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Surface Restructuring, Kinetic Oscillations, and Chaos in Heterogeneous Catalytic Reactions[1]

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Kinetic oscillations in catalytic reactions on single-crystal surfaces often result from the interplay of the purely chemical reaction steps and adsorbate-induced surface restructuring. A classical example is CO oxidation on Pt(100). We survey evolution of the models used to simulate this reaction and show how it can be described self-consistently by employing Monte Carlo simulations combined with the lattice-gas model, taking into account substrate-substrate, substrate-adsorbate and adsorbate-adsorbate lateral interactions. Under the reactive conditions, this approach predicts formation of mesoscopic restructured well ordered islands with atomically sharp boundaries.

KEY WORDS: Computer simulations; models of surface chemical reactions; surface reconstruction.

1. INTRODUCTION

Kinetic oscillations, chaos and pattern formation observed in liquid- and gas-phase reactions are usually simulated by using the conventional reaction-diffusion equations based on the mass-action law (see the excellent book by Nicolis and Prigogine$^{(1)}$ and later textbooks by Gray and Scott$^{(2, 3)}$). The structure of such equations is conceptually simple, because in this case the rate of elementary reaction steps is just proportional to the concentration,

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or the product of concentrations, of reactants. For this reason, the formulation and solution of a set of equations describing complex behaviour of chemical reactions in the liquid or gas phase is a challenge rather for chemists and mathematicians than for physicists.

The situation with heterogeneous catalytic reactions is more complex and simultaneously more interesting and intriguing from the physical point of view. The first report on oscillations in such reactions was published in the early 1970s by Hogo,$^{(4)}$ who studied CO oxidation on Pt in a flow reactor. Since then, regular and chaotic oscillations were found in about thirty reactions on practically all types of catalysts including single crystals, polycrystalline samples (foiles, ribbons and wires) and supported catalysts at a pressure range from 10^{-12} bar to atmospheric pressure.$^{(5, 6)}$ Often oscillations were connected with or influenced by thermal effects. However, in many cases, especially at ultrahigh vacuum (UHV) conditions, the temperature was kept constant. From the theoretical point of view, the data obtained at isothermal conditions are of particular interest, because then the oscillations are much more sensitive to details of a reaction mechanism. The experience accumulated indicates that, in analogy with liquid- and gas-phase reactions, the oscillatory regimes observed in heterogeneous reactions are sometimes connected with purely chemical reaction steps forming a catalytic cycle. Even in this case, however, one usually cannot employ simple mean-field equations based on the mass-action law, because the kinetics of elementary reaction steps occurring in the adsorbed overlayer are as a rule far from ideal due to adsorbate-adsorbate interactions and surface heterogeneity.$^{(7)}$ In addition, the elementary rate processes are often complicated due to spontaneous or adsorbate-induced changes in the surface. The latter purely physical factor actually lies behind kinetic oscillations and chaos in such catalytic reactions as $CO + O_2$, $CO + NO$, $NO + H_2$, and $NO + NH_3$ on Pt(100)$^{(10)}$ (among other possible causes of oscillations, it is appropriate to mention such relatively slow "side" processes as oxide formation$^{(8)}$ and carbon deposition$^{(9)}$). After the pioneering UHV experiments by Ertl *et al.*,$^{(11)}$ the first of these reactions has attracted considerable attention of theorists. In this paper, we discuss the models used to simulate this reaction and show how it can be described by using the methods of statistical physics.

2. MECHANISM OF OSCILLATIONS IN CO OXIDATION ON Pt(100)

CO oxidation on Pt occurs via the Langmuir–Hinshelwood (LH) mechanism

$$A_{\text{gas}} \rightleftharpoons A_{\text{ads}} \tag{1}$$

$$(B_2)_{\text{gas}} \to 2B_{\text{ads}} \tag{2}$$

$$A_{\text{ads}} + B_{\text{ads}} \to (AB)_{\text{gas}} \tag{3}$$

where A stands for CO, B_2 for O_2, and the subscripts "gas" and "ads" mark gas-phase and adsorbed particles, respectively.

On the clean Pt(100) surface, the (1×1) arrangement of metal atoms is metastable compared to a close packed quasi-hexagonal ("hex") arrangement. CO and oxygen adsorption may however stabilize the (1×1) phase. The latter provides a feedback between CO and oxygen adsorption, because the rate of oxygen adsorption on the (1×1) patches is much higher than on the "hex" patches, i.e., the ratio of the sticking coefficients for CO and O_2 changes dramatically upon reconstruction. This mechanism of oscillations proposed by Ertl and co-workers(11) is now generally accepted.

The experiments indicate that the (1×1) islands are formed during CO adsorption on Pt(100) already at low coverages, e.g., at $\theta_{\text{CO}} \simeq 0.08 \pm 0.05$ ML for $T \simeq 500$ K(12) or even at $\theta_{\text{CO}} \simeq 0.01$ ML for $T \simeq 400$ K.(13) The special features of the kinetics of thermal desorption of CO from Pt(100)(14) are also indicative of the phase separation in the adsorbed overlayer. This means that in the system under consideration *the adsorbate-induced surface restructuring should be described in terms of theory of first-order phase transitions*. In addition, it is desirable to use realistic values of the rate constants of various steps or at least a realistic *ratio* of the rate constants.

