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# Oscillations in the NO–CO reaction on Pt(100): NO decomposition on island boundaries

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We present the first Monte Carlo simulations of kinetic oscillations in heterogeneous catalytic reaction with one of the key reaction steps occurring on the boundaries between the islands formed due to adsorbate-induced surface restructuring. Specifically, we treat NO reduction by CO on the Pt(100) surface with NO decomposition on the interface between the "hex" and $(1 \times 1)$ phases. For this scenario, in agreement with experiment, our model predicts damped oscillations with correlation between broad maxima in the $CO_2$-formation rate and minima in the $(1 \times 1)$ area.

**KEY WORDS:** NO–CO reaction; Pt(100); kinetic oscillations; adsorbate-induced surface restructuring; role of island boundaries.

Kinetic oscillations and chaos observed in CO oxidation by $O_2$ and NO reduction by CO or $H_2$ on Pt(100) are intimately related to adsorbate-induced surface restructuring (AISR) [1,2]. The understanding of the complexity of these reactions is of great interest from the physical point of view due to the nontrivial interplay of chemistry and adsorbate-induced phase separation. In particular, adsorbed CO, NO, and O species are able to stabilize the $(1 \times 1)$ arrangement of Pt atoms, which is metastable on the clean surface compared to the "hex" arrangement. The size of the $(1 \times 1)$ islands lies in the range between 1 and 100 nm, as was first demonstrated in ref. [14] (the details of the growth of such islands were experimentally studied in refs. [3,4]). $O_2$ adsorption and NO dissociation occur primarily on the $(1 \times 1)$ phase. This feedback between the chemical steps and AISR results in oscillations. The mean-field (MF) and Monte Carlo (MC) models based on this general idea successfully reproduce the kinetic behavior of the reactions under consideration (see, *e.g.*, the MF treatments of CO oxidation [5] and NO reduction by $H_2$ [6], including the experimentally observed law of the growth of the $(1 \times 1)$ phase, and also the reviews [2,7]). Many details of the physics behind oscillations in these intriguing reactions in general and in the NO–CO reaction in particular are, however, still open for debate.

Oscillations in the NO + CO/Pt(100) system were first observed by Singh-Boparai and King [8] about 20 years ago. Later on, this phenomenon was studied in more detail by several groups [9–12] at $P_{CO} + P_{NO} \simeq 10^{-11}$–$10^{-8}$ bar and $T \simeq 400$–$500$ K. The reaction is found to exhibit damped, regular and chaotic oscillations occurring *via* the following steps

$$CO_{gas} \rightleftharpoons CO_{ads}, \tag{1}$$

$$NO_{gas} \rightleftharpoons NO_{ads}, \tag{2}$$

$$NO_{ads} \rightarrow N_{ads} + O_{ads}, \tag{3}$$

$$CO_{ads} + O_{ads} \rightarrow (CO_2)_{gas}, \tag{4}$$

$$2N_{ads} \rightarrow (N_2)_{gas}, \tag{5}$$

$$NO_{ads} + N_{ads} \rightarrow (N_2O)_{gas}. \tag{6}$$

Under chemically reactive conditions, at relatively low temperatures ($T < 430$ K), the Pt(100) surface is primarily in the $(1 \times 1)$ state [10,11] and the oscillations are entirely driven by autocatalytic NO decomposition (3). At higher temperatures, AISR is directly involved in oscillations [2,13]. The first MF analysis [10] of oscillations took into account AISR, but practically was focused on the case when AISR is negligible. The later MF treatment [13] was aimed primarily at AISR. The merit of these studies is that they have formed the framework for the understanding of the oscillations. The MF approximation does not, however, allow one to describe explicitly phase separation on the nanometer scale. The latter aspect of the reaction was explored [15] by using MC simulations based on the lattice–gas AISR model. One of the key assumptions in the MF and MC treatments [10,13,15] is that the oscillations are connected with NO decomposition on the $(1 \times 1)$ patches. In this case, the rate of the $CO_2$ formation is predicted to be maximum slightly after the moment when the area of the $(1 \times 1)$ islands is maximum. In contrast, experiment [10,12] indicates that at $T \simeq 450$ K during spontaneous damped oscillations or regular oscillations stabilized by a small temperature modulation the broad maxima in

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the $CO_2$-production rate coincide with minima in the $(1 \times 1)$ area. One of the likely reasons for this feature is NO decomposition on defects (see, *e.g.*, the discussion in refs. [12,13]). This idea is supported by recent DFT calculations [16] indicating that on defects this process seems to occur much faster than on regular sites.

