Monte Carlo model of oscillatory CO oxidation having regard to the change of catalytic properties due to the adsorbate-induced Pt(1 0 0) structural transformation

E.I. Latkin [a], V.I. Elokhin [b],*, V.V. Gorodetskii [b]

[a] *Novosibirsk State University, 630090 Novosibirsk, Russia*
[b] *Boreskov Institute of Catalysis, pr. Lavrentieva 5, 630090 Novosibirsk, Russia*

Abstract

The statistical lattice model has been constructed for the oscillatory $(CO + O_2)/Pt(1 0 0)$ reaction. The model takes into account the change of surface properties due to the adsorbate-induced reversible surface transformation hex $\leftrightarrow$ 1×1. The Monte Carlo simulations reproduce the hysteresis and the synchronous oscillations of reaction rate, O_{ads} and CO_{ads} coverages and hex and 1×1 surface phases under the conditions close to the experimental ones. Self-oscillations of the reaction rate are accompanied by autowave processes on the model platinum surface. The existence of the reaction zone between the moving adsorbate islands has been shown. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: CO oxidation; Surface phase transformation; Oscillations; Autowaves; Monte Carlo model

1. Introduction

More and more novel experimental issues revealing the nature of self-oscillations and surface waves [1–5] attract constant interest to the study of CO oxidation over platinum metals. The current knowledge of the $CO + O_2$ reaction mechanism makes possible to state rather justified theoretical models giving insight to the features of spatio-temporal dynamics of reaction on the platinum surface. Carbon monoxide oxidation over Pt(1 0 0) single-crystal has been studied comprehensively. It was shown that under certain conditions (partial pressures of reactants and temperature) the adsorbate coverages and the reaction rate undergoes self-oscillations attended by the spatio-temporal pattern of CO_{ads} and O_{ads} formation on the surface [1–3,6]. The observed phenomena are associated with the reversible adsorbate-induced surface phase transition hex $\leftrightarrow$ 1×1. The platinum state in unreconstructed 1×1 phase is catalytically active due to the ease of oxygen molecules dissociation: $S^{1 \times 1}(O_2) \approx 0.3/0.4 \gg S^{hex}(O_2) \approx 10^{-3}$. The CO adsorption on the reconstructed hex-surface is described by the nucleation and trapping mechanism. As STM-data evidence that upon attaining some critical coverages ≈ 0.05–0.1 ml, the hex to 1×1 surface phase transition proceeds with formation of $CO_{ads}/1 \times 1$ islands [1–3]. This phase transition is accompanied by the formation of structural defects since hex phase of Pt(1 0 0) is more than 20% dense than the 1×1 phase. When the CO_{ads} coverage falls below a critical value, than the reverse surface phase transition $(1 \times 1) \rightarrow$ hex is initiated. The (1×1) phase of Pt(1 0 0) is unstable and at $T > 400$ K transforms quickly into the non-active hex phase.

In the early theoretical models of $(CO+O_2)/Pt(1 0 0)$ reaction the rate of hex $\rightarrow$ (1×1) transition was

* Corresponding author. Fax: +7-3832-343056.
E-mail address: elokhin@catalysis.nsk.su (V.I. Elokhin).

assumed to be linearly dependent on the local CO_{ads} coverage over the hex-phase (e.g. [7]). However, it has been shown recently by molecular beam studies that the (1×1)-CO island growth rate and therefore, the (1×1) phase, is governed by a strongly non-linear power law $\Theta_{1 \times 1} \sim (\Theta_{CO}^{hex})^n$, where $\Theta_{1 \times 1}$ is a part of the surface transformed into (1×1) phase, Θ_{CO}^{hex} is the CO coverage on the hex phase, and $n \approx 4$ [8]. Subsequently this was included in the new model accounting for the oscillatory behaviour of $CO + O_2/Pt(1\,0\,0)$ reaction [9].

Among a great variety of models invoked for the theoretical inquiry on the microscopic level of critical phenomena in the heterogeneously catalysed reactions [4,5] the models based on the Monte Carlo and cellular automaton approaches [10–23] are the most attractive. In particular, in [12–20] both the dynamic behaviour of the CO oxidation reaction over Pt single-crystals and the processes of structural transformation of these surfaces were studied. The most important advantages of such models are the ability to reproduce almost any information about physical and chemical processes occurring on the catalyst surface, to obtain the visual pictures of spatio-temporal non-uniformities of catalytic reactions and (the last but not the least!) rather simple algorithmic realisation of any hypothesis about the systems under consideration.
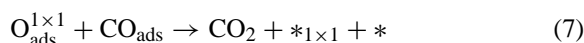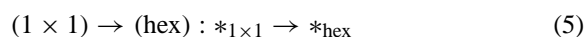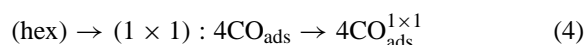
The aim of the present work is to create the statistical lattice model based on the Monte Carlo technique for describing of the self-oscillatory and autowave phenomena in the CO oxidation reaction over platinum metals. The model incorporates the modern view on the stages of reaction mechanism $(CO + O_2)/Pt(1\,0\,0)$, primarily the experimental data concerning the local change of catalytic properties under the reversible surface structure transformation hex $\leftrightarrow$ 1×1 of Pt(1 0 0) surface induced by CO adsorption.