A factor complicating simulations is that the sites for CO and oxygen adsorption on Pt are different. CO adsorbs on top or bridge sites, while oxygen prefers to adsorb on hollow sites. This difference is, however, expected to be of minor importance for a description of oscillations. To simplify the analysis, CO and oxygen are therefore usually assumed to adsorb on the same sites.

The most difficult part of the simulations is related with surface restructuring. On Pt(100), the surface densities of Pt atoms in the stable "hex" and metastable (1×1) structures are slightly different and the adsorbate-induced phase transition is then accompanied by "forcing up" some of the Pt atoms (the terms "stable" and "metastable" will hereafter always refer to the states which are stable and metastable on the *clean* surface). Full-scale simulations of the latter phenomenon are hardly possible at present. In the reported simulations of oscillations in CO oxidation on Pt(100), this complicating factor is ignored, i.e., the densities of Pt atoms in the stable and metastable structures are considered to be equal.

Depending on the chosen ways to describe adsorbate-induced changes in the surface, the available models of CO oxidation oscillations on Pt(100) can be divided into four groups as described in Sections 3–7. The early, purely phenomenological treatments were a natural first step identifying the right underlying qualitative mechanism. The later treatments successively incorporated more and more of the physics behind oscillations.

3. MEAN-FIELD MODELS

In theory of phase transitions, the term "mean-field approximation" means the simplest approach employing the average particle–particle or spin–spin interaction calculated by assuming that particles or spins are located at random. In surface chemistry, the meaning of the term "mean-field approximation" is slightly different. In the latter case, this term is usually used to introduce kinetic equations constructed on the basis of the mass-action law. Practically, this means that in analogy with the conventional mean-field approximation the adsorbed particles are considered to be located at random. In addition, all the particle–particle interactions are ignored. The readers familiar with statistical physics might expect that phase transitions in the framework of such an approximation would be impossible. This is not the case, however, because one can employ phenomenological equations taking into account that the adsorbed overlayer is in a two-phase state. An advanced approach of this type might be based on the kinetic equations for the size distribution of islands of one of the phases. From the experience available in the theory of spinodal decomposition, one can conclude that the latter approach is expected to be cumbersome and can hardly be realized self-consistently in the case when phase transition is combined with chemical reaction. Under such circumstances, the only real alternative is to additionally simplify the treatment and use kinetic equations for the adsorbate coverages and average coverages of the substrate phases. A mean-field model of this type was proposed first by Imbihl *et al.*(15) and later on by Gruyters *et al.*(16)

The equations used by Imbihl *et al.*(15) are as follows

$$d\theta_A^{1\times1}/dt = k_1 P_{\mathrm{CO}}\theta_{1\times1} - k_2\theta_A^{1\times1} + k_3\theta_A^{\mathrm{hex}}\theta_{1\times1} - k_4\theta_A^{1\times1}\theta_B^{1\times1}/\theta_{1\times1} \tag{4}$$

$$d\theta_A^{\mathrm{hex}}/dt = k_1 P_{\mathrm{CO}}\theta_{\mathrm{hex}} - k_6\theta_A^{\mathrm{hex}} - k_3\theta_A^{\mathrm{hex}}\theta_{1\times1} \tag{5}$$

$$d\theta_B^{1\times1}/dt = k_7 P_{\mathrm{O}_2}\theta_{1\times1} - k_4\theta_A^{1\times1}\theta_B^{1\times1}/\theta_{1\times1} \tag{6}$$

$$\frac{d\theta_{1\times1}}{dt} = \begin{cases} \dfrac{1}{\Theta_A^{\mathrm{gr}}}\dfrac{d\theta_A^{1\times1}}{dt}, & \text{if} \quad \Theta_A^{1\times1} > \Theta_A^{\mathrm{gr}} \quad \text{and} \quad \dfrac{d\theta_A^{1\times1}}{dt} > 0 \\[2ex] -k_8 c\theta_{1\times1}, & \text{if} \quad c = \dfrac{\Theta_A^{1\times1}}{\Theta_A^{\mathrm{cr}}} + \dfrac{\Theta_B^{1\times1}}{\Theta_B^{\mathrm{cr}}} < 1 \\[2ex] 0, & \text{otherwise} \end{cases} \tag{7}$$

where $\theta_{1\times1}$ and $\theta_{\text{hex}} = 1 - \theta_{1\times1}$ are the surface coverages corresponding to the (1×1) and "hex" phases, $\theta_A^{1\times1}$ and θ_A^{hex} the average CO coverages defined as the ratio of the number of CO molecules located, respectively, on the (1×1) and "hex" patches to the total number of adsorption sites, $\theta_B^{1\times1}$ the oxygen coverage defined in analogy with $\theta_A^{1\times1}$, and $\Theta_A^{1\times1} = \theta_A^{1\times1}/\theta_{1\times1}$, $\Theta_A^{\text{hex}} = \theta_A^{\text{hex}}/\theta_{\text{hex}}$, and $\Theta_B^{1\times1} = \theta_B^{1\times1}/\theta_{1\times1}$ the local CO and oxygen coverages of the (1×1) and "hex" phases.

