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Spiral concentration waves in the Monte Carlo model of CO oxidation over Pd(1 1 0) caused by synchronisation via CO_{ads} diffusion between separate parts of catalytic surface

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Abstract

The role of adsorbed CO diffusion as a synchronisation factor between the separate oscillating surfaces in CO oxidation reaction has been examined by means of Monte Carlo model. As a result of the chosen simulation strategy the spiral waves of adsorbed species on the palladium surface (imagined as a set of independent Pd(1 1 0) planes) have been observed. The dependence of the results on the details of the simulation experiment as well as on the size of the lattice representing the catalytic surface has been studied.

Keywords: CO oxidation; Palladium; Oscillations; Surface waves; Monte Carlo model; Synchronisation

1. Introduction

The mechanism of local oscillator synchronisation is one of the fundamental problems arising when studying the oscillatory behaviour of heterogeneous catalytic reaction [1]. The isothermal kinetic oscillations in different oxidation reactions are observed as a rule [1,2] on the supported metals and on metal tips considered as a superposition of the interrelated single crystal nanoplanes. The following factors should play the dominant role in synchronising a catalytic system consisting of separate oscillators with different properties, especially in the case of high pressure experiments: (i) the global coupling through the gas phase, or/and (ii) in the case of the support with high thermal conductivity, the coupling via heat transfer [3, and references therein]. In the case of single crystals and metal tips studies under UHV conditions the surface diffusion of the adsorbed species can be responsible in general for the synchronisation of local oscillators. Furthermore, according to Boudart [4] considering the kinetic features of CO oxidation reaction over Pd/Al_2O_3 it is necessary to take into account the contribution of CO_{ads} diffusion over the support onto the active metal particles surface (spillover). In our contribution we shall consider the possible consequences of the several catalytic surface sections coupling (in our case that is the surface of the palladium tip with four Pd(1 1 0) faces) exhibiting the surface wave behaviour with some time shift in the period of oscillations. The analysis would be provided by means of statistical lattice modelling by the example of the CO oxidation reaction over Pd(1 1 0).

2. Reaction mechanism and the corresponding Monte Carlo model

The following reaction mechanism based on our FEM data was used in simulation [5]:

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

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

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

$$O_{ads} + *_v \rightarrow [O_{ss}] \quad (4)$$

$$CO_{ads} + [O_{ss}] \rightarrow CO_{2(gas)} + 2 * + *_v \quad (5)$$

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

$$[CO_{ads}O_{ss}] \rightarrow CO_{2(gas)} + * + *_v \quad (7)$$

Here $*$ 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 (*cork-screw* reaction [5]). The adsorbed CO_{ads} can diffuse over the whole surface

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according to the following rules: (i) $CO_{ads} + * \leftrightarrow * + CO_{ads}$, (ii) $CO_{ads} + [O_{ss}] \leftrightarrow * + [CO_{ads}O_{ss}]$, (iii) $[CO_{ads}O_{ss}] + [O_{ss}] \leftrightarrow [O_{ss}] + [CO_{ads}O_{ss}]$. We suppose that the heat of CO adsorption on the *oxidised* centres $[O_{ss}]$ is less than that on the initial $[*]$ one, i.e. the probability of $[CO_{ads}O_{ss}]$ desorption (step 6) is greater than that of CO_{ads} (step 2) one. The parameters of the elementary steps were partly taken from the literature. The oscillatory behaviour was observed in simulation [5] in the neighbourhood 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. The rate coefficients for O_2 and CO adsorption (k_1, k_2, and k_6) can be treated as the product of the impingement rate ($k_i^0 P_i$) and of the sticking coefficient (S_i).

In this model the oscillations and surface waves of the adsorbed species are determined by purely kinetic reasons and not associated with the trigger switching of catalytic and adsorption properties in the course of the reaction. The $[O_{ss}]$ density in the adsorbed layer controls the reaction behaviour due to the change of O_2 or CO priority during the competition of their adsorption. CO_{ads} diffusion over the centres $*$ and $[O_{ss}]$ is very important for the synchronisation between local parts of the surface, but according to Elokhin and Latkin [6] at that surface diffusion of the adsorbed species is not necessary for the appearance of self-oscillations and of spatial–temporal behaviour in the model. The slow steps of formation (step 4) and especially consumption of subsurface oxygen (steps 5 and 7 restoring the centres for O_2 dissociative adsorption) play the decisive role in the appearance of oscillatory dynamics. Both the surface waves of the adsorbed species and the presence of the narrow reaction zone between the moving islands of adsorbates were observed by simulation of this model dynamics [5]. Let us briefly describe the details of the simulation algorithm. The simulation has been performed on the lattice with a size of $N \times N$ square cells with *zero* boundary conditions (see below). Each lattice cell can exist in one of the five states: $*$, CO_{ads}, O_{ads}, $[O_{ss}]$, $[CO_{ads}O_{ss}]$ according to the proposed detailed mechanism. For steps 1, 2, −2, 4, 5, 6, −6, and 7, the values of k_i were specified as a set of numbers, which can be considered as the rate constants of these elementary steps taking into account the partial pressures of O_2 (step 1) and CO (steps 2 and 6) (see the above table). The values of k_i were recalculated into the probabilities of the realisation of elementary processes w_i by the formula: $w_i = k_i \sum k_i$. Using a generator of random numbers uniformly distributed over the (0, 1) interval, we chose one of these processes according to the specified ratio of their occurrence (comb of probabilities). Using pairs of random numbers, the coordinates of one cell (or of two adjacent cells in the case of two-site processes—O_2 adsorption, reaction, or CO_{ads} diffusion in the inner cycle, see below) were determined from $N \times N$ cells of lattice. The states of the cells are determined according to the rules prescribed by the detailed reaction mechanism. Let us illustrate the realisation of the chosen process on the example of oxygen adsorption (step 1). If two randomly chosen adjacent cells are both in the state $*$, then the adsorption proceeds and the cells assume the state O_{ads}. If the required pair is not found out, the attempt is rejected. After every choice of one of the above-named processes and attempt to perform this process, the inner cycle of CO_{ads} diffusion was processed, which included *M* attempts of random choice of a pair of adjacent cells of the lattice. If the $\{CO_{ads}, *\}$, $\{CO_{ads}, [O_{ss}]\}$, $\{*, [CO_{ads}O_{ss}]\}$, $\{[CO_{ads}O_{ss}], [O_{ss}]\}$ pairs turned out to be these pairs, the states in these cells were interchanged according to rules (i)–(iii), i.e. diffusion took place. Otherwise, the attempt of diffusion was rejected. We suppose that reaction (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 (3). 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 zero boundary conditions are defined on the lattice. It means that if one of the two-site processes (reaction steps 3 and 5, oxygen adsorption or CO_{ads} diffusion) happens to occur from both sides of the boundary—this attempt should be rejected.

