Chemical Engineering Journal 107 (2005) 181–189

Chemical
Engineering
Journal
www.elsevier.com/locate/cej

Turbulent and stripes wave patterns caused by limited CO_{ads} diffusion during CO oxidation over Pd(1 1 0) surface: kinetic Monte Carlo studies

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Abstract

The dynamic behaviour of the CO oxidation reaction over Pd(1 1 0) has been studied by means of kinetic Monte Carlo modelling. The influence of the internal parameters on the shapes of surface concentration waves obtained in simulations under the limited surface diffusion intensity conditions has been studied. The hysteresis in oscillatory behaviour has been found under step-by-step variation of oxygen partial pressure. Two different oscillatory regimes could exist at one and the same parameters of the reaction. The parameters of oscillations (amplitude, period and the shape of spatio-temporal patterns on the surface) depend on the kinetic prehistory of the system. The possibility for the appearance of the cellular and turbulent patterns, spiral, ring and stripe oxygen waves on the surface in the cases under study has been shown.

Keywords: CO oxidation; Palladium; Oscillations; Surface waves; Monte Carlo model; Hysteresis in oscillatory regimes

1. Introduction

The complex dynamic behavior in oxidation reaction over platinum metals (bistability, oscillations, surface autowaves, etc.) can be directed by the structure of the reaction mechanism, specifically by the laws of physicochemical processes in the “reaction medium—catalyst” system. The most popular factors used to interpret the critical effects in high vacuum region are the following [1]: (i) phase transformations on the catalyst surface, including the formation and decomposition of surface and subsurface oxides during the reaction (e.g., Pd(1 1 0)) and (ii) structural phase transitions of the surface and its reconstruction due to the influence of the reaction media (e.g., Pt(1 0 0)).

A conventional approach to simulate the oscillatory behaviour based on solving of kinetic equations that reflect changes in the integral characteristics of the system, such as reaction rate and surface substances concentrations, cannot explain at the microscopic level the formation of spatial-wave structures having the forms of solitons, spiral waves, and turbulence pattern under the conditions of oscillations. The rare exceptions are the complicated reaction–diffusion models that permit to describe the intricate spatio-temporal structures using the deterministic approach [2]. Unlike this approach, imitation modelling based on the Monte Carlo methods makes it possible to reflect easily the spatio-temporal dynamics of adsorbate distribution [3,4] on real catalyst surfaces, whose structure may transform under the action of the reaction medium. Recently, the statistical lattice models for imitating the oscillatory and autowave dynamics in the adsorbed layer during CO oxidation over Pd(1 1 0) [5] and Pt(1 0 0) [6] single crystals with different structural properties of catalytic surfaces, has been studied.

The aim of this contribution is to study the influence of the change of internal parameters (e.g., partial pressure of oxygen) on the shapes of surface concentration waves obtained in simulations under the limited surface diffusion intensity conditions. Let us restrict our consideration by CO oxidation reaction over Pd(1 1 0 (similar results has been obtained by simulation of $CO + O_2$/Pt(1 0 0) [6]).

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1385-8947/$ – see front matter
doi:10.1016/j.cej.2004.12.041

2. Reaction mechanism and the corresponding Monte Carlo model

Detailed mechanism of this reaction has been established by means of FEM, TPR and XPS studies [7]:

$$O_{2(gas)} + 2* \rightarrow 2O_{ads} \quad (1)$$

$$CO_{gas} + * \leftrightarrow CO_{ads} \quad (2)$$

$$CO_{ads} + O_{ads} \rightarrow CO_{2(gas)} + 2* \quad (3)$$

$$O_{ads} + *_{v} \rightarrow [*O_{sub}] \quad (4)$$

$$CO_{ads} + [*O_{sub}] \rightarrow CO_{2(gas)} + 2* + *_{v} \quad (5)$$

$$CO_{gas} + [*O_{ss}] \leftrightarrow [CO_{ads}*O_{sub}] \quad (6)$$

$$[CO_{ads}*O_{sub}] \rightarrow CO_{2(gas)} + * + *_{v} \quad (7)$$

where * and $*_v$ are the active centres of the surface and subsurface Pd layer, respectively. Formation of the subsurface oxygen proceeds according to step 4, reduction of the initial surface—due to reactions 5 and 7. Molecules CO_{ads} can diffuse over the whole surface according to the rules: (i) $CO_{ads} + * \leftrightarrow * + CO_{ads}$, (ii) $CO_{ads} + [*O_{sub}] \leftrightarrow * + [CO_{ads}*O_{sub}]$ and (iii) $[CO_{ads}*O_{sub}] + [*O_{sub}] \leftrightarrow [*O_{sub}] + [CO_{ads}*O_{sub}]$. We suppose [7] that the heat of CO adsorption on the "oxidised" centres $[*O_{sub}]$ (with subsurface oxygen) is lower than that on the initial [*] one, i.e., the probability of $[CO_{ads}*O_{sub}]$ desorption (step 6) is higher than of CO_{ads} (step 2) one. The rate coefficients for O_2 and CO adsorption, k_1, k_2, and k_6, can be treated as product of the impingement rate ($k_i \times P_i$) and of the sticking coefficient (S_i). The parameters of the elementary steps were partly taken from the literature. The oscillatory behaviour was revealed in simulation [5] in the vicinity of the following set of the rate coefficients (s^{-1}):

k_1	k_2	k_{-2}	k_4	k_5	k_6	k_{-6}	k_7
1	1	0.2	0.03	0.01	1	0.5	0.02

For example, the self-oscillations of the reaction rate and adsorbed species concentrations accompanied by the autowave processes on the surface were observed in the k_1 range from 0.88 to 1.45.

