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Oscillatory Dynamics of CO Oxidation on Platinum-Group Metal Catalysts

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Abstract—Rate oscillations are theoretically studied for the CO + O_2 reaction proceeding according to a modified Langmuir–Hinshelwood mechanism on a platinum-group metal catalyst. A new hierarchical system of consistent mathematical models is suggested for the identification of oscillatory regimes in the stochastic model. This system includes the stochastic model based on the Monte Carlo method and a point deterministic model in the medium field approximation. Three fundamentally different types of oscillatory behavior of the stochastic model are revealed and studied. These are kinetic oscillations corresponding to autooscillations of the point model, fluctuation-induced oscillations occurring in an excitable medium in the region of the unique stable stationary solution of the point model, and fluctuation-induced random phase transitions between stable stationary solutions of the point model in the bistability region. The effect of internal fluctuations (which are inherent in stochastic models) on the oscillatory dynamics of the reaction is studied.

Rate autooscillations in a heterogeneous catalytic reaction were first observed more than 30 years ago [1–3]. Some 60 heterogeneous systems showing an oscillatory behavior on catalysts with various structures in a wide pressure range (from ultrahigh vacuum to atmospheric pressure) are presently known. In these systems, periodic variations of reaction rate may take place at constant values of external control parameters (the temperature and partial pressures of gas-phase components) and be accompanied by spatial self-organization phenomena such as the adsorption-induced reconstruction of the catalyst surface and chemical waves.

One of the most extensively studied heterogeneous catalytic reactions exhibiting oscillatory dynamics is CO oxidation on platinum catalysts. Depending on the catalyst type and experimental conditions, the oscillation of the CO + O_2 reaction rate may be due to slow reversible poisoning of the active catalyst surface [4–12], adsorption-induced surface reconstruction, microfaceting [13–16], or other phenomena.

Various mathematical models are used in detailed analyses of the mechanism of the rate oscillations in catalytic CO oxidation. They are generally based on the a set of nonlinear ordinary differential equations (ODEs) [12, 17–27]. These deterministic models are called point models. They provide a theoretical description for experimentally observed stationary states, hysteresis, and reaction rate oscillations. However, point deterministic models have found only limited application and can be used in reaction dynamics analysis only in a rather narrow range of external controls. Furthermore, they are inapplicable to the evolution of heterogeneous catalytic systems with significant internal fluctuations. These systems include, for example, reactions on a needle point, on active nanoclusters incorporated in a porous support, and on supported catalysts.

Microscopic stochastic models using the Monte Carlo method [22, 26–33] are the most promising for theoretical investigation of the dynamics of fluctuating reaction systems. These stochastic models are based on detailed information concerning the elementary steps of the reaction, the structure of the catalyst surface, and the mobility of species in the adsorption layer. In a stochastic model, it is possible to correctly take into account the internal fluctuations, spatial correlations in the adsorption layer, and other factors that cannot be investigated using point models. The key problem in stochastic modeling is to preliminarily determine the domains of existence of qualitatively different solutions in the space of external controls. For this purpose, the bifurcation analysis of stationary and periodic solutions using numerical parameter continuation methods is carried out in ODE sets. The mathematical apparatus of the qualitative analysis of stochastic models has not been properly advanced as yet, even though the first steps towards that end were promising [34, 35].

Therefore, the theoretical investigation and explanation of complex dynamic phenomena on a catalyst surface in the framework of one class of models cannot be comprehensive. It is necessary to develop systems of consistent mathematical models describing the evolution of reaction systems on different spatial scales. This would allow the advantages of different classes of mathematical models to be combined.

Here, this approach is applied to oscillatory regimes of CO oxidation over platinum-group metal catalysts. Different oxygen species were detected in experiments

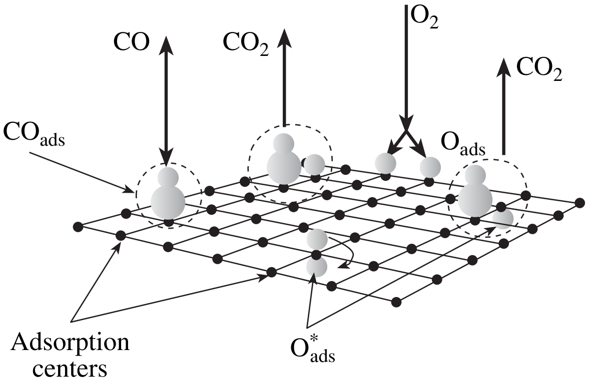

Fig. 1. Schematic representation of the lattice gas model as applied to CO oxidation by the TSM mechanism.

on CO oxidation over palladium [4–6], platinum [7], rhodium [8], and ruthenium [9], including oxygen adsorbed on the catalytic surface, subsurface oxygen, and oxygen in the catalyst bulk. In such heterogeneous systems, oscillations of the CO oxidation rate can arise from the slow reversible oxidation of the catalyst surface (the TSM mechanism) [10–12]. Chemisorbed oxygen can penetrate under the surface to form an oxide. The oxidized surface has a low catalytic activity. The surface is reduced through a reaction between metal oxide and adsorbed CO. Note that the TSM mechanism is a particular case of a feedback based on a hypothetical inert substance (buffer) that is slowly and reversibly adsorbed onto the active surface, thus oxidizing this surface [17–19].