The so-called MC-step consisting of $N \times N$ attempts of choice and realisation of *main* elementary processes {1 and 2, 4–7} is used as a time unit in the Monte Carlo models. During the MCS, each cell is tested on the average once. The reaction rate (and surface coverages) was calculated after each MCS as a number of CO_2 molecules formed (or the number of cells in the corresponding state for the surface coverages) divided by the total value of the lattice cells, N^2. The following simulation experiment has been carried out to prove the possible consequences of the synchronisation between several catalytic surface parts coupled with CO_{ads} diffusion as it has been experimentally found on the Pt-tip surface [7]. The whole model surface (768 × 768 or 1536 × 1536 active centres) was divided into four square parts that initially are *opaque* to surface diffusion: northwest (1), northeast (2), southeast (3), and southwest (4). Contrary to Latkin et al. [5] the lattice has no periodic boundary conditions, therefore it can serve as a model for a palladium surface with four separate Pd(1 1 0) faces connected with CO_{ads} diffusion. Let us first suppose that the separate parts are perfectly isolated from each other and the boundaries between them apparently act as strong barriers for CO_{ads} diffusion (zero boundary conditions between the sections). Let us also imagine that the oscillations on these faces start with the time shift equal to ∼1/4 of the period. At the chosen set

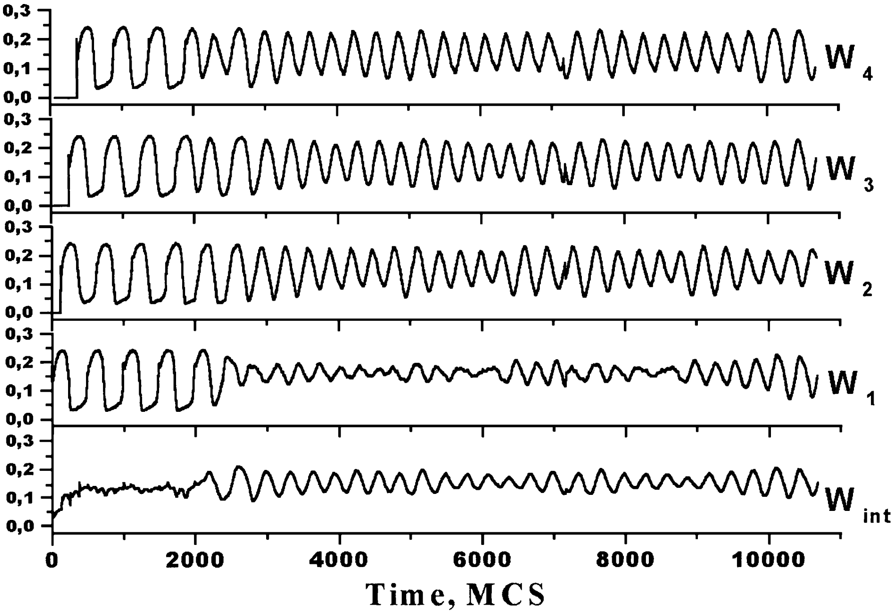


Fig. 1. Dynamics of the specific rate of CO_2 formation on the separate sections of the surface (W_1–W_4) and on the whole surface (W_{int}) at k_i from the table given in Section 2.

of the parameters (see the table) the oscillation period has the value ~500 Monte Carlo steps [5] and so the reaction in section 1 starts at 0 MCS, in section 2 at 125 MCS, in section 3 at 250 MCS, and in section 4 at 375 MCS (Fig. 1). Then the reaction oscillates separately over the time of 2000 MCS (Figs. 1–3). In the course of this time interval the autowave processes in sections 1–4 were observed to have a shape of propagating oxygen islands (high reaction rate) changed by the CO_{ads} coverage blocking the surface (low reaction rate). The overall reaction rate on the whole surface W_{int} in this time interval remains approximately constant (Fig. 1). But after the 2000 MCS we eliminated the borders between the sections and made it *transparent* for the CO_{ads} diffusion. In all simulation experiments the parameter of the diffusion cycle was equal to 50 and the size of the model lattice was 768 × 768 (except for the final simulation experiments where $N = 1536$). Let us recall that the surface coverage and the reaction rate