The first two terms in Eqs. (4) and (5) describe adsorption and desorption of CO molecules on the (1×1) and "hex" patches, respectively (P_{CO} is the CO pressure, k_1 is the adsorption rate constant dependent on local adsorbate coverages, and k_2 and k_6 are the desorption rate constants). The third term in Eqs. (4) and (5) takes into account jumps of CO molecules from the "hex" patches to the (1×1) patches (this process is considered to be irreversible, and the rate constant k_3 is assumed to be independent of coverage). The first term in Eqs. (6) describes oxygen adsorption on the (1×1) patches (P_{O_2} is the O_2 pressure, and k_7 is the adsorption rate constant dependent on local adsorbate coverages). Oxygen adsorption on the "hex" patches is neglected. The fourth term in Eq. (4) and the second term in Eq. (6) result from the LH reaction between adsorbed CO and oxygen (the rate constant of this reaction is assumed to be independent of coverage). Equation (7) describes surface restructuring. The coverage corresponding to the (1×1) phase increases if the local CO coverage is higher than the critical coverage, $\Theta_A^{\text{gr}} \simeq 0.5$ (the growth of the (1×1) patches is assumed to be limited by the supply of CO molecules). The (1×1) phase shrinks if the local CO and oxygen coverages are low ($\Theta_A^{\text{cr}} \simeq 0.3$ and $\Theta_B^{\text{cr}} \simeq 0.4$ are the corresponding critical coverages). Typical values of the Arrhenius parameters of the temperature-dependent rate constants for the elementary steps above are given in Table 1.

Table 1. Typical Values of the Arrhenius Parameters of the Temperature-Dependent Rate Constants for the Elementary Steps of the $\text{CO} + \text{O}_2$ Reaction on Pt(100)[a]

Step	k	E_a (kcal/mol)	ν (s^{-1})
CO desorption	k_2	37	10^{15}
CO desorption	k_6	28	10^{15}
LH reaction	k_4	14	10^{10}
Phase transition	k_8	25	10^{11}
CO diffusion	k_D	7	10^{12}

[a] For CO diffusion, the pre-exponential factor corresponds to the rate constants of jumps to nearest-neighbour sites. Oxygen diffusion is expected to be negligibly slow. (Adapted from ref. 15.)

The full and reduced versions Eqs. (4)–(7) were used Imbihl *et al.*(15) to mimic the temporal behaviour of the reaction. To explore spatio-temporal patterns observed on the 0.1-mm scale, they complemented Eq. (4) by the term describing CO diffusion on the (1×1) patches (for more recent work in this direction, see the reviews(6, 17)).

Gruyters *et al.*(16) introduced a few new ingredients into the model above. In particular, they took into account that the CO jumps from the (1×1) patches to the "hex" patches are reversible. The fact that this is the case is actually evident from Table 1, because the difference of the CO binding energies on the (1×1) and "hex" patches, $\simeq 9$ kcal/mol, is lower than the activation energy for the LH step. In addition, referring to their own experimental studies, Gruyters *et al.* proposed a new power law for describing surface restructuring,

$$\frac{d\theta_{1\times 1}}{dt} = \begin{cases} k_9(\Theta_A^{\text{hex}})^n \, \theta_{\text{hex}}, & \text{if} \quad c \geqslant 1 \\ -k_8(1-c)\, \theta_{1\times 1}, & \text{if} \quad c < 1 \end{cases} \tag{8}$$

where $n = 4$, and c is defined as in Eq. (7).

The merit of the mean-field equations is that they reproduce experimentally observed kinetic oscillations with realistic values of the rate constants of the elementary steps. Thus, these equations confirm that the mechanism proposed for oscillations is robust. The main shortcoming of the mean-field equations is that they do not provide any information on the reactant distribution on the mesoscopic scale. In particular, these equations do not contain such a physically relevant parameter as the average size of the (1×1) patches.

4. PHENOMENOLOGICAL LANDAU EQUATIONS

Near the critical points, some features of the kinetics of phase transitions can be described on the basis of the phenomenological Landau equations.(18) For CO oxidation on Pt(100), this approach was used by Andrade *et al.*(19, 20) To simulate kinetic oscillations, they combined(19) Eqs. (4)–(6) with the Landau–Khalatnikov equation for $\theta_{1\times 1}$,

$$\frac{d\theta_{1\times 1}}{dt} = -\gamma \frac{\partial F}{\partial \theta_{1\times 1}} \tag{9}$$

where F is the free energy of the interface, and γ the kinetic coefficient. The free energy was represented as

$$F = F_{\text{s}}(\theta_{1\times 1}) + F_{\text{as}}(\theta_{1\times 1}, \Theta_A^{1\times 1}, \Theta_B^{1\times 1}, \Theta_A^{\text{hex}}) \tag{10}$$

where F_s is the term corresponding to the clean surface, and F_{as} the adsorbate–substrate interaction (the adsorbate entropic contribution and adsorbate–adsorbate interactions were for simplicity ignored). Both terms were first calculated in the mean-field approximation (the term "mean-field" is used here in the sense employed in statistical physics), and then the former term was represented in the Landau form, i.e.,

$$F_s = \eta_2 \theta_{1\times1}^2 + \eta_3 \theta_{1\times1}^3 + \eta_4 \theta_{1\times1}^4 \tag{11}$$

$$F_{as} \simeq -\varepsilon_1 (\Theta_A^{1\times1} + \Theta_B^{1\times1})\, \theta_{1\times1} \tag{12}$$

where η_2, η_3 and η_4 are the expansion coefficients, and $\varepsilon_1 > 0$ is the parameter characterizing the adsorbate–substrate interaction stabilizing the (1×1) phase (the dependence of F_{as} on Θ_A^{hex} is neglected because the latter coverage is usually low).