In the system under consideration, there are two types of defect. The first is connected with the fact that the surface densities of Pt atoms in the "hex" and $(1 \times 1)$ structures are slightly different. For this reason, AISR is accompanied by "forcing up" some of the Pt atoms. In addition, defects are formed on the boundaries between the "hex" and $(1 \times 1)$ phases. Our lattice–gas AISR model [15] explicitly describes the latter defects and accordingly makes it possible to scrutinize their role in oscillations. Using this opportunity, we have simulated the oscillatory kinetics assuming the NO decomposition to occur on the island boundaries. This is the key new ingredient in our present work. The other ingredients briefly described below are the same as in ref. [15]. In particular, we use basically the same energetic parameters and the same ratio of the main kinetic parameters as earlier [15]. (For validation of the energetic and kinetic model parameters, see ref. [15] and/or sec. 4.8 in ref. [7].)

In our simulations, $N_2O$ formation (6) is neglected. $N_2$ desorption (5) is considered to be rapid so that the N coverage is negligible. Practically, this means that N atoms are removed from the lattice just after NO decomposition.

Pt atoms form a square lattice. Every Pt atom may be in the stable or metastable state [the terms "stable" and "metastable" are associated with the "hex" and $(1 \times 1)$ arrangements which are stable and metastable on the *clean* surface]. The energy difference of these states is $\Delta E$. The nearest-neighbor (nn) Pt–Pt lateral interaction is attractive, $-\varepsilon_{MM}$ ($\varepsilon_{MM} > 0$; $M \equiv \mathrm{Pt}$), if the atoms are in the same state, and repulsive, $\varepsilon_{MM}$, if the states are different.

Adsorbed particles occupy hollow sites. The adsorption energy of a given particle increases linearly with the number of nn substrate atoms in the metastable state. In particular, the increase of the adsorption energy of CO, NO, and O after the transition of one nn substrate atom from the stable to the metastable state is $\varepsilon_{AM}$, $\varepsilon_{BM}$, and $\varepsilon_{CM}$ ($A \equiv \mathrm{CO}$, $B \equiv \mathrm{NO}$, and $C \equiv \mathrm{O}$), respectively. These adsorbate–substrate interactions stabilize the $(1 \times 1)$ phase. Adsorbate–adsorbate lateral interactions are ignored.

CO and NO adsorption occurs on vacant adsorption sites. CO and NO desorption is affected by CO–Pt and NO–Pt lateral interactions, $\varepsilon_{AM}$ and $\varepsilon_{BM}$, respectively. The normalized dimensionless probability of desorption of a given molecule is defined as $W_{\mathrm{des}} = \exp(\mathcal{E}_i/k_{\mathrm{B}}T)$, where $\mathcal{E}_i$ is the sum of nn lateral interactions. The Langmuir–Hinshelwood reaction (4) occurs between nn CO and O species. The probability of this process is independent of the arrangement of particles in adjacent sites.

NO decomposition requires an nn vacant site. In the earlier simulations [15], this process was considered to be possible provided that an NO molecule and vacant site were located on *perfect* $(1 \times 1)$ patches (practically this means that all the Pt atoms adjacent to an NO molecule and vacant site were required to be in the metastable state). In this work, NO decomposition is assumed to occur if (i) an NO molecule is surrounded by nn Pt atoms in the metastable state and (ii) a vacant site has at least one nn Pt atom in the stable state. These two conditions can be met only on the boundaries between the two phases or near defects inside the $(1 \times 1)$ patches. With our model parameters, these patches are, however, well ordered [see, *e.g.*, the snapshots shown below in figures 2(c) and (d)] and accordingly the role of interior defects is nearly negligible. Thus, *NO decomposition runs primarily on island boundaries*. In reality, NO decomposition may occur in parallel on the $(1 \times 1)$ islands and island boundaries. The former channel can be neglected if the latter one is faster.