Let us briefly describe the algorithms used in simulations. The square lattice N × N (N = 400–1600) with periodic boundary conditions represents the model catalyst surface. States of the lattice cells (in this case—*, O_{ads}, CO_{ads}, $[*O_{sub}]$ and $[CO_{ads}*O_{sub}]$) are determined according to the rules prescribed by the detailed reaction mechanisms used in the cases under study. So-called Monte Carlo step (MCS) consisting from $N \times N$ elementary actions was used as a time unit. During the MCS, each cell is tested on the average once. By elementary action, it is meant a trial to change a state of the randomly chosen centre in such a manner, as it will with the substances taking part in the elementary processes (steps) constitute the detailed reaction mechanism. The probability of the particular process w_i is determined by a ratio between the rate coefficients, therewith the rate coefficients for the adsorption processes are multiplied by the relevant partial pressures. During the MCS, after each of $N \times N$ trial to carry out one of the elementary action, the inner cycle of CO_{ads} diffusion has been arranged (usually $M = 50$–100 attempts of diffusion). Adsorbed carbon monoxide can diffuse via hopping from their sites to vacant nearest neighbour site (both sites has been chosen randomly) and the types of active centres remain the same. The diffusion is necessary for the spatio-temporal processes synchronization occurring on the different regions of the model surface. We suppose that reaction (step 3) proceeds immediately as soon as adsorbed CO_{ads} and O_{ads} appear in the nearest neighbourhood. After each successful CO or O_2 adsorption as well as of CO_{ads} diffusion, the neighbouring cells were checked to find the partners in reaction. If the partners were found then the cells were given the state *, and one more CO_2 molecule was added to the reaction rate counter. The reaction rate and surface coverages were calculated after each MCS as a number of CO_2 molecules formed (or the number of cells in the corresponding state) divided by the total number of the lattice cells N^2. For a more detailed description of the employed algorithms, please see [5–6].

3. Results and discussion

In both cases [5–6], the synchronous oscillations of the reaction rate and surface coverages are exhibited within the range of the suggested model parameters under the conditions very close to the experimental observations—e.g., Fig. 1, in the case of Pd(1 1 0). These oscillations are accompanied by the autowave behaviour of surface phases and adsorbate coverages (Fig. 2). One can see from Figs. 1 and 2 that the oscillations are quite regular, and the shape of oxygen waves is of prominent cellular pattern of change: the initiation of oxygen fronts propagation proceeds simultaneously at different local regions of the model surface, and the O_{ads} and CO_{ads} coverages alternate during the period of oscillations. Fig. 2 demonstrates the change of the adsorbed layer composition during separate period of oscillations. The low reactive, CO covered state of the surface is characterised by spatial homogeneity of both types of adsorbed CO (first snapshot). Adsorbed oxygen is almost absent on the surface, whereas the concentration of the subsurface oxygen $[*O_{sub}]$ diminishes slowly due to actions of 5 and 7 steps of the detailed reaction mechanism. The decrease of $[*O_{sub}]$ concentration to a certain critical value makes reaction ignition favourable due to the appearing on the surface of the pairs of free active centres of Pd. Oxygen adsorbs on these neighbouring free centres and the oxygen islands begin to propagate over the surface (second snapshot). The system undergoes a transition to the high reactive state. The concentration of O_{ads} attains its maximum quite quickly (third snapshot) but at the same time the concentration of $[*O_{sub}]$ begins to grow. Remember that adsorption of O_2 on the "oxidised" centres $[*O_{sub}]$ is prohibited therefore at the $[*O_{sub}]$ maximum the slow transition to the low reactive state

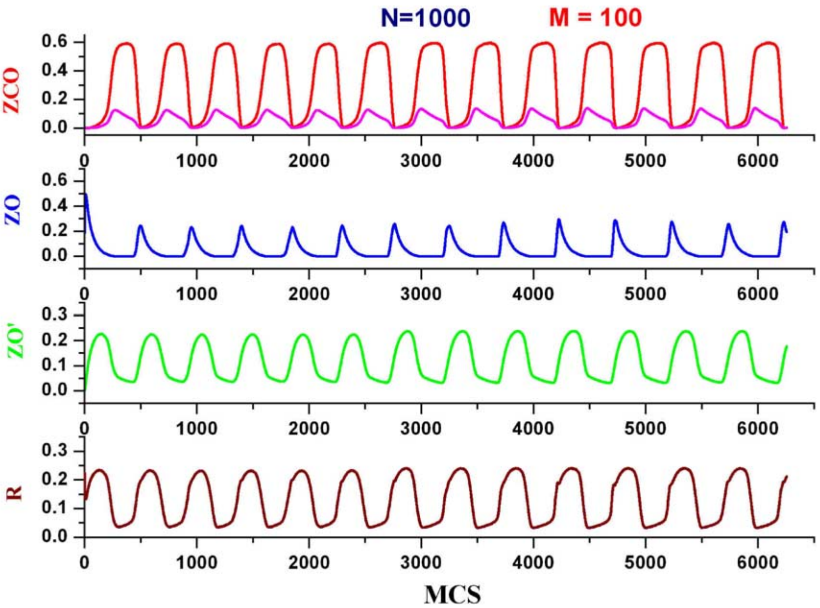

Fig. 1. Dynamics of changes in the surface coverages CO_{ads} (red line), $[CO_{ads}{*}O_{sub}]$ (pink line), $[{*}O_{sub}]$ (green line), O_{ads} (blue line), R (brown line)—Monte Carlo model for CO oxidation over Pd(1 1 0). $N = 1000$, $M = 100$. The values of the rate constants of steps (s^{-1}) (see scheme): $k_1 = 1$, $k_2 = 1$, $k_{-2} = 0.2$, $k_3 = \text{inf}$, $k_4 = 0.03$, $k_5 = 0.01$, $k_6 = 1$, $k_{-6} = 0.5$, $k_7 = 0.02$. The partial pressures of reagents (CO and O_2) are included in the rate constants of adsorption (k_1, k_2, k_6). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

