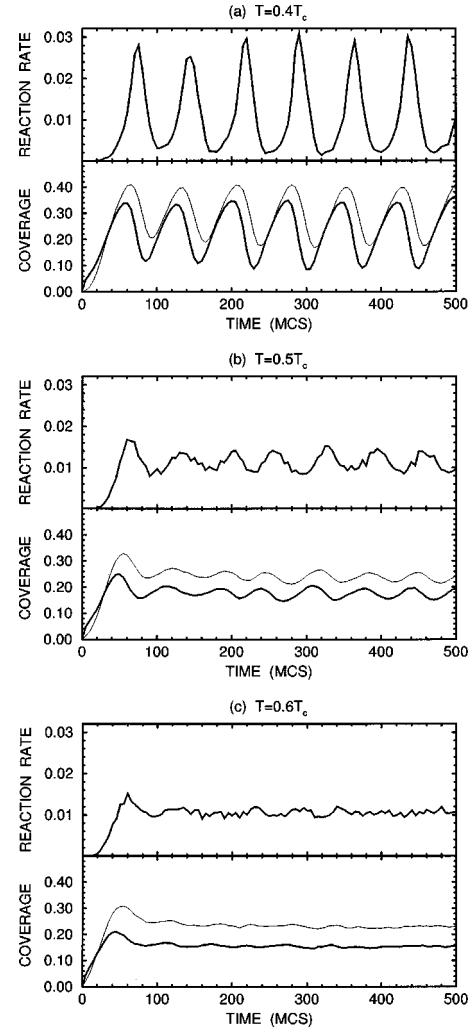

FIG. 1. NO decomposition rate (per site per MCS), NO coverage (thick solid line), and fraction of Pt atoms in the metastable state (thin solid line) as a function of time for $p_{NO} = 0.03$ and $T/T_c = 0.40$ (a), 0.50 (b), and 0.60 (c). The other parameters are as in the standard case.

above T_c, one might expect that oscillations would occur up to T_c. To address this question, we have simulated the reaction kinetics with proportionally reduced values of the dimensionless parameters $\Delta E/T$, ϵ_{MM}/T, and ϵ_{AM}/T (this corresponds to an increase of the ratio T/T_c). All the other parameters were kept as in the standard case described in Sec. II. The calculations executed for $p_{NO} = 0.03$ and $T/T_c = 0.40$, 0.50, and 0.60 show (Fig. 1) that with increasing the ratio T/T_c the oscillations disappear already at $T/T_c = 0.60$. The latter occurs despite well-developed phase separation on the surface [Fig. 2(c)]. For other p_{NO} values, the situation is similar. Thus we may conclude that for the model under consideration the phase separation is necessary but not sufficient for observation of oscillations.

IV. SYNCHRONIZATION OF OSCILLATIONS

At isothermal conditions, synchronization of oscillations in heterogeneous catalytic reactions usually occurs via surface diffusion or gas-phase coupling. The former channel is conventionally considered [3,9] to be effective provided that the typical diffusion length, $(D\tau)^{1/2}$, corresponding to the
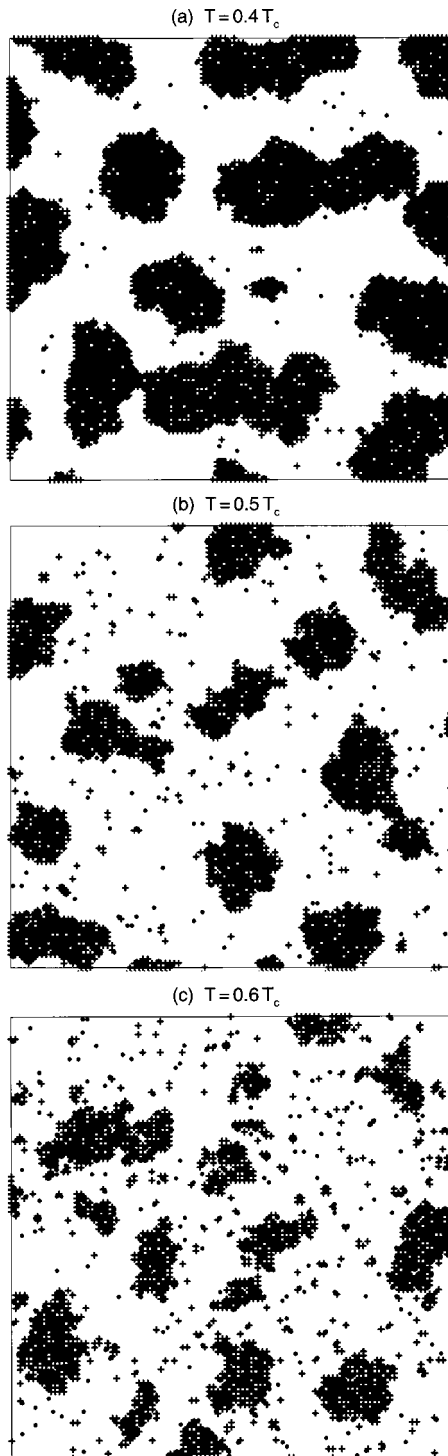
FIG. 2. A 100×100 fragment of the 200×200 lattice at the end of the runs, exhibited in Fig. 1. Filled circles and pluses indicate adsorbed particles and substrate atoms in the metastable state, respectively. Metal atoms in the stable state are not shown.