2. The model

The catalyst surface is modelled by means of the lattice ($N \times N$ square cells) with periodic boundary conditions. Each cell corresponds to the active centre ($*$) of the platinum surface. If the centre is marked as $*_{hex}$ (or $*_{1 \times 1}$) it will be considered to belong to (hex) type structure, or (1×1), respectively. Under certain conditions, to be discussed below, the centre can change

its type. For simplicity sake the structural characteristics of the surface are assumed to be invariant and only the catalytic properties of the active centres vary. Of course, the processes of the change of active centres co-ordination and appearance of the excess atoms (structure defects) upon the surface structure transformations could be included in the surface model (e.g. similar to [15–17]). However, this may result in the model unwarranted complexity and at the same time scarcely affects the variations in spatio-temporal dynamics of the adsorbed layer (though gives a better explanation of the results obtained). The local structure (hex or 1×1) in our model could consist of a single centre; the surface coverage by the phases hex or 1×1 (Θ_{hex} and $\Theta_{1 \times 1}$) is defined as a number of centres, marked correspondingly, divided by a total number of N^2 centres. It is evident, that $\Theta_{hex} + \Theta_{1 \times 1} = 1$.

Therein lies one of the most simplifying presumptions of our model: no allowance is made for difference in atomic density between the hex and 1×1 phases, we do not take account of change in number of active centres, in number of neighbours, etc. We used the Monte Carlo algorithm that has been recently extended for the modelling of spatio-temporal dynamics of catalytic CO oxidation caused by the processes of subsurface oxygen formation and consumption [22,23]. The statistical lattice model presented is characterised by inclusion of a strongly non-linear step of hex $\rightarrow$ (1×1) phase transition. Let us describe briefly the main processes governing the dynamics of the model under consideration:

$$CO + * \rightarrow CO_{ads} \tag{1}$$

$$CO_{ads}^{hex} \rightarrow CO + *_{hex} \tag{2}$$

$$CO_{ads}^{1 \times 1} \rightarrow CO + *_{1 \times 1} \tag{3}$$

$$(hex) \rightarrow (1 \times 1) : 4CO_{ads} \rightarrow 4CO_{ads}^{1 \times 1} \tag{4}$$

$$(1 \times 1) \rightarrow (hex) : *_{1 \times 1} \rightarrow *_{hex} \tag{5}$$

$$O_2 + 2*_{(1 \times 1)} \rightarrow : 2O_{ads}^{1 \times 1} \tag{6}$$

$$O_{ads}^{1 \times 1} + CO_{ads} \rightarrow CO_2 + *_{1 \times 1} + * \tag{7}$$

$$CO_{ads} + * \rightarrow * + CO_{ads} \tag{8}$$

(1) Carbon monoxide adsorption: The absence of indices near the centre $*$ implies that CO, in contrast to oxygen, is considered to have equal sticking

probability on both $*_{hex}$ and $*_{1\times1}$. The estimation of the rate coefficient for CO adsorption ($k_1 = 2.94 \times 10^{-5}$ mL/s Torr) was adopted from ([7], Table 1). The CO partial pressures were varied around 10^{-5} Torr.

(2 & 3) Carbon monoxide desorption: The rate coefficients for CO desorption on hex and 1×1 phases differ widely (approximately by three-four orders of magnitude, e.g. [7,9]), therefore, in our simulation we accept for CO desorption the following values [7]: $k_2 = 4\,s^{-1}$, $k_3 = 0.03\,s^{-1}$.

(4) Structural phase transformation (hex) $\rightarrow$ (1×1): In accordance with [9] let us assume that the adsorption of four CO molecules on the 2×2 neighbouring centres of the lattice would transform these centres (with some probability) into the (1×1) structure. The similar procedure was used in [12] while modelling the same (CO + O_2)/Pt(1 0 0) reaction by the cellular automaton technique: if eight from the 3×3 neighbouring centres appear to be covered by CO_{ads}, then all the nine centres (with a unit probability) transforms into the state (1×1). In our case rate coefficient k_4 of structure transition from hex to (1×1) was taken approximately equal to k_5 of reverse transition from (1×1) to hex ($k_4 = 3\,s^{-1}$).

(5) Structural phase transition (1×1) $\rightarrow$ (hex): Value of k_5 at $T \sim 500\,K$ was taken from ([7], Table 1), as a $k_5 = 2\,s^{-1}$.