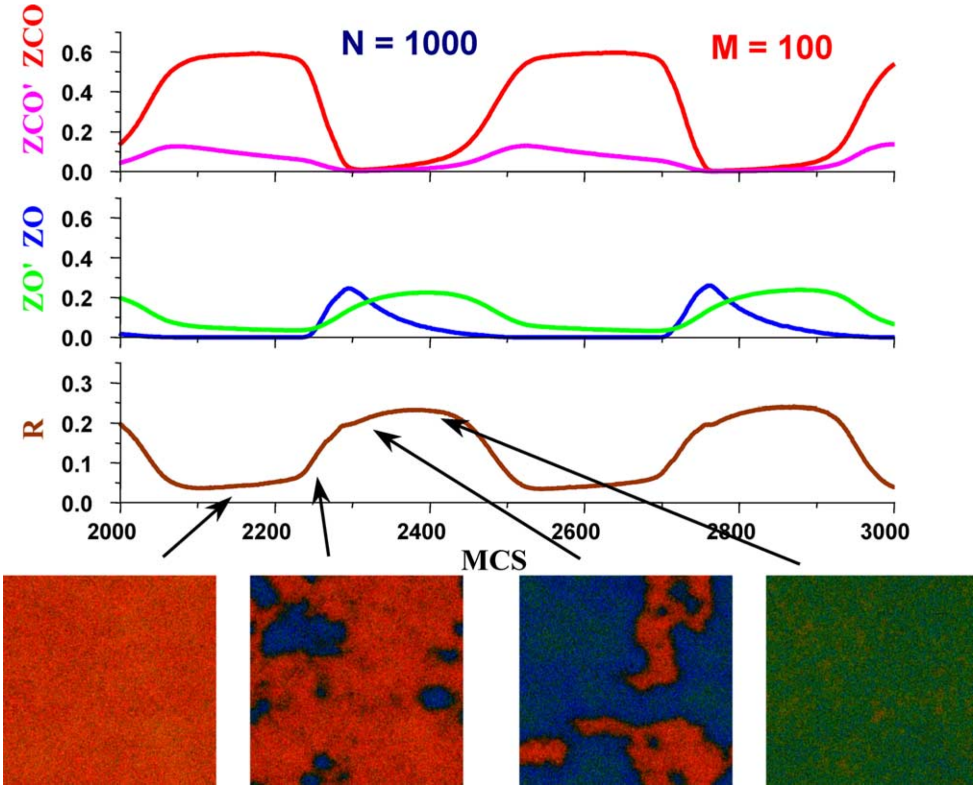

Fig. 2. Reaction rate and coverages of surface species along with simulated snapshots displaying spatial distribution of different adsorbates over the surface at specific times. On the snapshots O_{ads} is painted blue, $[{*}O_{sub}]$ as green, CO_{ads} as red, $[CO_{ads}{*}O_{sub}]$ as yellow, empty Pd sites as black. The parameters of simulation are the same as for Fig. 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

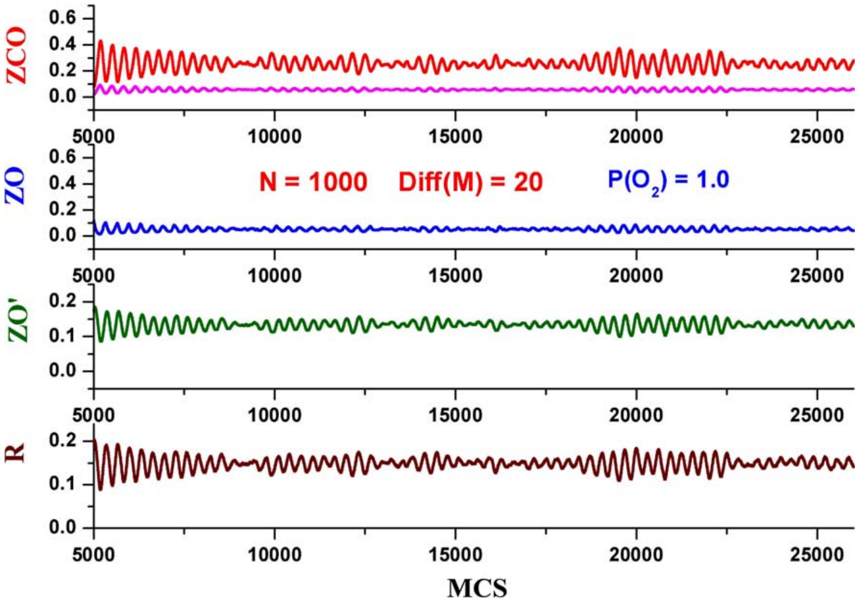

Fig. 3. Dynamics of changes in the surface coverages and reaction rate at $M = 20$. The rest of parameters are the same as for Fig. 1.

begins (forth snapshot). Let us notice that the surface species distribution at this reverse transition is homogeneous in contrast with the forward transition to the high reactive state.

The employed algorithms [5–6] permit to calculate not only the surface species distribution but also the local intensity of the reaction rate over the model surface. The simulations show that the intensity of CO_2 formation in the CO_{ads} layer is low, inside oxygen island it is intermediate and the highest intensity of CO_2 formation is related to a narrow zone between the propagating O_{ads} island and surrounding CO_{ads}