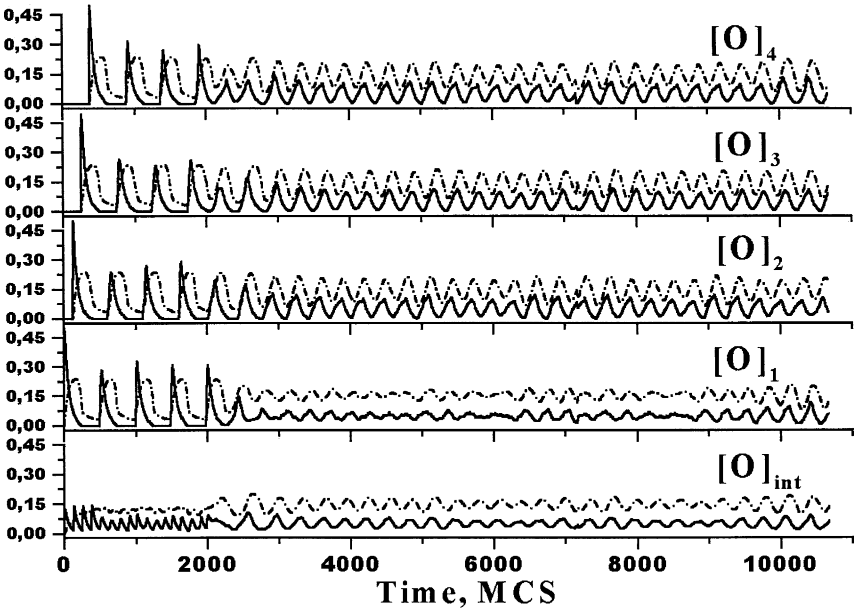


Fig. 2. Dynamics of O_{ads} (solid lines) and $[O_{ss}]$ (dash-dotted lines) on the separate sections of the surface (O_1–O_4) and on the whole surface (O_{int}).

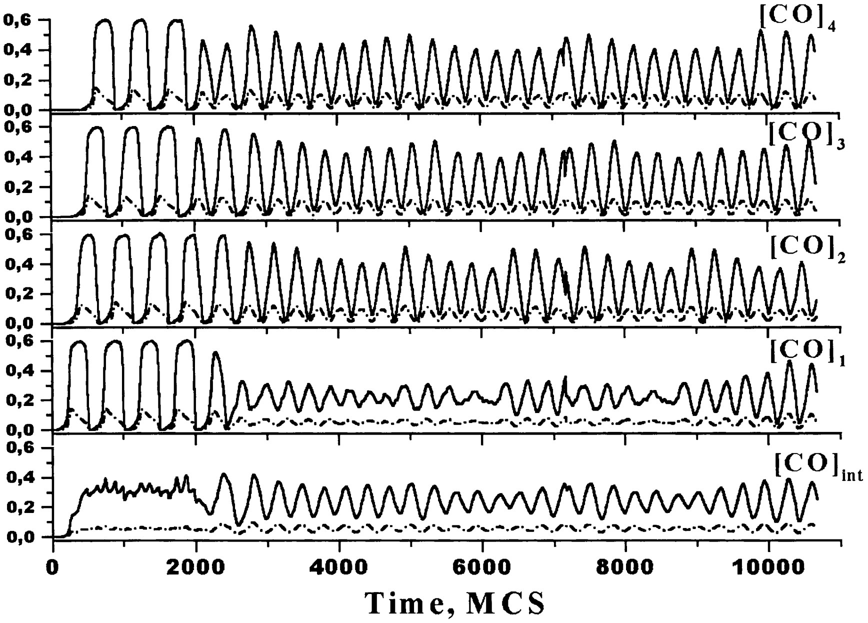


Fig. 3. Dynamics of CO_{ads} (solid lines) and $[CO_{ads}O_{ss}]$ (dash-dotted lines) on the separate sections of the surface (CO_1–CO_4) and on the whole surface (CO_{int}).

were calculated after each MCS for each section as a number of adsorbed species and of CO_2 formation events divided on the area of the section ($N^2/4$). If we calculate the integral parameters for the whole lattice ($[O_{int}]$, $[CO_{int}]$ and W_{int}) then we shall divide the corresponding values on the whole lattice area (N^2).

3. Results and discussion

The synchronisation leads, first, to the decreasing of the period of oscillations by 1.5–2 times (Figs. 1–3), and second, to the appearance of counterclockwise spiral waves over the whole surface (Figs. 4 and 5). It should be noted that the