Here, we suggest a new system of consistent mathematical models for investigation of the oscillatory dynamics of the TSM mechanism of the CO + O_2 reaction on platinum group metals. This system includes a microscopic stochastic model involving a Monte Carlo dynamic algorithm [36] and a point deterministic model as an ODE set obtained in the ideal adsorption layer approximation [37, 38]. Although both models are based on the same kinetic network for CO oxidation by a modified Langmuir–Hinshelwood mechanism [10–12], they may lead to qualitatively different results. While the stochastic model allows for oscillatory reaction regimes in a wide range of CO pressures, the deterministic model may predict a single stationary state or a multiplicity of stationary states and, accordingly, a hysteresis at the same parameter values. The difference between the models arises from the specific features of processes at the atomic level, namely, spontaneous fluctuations and spatial correlations in the adsorption layer, which are taken into account by the stochastic model.

We distinguish and analyze three types of oscillatory behavior of the reaction system within the stochastic model.

The first type is to denote kinetic oscillations existing in the region of autooscillations in the point model.

The second type is to denote fluctuation-induced oscillations in the region of existence of the single stable stationary solution of the ODE set. A necessary condition for the onset of oscillations in the stochastic model is that the point model has excitable dynamics, which arise from a special spatial configuration of isoclines.

The third type of oscillatory dynamics is fluctuation-induced transitions from one stationary state of the point model to another in a bistable medium.

Here, we thoroughly investigate the mechanism of realization of each type of oscillatory behavior of the reaction system, as well as the role of internal fluctuations and of the migration of adsorbed species. For this purpose, we perform a qualitative analysis of the point model, process time series calculated using the stochastic and deterministic models, and construct energy spectra and correlation functions.

MATHEMATICAL MODELS

Kinetic Network

The dynamics of catalytic CO oxidation in the framework of the TSM kinetic network will be described using the multicomponent two-dimensional lattice gas model. As a rule, the reversible formation of a surface oxide is considered in terms of two active-site sublattices exchanging oxygen atoms, one on the surface and the other in the subsurface layer. However, under the assumption that the arrangement of adsorption sites on the surface is identical to the arrangement of vacant sites in the subsurface layer and that oxide oxygen completely disables all of the nearest adsorption sites on the surface, it is possible to consider a single adsorption-site lattice [28, 29]. In this case, any lattice site may be free (*) or occupied by an adsorbed carbon monoxide molecule CO_{ads}, an adsorbed oxygen atom O_{ads}, or an adsorbed oxide oxygen atom O^*_{ads}.

The surface and the subsurface layer of the catalyst will be modeled as a single regular two-dimensional lattice of energetically equivalent adsorption sites with a square unit cell (Fig. 1).

The TSM kinetic network includes the Langmuir–Hinshelwood mechanism,

$$CO_{gas} + (*) \longleftrightarrow CO_{ads}, \qquad (I)$$

$$O_{2,\,gas} + 2(*) \longrightarrow 2O_{ads}, \qquad (II)$$

$$CO_{ads} + O_{ads} \longrightarrow CO_2\uparrow + 2(*) \qquad (III)$$

and the formation and removal of surface oxide,

$$O_{ads} \longrightarrow O^*_{ads}, \qquad (IV)$$

$$O^*_{ads} + CO_{ads} \longrightarrow CO_2\uparrow + 2(*). \qquad (V)$$

Furthermore, we consider the migration of adsorbed species via a vacant-site mechanism:

$$CO_{ads} + (*) \longleftrightarrow (*) + CO_{ads}, \qquad (VI)$$

$$O_{ads} + (*) \longleftrightarrow (*) + O_{ads}, \qquad (VII)$$

$$O^*_{ads} + (*) \longleftrightarrow (*) + O^*_{ads}. \qquad (VIII)$$

Here, $(CO)_{gas}$ and $(O_2)_{gas}$ are molecules in the gas phase. Two-site processes occur on adjacent lattice sites. The rate of a two-site process is defined for a pair of sites, and the rate of a one-site process is defined for one site. The surface oxide formation step (IV) is viewed as a one-site process, and step (V) is a two-site process. It is assumed that oxide oxygen retains its reactivity (see step (V)) and markedly decreases the activity of the catalyst in reactant adsorption from the gas phase.