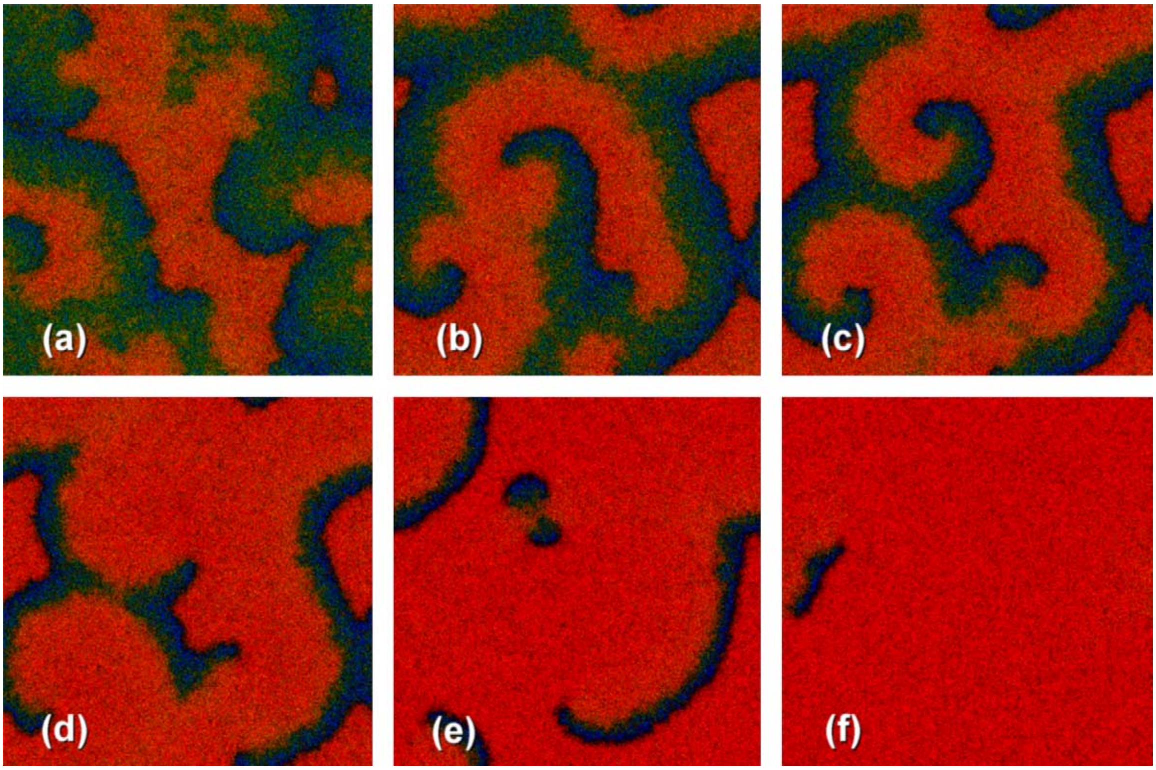

Fig. 4. Typical snapshots of the adsorbate distribution over the surface ($N = 1000$) at step-by-step reducing of k_1 in the case of restricted diffusion intensity of CO_{ads} ($M = 20$). The designations of adsorbate are the same as for Fig. 2.The values of partial pressure of oxygen (i.e., k_1) are the following: 1 (a), 0.9 (b), 0.85 (c), 0.8 (d), 0.73 (e), and 0.71 (f).

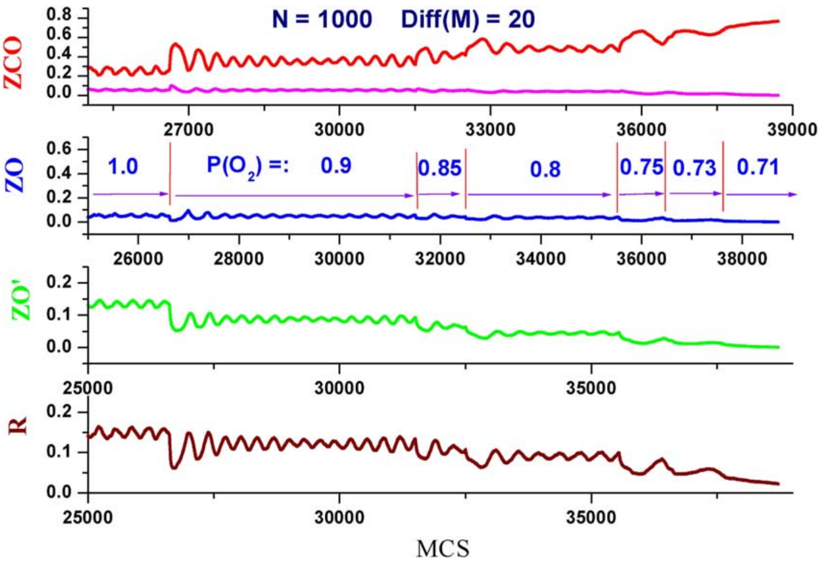

Fig. 5. Dynamics of changes in the surface coverages and reaction rate at step-by-step reducing of k_1 (or P_{O_2}). $M = 20$. The rest of parameters are the same as for Fig. 1.

layer—“reaction zone”, characterised by the elevated concentration of the free active centres [5–6]. The presence of the narrow reaction zone between O_{ads} and CO_{ads} layers was found experimentally by means of the field ion probe-hole microscopy technique with 5 Å resolution [8]. The important role of the diffusion rate and of the lattice size on the synchronisation and stabilisation of surface oscillations has been demonstrated [5–6]. Particularly, in the case of Pt(1 0 0), the decrease of the diffusion intensity (parameter M) from 100 to 30 leads to irregular oscillations and to the turbulent patterns on the model surface—in this case, the mobile islands of O_{ads} shaped as cellular waves, spiral fragments, etc., are formed [6]. Similar spatio-temporal behavior was experimentally observed in $CO + O_2$/Pt(1 0 0) using the ellipsomicroscopy for surface imaging (EMSI) technique [9].

Let us study the influence of diffusion intensity M on the shape of the surface waves in the case shown in Fig. 2. Decrease of M up to value $M = 50$ doesnot change significantly the oscillatory and wave dynamics, but decreasing M up to the value $M = 20$ drastically changes both the shape of oscillations and the spatio-temporal behaviour of simulated surface waves. Period and amplitude of oscillations decrease