CO and NO molecules diffuse *via* jumps to nn vacant sites. O atoms are immobile. Surface restructuring is performed *via* changes of the state of Pt atoms. The transition probabilities corresponding to diffusion and restructuring satisfy the Metropolis rule.

To characterize the relative rates of the surface restructuring and catalytic cycle, we use the dimensionless parameters $p_{\mathrm{res}}$ and $p_{\mathrm{rea}}$. Inside the catalytic cycle, the relative rates of CO and NO adsorption and desorption, NO decomposition, and LH reaction between CO and O are considered to be proportional to $p_{\mathrm{CO}}$, $p_{\mathrm{NO}}$, $p_{\mathrm{CO}}^{\mathrm{des}}$, $p_{\mathrm{NO}}^{\mathrm{des}}$, $p_{\mathrm{dec}}$, and $1 - p_{\mathrm{CO}}^{\mathrm{des}}$, respectively. CO and NO diffusion is two orders of magnitude faster compared to other steps (*i.e.*, the ratio of the rates of these processes is $N_{\mathrm{dif}} = 100$).

The MC algorithm and definition of MC time are identical to those employed earlier [15]. In particular, the MC and real times are interconnected as $t_{\mathrm{MC}} = (k_{\mathrm{CO}}^{\mathrm{des}} + k_{\mathrm{LH}} + k_{\mathrm{res}})t$, where $k_{\mathrm{CO}}^{\mathrm{des}}$ is the maximum value of the desorption rate constant, $k_{\mathrm{LH}}$ the LH reaction rate constant, and $k_{\mathrm{res}}$ the maximum value of the rate constant of surface restructuring.

Our earlier simulations [15] indicate that in the case of NO decomposition on perfect $(1 \times 1)$ patches the model easily predicts sustained oscillations. If, however, NO decomposition occurs on the island boundaries as described above, it becomes harder to find sustained oscillations. In particular, our attempts to get such regimes did not succeed. However, there were no problems in obtaining damped oscillations which were experimentally observed [10,12] at $T \simeq 450$. (In analogy with the experiment [12], damped oscillations might be stabilized, *e.g.*, by a small temperature modulation. However, we have not used this trick.) Typically, such oscillations exhibit a couple of maxima in adsorbate coverages and reaction rate as shown in figures 1 and 2. By tuning the kinetic parameters, we were able to generate kinetics