oscillation period, τ, is larger that the sample size, L, i.e.

$$(D\tau)^{1/2} > L, \tag{1}$$

where D is the diffusion coefficient. For CO or NO molecules (these species are often responsible for oscillations), the typical values of the Arrhenius parameters for diffusion on Pt or Rh are $D_o = 10^{-3}$ cm²/s and $E_o = 7$ kcal/mol [10]. Using these data and assuming $T = 500$ K and $\tau = 10$ s, one

obtains $(D\tau)^{1/2} \simeq 3 \times 10^{-3}$ cm. This length is small compared to the typical length of samples, $L \sim 0.5$ cm. Thus one might argue [9] that surface diffusion is usually not able to synchronize oscillations, and accordingly the priority should be given to the gas-phase coupling. However, this conclusion does not appear to be in agreement with the bulk of experimental data indicating that oscillations are often observed without any special care about synchronization via the gas phase. Under such circumstances, it seems to be reasonable to scrutinize condition (1).

Physically, it is clear that condition (1) is just a scaling estimate based on the random walk theory. *A priori*, there is no guarantee that it should be applicable to oscillations. The only attempt to prove condition (1) has recently been executed in MC simulations [3] of CO oxidation on the Pt(100) and (110) surfaces. The results obtained are in general agreement with condition (1). However, the model employed [3] does not predict well developed phase separation on the surface. In contrast, our model shows the formation of mesoscopic restructured islands. Taking into account this difference, it is of interest to verify whether condition (1) holds in our case.

To prove criterion (1), we first need to discuss two complementary aspects of MC simulations of oscillations of heterogeneous reactions. The first one concerns the boundary conditions used in calculations. The bulk of simulations employ the periodic boundary conditions. An alternative choice is open boundary conditions. Intuitively, it is clear that the periodic boundary conditions make oscillations slightly better. This is the main reason why such boundary conditions are popular. The open boundary conditions are, however, more realistic. If we are interested in the shape of kinetic curves during oscillations, the periodic boundary conditions are slightly preferable. If, however, our goal is to verify criterion (1), the open boundary conditions seem to be more reasonable, because they are closer to reality. For this reason, we use the latter conditions in this section.

Second, we need to recall how to calculate the diffusion coefficient. In our model [8], the rate of diffusion jumps of A particles depends on their arrangement and also on the arrangement of M atoms. For example, the jumps on the interface from the restructured phase to the unrestructured phase are slow compared to the jumps in the opposite direction (because the binding energy on the restructured patches is higher). On the other hand, the jumps on the perfect restructured and unrestructured patches are relatively fast and occur at the same rate. Taking into account that A diffusion takes place primarily on almost perfect patches, in Eq. (1) we may use a diffusion coefficient corresponding to such patches. The value of the diffusion coefficient depends on the length and time units employed in simulations. We use the dimensionless units. In particular, length is calculated in the lattice spacing. For time, we employ the MC steps related to the adsorption-reaction-surface-restructuring events (Sec. II). Per one MC step, we realize N_{dif} attempts of diffusion. According to the random walk theory, in this case we have