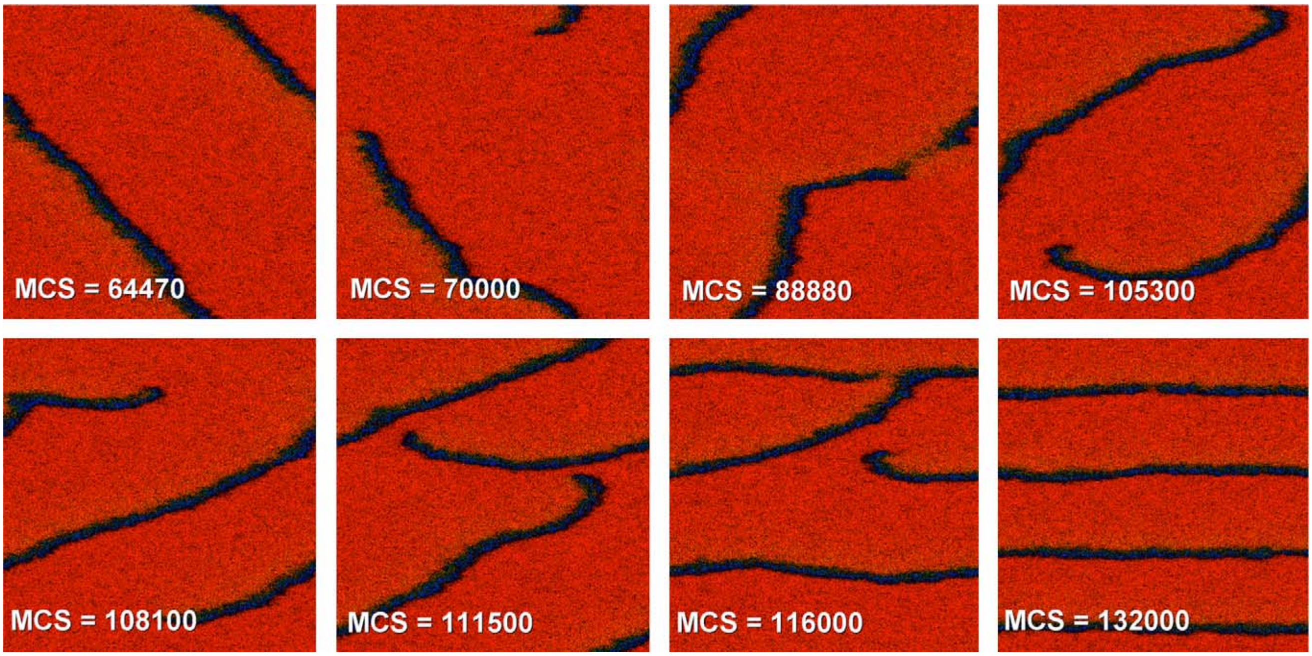

Fig. 6. Consequent snapshots of the oxygen stripes evolution over the surface at diffusion anisotropy: $M_x = 18$, $M_y = 2$; $P_{O_2} = 0.72$.

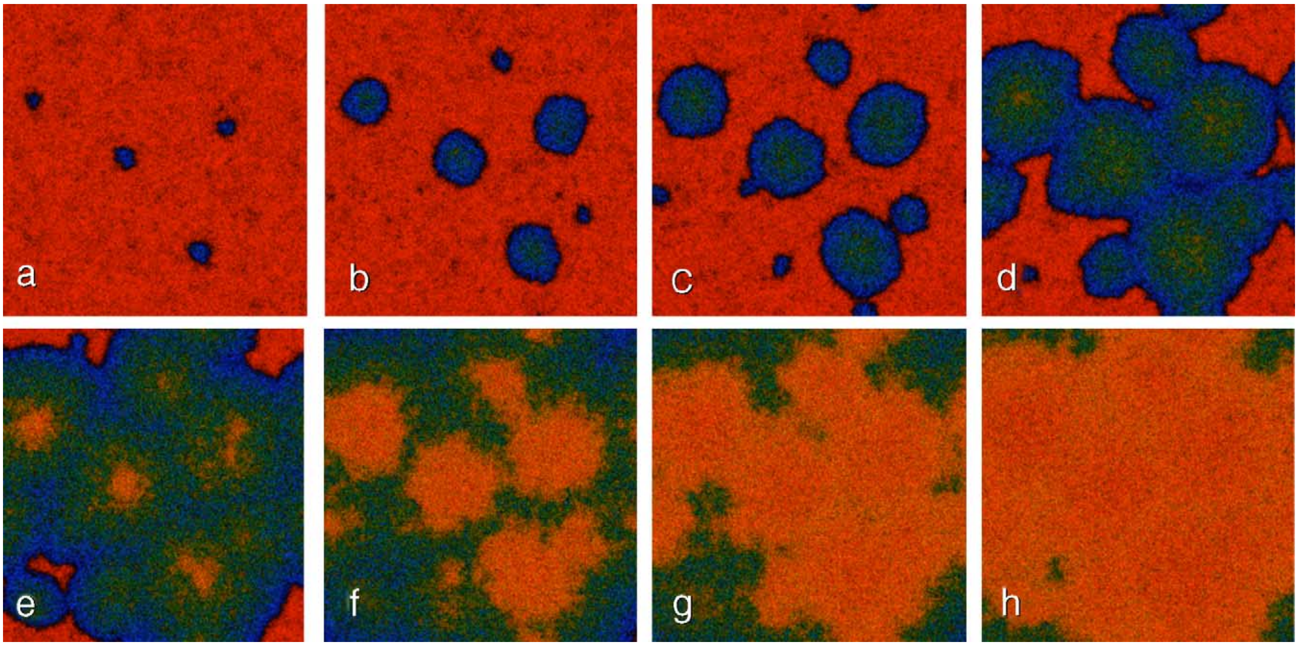

Fig. 7. The snapshots illustrating the rise of oscillations at inverse step-by-step increasing of k_1, $k_1 = 0.85$. The difference between the frames is 50 MC steps.

considerably, the dynamic behaviour of reaction rate and surface coverages demonstrate the intermittence (Fig. 3, oscillatory regime I). During these oscillations, oxygen (O_{ads}) is always present on the surface (in contrast to the case of Figs. 1 and 2) in the form of turbulent spatio-temporal structures (Fig. 4a). It is seen from Fig. 4a that the whole surface is divided in several islands oscillating with the same period but with a phase shift relative to each other, therefore the reaction rate and coverage's time dependencies demonstrate the intermittence peculiarities. Here, one can observe the spatio-temporal pattern of complicated turbulent shape on the surface. The colliding oxygen islands form the spiral-like patterns. The nature of the appearing of spiral-like patterns could be explained using the results obtained in [10]. In this paper, we studied the oscillations in the $CO + O_2$/Pd(1 1 0) over the few nanocrystals of Pd initially independent of each others, i.e., the CO_{ads} diffusion between the different parts of the surface was prohibited. After the removing boundaries for the CO_{ads} diffusion, the colliding oxygen waves generate the stable spiral wave. The main conclusion of [10] was that namely the phase shift between colliding local oscillators could lead to the spiral patterns formation.