(6) Oxygen adsorption: Oxygen adsorbs dissociatively only on the two neighbouring (1×1) centres. Rate coefficient for O_2 adsorption k_6 is estimated from Table 1 in [7], as $k_6 = 5.6 \times 10^5$ ML/s Torr. The oxygen partial pressure is $\sim10^{-4}$ Torr. Oxygen desorption in the temperature range being of interest ($\sim500\,K$) is usually neglected; either do we.

(7) CO_2 formation: The surface reaction proceeds via the Langmuir–Hinshelwood mechanism conserving the type of the active centres. Adsorbed oxygen interacts equally with both CO_{ads}^{hex} and $CO_{ads}^{1\times1}$. In the imitation modelling of surface reactions via Monte Carlo technique the reaction AZ + BZ is usually assumed to occur with the infinite rate (e.g. [12,23,24]): i.e. when adatoms AZ and BZ appear in the neighbour lattice cells, they abandon these cells (with a unit probability) producing AB. In our model the rate of O_{ads} interaction with CO_{ads} is determined by the intensity of CO_{ads} diffusion (see below): at large $O_{ads}^{1\times1}$ coverages and sufficiently intensive CO_{ads} diffusion the reaction rate is practically "infinite", while

at small $O_{ads}^{1\times1}$ coverages the reaction rate is limited by CO_{ads} transfer to small oxygen clusters. This correlates with a hypothesis proposed in [25].

(8) CO_{ads} diffusion: Adsorbed carbon monoxide can diffuse via hopping from their sites to vacant nearest neighbour site and the type of active centres remains the same (in case of trapping and untrapping processes). Along with the stage (7) this process offers an additional source of empty active centres $*_{1\times1}$ required for dissociative oxygen adsorption.

3. The algorithm

Each centre of square ($N \times N$) lattice (in our simulations N was varied from 100 to 1000) can exist in
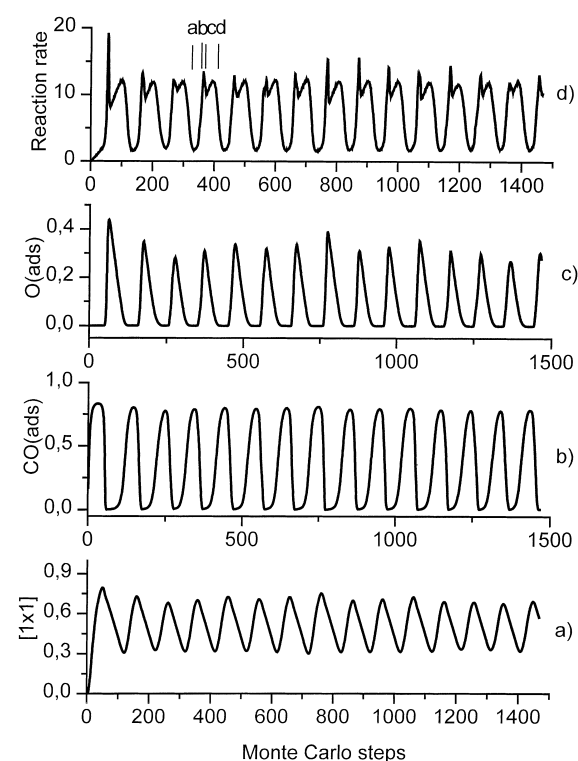

Fig. 1. Self-oscillations of the model variables at $M = 100$ and $N = 384$ (a) $\Theta_{1\times1} = \Theta_*^{1\times1} + \Theta_{CO}^{1\times1} + \Theta_O^{1\times1}$; (b) $\Theta_{CO} = \Theta_{CO}^{hex} + \Theta_{CO}^{1\times1}$; (c) $\Theta_O^{1\times1}$; (d) specific reaction rate. Parameter values: $k_1 = 2.94 \times 10^5$ ML/s Torr, $P_{CO} = 5 \times 10^{-5}$ Torr, $k_2 = 4\,s^{-1}$, $k_3 = 0.03\,s^{-1}$, $k_4 = 3\,s^{-1}$, $k_5 = 2\,s^{-1}$, $k_6 = 5.6 \times 10^5$ ML/s Torr, $P_{O_2} = 10^{-4}$ Torr.