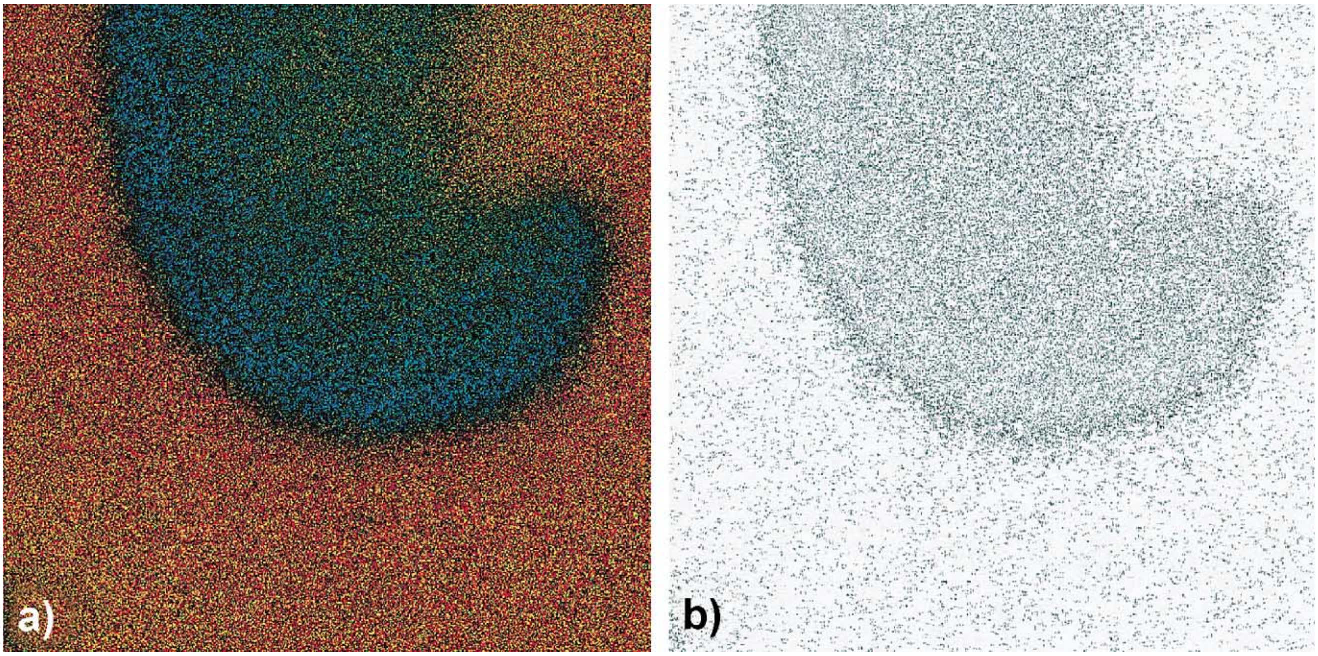


Fig. 4. Snapshots reflecting the spiral waves propagation at 3200 MCS. (a) The adsorbate distribution over the surface: O_{ads} is painted blue, $[O_{ss}]$ as green, CO_{ads} as red, $[CO_{ads}O_{ss}]$ as yellow, empty Pd sites as black. (b) The CO_2 formation rate intensity is reflected by the greyscale.

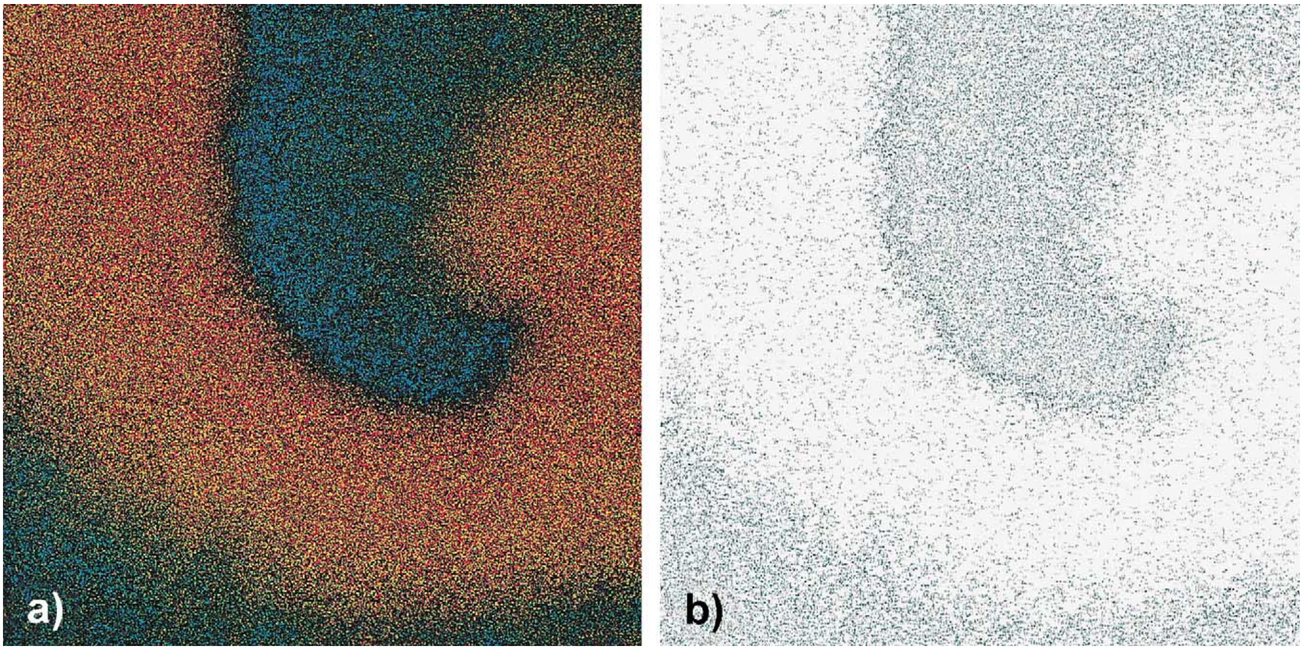


Fig. 5. Snapshots reflecting the spiral waves propagation at 9600 MCS. The designations are the same as for Fig. 4.