Step-by-step decrease of oxygen partial pressure P_{O_2} (remember, that the values for O_2 and CO adsorption coefficients, k_1, k_2, and k_6, can be treated as product of the impingement rate ($k_i \times P_i$) and of the sticking coefficient (S_i)) leads to the gradual thinning of oxygen travelling waves (Fig. 4b–e). Each time at stepwise changing of P_{O_2} (or k_1),

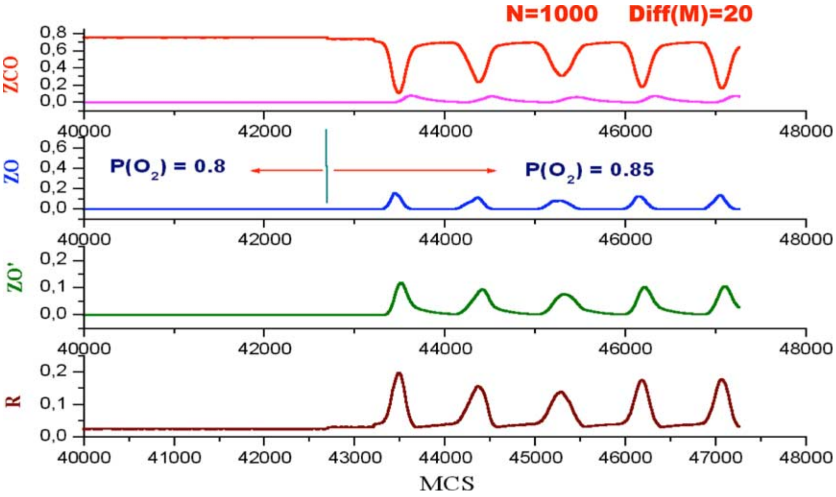

Fig. 8. Ignition of oscillatory regime II in the course of step-by-step increasing of k_1.

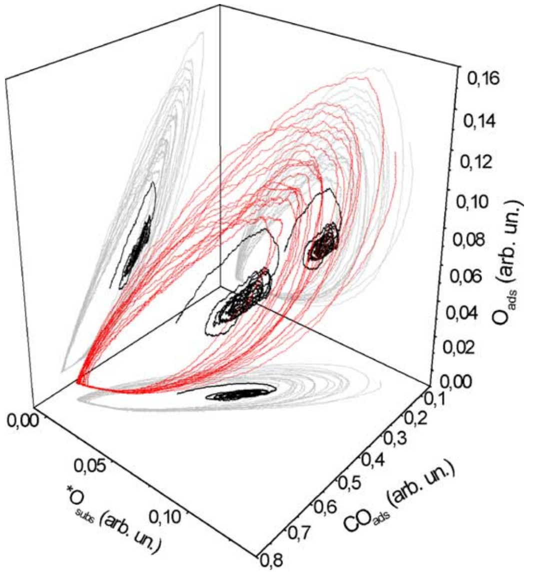

Fig. 9. Phase trajectories belonging to different oscillatory regimes in the phase subspace $\{O_{ads} \times [{}^*O_{sub}] \times CO_{ads}\}$ at $k_1 = 0.85$. Regime I is painted black and regime II as red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

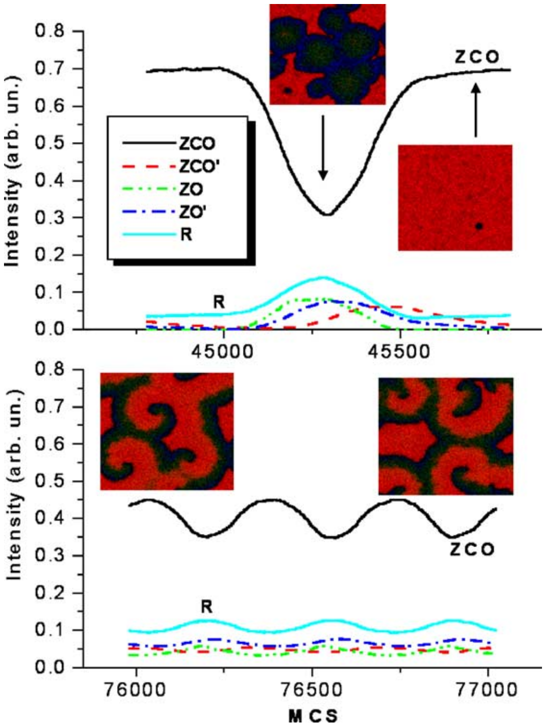

Fig. 10. The characteristics of two different oscillatory regimes at $k_1 = 0.85$. At the bottom, characteristics of the regime I: period of oscillations ∼250 MCS, turbulent spiral-like patterns on the surface. On the top, characteristics of the regime II: period of oscillations ∼1000 MCS, the alternately change of O_{ads} and CO_{ads} layers via growing cellular oxygen islands.

we start from the preceding configuration of the adsorbed species, i.e., we keep in mind the previous spatio-temporal dynamics on the surface (this is important for subsequent discussion). At low values of P_{O_2} (Fig. 4d–f), the long and thin oxygen stripe (or worm-like) patterns are formed on the simulated surface, and the clear tendency of turbulent patterns to combine into spirals disappeared at $P_{O_2} < 0.8$. The width of the oxygen stripes gets thin and the amplitude of oscillations diminishes with decreasing of k_1 (Fig. 5). At last, at $P_{O_2} = 0.71$, the oxygen stripe wave vanish slowly from the surface and the system transform to the low reactive state (the surface is predominantly covered by CO_{ads}).