Basic Kinetic Equation

We will consider a terminal lattice fragment containing $N \times N$ sites and impose periodic boundary conditions. The evolution of fragment state probabilities in the Markovian approximation is described by the basic kinetic equation

$$\mathrm{d}P_{\vec{S}}/\mathrm{d}t = \sum_{\vec{S}'}[P_{\vec{S}'}\lambda(\vec{S}' \longrightarrow \vec{S}) - P_{\vec{S}}\lambda(\vec{S} \to \vec{S}')] \quad (1)$$

subject to the initial condition $P_{\vec{S}}(t^0) = P^0_{\vec{S}}$. Here, t (s) is time, s; $\vec{S}$ is the state of the fragment at the time point t defined by the occupancies s_i of all active sites of the fragment, $i = 1, \ldots, N^2$, $s_i \in \Psi = \{(*), \mathrm{CO_{ads}}, \mathrm{O_{ads}}, \mathrm{O^*_{ads}}\}$; $P_{\vec{S}}(t)$ is the absolute probability of the state $\vec{S}$ at the time point t; and $\lambda(\vec{S}' \longrightarrow \vec{S}, t)$ (s^{-1}) is the rate of transition from the state $\vec{S}'$ to the state $\vec{S}$ at the time point t. The rate of transition is determined by the rates of possible surface processes bringing the fragment from one state to another and depends on the current state of the lattice fragment.

Stochastic and Deterministic Models

Since the basic kinetic equation is a multidimensional system even for a small lattice, it will be solved by approximate methods. In Monte Carlo stochastic modeling, state trajectories are constructed for the reaction system in the state space. Stochastic models describe the evolution of a selected lattice fragment at the atomic level. Here, we use a dynamic Monte Carlo algorithm with a variable time step [36].

Our deterministic description is based on the ideal adsorption layer model. According to the above kinetic network, the variation of $\mathrm{CO_{ads}}$, $\mathrm{O_{ads}}$, and $\mathrm{O^*_{ads}}$ concentrations is described by a set of three ODEs derived from Eq. (1) under the assumption that surface processes are equiprobable on each lattice site:

$$\left\{\begin{aligned}
&\frac{\mathrm{d}\theta_{CO}}{\mathrm{d}t} = k_1(1 - \theta_{CO} - \theta_O - \theta_{O*}) \\
&- k_{-1}\theta_{CO} - 4k_3\theta_{CO}\theta_O - 4k_5\theta_{CO}\theta_{O*} \\
&\frac{\mathrm{d}\theta_O}{\mathrm{d}t} = 4k_2(1 - \theta_{CO} - \theta_O - \theta_{O*})^2 - 4k_3\theta_{CO}\theta_O - k_4\theta_O \\
&\frac{\mathrm{d}\theta_{O*}}{\mathrm{d}t} = k_4\theta_O - 4k_5\theta_{CO}\theta_{O*}
\end{aligned}\right. \quad (2)$$

with the initial conditions

$$\theta_{CO}(t_0) = \theta^0_{CO}, \quad \theta_O(t_0) = \theta^0_O, \quad \theta_{O*}(t_0) = \theta^0_{O*}. \quad (3)$$

Here, $\theta_{CO}(t)$, $\theta_O(t)$, and $\theta_{O*}(t)$ are the concentrations of adsorbed CO molecules and O atoms and oxide oxygen, respectively, and $k_1, k_{-1}, k_2, \ldots, k_8$ are the rate constants of elementary steps. The normalization conditions are as follows: $0 \le \theta_{CO} \le 1$, $0 \le \theta_O \le 1$, $0 \le \theta_{O*} \le 1$, and $0 \le \theta_{CO} + \theta_O + \theta_{O*} \le 1$.

The point deterministic model (2) describes the variation of average parameters of the reaction system. At the same time, it allows a rigorous microscopic interpretation and its solutions can be approximated with any degree of accuracy by solutions of the corresponding stochastic model on condition that the state of the adsorption layer is nearly ideal. A good quantitative agreement between the models can be achieved, for example, by applying the Monte Carlo modeling method to a highly mobile adsorption layer on a sufficiently large lattice.

Note that the ODE set (2) and the model presented in [12] contain different expressions for the rate of surface oxide formation (step (IV)).