shape of oscillations both in coverage (Figs. 2 and 3) and reaction rate (Fig. 1) changes from the relaxation-type (first 2000 MCS in Figs. 1–3) to the saw-toothed curves. It should be emphasised that the appearance of the spiral waves is exclusively the consequence of our simulation strategy described above. If from the very beginning we had started the simulation on the whole surface without boundaries between different parts, we should have obtained the synchronous oscillations with the same period ∼500 MCS accompanied with autowave processes over the whole surface (propagating O_{ads} islands altering by CO_{ads} blocking). The spiral motion arises in our model from the time shift in the period between different parts of oscillating catalytic surface when to the moment of the communication via CO_{ads} diffusion the neighbouring sections have different compositions of the adsorbed layer. The colliding oxygen islands propagating from one section to another form the spiral waves on the surface. Fig. 6 illustrates the initial stages of the spiral wave formation (2000, 2020, 2040 and 2050 MCS). By the time of elimination of the borders between the sections (2000 MCS) in section 1 the very beginning of the oxygen wave propagation can be seen; section 2 is fully covered by CO_{ads}; in section 3 the process of the subsurface oxygen consumption comes to the end; section 4 is predominantly covered by O_{ss}. Then the oxygen island propagates into section 2 (2020, 2040 and 2050 MCS) and CO_{ads} from section 3 starts to react with O_{ss} in section 4, forming correspondingly the head and tail of the oxygen spiral wave.

The shape of the spiral waves obtained in the above described simulations is represented in Figs. 4 and 5. The local distributions of the adsorbed particles (a) and intensity of CO_2 formation (b) are depicted in these figures (the rate intensity is reflected by the greyscale). There is a strong correlation between (a) and (b) pictures. The CO_2 formation rate is minimal within the CO_{ads} adlayer, it is intermediate within O_{ads} adlayer, and the maximal intensity of CO_2 production exists right in the *reaction zone*—at the boundary of the propagating oxygen adlayer where the local concentration of the free active centres is maximal. The reaction zone was found experimentally (field ion probe-hole microscopy technique with 5 Å resolution) in [7]. The direction of the oxygen adlayer propagation over the surface is clearly seen from Figs. 4a and 5a. Oxygen *win* in the adsorption competition with CO over the reaction zone and the oxygen adlayer front move towards the CO adlayer. Right after the O_{ads} adlayer the $[O_{ss}]$ layer is formed occupying approximately 2/3 of oxygen spiral width. The $[CO_{ads}O_{ss}]$ concentration is low (Figs. 3–5), therefore the primary consumption of $[O_{ss}]$ proceeds due to reaction step 5, but not due to step 7.

The simulated spiral waves are qualitatively close to the experimentally founded wave propagation over the separated (1 0 0) Pt planes in the course of the CO oxidation reaction [8] (unfortunately, we do not have the experimental information about Pd-catalysed CO oxidation over the Pd tips). Fig. 7 reproduces the various stages of CO oxidation reaction oscillating over the (1 0 0)-oriented Pt-tip—a pre-adsorbed oxygen layer reacted with CO in an unexpected consecutive way. Separate regions showed a *switch-on* reaction when O_{ads} was reacting with CO_{ads}. The initial reaction was