$$D = N_{\text{dif}}/4. \tag{2}$$

Using Eq. (2), it is instructive to apply condition (1) to our standard case, where we have $N_{\text{dif}} = 1000$, $L = 200$, and $\tau \simeq 80$ (Fig. 1). With these values, the right and left parts of condition (1) are nearly equal. Thus one could argue that
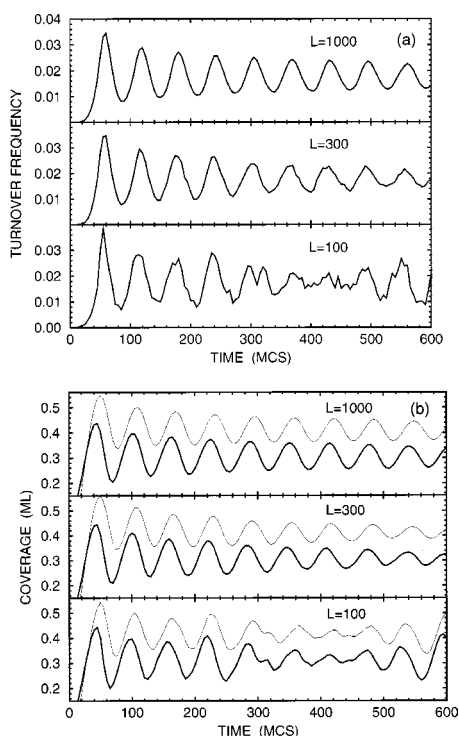
FIG. 3. (a) NO decomposition rate (per site per MCS), and (b) NO coverage (thick solid line) and fraction of Pt atoms in the metastable state (thin solid line) as a function of time for $p_{NO}=0.05$, $N_{dif}=100$, and $L=100$, 300, and 1000. The other parameters are as in the standard case.

FIG. 4. A 100×100 fragment of the 1000×1000 lattice at $t=40$ (a) and 600 MCS (b) for the run shown in Fig. 3. The designations are as in Fig. 2.

synchronization of oscillations should not be too good. Really, however, the oscillations are synchronized very well [Fig. 1(a)]. In particular, the amplitude of oscillations is large and the shape is almost perfect.

To analyze the applicability of condition (1) in more detail, we have reduced N_{dif} down to 100 and calculated the reaction kinetics for $L=100$, 300, and 1000 (Fig. 3). For $L=100$, the oscillations are found to be irregular (due to the boundary effects). For $L=300$, the synchronization is better, but the amplitude of oscillations slightly decreases with increasing time. The best synchronization is observed for $L=1000$. In the latter case, the left part of condition (1), $(D\tau)^{1/2}\simeq40$, is 25 times lower compared to the right part.

In summary, our simulations indicate that condition (1) can hardly be used as a quantitative criterion for synchronization of oscillations, because it may considerably underestimate the effect of surface diffusion on synchronization. In other words, well developed oscillations may be observed not only when condition (1) is fulfilled but also in the cases
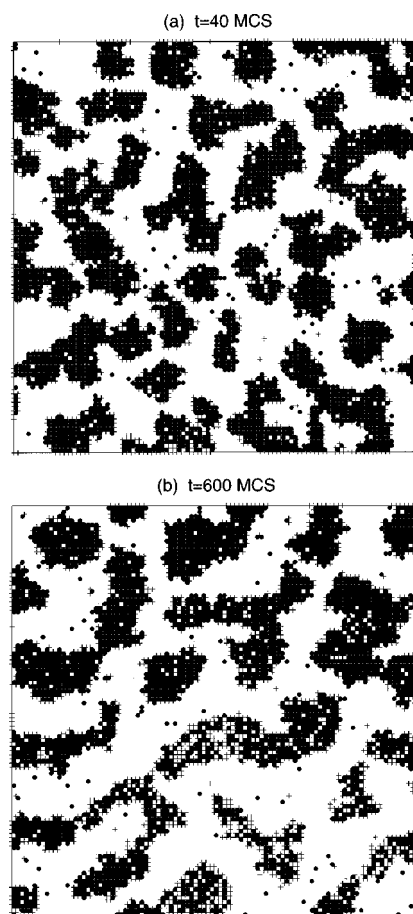
when its left part is much lower compared to the right part. We believe that the failure of condition (1) in our case is directly connected with the formation of mesoscopic islands (Fig. 4). Such islands arise already during the first period of oscillations. In fact, the oscillations are well synchronized in the beginning, because we start from a clean perfect surface. Thus diffusion of A particles should only maintain oscillations. The latter is not so difficult because the changes of the shape of islands during the oscillation period are relatively small. It is not surprising that under such circumstances criterion (1), based on the random walk theory, is no longer applicable.

ACKNOWLEDGMENT

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