one of five states: $*_{hex}$, CO_{ads}^{hex}, $*_{1\times1}$, $CO_{ads}^{1\times1}$ and $O_{ads}^{1\times1}$. So-called Monte Carlo step (MCS) consisting from $N \times N$ elementary action was used as a time unit, i.e. on average every MCS calls each cell at least once (except for diffusion and reaction processes, see below). In our model by elementary action it is meant a trial to change a state of the randomly chosen centre in such a manner as it was with the substances named in above mentioned processes (1)–(6). The probability of some particular process w_i is determined by a ratio between the rate coefficients for stages (1)–(6): $w_i = k_i/(k_1 + k_2 + k_3 + k_4 + k_5 + k_6)$, therewith the rate coefficients for the adsorption processes are multiplied by the relevant partial pressures. When appropriate process is chosen according to the adjusted w_i ratio then an attempt of its realisation is undertaken. Depending on the state of the randomly chosen cell (one in case of 1st, 2nd, 3rd and 5th processes; two in case of 6th; four in case of 4th) the chosen process can either occur or not. E.g., if the CO adsorption is chosen then for the success of this attempt the randomly chosen cell ($*_{hex}$ or $*_{1\times1}$) must be empty. In case of the O_2 adsorption two randomly chosen neighbouring cells must be in the $*_{1\times1}$ state. If according to the ad-

justed probability w_4 the process of (hex) $\to$ (1×1) is chosen, we randomly choose the block from four (2×2) neighbouring centres of the lattice, and if all of them are covered with CO_{ads}, then they become state $CO_{ads}^{1\times1}$ etc. Otherwise the state of the chosen cell (cells) remains unchanged. This procedure reflects indirectly the dependence of the stage rates on the surface coverages by adsorbed substances and, in our case, on the surface coverages by the different surface phases.

Monte Carlo technique does not permit now to model too intensive adsorbate diffusion on the surface due to huge consumption of computer time. However, diffusion is necessary for the spatio-temporal processes synchronisation occurring on the different regions of the model surface. In our model after each of $N \times N$ trial to carry out one of the processes (1)–(6) the inner cycle of CO_{ads} diffusion is arranged. The cycle consists of M attempts of random choice of two neighbour lattice cells (in our computations M was varied from 20 to 100). If such pair is $\{CO_{ads}, *\}$, then CO_{ads} and $*$ interchange their position, i.e. diffusion happens (stage 8). For all other pairs except for $\{CO_{ads}, O_{ads}^{1\times1}\}$, an attempt of diffusion is
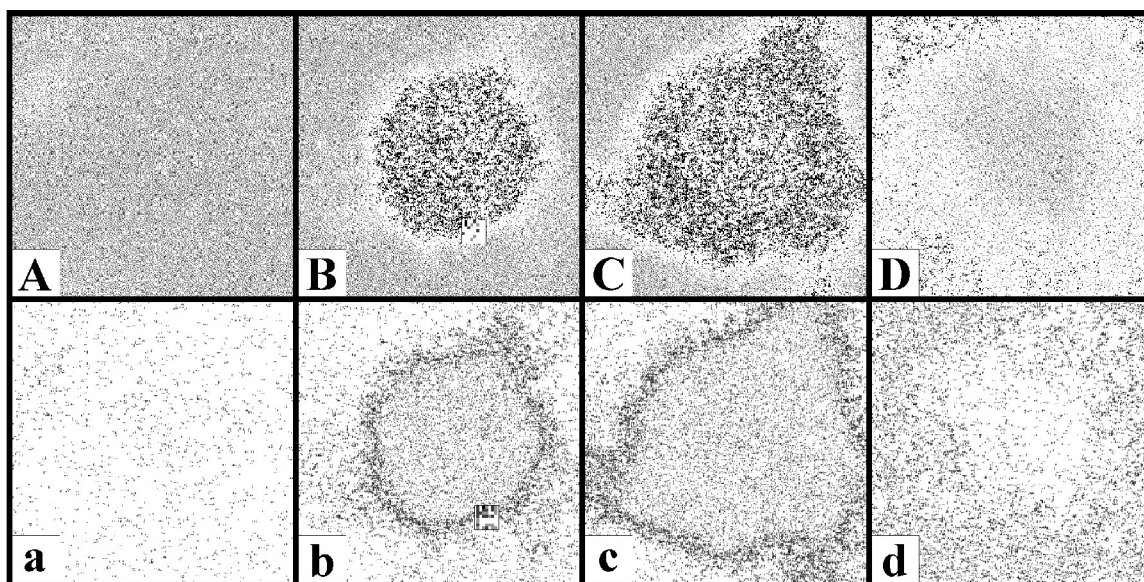

Fig. 2. Snapshots reflecting the adsorbate distribution over the surface (capital letters) and the appropriate CO_2 formation rate intensity (small letters). On the A–D snapshots O_{ads} is painted black, CO_{ads} as grey, empty Pt sites as white. On the a–d snapshots a grey scale reflects the rate intensity. Snapshots A,a–D,d correspond to 332, 360, 364, and 408 MCS (vertical bars on the Fig. 1d).

rejected. If the pair is $\{CO_{ads}, O_{ads}^{1\times1}\}$, reaction (stage 7) occurs with releasing of active sites and forming of CO_2 (reaction rate counter increased therewith by a unit). The type of active sites remains the same. Thus, the rate of $CO_{ads} + O_{ads}$ interaction is determined by a number of diffusion trials (i.e. by M parameter). Realisation of the 7th stage indirectly assumes that for the interaction of surface species the diffusion of mobile CO_{ads} is required to overcome the potential barrier, in such a manner that CO_{ads} faced with O_{ads}.