Substituting Eqs. (10)–(12) into Eq. (9), assuming that $\theta_{1\times1}$, $\Theta_A^{1\times1}$ and $\Theta_B^{1\times1}$ are independent variables, and replacing γ by k_8/ε_1 in Eq. (9), Andrade *et al.* obtained

$$\frac{d\theta_{1\times1}}{dt} = k_8 (\Theta_A^{1\times1} + \Theta_B^{1\times1} - \bar{\eta}_2 \theta_{1\times1} - \bar{\eta}_3 \theta_{1\times1}^2 - \bar{\eta}_4 \theta_{1\times1}^3) \tag{13}$$

where $\bar{\eta}_2 = 2\eta_2/\varepsilon_1$, $\bar{\eta}_3 = 3\eta_3/\varepsilon_1$, and $\bar{\eta}_4 = 4\eta_4/\varepsilon_1$.

To describe the formation of spatio-temporal patterns, Andrade *et al.*(20) used the Landau–Ginzburg equation for $\theta_{1\times1}$,

$$\frac{\partial\theta_{1\times1}}{\partial t} = k_8 (\Theta_A^{1\times1} + \Theta_B^{1\times1} - \bar{\eta}_2 \theta_{1\times1} - \bar{\eta}_3 \theta_{1\times1}^2 - \bar{\eta}_4 \theta_{1\times1}^3) + k_{10} \nabla^2 \theta_{1\times1} \tag{14}$$

At first sight, the phenomenological equations above are quite general. In reality, this is however not the case. The problem is that the Landau–Khalatnikov and Landau–Ginzburg equations can be justified provided that the order parameter (i.e., $\theta_{1\times1}$) is the only variable deviating from equilibrium. Under the reaction conditions, the deviations from equilibrium are often much stronger and accordingly there is no guarantee that the phenomenological equations hold. In addition, Andrade *et al.*(19, 20) assumed that $\theta_{1\times1}$, $\Theta_A^{1\times1}$ and $\Theta_B^{1\times1}$ are independent variables. This assumption does not seem to be fulfilled. Indeed, with increasing or decreasing $\theta_{1\times1}$, the local coverages $\Theta_A^{1\times1}$ and $\Theta_B^{1\times1}$ will almost inevitably change because they are defined as the ratio of the average coverages $\theta_A^{1\times1}$ and $\theta_B^{1\times1}$ to $\theta_{1\times1}$. Thus, $\theta_{1\times1}$, $\Theta_A^{1\times1}$ and $\Theta_B^{1\times1}$ can hardly be treated as independent variables.

5. GENERAL COMMENTS ON MONTE CARLO SIMULATIONS

To improve the mean-field models, one can try to employ more sophisticated analytical approaches, but as noted in the beginning of Section 3 this strategy is not expected to succeed. Alternatively, one can use the Monte Carlo (MC) method (or cellular automaton technique) to simulate oscillations. In principle, this method is superior, because it makes it possible to take into account and explore in detail various complicating factors which can hardly be treated analytically. Active use of the MC method for simulations of the kinetics of heterogeneous reactions started after the nowadays classical paper by Ziff, Gulari and Barshad.(21) The bulk of simulations executed in this field concerns reactions occuring on stable surfaces (see, e.g., the reviews(22–25)).

Available MC simulations of reactions accompanied by surface restructuring can be divided into two groups (Sections 6 and 7) depending on the principles employed to treat surface restructuring. As explained in Section 2, this process is complex and accordingly can hardly be described in all the details. To simplify an analysis, one may choose between two strategies. The first "engineering" strategy (Section 6) is based on the use of semi-empirical kinetic rules for elementary steps involved into the game in order to fit experimentally observed kinetics. The second strategy (Section 7) is to formulate a reasonably simple well-defined statistical model of a system under consideration and to explore the corresponding kinetics by employing the standard prescriptions of the theory of phase transitions. Specifically, taking into account that phase transitions result from interactions between particles, one needs to introduce a least a minimal set of such interactions. Then, simulating the kinetics, one should define the probability of reversible steps in agreement with the detailed balance principle (this is the main prescription of general theory for simulations of kinetic processes).

6. SIMULATIONS USING AN "ENGINEERING" APPROACH

First, the simulations of oscillations and pattern formation during CO oxidation on Pt(100) were based exclusively on semi-empirical kinetic rules combined with the cellular automaton technique(26–29) or MC method.(30–33) The merit of these simulations is that they show that with current computer facilities one can directly calculate the arrangement of particles in the adsorbed overlayer on the nm scale. In addition, the results obtained there illustrate richness of spatio-temporal patters which are possible in 2D systems (see especially refs. 27, 28, and 32). The shortcomings are connected with the rules employed to describe CO diffusion and surface restructuring. In all the studies quoted, CO diffusion was neglected, or considered to be slow compared to the LH step. In reality, this is however not the case, because the activation energy for CO diffusion is much lower than that for the LH step (Table 1). In addition, the rate of CO diffusion was considered to be independent of the state of adsorption sites. In particular, the effect of phase boundaries on diffusion was neglected. In reality, the jump rate of CO molecules from the "hex" to (1×1) sites is much higher than that in the opposite direction, because the CO binding energy on the "hex" sites is lower than that on the (1×1) sites (Table 1).