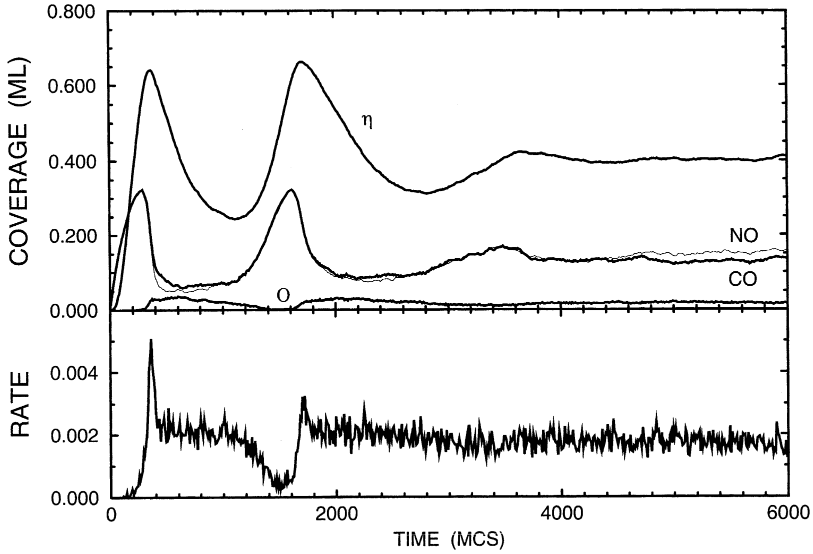
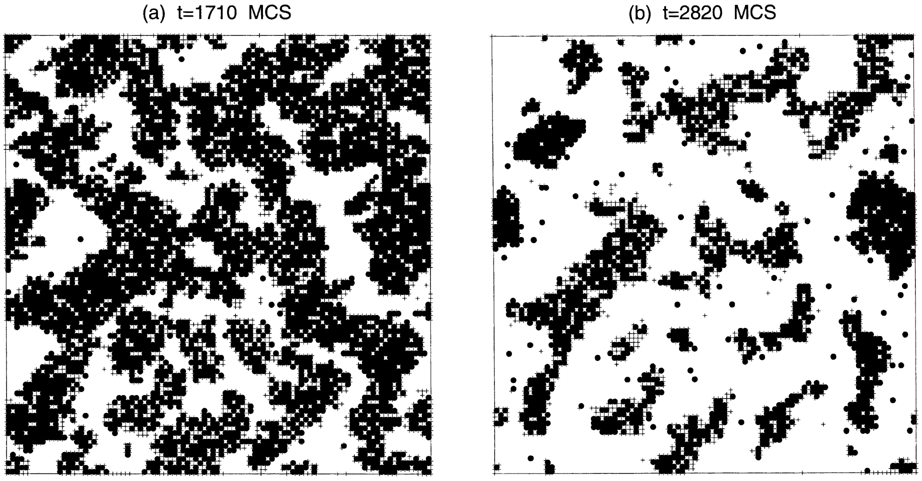
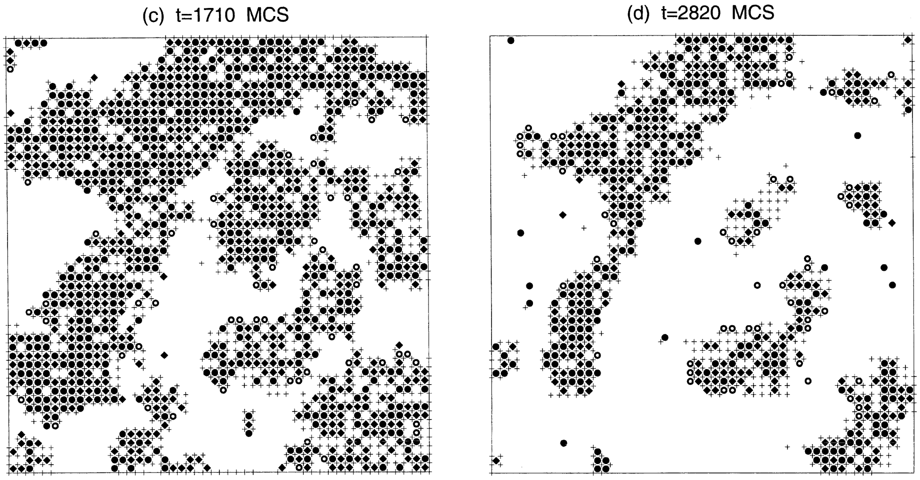


Figure 1. CO, NO, O coverages, fraction of Pt atoms ($\eta$) in the state corresponding to the (1 × 1) phase, and reaction rate ($CO_2$ molec. per site per MCS) as a function of time for $p_{\mathrm{CO}} = p_{\mathrm{NO}} = 0.0025$, $p_{\mathrm{CO}}^{\mathrm{des}} = p_{\mathrm{NO}}^{\mathrm{des}} = 0.002$, $p_{\mathrm{res}}/(p_{\mathrm{res}} + p_{\mathrm{rea}}) = 0.01$, $p_{\mathrm{NO}}^{\mathrm{des}} + p_{\mathrm{dec}} = 0.2$, $\Delta E/k_{\mathrm{B}}T = 2$, $\varepsilon_{MM}/k_{\mathrm{B}}T = 0.5$, and $\varepsilon_{AM}/k_{\mathrm{B}}T = \varepsilon_{BM}/k_{\mathrm{B}}T = \varepsilon_{CM}/k_{\mathrm{B}}T = 2$. The kinetics has been calculated on a (100 × 100) lattice with periodic boundary conditions.