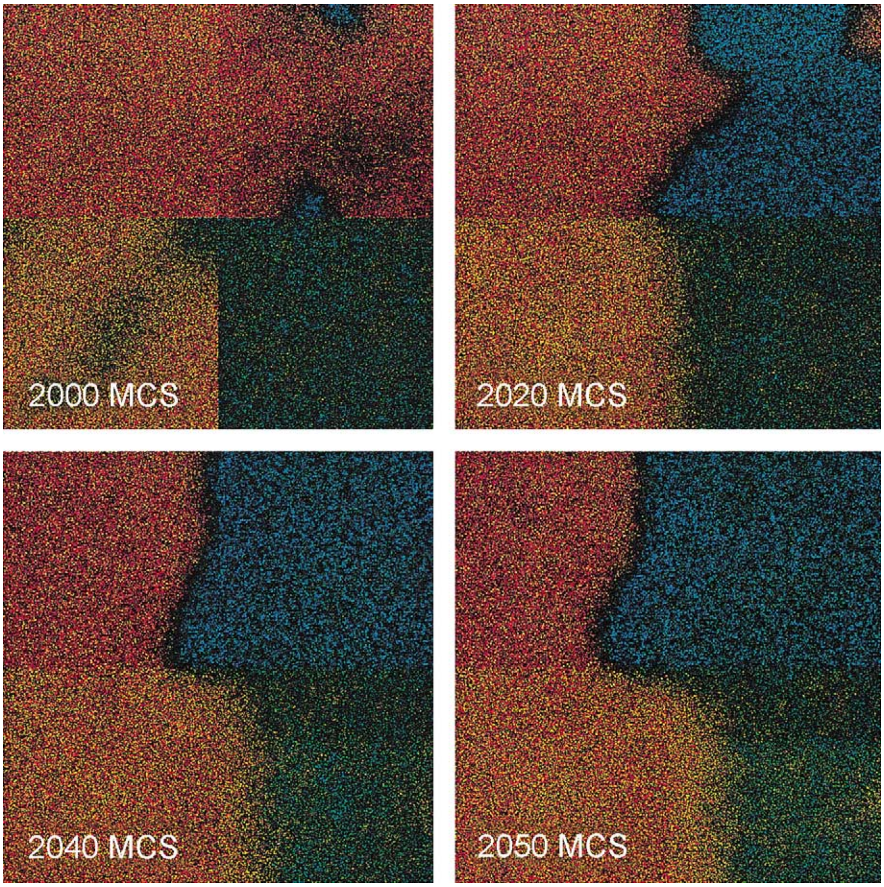
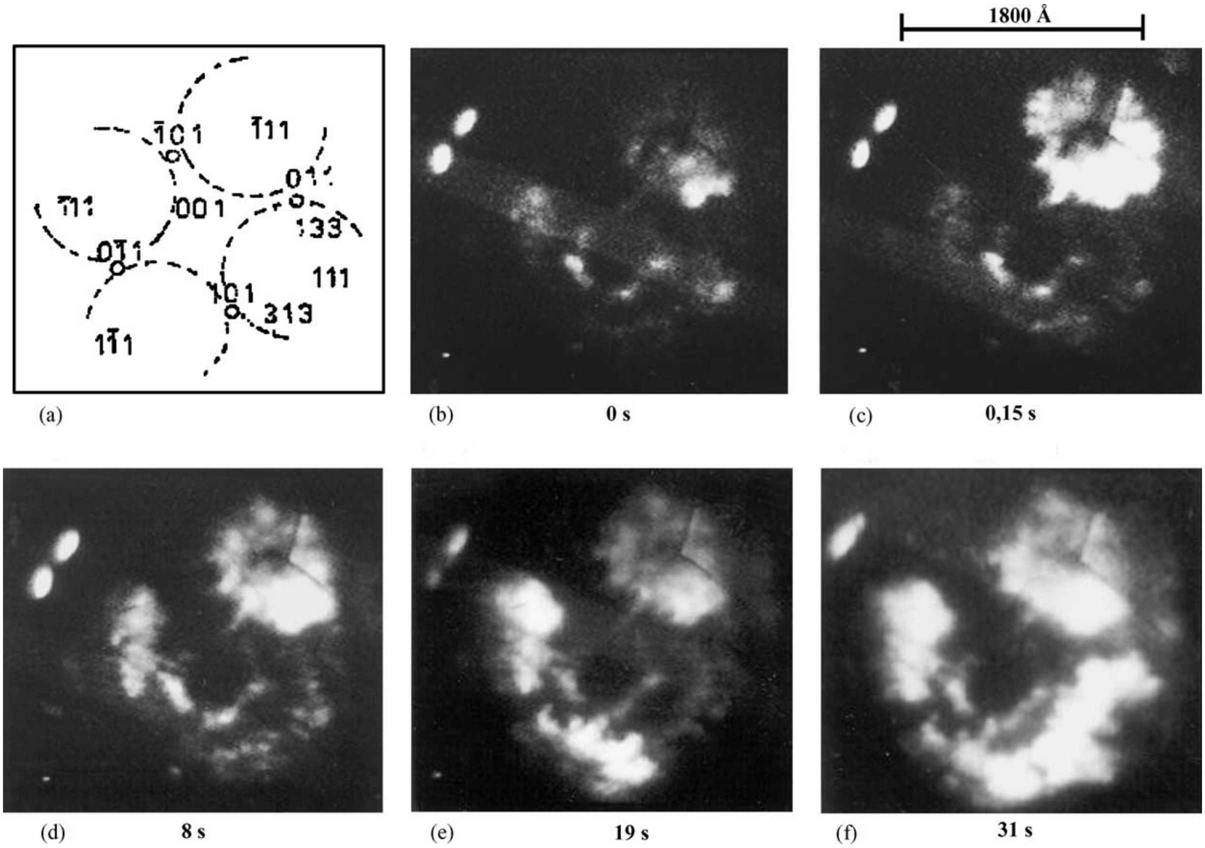


Fig. 6. Snapshots showing the initial stages of the spiral wave formation.



(a)

(b) 0 s

(c) 0,15 s

(d) 8 s

(e) 19 s

(f) 31 s

Fig. 7. FEM images at various stages of the oscillating CO oxidation over the (1 0 0)-oriented Pt-tip [8]; $P(O_2) = 10^{-4}$ mbar, $P(CO) = 10^{-5}$ mbar: (a) stereographic projection and (b)–(f) formation of large CO_{ads} islands (bright regions), switch-on reaction.

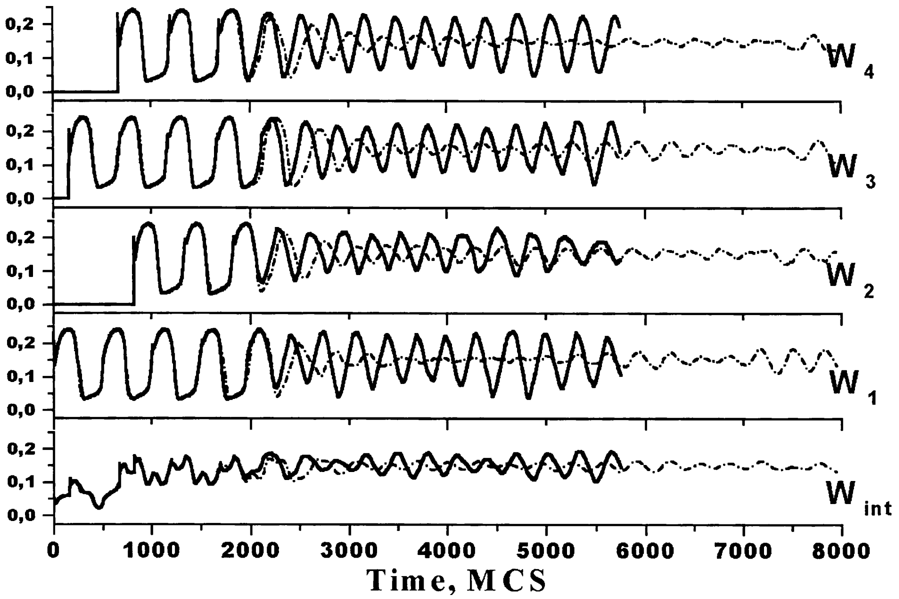


Fig. 8. Dynamics of the specific rate of CO_2 formation on the separate sections of the surface (W_1–W_4) and on the whole surface (W_{int}) at the random choice of the beginning of the reaction on the random chosen sections. The size of the lattice is 768 × 768 (solid line) and 1536 × 1536 (dash-dotted line).