It should be mentioned here, that the main body of simulation under discussion has been performed on the assumption, that the model surface is homogeneous, i.e., the surface structure of the palladium single crystal was not taken into account. However, it is well known, that CO or oxygen adsorption over the Pd(1 1 0) surface leads to the reversible surface structure transformation into the so called “missing-row” structure: $(1 \times 1) \leftrightarrow (1 \times 2)$. The presence of steps introduces diffusion anisotropy and the diffusion rate of CO_{ads} along and across the rows can differ noticeably. The anisotropy of surface diffusion should reflect in the shape of the chemical wave propagation observed in the oscillatory reaction regimes [11]. Let us study the influence of the diffusion anisotropy on the spatio-temporal patterns observed during our simulations. As an illustrative example of the anisotropic effect, we will choose the case of steadily existing oxygen stripes on the surface, $P_{O_2} = 0.72$ (Fig. 6). In the case of isotropic diffusion ($M = M_x + M_y = 20$, $M_x = M_y$), the direction of stripes propagation is arbitrary and depends on the systems prehistory (in our particular case – from left lower corner to right upper corner of the model lattice with periodic boundary conditions,

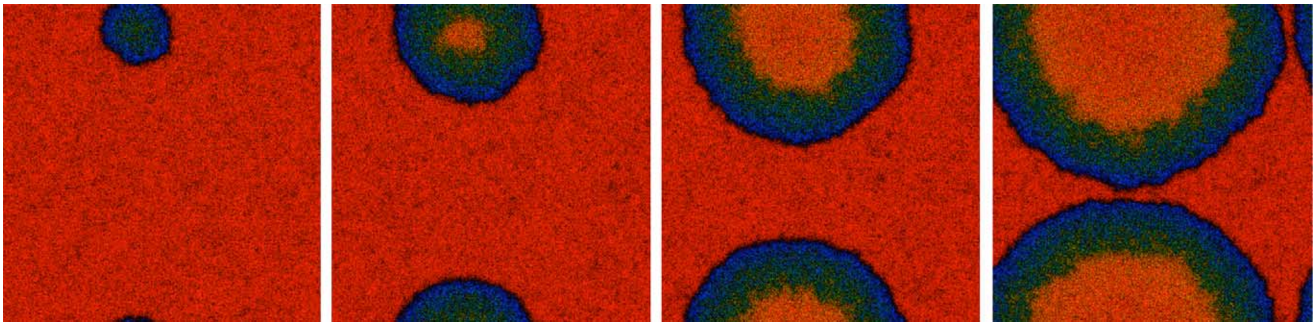

Fig. 11. The snapshots illustrating the propagation of ring-like islands of oxygen at $k_1 = 0.83$. The time interval between the frames is 100 MC steps.

Fig. 6, MCS = 64,470). Introducing an anisotropic diffusion via setting the values $M_x = 18$, $M_y = 2$ leads to the stripe wave instability: the stripe breaks (Fig. 6, MCS = 70,000), different parts of the stripes collide with each other (MCS = 88,880, 105,300, 108,100 and 111,500) and, as a result, the preferred direction of stripes propagation change gradually. Finally, the stripes become stretched along abscissa axis in accordance with preferred direction of CO_{ads} molecules diffusion (Fig. 6, MCS = 116,000 and 132,000), and the direction of the stripes propagation become top–down. Let us notice that when the parts of oxygen stripes move from left to right (e.g., MCS = 88,880), the width of this strip is maximal, as a consequence of strongly anisotropic diffusion of CO_{ads} molecules. The anisotropic effect on the turbulent spiral-like patterns (e.g., at $P_{O_2} = 0.9$ and 0.8) leads, as well, to the gradual stretching of these patterns along *X*-direction.

The reverse increasing of k_1 leads to hysteresis in oscillatory behaviour. The oscillations appear only at $P_{O_2} = 0.85$ via very fast "surface explosion" (Fig. 7a–h). It is surprising that the characteristics of these oscillations differ drastically from those observed at gradual decreasing of P_{O_2} at the same value of $P_{O_2} = 0.85$ (in oscillatory regime I). Now the amplitude of oscillations (coverage's and reaction rate) is larger than that in regime I (Fig. 8) and instead of turbulent spiral-like pattern (Fig. 4c), we observe the alternately change of O_{ads} and CO_{ads} layers via growing cellular oxygen islands (Fig. 7) similar to the case with large diffusion intensity (Fig. 2). Our attempts to switch from this oscillatory regime (II) to previous regime (I) by means of setting the various initial conditions on the concentrations of the surface species (i.e., *, O_{ads}, CO_{ads}, [$*O_{sub}$] and [$CO_{ads}*O_{sub}$]) proved to be unsuccessful. Starting both from the bare surface and from the surface predominantly covered by O_{ads} or CO_{ads} (similar to the case of Fig. 7) we fall each time in the same regime II. The point is that due to the algorithm of our Monte Carlo model, we always create the initial configuration of the adsorbed layer with uniformly distributed species over the surface. That means, that despite of apparent intersection of phase trajectories belonging to different oscillatory regimes in the phase space during the Monte Carlo simulations (Fig. 9) we could not obtain the oscillatory regime I from any surface composition with uniformly distributed species over the surface. Only if we compose the specific spatio-temporal patterns on the surface, similar to those on Fig. 4, we could fall into regime I. In other words, the hysteresis in oscillatory and spatio-temporal behaviour, revealed in our Monte Carlo simulations, depends on the system prehistory (shape–memory effect).

It has been found in experiments, e.g., [8], that the different oscillatory windows could exist in the parameter space of the particular system, e.g., CO oxidation over Pt(1 0 0) [8], i.e., at different parameters (temperature and CO/O_2 ratio) two regions has been found at a constant total pressure where the rate oscillations and spatio-temporal formation has been