The purely mathematical rules used for surface restructuring were somewhat arbitrary. Usually, the "hex" $\rightarrow (1 \times 1)$ transitions were considered to occur if the local CO coverage was appreciable, which is qualitatively reasonable, but not consistent with the rules employed for CO diffusion. For these reasons, the models under consideration do not predict well-developed phases with atomically sharp phase boundaries. In particular, they do not reproduce the formation of (1×1) islands at relatively low CO coverages, because the kinetic rules used do not describe properly phase separation. In contrast, the experiments indicate that such islands are easily formed during CO adsorption (see Section 2).

To illustrate the statements above, it is instructive to reproduce the rules employed, e.g., by Kuzovkov *et al.*(33) for CO diffusion, LH reaction and surface restructuring. (i) In their study, CO diffusion is considered to occur via jumps to nearest-neighbour vacant sites. The rate of jumps is assumed to be independent of the phase state of the sites involved. (ii) The LH reaction is considered to occur if an adsorbed CO molecule jumps onto a site occupied by an oxygen atom. This means that the reaction is assumed to be limited by CO diffusion. (iii) The propagation of phase boundaries is simulated by analyzing the state of pairs of nearest-neighbour sites. If one of the sites is in the (1×1) state and in addition the pair is occupied at least by one CO molecule, the other site transits to the (1×1) state. If one of the sites is in the (1×1) state and the pair does not contain CO molecules, this site transits to the "hex" state. The rates of these transitions are assumed to be equal. All these assumptions [(i)–(iii)] are far from the reality.

7. MONTE CARLO MODELS BASED ON PRESCRIPTIONS OF STATISTICAL PHYSICS

To make the treatment of the reaction steps, adsorbate diffusion and surface restructuring self-consistent, one needs to use a physically robust model of adsorbate-induced surface restructuring. The main factor complicating the construction of such a model is that the surface densities of Pt atoms in the stable "hex" and metastable (1×1) structures are slightly different. This difference does not, however, seem to be crucial for describing oscillations and accordingly can to a first approximation be ignored. In this case, surface restructuring can be described by using a lattice-gas model taking into account substrate–substrate, adsorbate–substrate and adsorbate–adsorbate lateral interactions. Such a model of CO and hydrogen adsorption on Pt(100) was first proposed in ref. 34 and then used to treat CO and H_2 thermal desorption spectra,(35, 36) propagation of chemical waves,(36) and oscillations in CO oxidation on Pt(100).(37) A similar approach for describing oscillations was employed in ref. 38.

The model used by Rose *et al.*(38) was one-dimensional. CO diffusion from stable to metastable sites was considered to be irreversible. Surface restructuring was described by employing the Glauber dynamics.

The main ingredients of a more general two-dimensional model(36, 37) are as follows:

(i) M (Pt) atoms are assumed to form a square lattice. Every M atom may be in the stable or metastable state. The energy difference of these states is ΔE. The nearest-neighbour (nn) M-M interaction is considered to be attractive, $-\varepsilon_{MM}$ ($\varepsilon_{MM} > 0$), if the atoms are in the same states, and repulsive, ε_{MM}, if the states are different (really, the total nn M-M interactions are of course attractive; the interactions $-\varepsilon_{MM}$ and $+\varepsilon_{MM}$ describe the deviation from the average value). The next-nearest-neighbour (nnn) interactions are ignored. With this choice of the M-M interactions, the model describes the tendency of substrate atoms to be either all in the stable or all in the metastable state.

(ii) Adsorbed particles are assumed to occupy hollow sites (this assumption is not essential, because in the case of adsorption on on-top sites the structure of the formal equations will be the same). The adsorption energy of a given adparticle 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 or B particle after the transition of one nn substrate atom from the stable to the metastable state is ε_{AM} or ε_{BM} ($\varepsilon_{AM} > 0$ and $\varepsilon_{BM} > 0$), respectively.

(iii) The nn adsorbate–adsorbate interaction is considered to be negligible or repulsive, $\varepsilon_{AA} \geqslant 0$, $\varepsilon_{BB} \geqslant 0$, and $\varepsilon_{AB} \geqslant 0$.

The Hamiltonian corresponding to the assumptions above contains the substrate, adsorbate–substrate, and adsorbate–adsorbate interactions,

$$H = H_{\mathrm{s}} + H_{\mathrm{as}} + H_{\mathrm{a}} \tag{15}$$

$$H_{\mathrm{s}} = \Delta E \sum_{i} n_i^M - 4\varepsilon_{MM} \sum_{i,\,j} (n_i^M - 1/2)(n_j^M - 1/2) \tag{16}$$

$$H_{\mathrm{as}} = -\sum_{i,\,j} (\varepsilon_{AM} n_i^A + \varepsilon_{BM} n_i^B)\, n_j^M \tag{17}$$

$$H_{\mathrm{a}} = \sum_{i,\,j} (\varepsilon_{AA} n_i^A n_j^A + \varepsilon_{BB} n_i^B n_j^B,\, + \varepsilon_{AB} n_i^A n_j^B) \tag{18}$$

where n_i^M is the variable characterizing the state of atom i ($n_i^M = 1$ or 0 is assigned to the metastable and stable states, respectively), n_i^A and n_i^B are the occupation numbers of the adsorption sites, and $\sum_{ij}$ means summation over nn pairs.