(a) t=1710 MCS

(b) t=2820 MCS


(c) t=1710 MCS

(d) t=2820 MCS

Figure 2. Snapshots of the 100 × 100 lattice for the MC run shown in figure 1 at the stages when the (1 × 1) area reaches second (a) maximum and (b) minimum. Filled circles show adsorbed particles. Pluses indicate Pt atoms in the metastable state associated with the (1 × 1) phase. Pt atoms in the stable state are not shown. Panels (c) and (d) exhibit 50 × 50 fragments of lattices (a) and (b), respectively. In the latter case, filled and open circles and diamonds correspond to CO, O, and NO species, respectively. Notice that the (1 × 1) phase is well ordered. Oxygen atoms produced due to NO decomposition are located primarily near the island boundaries.

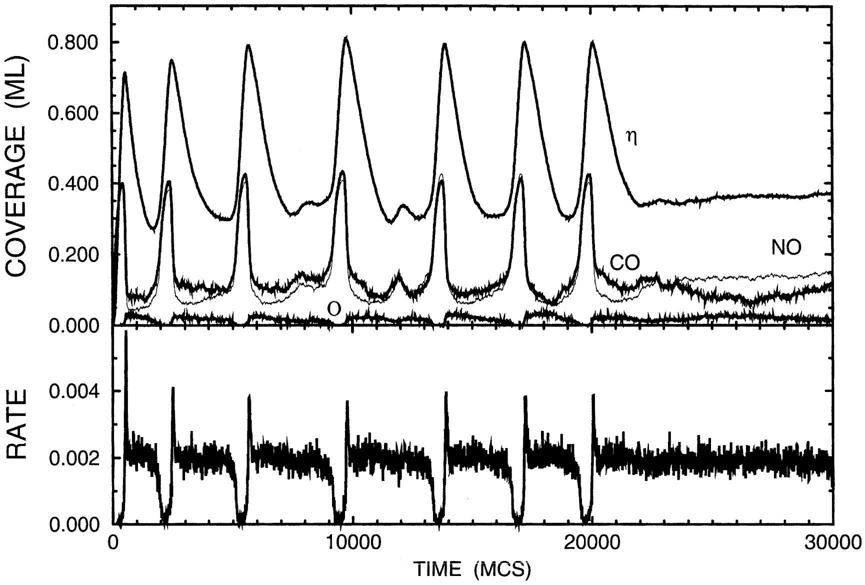


Figure 3. As for figure 1 for $p_{\mathrm{res}}/(p_{\mathrm{res}}+p_{\mathrm{rea}}) = 0.005$.