4. Results and discussions

The synchronous variations of the reaction rate, O_{ads} and CO_{ads} coverages and hex and 1×1 surface phases exhibited within the above-mentioned range of the suggested model parameters. The wave processes on the surface attend these oscillations. These processes are shown in Figs. 1 and 2 ($N = 384$, $M = 100$, other parameters are given in Figure captions). We start with the clean surface Pt(1 0 0)-hex, Fig. 1a,b (i.e. only CO adsorption is permitted). Despite of the small value of the rate coefficient for the reconstruction process (stage 4) (hex) $\rightarrow$ (1 × 1) the surface portion in state 1×1 ($\Theta_{1\times1} = \Theta_*^{1\times1} + \Theta_{CO}^{1\times1} + \Theta_O^{1\times1}$) grows rather quickly (Fig. 1a). The centres suitable for O_2 adsorption are produced as a result of CO_{ads} diffusion, but the $O_{ads}^{1\times1}$ coverage is negligibly low due to very fast reaction with neighbouring CO_{ads} (compare Fig. 1a,b,c). When the Co_{ads} coverage attains its maximum ($\Theta \approx 0.8$), the adsorbed layer is composed from CO_{ads}^{hex} and $CO_{ads}^{1\times1}$ (Fig. 2A). This adlayer composition corresponds to the minimum of the reaction rate (Fig. 1d) calculated as a number of the formed CO_2 molecules per one MCS divided by N^2 (i.e. specific reaction rate per one active centre). Moreover, we calculated the distribution of local intensity of CO_2 formation. Fig. 2a shows that the intensity of CO_2 formation in the CO_{ads} layer is low, but it increases over the zones with elevated concentration of free active centres (Fig. 2A). These are just the zones where the $O_{ads}^{1\times1}$ islands are generated and then propagated over the surface as a wave with a sharp boundary (Fig. 2B,C and b,c). Fig. 2b,c show that the highest intensity of CO_2 formation is related to a narrow zone between the growing O_{ads} island and surrounding CO_{ads} layer ("reaction zone"). Inside oxygen island the intensity of

CO_2 formation is intermediate. The peak of the integral reaction rate corresponds to the maximal perimeter of the oxygen island (Fig. 2c). The final phase of the oscillation cycle is an increase of the CO_{ads} coverage on the free centres $*_{hex}$ and $*_{1\times1}$, in the same time the latter undergoes the reverse transformation into $*_{hex}$ (Fig. 2D,d). Due to sufficiently high rates of CO_{ads} diffusion and $O_{ads} + CO_{ads}$ reaction ($M = 100$) the oscillations are characterised by nearly constant amplitude and period. The shape of oscillations also remains almost unchanged, though the active zones with elevated concentration of free active centres appear every time on new regions of the model lattice.

The competition of the mechanisms of O_2 and CO adsorption in combination with the processes of the surface structure transition hex $\rightarrow 1 \times 1$ is a driving force for self-oscillations. At a proper choice of model parameters k_i on the surface regions with elevated concentration of the active centres $*_{1\times1}$ the oxygen
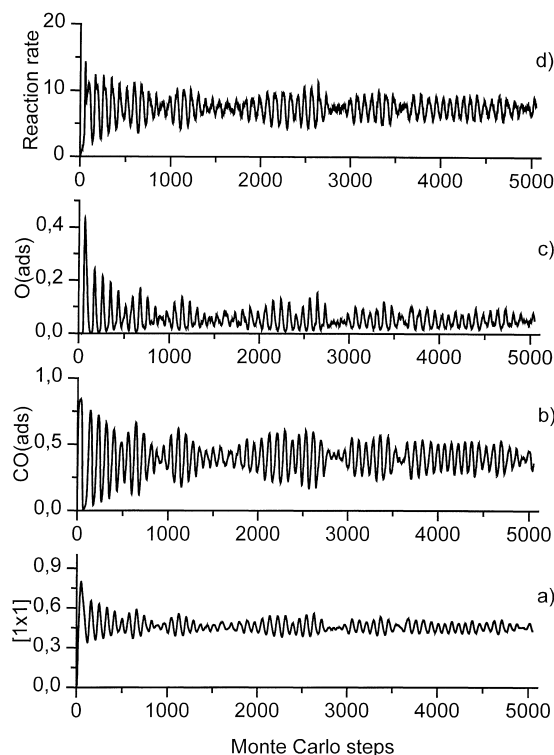