The model outlined above predicts an adsorbate-induced first-order phase transition provided that the adsorbate–substrate interaction is sufficiently strong. This fact is in fact obvious, because what we basically have here is the interacting lattice-gas and Ising systems [Eqs. (18) and (16), respectively]. To simulate oscillations, Eqs. (15)–(18) were complemented by the following kinetic rules:(37)

Adsorption of A is assumed to occur on vacant adsorption sites. The normalized dimensionless probability of desorption of a given A molecule depends on lateral interactions and is defined as $W_{\mathrm{des}} = \exp(\mathscr{E}_i/k_{\mathrm{B}} T)$, where $\mathscr{E}_i = \sum_j (\varepsilon_{AA} n_j^A + \varepsilon_{AB} n_j^B - \varepsilon_{AM} n_j^M)$ is a sum of nn interactions. In this case, the rates of adsorption and desorption are in agreement with the detailed balance principle.

Diffusion of A particles occurs via jumps to nn vacant sites. The probabilities of these jumps usually depend on lateral interactions in the ground and activated states (the terms "activated" and "ground" correspond here to the transition state theory). Taking into account that the details of diffusion, complicated by adsorbate–substrate lateral interactions, are not well established, the jump probabilities were calculated by using the Metropolis rule satisfying the detailed balance principle. This rule is a reasonable first approximation because it predicts rapid diffusion on perfect stable or metastable patches, rapid jumps on the phase boundaries from the perfect to the metastable phase, but slow jumps in the opposite direction (because the adsorption energy on metastable patches is higher).

Dissociative adsorption of B_2 molecules is considered to occur on pairs of nnn vacant adsorption sites provided that (i) these sites have no nn sites occupied by B particles and (ii) at least one of the nn M atoms is in the metastable state (B_2 dissociation on perfect stable patches is ignored). Prohibiting B_2 dissociation and adsorption on nn sites is motivated if the repulsive interaction between nn B particles, ε_{BB}, is very strong. The latter is the case for oxygen adsorption on close-packed faces of Pt (at UHV conditions the saturation O coverage on these faces is only a fraction of ML). Neglecting B_2 dissociation on perfect stable patches is justified because the O_2 sticking coefficient on the "hex" Pt surface is known to be much lower compared to that on the (1×1) surface.

Diffusion of *B* particles is neglected because this process is assumed to be slow compared to the reaction steps (this may not be quite right for the LH step).

The LH reaction (3) is considered to occur between nn *A* and *B* particles. The probability of this process is for simplicity assumed to be independent of the arrangement of particles in adjacent sites. The latter is the case if lateral interaction in the activated state is about the same as in the ground state.(7)

Surface restructuring is assumed to occur via changes of the state of *M* atoms. The probabilities of the transitions from the metastable to the stable state and back were defined by the Metropolis rule (as in the case of *A* diffusion).

The relative rates of surface restructuring, adsorption-reaction steps, and diffusion of *A* particles are characterized by the dimensionless parameters, p_{res} and p_{rea} ($p_{\mathrm{res}} + p_{\mathrm{rea}} \leqslant 1$). Specifically, the rates of these processes are considered to be proportional to p_{res}, p_{rea}, and $1 - p_{\mathrm{res}} - p_{\mathrm{rea}}$, respectively. The simulations(37) were performed with qualitatively realistic ratios between the rates of different steps. In particular, *A* (CO) diffusion was much faster than the LH step (i.e., $p_{\mathrm{res}} + p_{\mathrm{rea}} \ll 1$) which in turn was faster than surface restructuring (i.e., $p_{\mathrm{res}} < p_{\mathrm{rea}}$).

The MC algorithm consisted of attempts to execute one of the steps involved into the game. As usual, a random number ρ ($\rho \leqslant 1$) is generated. If $\rho < p_{\mathrm{rea}}$, an adsorption-reaction trial is realized. For $p_{\mathrm{rea}} < \rho < p_{\mathrm{rea}} + p_{\mathrm{res}}$, an attempt of surface restructuring is executed. If $\rho > p_{\mathrm{rea}} + p_{\mathrm{res}}$, an *A*-diffusion trial is performed. All these processes are characterized by the dimensionless probabilities. Due to lateral interactions, the probabilities of *A* desorption, *A* diffusion, and surface restructuring depend on the local arrangements of particles as described above. The probability for *A* adsorption (this probability is proportional to *A* pressure) was chosen as a governing parameter.

Typical results obtained for the case when *A* diffusion is two orders of magnitude faster compared to all other steps are shown in Figs. 1 and 2. The mesoscopic restructured islands predicted are seen [Fig. 2a] to be well ordered when the *A* coverage is appreciable. The island boundaries are atomically sharp, and almost all *A* molecules are located inside islands. If the *A* coverage is close to minimum [Fig. 2b], the ordering of islands is worse, because in the latter case the driving force for phase separation is weak. At relatively high rates of *A* diffusion, the size of islands was found to be fairly insensitive to the diffusion rate. This means that the size of islands depends first of all on the interplay of the reaction steps and surface restructuring.