RESULTS OF MATHEMATICAL MODELING

Theoretical study of the oscillatory dynamics of CO oxidation at the atomic level in the framework of the kinetic network (I)–(VIII) has been performed for more than 10 years. Researchers' primary concern has been the search for the regions of reaction rate oscillations in the parameter space. The purpose of this work is to clear up the fundamental questions related to the nature of the mechanisms of the oscillatory behavior of the reaction within stochastic models on small lattices and to the qualitative changes in the behavior of the reaction system that will be brought about by increasing the lattice size.

These questions were answered by the construction and qualitative analysis of consistent mathematical models describing the dynamics of the reaction on various space scales. The most detailed descriptions are provided by Monte Carlo methods. However, using stochastic modeling, it is difficult to predict the behavior of the system and to offer a substantiated explanation for observed phenomena, because no mathematical apparatus has been developed for the a priori qualitative

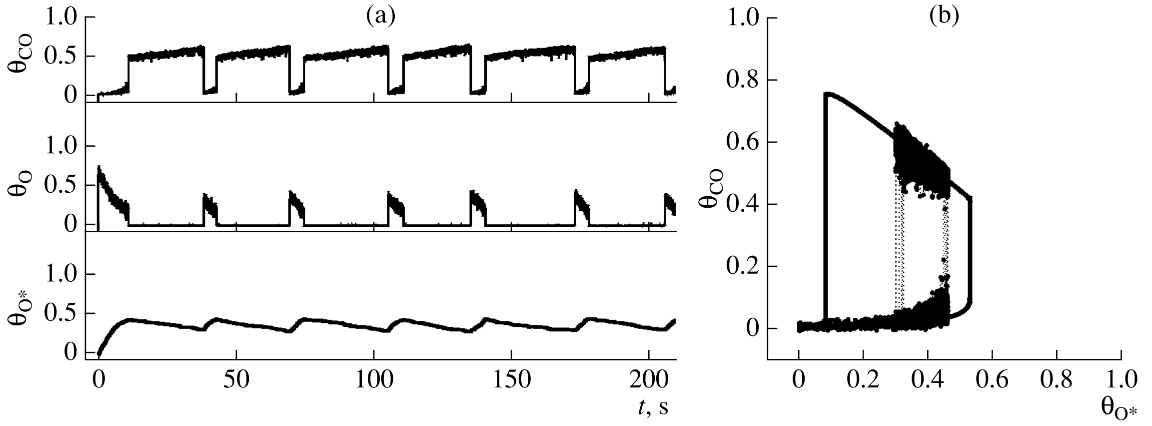

Fig. 2. Kinetic oscillations. $P_{CO} = 0.3$ Torr. (a) $\theta_{CO}(t)$, $\theta_O(t)$, and $\theta_{O^*}(t)$ curves obtained by the Monte Carlo method ($h = 10^5$ s^{-1}; 20×20 lattice). (b) Comparison of the results of stochastic and deterministic modeling. The solid line is the projection of the limit cycle of the ODE set (2) on the phase plane (θ_{O^*}, θ_{CO}). Data obtained by the Monte Carlo method are shown as dots and are connected with dotted lines.

analysis of stochastic models. For solving these problems, we suggest a consistent deterministic model represented as an ODE set of low dimensionality and propose analyzing this system using the well-developed theory of ODEs.

This approach allows the oscillatory behavior patterns of CO oxidation within the stochastic model to be classified. We distinguish and investigate autooscillations, fluctuation-induced oscillations, and fluctuation-induced random reversible transitions between the high- and low-reactivity states.

Autooscillations

One of the most adequate models for the $CO + O_2$ reaction accompanied by the formation of a surface oxide is the ODE set in CO_{ads}, O_{ads}, and O^*_{ads} concentrations reported in [12]. This model satisfactorily reproduces the basic qualitative features of CO oxidation on the surface of a polycrystalline platinum wire.

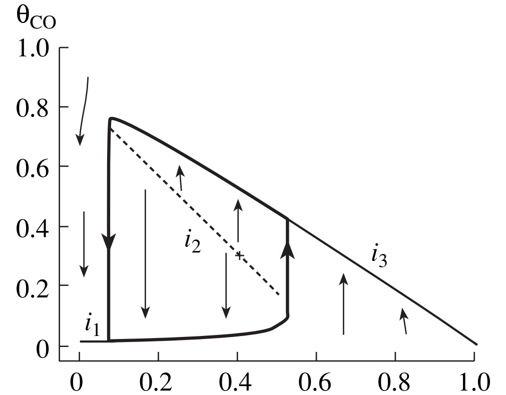

Fig. 3. Projections of the isoclines of the variables θ_{CO} and θ_O and of the limit cycle of the ODE set (2) on the phase plane (θ_{O^*}, θ_{CO}) at $P_{CO} = 0.3$ Torr. The thin solid lines are the attractive isocline branches i_1 and i_3, the dashed line is the repulsive isocline branch i_2, and + is the unstable stationary point. The arrows show the directions of trajectories.