Fig. 3. Self-oscillations of the model variables at $M = 30$ and $N = 384$ (a) $\Theta_{1\times1} = \Theta_*^{1\times1} + \Theta_{CO}^{1\times1} + \Theta_O^{1\times1}$; (b) $\Theta_{CO} = \Theta_{CO}^{hex} + \Theta_{CO}^{1\times1}$; $\Theta_O^{1\times1}$; (d) specific reaction rate. The parameter values are the same as for Fig. 1.

adsorption dominates, needed two neighbouring free centres $*_{1 \times 1}$. Carbon monoxide adsorption prevails in zones with low local concentration of the active centres. CO_{ads} diffusion and surface reaction represented by M parameter synchronise the situation on different local regions of the surface thus governing the oscillation regularity. The increase of the rate coefficient for structural phase transformation (hex) $\rightarrow$ (1×1) up to 10^4 (close to the value recommended in [26]) leads to the disappearing of the wave phenomena on the sur-

face, however, the reaction rate and surface coverage's continue to oscillate.

The lowering of M parameter down to 50 does not influence the regularity and uniformity of the oscillations but results in some decrease of period and amplitude. The further lowering of M down to 30 leads to the non-regularity (chaotisation) of the period and amplitude of oscillations and even to intermittence phenomena (Fig. 3). The concentration of the 1×1 phase at $M = 30$ is varied within 0.1 ML range. In this case
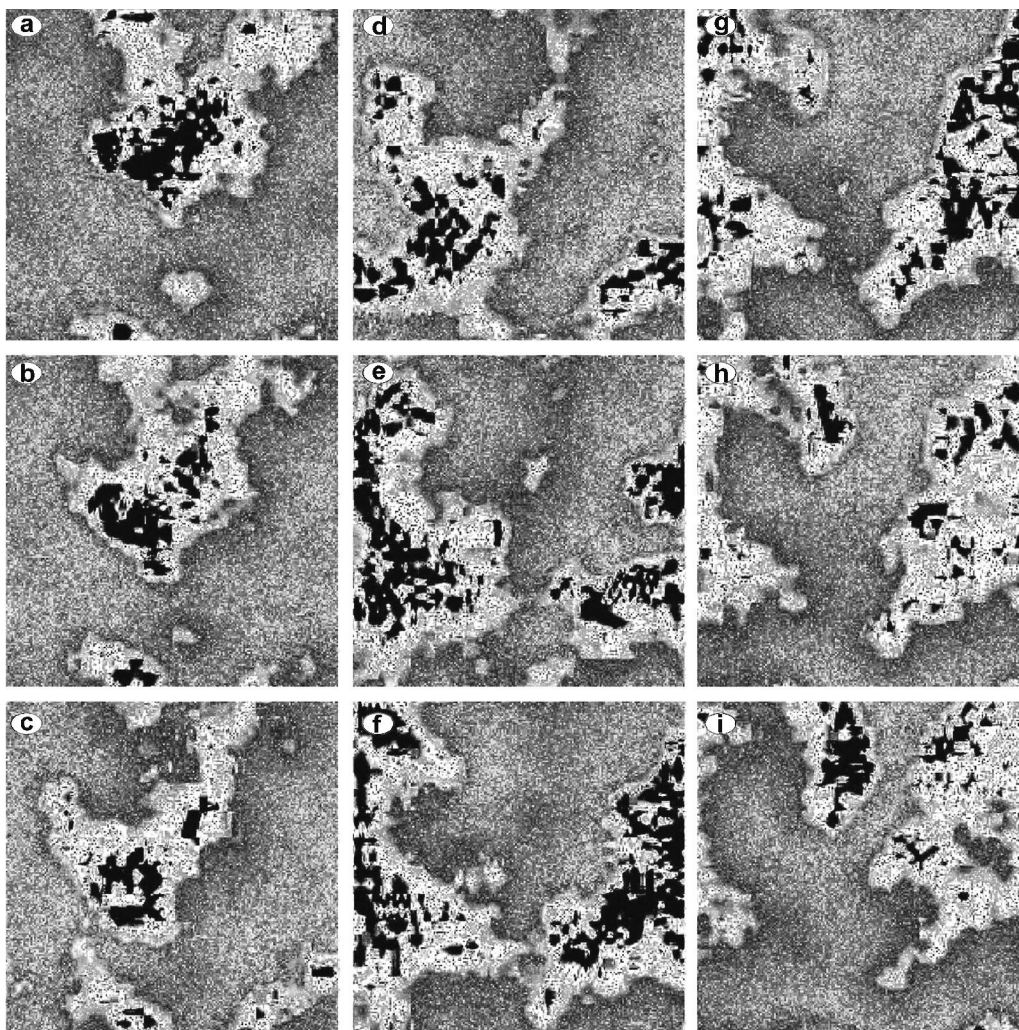

Fig. 4. Snapshots reflecting the adsorbate distribution over the surface in the case of low diffusion intensity (Fig. 3). On the snapshots O_{ads} is painted black, CO_{ads} as grey, empty Pt sites as white.

the adsorbed oxygen is always present on the surface in a shape of moving spots (cellular structure, fragments of spirals, strips, etc.), Fig. 4. Similar turbulent spatio-temporal behaviour of adsorbate coverages in the CO+O_2/Pt(1 0 0) reaction has been experimentally observed by Rotermund (PEEM) [27] and Lauterbach et al. (EMSI) [28]: the structures with a higher symmetry, i.e. spirals, appears only for short periods of time.