observed around the (1 1 1) plane, where in Fig. 7b, a bright emitting domain of CO_{ads} island is formed. This domain expands suddenly, starting at the (0 1 1) region, and proceeds towards the direction of (0 0 1) and (1 1 1) planes. In a counterclockwise motion the different planes were switched-on (Fig. 7c–e) and the emission pattern of Fig. 7f showed that the CO_{ads} layer was completed. As it was stated in [9], the reaction started randomly only at one of the (0 1 1) plane. The further population of (0 1 1) planes with oxygen in a counterclockwise sequence seems to be governed by mass transportation at the surface. Namely, a slow diffusion of CO_{ads} towards the freshly formed rather immobile O_{ads} layer determines the reaction sequence of the (0 1 1) planes in experiments.

To prove the phenomena of spiral wave appearance from the simulation strategy the following experiment has been carried out. In the chosen section the moment of the oscillations onset has been randomly chosen. Namely, the reaction in section 1 starts at 0 MCS, in section 2 at 863 MCS, in section 3 at 161 MCS, and in section 4 at 670 MCS.

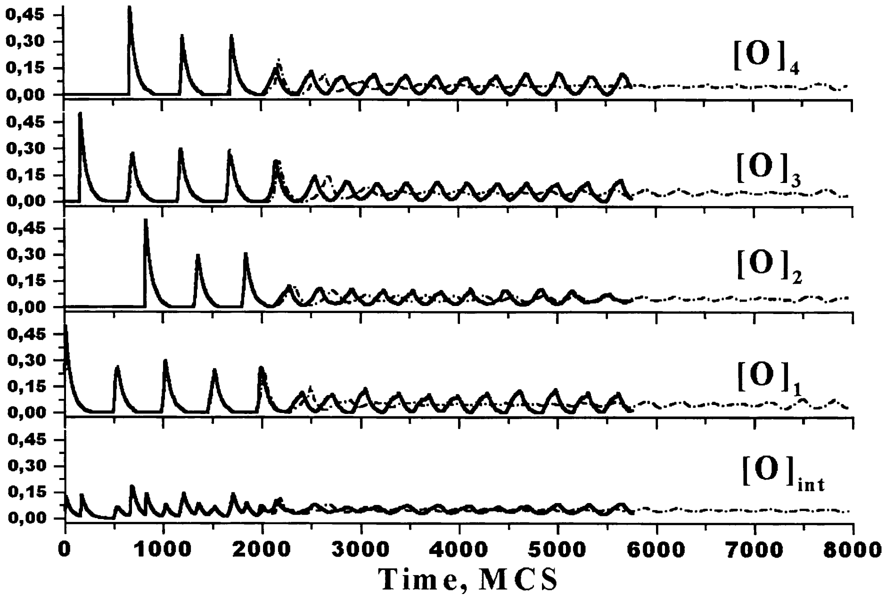


Fig. 9. Dynamics of O_{ads} oscillations on the separate sections of the surface (O_1–O_4) and on the whole surface (O_{int}) at the random choice of the beginning of the reaction on the random chosen sections. The size of the lattice is 768 × 768 (solid line) and 1536 × 1536 (dash-dotted line).

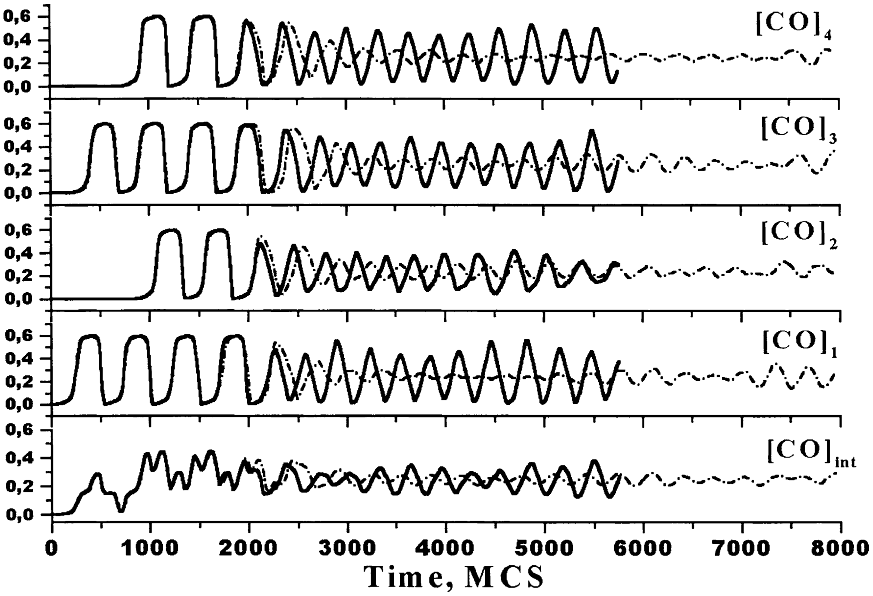


Fig. 10. Dynamics of CO_{ads} oscillations on the separate sections of the surface (CO_1–CO_4) and on the whole surface (CO_{int}) at the random choice of the beginning of the reaction on the random chosen sections. The size of the lattice is 768 × 768 (solid line) and 1536 × 1536 (dash-dotted line).