We will use the following similar values of the rate constants of the elementary steps at $T = 550$ K: $k_1 = \bar{k}_1 P_{CO} = 3 \times 10^3$ s^{-1}, $k_{-1} = 3 \times 10^2$ s^{-1}, $k_2 = 2.5 \times 10^3$ s^{-1}, $k_3 = 2.5 \times 10^4$ s^{-1}, $k_4 = 0.11$ s^{-1}, and $k_5 = 6.5 \times 10^{-3}$ s^{-1}. Let us set $\bar{k}_1 = 10^4$ s^{-1} Torr^{-1} [12].

The results of the Monte Carlo modeling of the dynamics of the $CO + O_2$ reaction on a 20×20 lattice at a high mobility of adsorbed species ($h = k_6 = k_7 = k_8 = 10^5$ s^{-1}) are presented in Fig. 2. The state trajectories of the reaction system are oscillations with a nearly constant amplitude and a variable period. The solution of the ODE set (2) at the same values of model parameters is a limit cycle describing the kinetic oscillations (Fig. 2b).

The projections of the limit cycle and of the principal isoclines of the point model on the phase plane (θ_{O^*}, θ_{CO}) at $P_{CO} = 0.3$ Torr are shown in Fig. 3. The isoclines intersect at the unstable stationary point. The arrangement of the isocline curves is typical of relaxation oscillations in a system with a small parameter. Here, this parameter is the reciprocal reaction rate in the adsorption layer. Since this small parameter is implicitly involved in the first two equations of the ODE set (2), θ_{CO} and θ_O are rapid variables and θ_{O^*} is a slow variable. The oscillation period is primarily determined by the time over which the reaction system moves along the principal isoclines of the first two equations. The movement of the system along the attractive branches of the isoclines i_1 and i_3 (solid lines) means a comparatively rapid oxidation and a slow reduction of the catalytic surface. The transitions from one attractive branch to another are almost instantaneous.

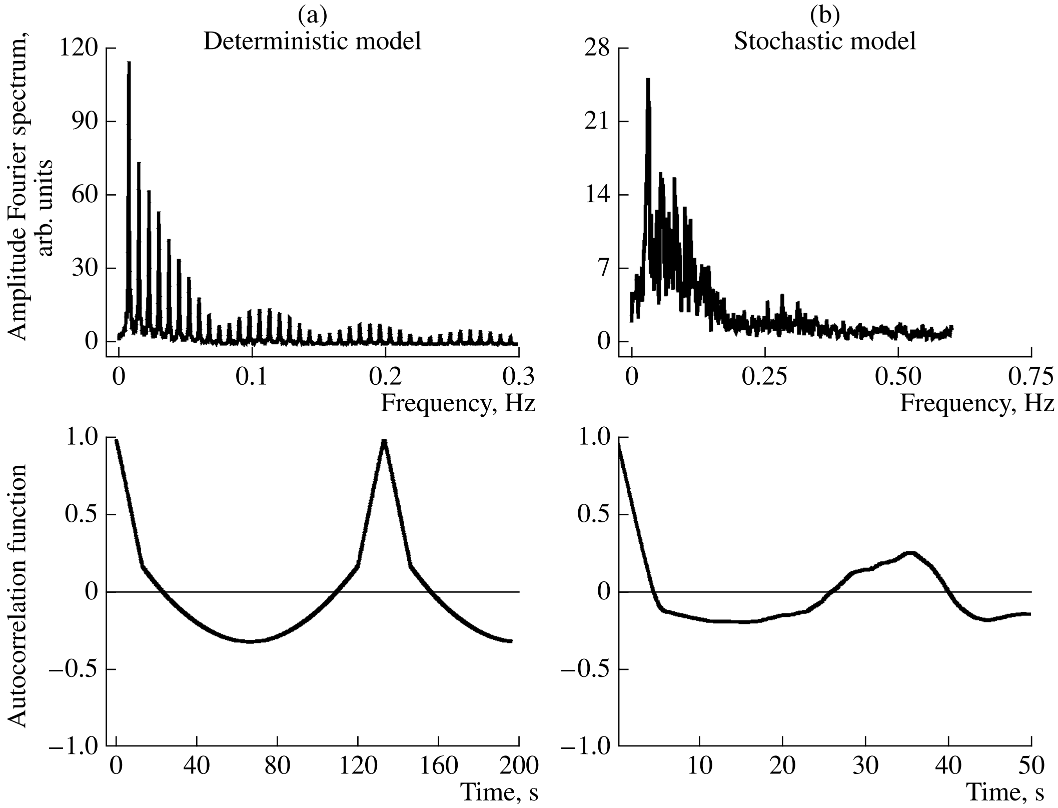

Fig. 4. Amplitude Fourier spectrum and autocorrelation function for the $\theta_{CO}(t)$ relationships obtained using (a) the point model and (b) the Monte Carlo method. The model parameters are the same as in Fig. 2.