Let us consider the fine structure of the above mentioned reaction zone (Fig. 5, an enlarged inset of Fig. 2B). The presence of the narrow reaction zone with atomic resolution has been found experimentally (field ion probe-hole microscopy technique with 5 Å resolution) by Gorodetskii et al. [29]. In the left upper corner of the Fig. 4 an edge of the oxygen island with free active centres $*_{hex}$ and $*_{1 \times 1}$ inside them has been shown. The greatest concentration of the empty Pt centres is observed in the narrow zone between O_{ads} and CO_{ads} layers. Due to rapid O_2 adsorption and subsequent fast reaction with neighbouring CO_{ads} the formation of CO_2 molecules proceeds most intensively in this reaction zone.

The Monte Carlo technique permit us to study the dependencies of oscillation features versus reaction
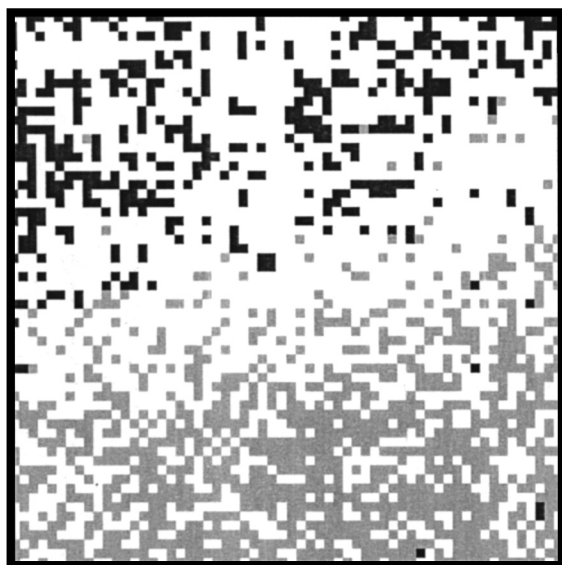

Fig. 5. Fine structure of the reaction zone (an enlarged inset from Fig. 2B). Black cells — $O_{ads}^{1 \times 1}$; grey cells — CO_{ads}; white cells — empty Pt centres.

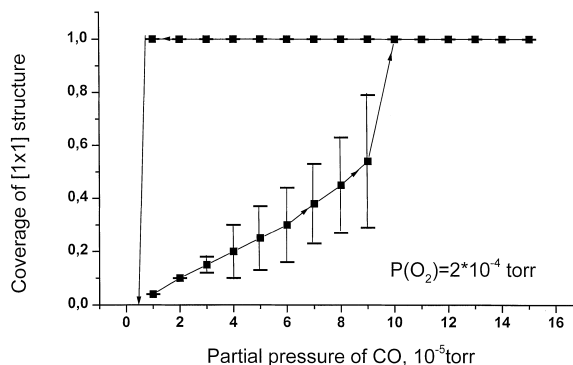Fig. 6. Hysteresis of $\Theta_{1 \times 1}$ vs. P_{CO} (step-by-step changing), $P_{O_2} = 2 \times 10^{-4}$ Torr, vertical bars show the amplitude of oscillations.

parameters (e.g. CO partial pressure) by changing the parameter step-by-step and using the surface configuration after the previous simulation run as an initial for the next one. Fig. 6 shows the hysteresis in $\Theta_{1 \times 1} = \Theta_*^{1 \times 1} + \Theta_{CO}^{1 \times 1} + \Theta_O^{1 \times 1}$ by consecutive increasing and lowering P_{CO}. At very high ratio P_{O_2}/P_{CO} the surface Pt(1 0 0)-hex is practically empty. The increasing of P_{CO} leads to the appearance of (1×1) surface structure covered by CO_{ads} and at $P_{CO} = 3 \times 10^{-5}$ Torr the oscillations of reaction rate and surface coverages arises following the aforementioned scenario. The amplitude and the period of oscillations grows with increasing of P_{CO}. Then at $P_{CO} = 10^{-4}$ Torr the surface is saturated by $CO_{ads}^{1 \times 1}$. Due to very low probability of desorption this state of the Pt(1 0 0) surface preserves up to very low P_{CO}. The CO desorption rate constant k_3 determines the lower boundary of hysteresis. Back structural phase transition $(1 \times 1) \rightarrow$ (hex) proceed though the rapid clean-off reaction (steps 7 and 5).