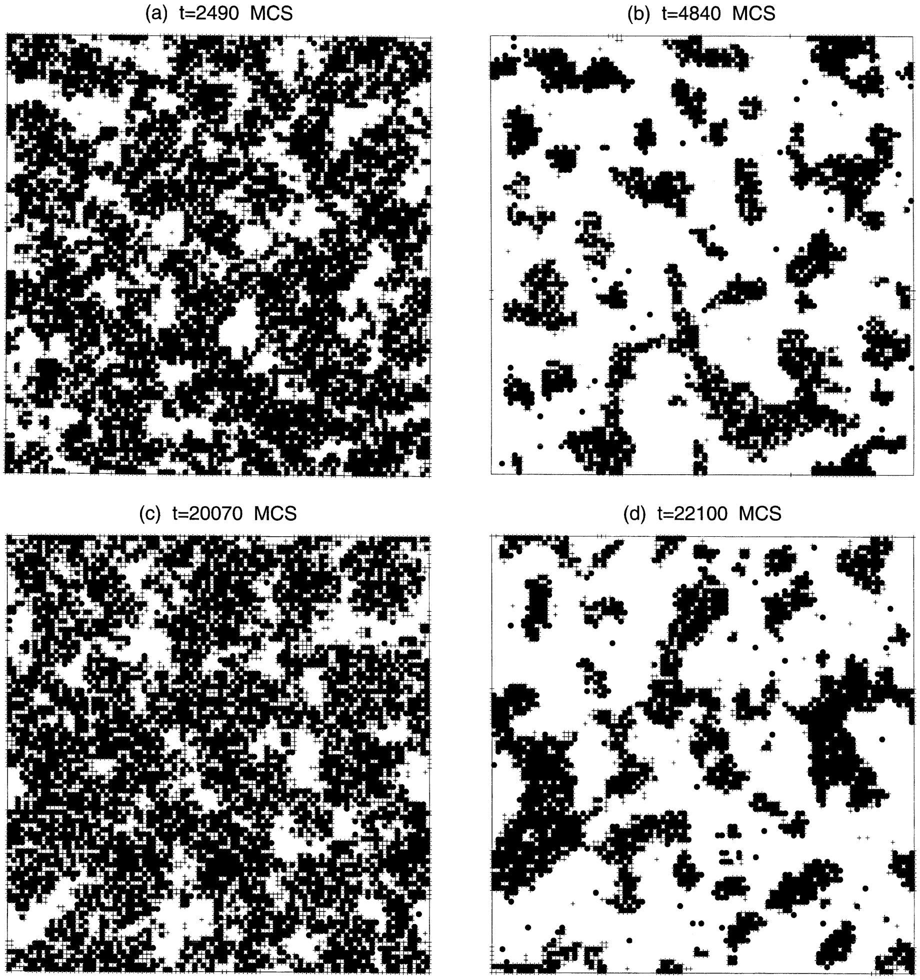


Figure 4. Snapshots of the 100 × 100 lattice for the MC run shown in figure 3 at the stages when the (1 × 1) area reaches second (a) maximum and (b) minimum and seventh (c) maximum and (d) minimum. Filled circles show adsorbed particles. Pluses indicate Pt atoms in the state associated with the (1 × 1) phase.

containing more (up to ten) periods (see, *e.g.*, figures 3 and 4). The reason why oscillations eventually damp seems to be connected with slow growth of the average (over time) size of the $(1 \times 1)$ islands. This process appears to violate the balance between NO decomposition on the island boundaries and other processes and then the oscillations cease.

Looking through the kinetics presented in figures 1 and 3, one can notice that the $CO_2$-formation rate exhibits very narrow peaks located between the minima and maxima in the area of the $(1 \times 1)$ patches. Broad maxima in the $CO_2$-formation rate coincide with minima in the $(1 \times 1)$ area.

Narrow peaks in the reaction rate are a general feature of the "relaxation"-type oscillations. In experiments, such peaks are often smeared (especially in the case of damped oscillations) or absent (if oscillations are nearly harmonic). In particular, the measured damped oscillatory kinetics [10,12] of the reaction under consideration do not contain narrow peaks. Broad maxima in the measured $CO_2$-formation rate were found to correlate with minima in the $(1 \times 1)$ area. The latter feature is reproduced in our simulations.

In summary, we have presented the first MC simulations of oscillatory reaction kinetics in the case where one of the key reaction steps occurs on the boundaries between the islands formed due to adsorbate-induced surface restructuring. Specifically, we have treated NO reduction by CO on the Pt(100) surface with NO decomposition on the interface between the "hex" and $(1 \times 1)$ phases. For this scenario, our model predicts damped oscillations with correlation between broad maxima in the $CO_2$-formation rate and minima in the $(1 \times 1)$ area. This feature is in agreement with UHV experimental data [10,12] obtained at $T \simeq 450\,\mathrm{K}$. Thus, at these temperatures, NO decomposition on the island boundaries may really play a significant or even crucial role in oscillations observed on Pt(100) in the NO–CO reaction and perhaps in other reactions (*e.g.*, in NO reduction by $H_2$). With increasing temperature, the role of the island boundaries is expected to lower and we cannot exclude that at $T \simeq 500\,\mathrm{K}$ NO decomposition occurs primarily on the $(1 \times 1)$ patches.

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