Comparison of Figs. 2 and 3 suggests that the trajectories of the reaction system in the stochastic model lie near the attractive branches of the isoclines i_1 and i_3 of the point model; however, the cycle narrows and the oscillation period shortens. This specific feature is due to the effect of internal fluctuations, which shift the reaction system to the attraction domain of the other isocline branch. An increase in the migration rate of adsorbed species lowers the level of fluctuations in the system, bringing the solution of the stochastic model closer to the solution of the deterministic model. For a better quantitative agreement between the models, it is necessary to increase the lattice size or, in other words, to consider a larger catalyst sample. As the mobility of the adsorbed species decreases, the kinetic oscillations are replaced by random fluctuations and then oxide poisoning of the catalyst.

For numerical analysis of the results of modeling, let us construct amplitude Fourier spectra and autocorrelation functions for the time series $\theta_{CO}(t)$ obtained using the point model and the Monte Carlo method (Fig. 4). The amplitude Fourier spectrum describes the frequency distribution of the oscillation amplitude. This spectrum for the point model is discrete. It corresponds to complicated, periodic relaxation oscillations. The spectrum obtained by the Monte Carlo method is continuous. It shows a fundamental frequency and several well-defined harmonics, indicating that the oscillations are near-periodic. The autocorrelation function characterizes the degree of interdependence between different time sections of a given function. The amplitude spectra and autocorrelation functions for the time series obtained by deterministic and stochastic modeling are in essence similar. The more rapid decrease of the autocorrelation function in the latter case is explained by the fact that the oscillations in the stochastic model are less ordered.

Thus, in spite of the quantitative difference, the reaction rate oscillations in the deterministic and stochastic models are qualitatively the same. The surface of the catalyst is periodically oxidized, passing into the low-reactivity state, and is reduced, returning to the high-reactivity state. The mechanism of these autooscillations can be described as follows:

(1) Let the system be in a low-reactivity state characterized by a high concentration of adsorbed CO (θ_{CO}), a low concentration of adsorbed O (θ_O), a high concentration of the surface oxide (θ_{O^*}), and a low CO_2 formation rate.

(2) Since there are very few adsorbed oxygen atoms on the surface, the surface oxide does not form. The reaction between CO_{ads} and O^*_{ads} slowly diminishes the concentration of the latter. The surface undergoes

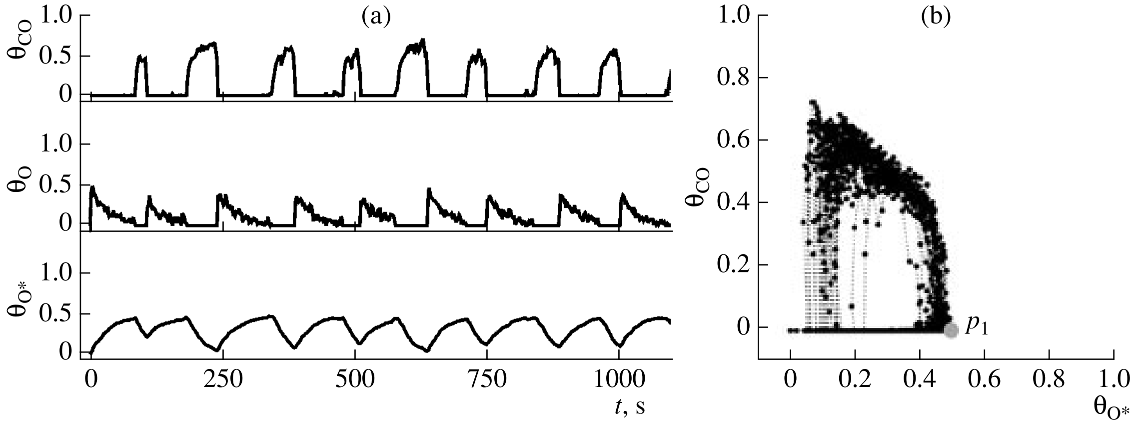

Fig. 5. Fluctuation-induced kinetic oscillations. $P_{CO} = 10^{-7}$ Torr. (a) $\theta_{CO}(t)$, $\theta_O(t)$, and $\theta_{O*}(t)$ curves obtained by the Monte Carlo method ($h = 10^4$ s^{-1}; 20 × 20 lattice). (b) Comparison of modeling data. ● is the projection of the stable stationary solution p_1 of the ODE set (2) on the phase plane (θ_{O*}, θ_{CO}). Monte Carlo data are plotted as dots and are connected with dotted lines.

reduction. θ_{CO} increases, but the total concentration $\theta_{CO} + \theta_O + \theta_{O*}$ falls.