5. Conclusions

The statistical lattice model was constructed for the $(CO + O_2)$/Pt(1 0 0) reaction which takes into account the change of surface properties due to the adsorbate-induced reversible surface transformation hex $\rightarrow$ 1×1. The model reproduces qualitatively the hysteresis and the synchronous variations of reaction rate, O_{ads} and CO_{ads} coverages, hex and 1×1 surface phases under the conditions close to the experimental ones ($P_{O_2} \cong 10^{-4}$ Torr, $P_{CO} \cong$

10^{-5} Torr, $T \approx 500$ K). Autowave processes accompany self-oscillations of the reaction rate. The existence of a reaction zone between the moving adsorbate islands has been shown. The results obtained make possible to interpret the surface processes on the atomic scale. The computer movies illustrating the spatio-temporal dynamics of the adsorbed layer distribution and the local intensity of the reaction rate at different rates of reaction and CO_{ads} diffusion are available at http://catalysis.nsk.su/~latkin/.

References

[1] R. Imbihl, Progr. Surf. Sci. 44 (1993) 185.
[2] G. Ertl, Adv. Catal. 37 (1990) 213.
[3] G. Ertl, Surf. Sci. 299/300 (1994) 742.
[4] F. Schüth, B.E. Henry, L.D. Schmidt, Adv. Catal. 39 (1993) 51.
[5] M.M. Slin'ko, N.L Jaeger, Stud. Surf. Sci. and Catalysis, Vol. 86, Oscillating Heterogeneous Catalytic Systems, Elsevier, Amsterdam e.a., 1994.
[6] G. Ertl, P.R. Norton, J. Rustig, Phys. Rev. Lett. 49 (1982) 177.
[7] R. Imbihl, M.P. Cox, G. Ertl, H. Müller, W. Brenig, J. Chem. Phys. 83 (1985) 1578.
[8] A. Hopkinson, X.C. Guo, J.M. Bradley, D.A. King, J. Chem. Phys. 99 (1993) 8862.
[9] M. Gruyters, T. Ali, D.A. King, J. Phys. Chem. 100 (1996) 14417.
[10] V.P. Zhdanov, B. Kasemo, Surf. Sci. Rep. 20 (1994) 111.
[11] R. Kapral, J. Math. Chem. 6 (1991) 113.
[12] P. Möller, K. Wetzl, M. Eiswirth, G. Ertl, J. Chem. Phys. 85 (1986) 5328.
[13] R.J. Schwankner, M. Eiswirth, P. Möller, K. Wetzl, G. Ertl, J. Chem. Phys. 87 (1987) 742.
[14] M. Eiswirth, P. Möller, K. Wetzl, R. Imbihl, G. Ertl, J. Chem. Phys. 90 (1989) 510.
[15] A.E. Reynolds, D. Kaletta, G. Ertl, R.J. Behm, Surf. Sci. 218 (1989) 452.
[16] R. Imbihl, A.E. Reynolds, D. Kaletta, Phys. Rev. Lett. 67 (1991) 275.
[17] R. Imbihl, J. Falta, D. Kaletta, M. Henzler, J. Vac. Sci. Technol. A 9 (1991) 1749.
[18] X.-G. Wu, R. Kapral, Physica A 188 (1992) 284.
[19] H. Rose', H. Hempel, L. Schimansky-Geier, Physica A 206 (1994) 421.
[20] R.J. Gelten, A.P.J. Jansen, R.A. van Santen, J.J. Lukkien, J.P.L. Segners, P.A.J. Hilbers, J. Chem. Phys. 108 (1998) 5921.
[21] L.V. Lutsevich, O.A. Tkachenko, J. Catal. 136 (1992) 309.
[22] A.L. Vishnevskii, E.I. Latkin, V.I. Elokhin, Surf. Rev. Lett. 2 (1995) 459.
[23] V.I. Elokhin, E.I. Latkin, Dokl. Acad. Nauk (Russia) 344 (1995) 56.
[24] R.M. Ziff, E. Gulari, Y. Barshad, Phys. Rev. Lett. 56 (1986) 2553.
[25] X. Xu, D.W. Goodman, J. Phys. Chem. 97 (1993) 7711.
[26] A. Hopkinson, D.A. King, Chem. Phys. 177 (1993) 433.
[27] H.H. Rotermund, Physica Scripta 49 (1993) 549.
[28] J. Lauterbach, G. Bonilla, T.D. Pletcher, Chem. Eng. Sci. 54 (1999) 4501.
[29] V. Gorodetskii, W. Drachsel, J.H. Block, in: Proceedings of the 11th International Congress on Catalysis, June 30–July 5, 1996, Baltimore, Maryland, USA, Posters, Catalyst Characterization, p. 138.