It can be distinctly seen in Figs. 8–10. After 2000 MCS the borders between the sections were eliminated and CO_{ads} diffusion began to join the differing adlayer compositions in the sections. As in the previous case, the spiral wave appears, but now in the clockwise direction. To prove the dependence of the reaction performance on the size of the lattice used we have enlarged it twice and repeated the previous simulation experiment. It is interesting to note that the kinetic curves obtained on the *large* (1536 × 1536) and the *small* (768 × 768) lattices coincide entirely up to the moment of the borders removal (2000 MCS). Then the amplitudes of the coverage and reaction rate oscillations corresponding to the large lattice (dash-dotted curves) become substantially smaller. However, on the whole surface the well pronounced spiral wave is observed (Fig. 11). Of course, we understand that this behaviour is stimulated by our simulation strategy.

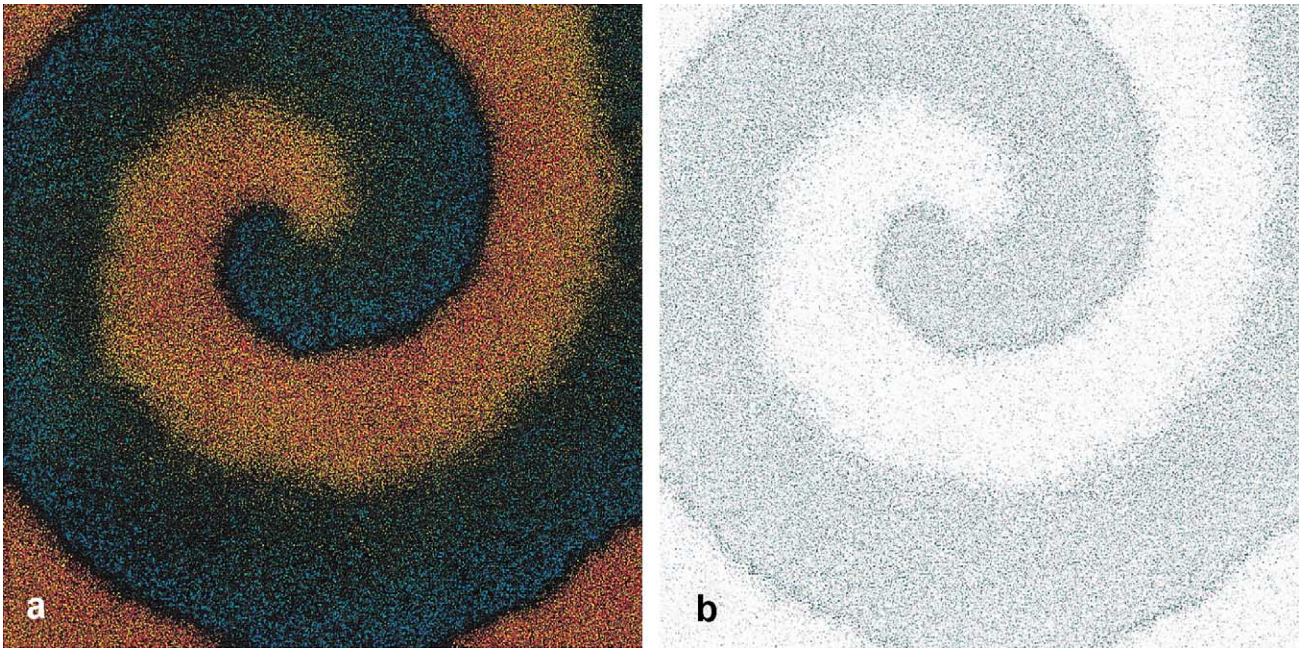


Fig. 11. Snapshots reflecting the spiral waves propagation at 4000 MCS. (a) The adsorbate distribution over the surface: O_{ads} is painted blue, $[O_{ss}]$ as green, CO_{ads} as red, $[CO_{ads}O_{ss}]$ as yellow, empty Pd sites as black. (b) The CO_2 formation rate intensity is reflected by the greyscale. The size of the lattice is 1536 × 1536.

4. Conclusion

In this work, a comparison of non-linear phenomena in CO oxidation on a flat Pd(1 1 0) and several independent parts of Pd(1 1 0) surface coupled by CO_{ads} diffusion has been presented in an attempt to bridge the gap between single crystals and randomly distributed metal particles on supported catalysts. It has been demonstrated that chemical spiral waves can be initiated in the catalytic CO oxidation over separate oscillating surfaces if the reaction conditions are held such that CO_{ads} diffusion exists on the whole surface. The theoretical modelling demonstrates the occurrence of a rich scenario of spatiotemporal patterns (islands, rotating spirals) with a spatially resolved of thin wave front structures during the reaction. The modelling and design of catalytic reactors are generally based on the assumption that the surface concentrations are spatially uniform. The present results show that the activity of catalyst exhibiting spatiotemporal patterns differs from those having a uniform concentration. Consequently, it is necessary to get a better understanding of the reaction conditions under which the spatial patterns can exist on the surface.

Acknowledgements

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