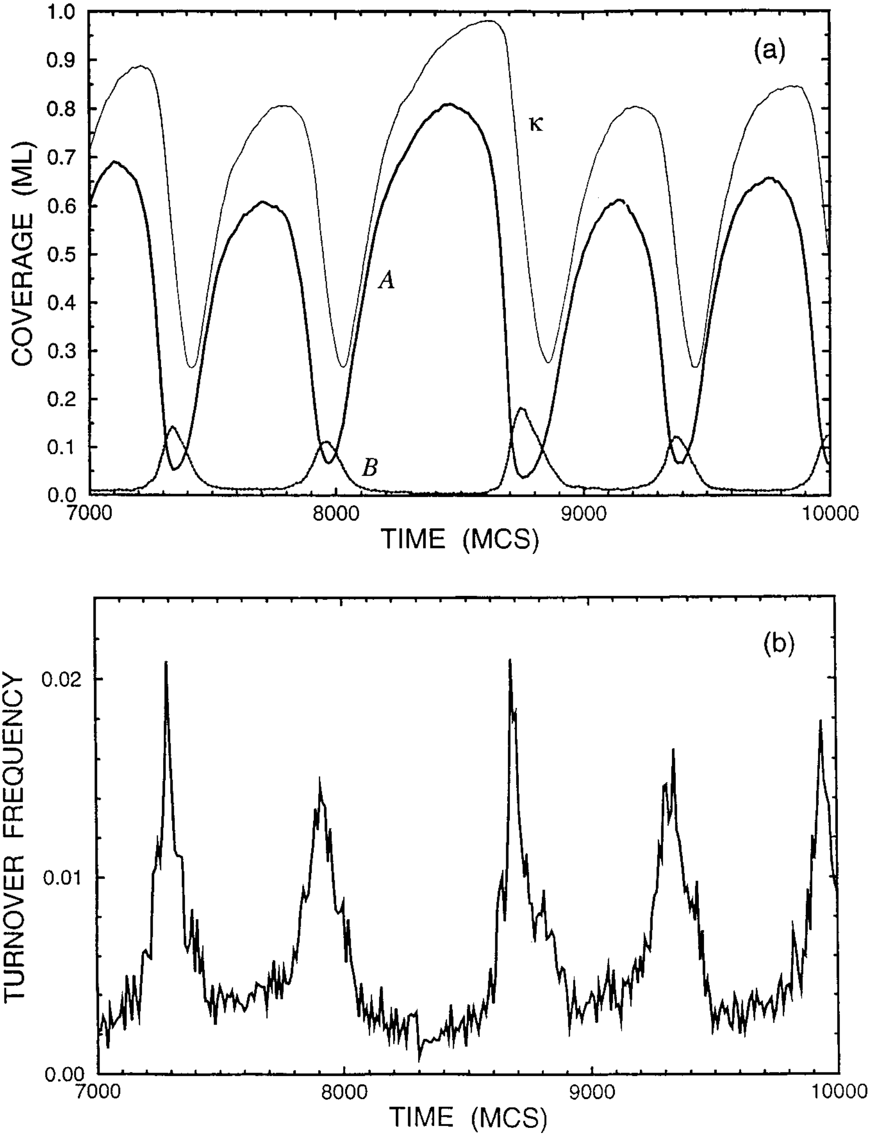
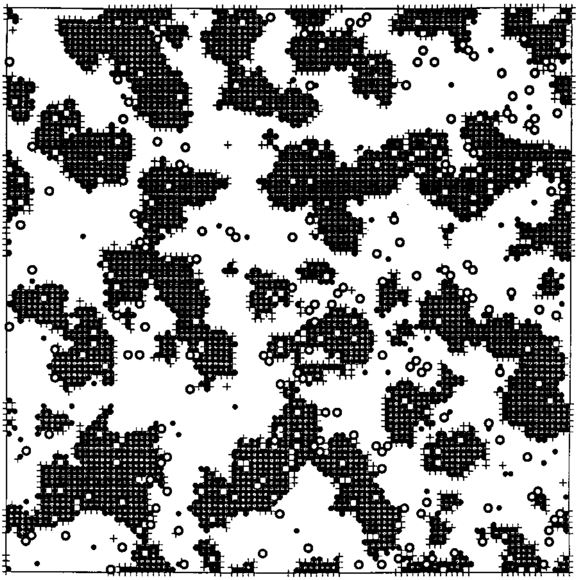


Fig. 1. Example of the oscillatory reaction kinetics calculated[37] in the framework of the lattice-gas model treating surface restructuring as a first-order phase transition: (a) A and B coverages, fraction of M atoms in the metastable state, κ, and (b) reaction rate [AB molec. per site per Monte Carlo step (MCS)] as a function of time. The results were obtained on the (100×100) lattice with periodic boundary conditions. One MCS is defined as (100×100) attempts to realize the adsorption-reaction-surface-restructuring steps. The rate of these steps is two orders of magnitude lower compared to that of A diffusion.