(3) As the concentration of vacant sites increases, the probability of the adsorption of O_2 molecules grows. Oxygen atoms on the surface either react rapidly with adsorbed CO or turn slowly into O^*_{ads}. The surface reaction yields vacant sites, favoring further oxygen adsorption. The rate of CO_2 formation by the Langmuir–Hinshelwood mechanism increases, and the reaction system passes into the high-reactivity state, which is characterized by a high concentration of surface oxygen, a low concentration of adsorbed CO, and a comparatively high rate of surface oxide formation.

(4) The gradual increase in θ_{O*} is accompanied by a reduction in θ_O and in the rate of reaction in the adsorbed layer. However, the total concentration of adsorbed species increases due in part to the rapid one-site adsorption of CO. As θ_{CO} increases, the system approaches the low-reactivity state. The cycle is thus closed.

Thus, the oscillatory behavior of the stochastic model of the reaction system is observed in the autooscillation region of the deterministic model. To excite oscillatory dynamics at the atomic level, it is necessary to reduce the internal fluctuations, which are inherent in small-size systems because of the stochastic nature of elementary surface processes. In particular, the probability of the onset of the above oscillatory regime is much higher at a high species mobility than in a low-mobility or immobile adsorption layer.

In the last two sections, we will demonstrate that the internal fluctuations can not only damp but also excite reaction rate oscillations.

Fluctuation-Induced Kinetic Oscillations

The stochastic model can execute oscillations that do not correspond to the kinetic oscillations of the point model and that take place in the region of parameters where the ODE set (2) has a single stationary solution—another type of oscillations. Since these oscillations are near-regular, some authors mistakenly consider them to be kinetic oscillations defining the limit cycle of the point model [28]. We will set $k_1 = \bar{k}_1 P_{CO} = 1$ s^{-1} at $P_{CO} = 10^{-7}$ Torr, $k_{-1} = 0.2$ s^{-1}, $k_2 = 0.5$ s^{-1}, $k_3 = 10^5$ s^{-1}, $k_4 = 0.03$ s^{-1}, and $k_5 = 0.02$ s^{-1}, as was done in [28].

Typical Monte Carlo state trajectories of the reaction system are shown in Fig. 5. At the same parameters, the point model (2) has a single stable stationary state (point p_1 in Fig. 5b).

Consider the phase portrait of the deterministic model. In Fig. 6, we plot the trajectory of the system in the phase plane (θ_{O*}, θ_{CO}) and show the isocline of the first two equations, which intersects the isocline of the third equation at two points. One of these points, with the coordinates $\theta_{CO} = 0$, $\theta_O = 0$, and $\theta_{O*} = 1$, is at the boundary of the physically possible concentration region. It exists at all values of the parameters, is saddle-type, and has no effect on the dynamic behavior of the system. The other stationary point corresponds to the above-mentioned stable stationary state p_1. Near p_1, one can see trajectories that take the system away from this point and approach the stable branch of the isocline, i_3. Next, these trajectories run along the branch i_3 up to the turning point, at which this branch merges with the unstable branch i_2. Near the turning point, the trajectories also make a turn to bring the system to the other stable branch of the S-shaped isocline (i_1), along which the system returns to the stationary state p_1.

This run of trajectories in the vicinity of the stable stationary point is typical of an excitable medium. The

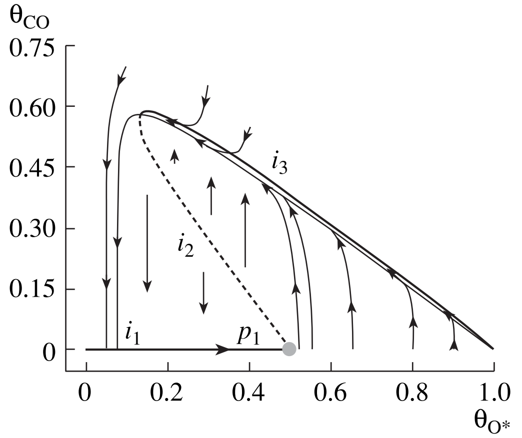

Fig. 6. Projections of the isoclines of the variables θ_{CO} and θ_O and of the trajectories of the ODE set (2) on the phase plane (θ_{O*}, θ_{CO}) at $P_{CO} = 10^{-7}$ Torr. The solid lines are the attractive isocline branches i_1 and i_3, the dashed line is the repulsive isocline branch i_2, and ● is the stable stationary point. The arrow-ended lines are trajectory projections.

stationary point p_1, which is stable both in the small and globally, is unstable towards finite perturbations. Its domain of attraction is small in some directions. A slight finite perturbation will take the trajectory of the system away from this point. After moving along the stable branch i_3, the system will return to its stationary state.