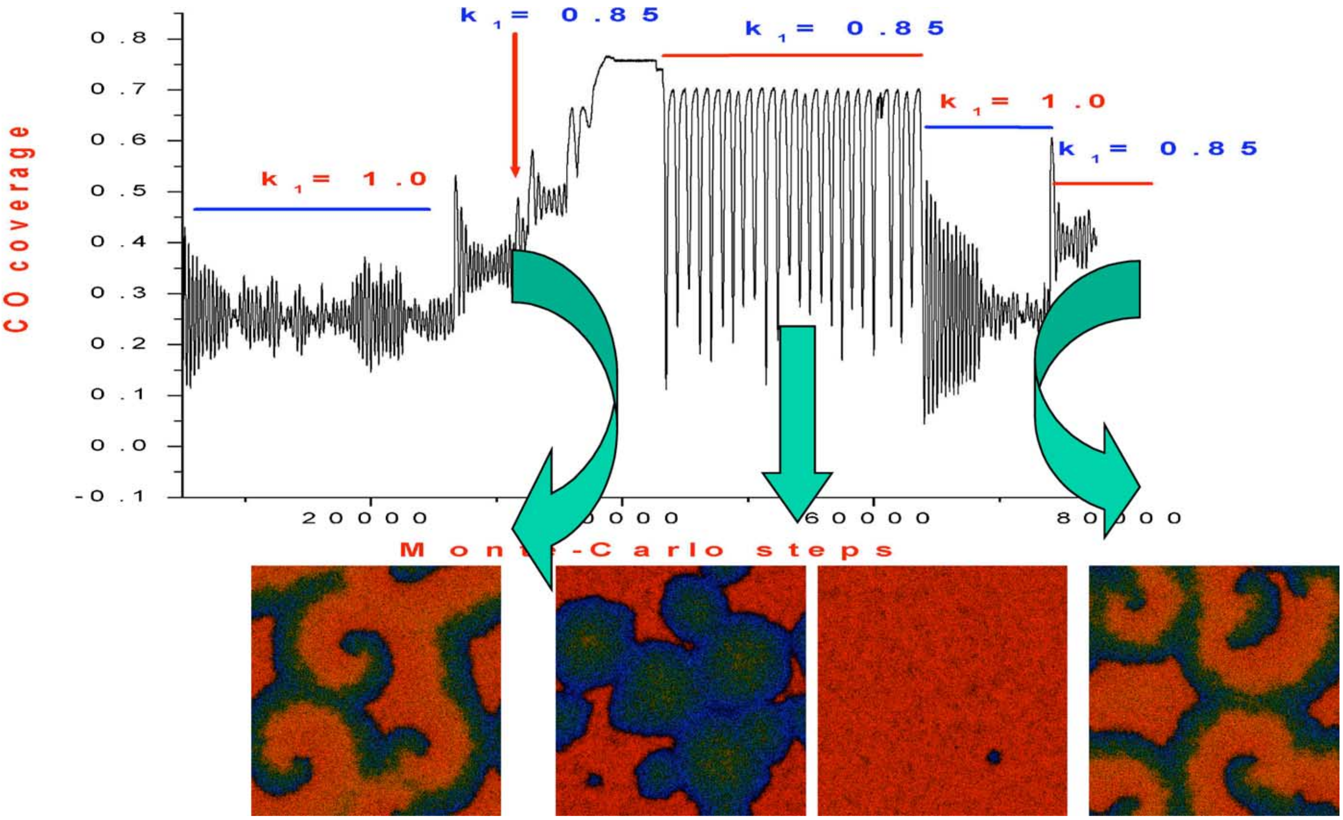

Fig. 12. The whole scenario of k_1 change during our simulation experiments, exemplified by CO_{ads} temporal dynamics.

observed. In our case, two different oscillatory regimes in the same variation interval of P_{O_2} has been found in simulations with discriminate spatio-temporal dynamics, Fig. 10.

The interval of existence of oscillatory regime II is quite large: $0.98 > k_1 > 0.82$. Increase of k_1 in this interval leads to the increasing of the amplitude and decreasing of the period of oscillations. At low bound of this interval (i.e., at $k_1 = 0.83$), the ring structures of growing oxygen islands has been observed (Fig. 11)—during the oxygen island propagation CO have time to adsorb into its centre. In this case, the period of oscillations increased significantly (∼2000 MCS). And only if we fall outside the upper limit of oscillatory regime II (at $k_1 = 1$), the transformation occurs from the regime II to the regime I—we observe again the turbulent patterns over the surface (Fig. 4a). When we switch over from $k_1 = 1$ to $k_1 = 0.85$, we observe again the oscillatory regime I (Fig. 4c). Fig. 12 illustrates the whole scenario of k_1 change during our simulation experiments, exemplified by CO_{ads} dynamics. First, we carried out the simulations at restricted CO_{ads} diffusion intensity ($M = 20$) with P_{O_2} (or k_1) equal to 1.0 till MCS = 26,600 (see Fig. 3 as well). Then, we began to decrease the k_1 parameter (or, the same, P_{O_2}) step-by-step manner down to the vanishing of the oscillatory regime I at $P_{O_2} = 0.71$ (MCS ∼ 40,000). The details of this action are shown in Fig. 5. The interval of simulations at $P_{O_2} = 0.85$ was from 31,500 to 32,500 MCS. The inverse step-by-step increase of P_{O_2} leads to the rise of oscillatory regime II at $P_{O_2} = 0.85$ (MCS = 43,500; Fig. 8). The characteristics of oscillations (period and amplitude) differ drastically in these two oscillatory regimes, and what is more, the spatio-temporal patterns are distinctly different (insets on Fig. 12). Whereas in oscillatory regime I, oxygen is always present on the surface in the form of small islands, spirals and stripes, oscillatory regime II characterised by alternate high and low reactive states changing due to periodic oxygen cellular patterns propagation (cf. Figs. 4c and 7). The further increase of P_{O_2} up to 0.98 (the upper bound of oscillatory regime II) is not shown on this graph. But the transition to the $P_{O_2} = 1$ both from the values 0.98 and 0.85 (Fig. 12, MCS = 64,000) leads to the oscillatory regime I. After the establishment of the regime I, we turn back to the $P_{O_2} = 0.85$ at MCS = 74,000 and observe again the spiral-like spatio-temporal structures of oxygen on the surface (the last inset on Fig. 12). That means, that at the same value of the key parameter (e.g., $k_1 = 0.85$) two different "cycles" could exist. The shape of "integral" oscillations and spatio-temporal patterns depends on the dynamic prehistory (shape–memory effect).

4. Conclusion

Thus, the hysteresis in oscillatory behaviour has been found by kinetic Monte Carlo modelling of CO oxidation reaction over Pd(1 1 0). Two different oscillatory regimes could exist at one and the same parameters of the reaction (e.g., oxygen partial pressure). The parameters of oscillations (amplitude, period and the shape of spatio-temporal patterns on the surface) depend on the kinetic prehistory of the system. The possibility for the appearance of the cellular and turbulent patterns, spiral, ring and stripe oxygen waves on the surface in the cases under study has been shown. The results obtained make possible to interpret the surface processes on the atomic scale.

Acknowledgements

The financial support of the NWO grant # 047.015.002 and RFBR grant # 02-03-32568 is highly appreciated.

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