(a) t=9520 MCS



(b) t=10^4 MCS

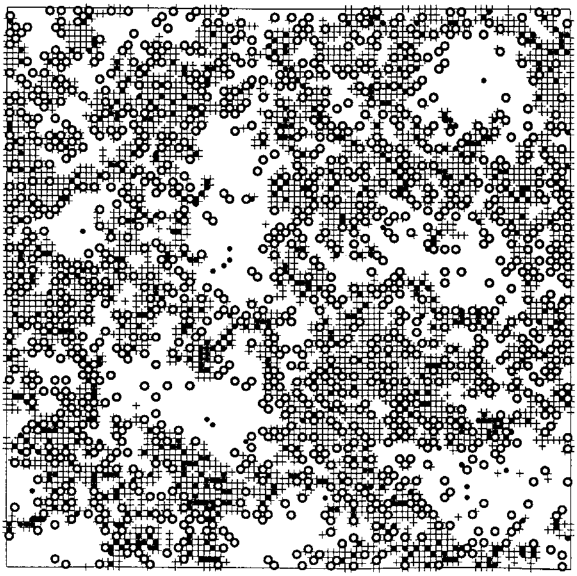


Fig. 2. Snapshots of the lattice for the MC run shown in Fig. 1. Plus signs indicate substrate atoms in the metastable state (atoms in the stable state are not shown). Filled and open circles exhibit *A* and *B* particles adsorbed at hollow sites.

8. OSCILLATIONS AND CHAOS ON NM CATALYST PARTICLES

The simulations described in the previous sections concerned primarily CO oxidation on a single-crystal Pt(100) surface. Practical catalysts frequently consist of small, active metal particles of 1–100 nm in size, carried by an inert porous support. The reaction kinetics on such catalyst particles exhibiting primarily (111) and (100) facets can be complicated by adsorbate interfacet diffusion.(39) This effect is especially interesting when the reaction occurs in the oscillatory regime. Detailed experimental data on such reaction regimes, complicated by interfacet diffusion, are yet lacking. Theoretically, kinetic oscillations of this type were recently analyzed in ref. 40. The catalyst Pt particles were assumed to be shaped into a truncated pyramid, with top and bottom (100) faces and (111) side faces and with the largest (100) facet attached to the substrate. The sizes of the top and bottom facets were respectively (50×50) and (100×100). The top (100) facet was allowed to reconstruct during A adsorption, as in the case of CO adsorption on the Pt(100) single-crystal surface. This phenomenon was treated as a first-order phase transition by using the model described in the previous section.

First, the $A + B_2$ reaction kinetics were calculated for the isolated (50×50) facet. With the chosen model parameters, the amplitude of oscillations was high. The large-scale changes in adsorbate coverages were accompanied by small-scale fluctuations with the amplitude comparable with that predicted by the Poissonian distribution. The fluctuations in the reaction rate were larger, because the rate depends on the distribution of both reactants.

In the case of communicating facets, the main role of the peripheral facets is to provide additional supply of A particles to the central facet via adsorption and surface diffusion. This supply was found to result in a strongly nonuniform phase distribution on the central facet (the facet was restructured primarily near the boundaries). As a consequence, the conditions for oscillations on different regions of the central facet were quite different. The latter resulted in chaotic oscillations. Such chaos, connected with the interplay of the reaction kinetics on adjacent (100) and (111) facets, seems to be inherent for reactions on nm particles (or on a tip of a field ion microscope(41, 42)) and does not have its counterpart in reactions on single-crystal surfaces.

9. CONCLUSION

During the past fifteen years, kinetic oscillations in CO oxidation on Pt(100) have attracted considerable attention of theorists. The first models used to simulate this process were purely phenomenological. The last studies are based on the well-defined lattice models taking into account lateral interactions between adsorbed particles and metal atoms and describing adsorbate-induced surface restructuring in terms of the theory of first-order phase transitions. The latter approach predicts the formation of mesoscopic restructured well ordered islands with atomically sharp boundaries. The reliable *in-situ* experimental data on the reactant distribution on the nm scale during kinetic oscillations are in fact still lacking. But from complementary experimental studies, one can estimate(43) that in such reactions as $CO + O_2$, $CO + NO$ or $NO + H_2$ on Pt(100) the (1×1)-island size lies in the range between 1 and 100 nm. The size of islands observed a Pt(100) tip of a field ion microscope(41, 42) is about 10–20 nm and their boundaries are atomically sharp. Thus, the theory match up with experiment.

Despite a large number of simulations executed in this field, some of the aspects of the reaction under consideration are still open for discussions and further studies. It is of interest for example to explicitly describe the forcing up some of the Pt atoms during surface restructuring, to interpret the experimentally observed power-law growth of the (1×1) phase, and to explore the relationship between macroscopic and mesoscopic spatio-temporal patterns. It is also of interest to construct microscopic statistical models describing kinetic oscillations in CO oxidation on Pt(110) [in this case, CO adsorption results in the $(2 \times 1) \rightarrow (1 \times 1)$ phase transition] and in other catalytic reactions accompanied by surface restructuring or such processes as oxide or carbon formation (for recent simulations treating some of these problems, see refs. 44 and 45). An area still open to experimental studies is oscillations on mesoscopic crystallites, with communicating facets (by diffusive transport).

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