The behavior of the stochastic model of the reaction system is easy to predict. The fluctuations that increase the CO and oxide oxygen coverage of the surface will occasionally take the system away from the domain of attraction of the stationary point p_1. This is clear from the phase portrait shown in Fig. 5b. Most of the time, the reaction system is near the stable isocline branches of the point model, i_1 and i_3, randomly jumping from one to the other. As in the previous case, these oscillations correspond to an alternating oxidation and reduction of the surface. As the system moves along the branch i_1, θ_{O*} increases, implying the oxidation of the surface. As the system moves along the branch i_3, the surface is reduced.

As the lattice size is increased, the effect of the internal fluctuations on the dynamics of the stochastic model of the reaction system weakens. It can be stated that, if the lattice is sufficiently large and the adsorption layer is highly mobile, there will be a state corresponding to the stable stationary state p_1 of the deterministic model (2).

Note the following feature of the reaction–diffusion model, which is obtained by adding a diffusion term to the point model: in an excitable medium, solitary pulses running through the stable stationary point p_1 are excited in the one-dimensional case and helical waves are observed in the two-dimensional case. It was found that, on a small lattice, the oscillation pattern of the mean concentrations in the stochastic model corresponds to the running solitary pulses excited in the reaction–diffusion model.

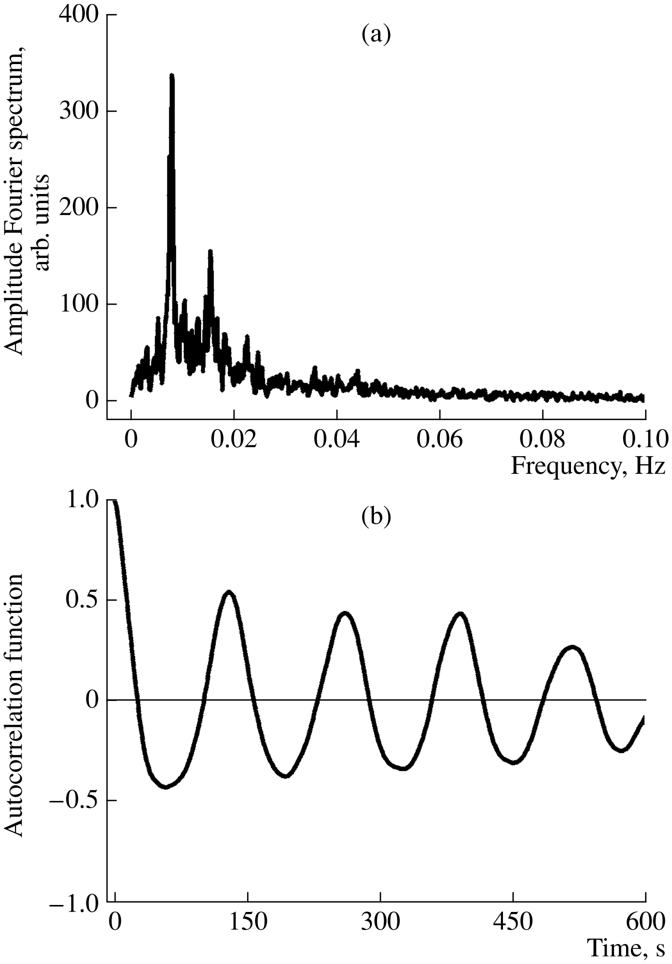

Fig. 7. (a) Amplitude Fourier spectrum and (b) autocorrelation function for the $\theta_{CO}(t)$ relationships calculated using the Monte Carlo method (see Fig. 5a).

To characterize the oscillatory behavior of the reaction system, we constructed an amplitude Fourier spectrum and an autocorrelation function for the time series $\theta_{CO}(t)$ (Fig. 7). The amplitude spectrum shows a number of peaks and has a fundamental frequency with the largest amplitude. The autocorrelation function proves the existence of correlations in the time series examined. Therefore, this time series defines oscillations.

Thus, we have demonstrated in this section that, in the parameter region where the point model has a single stable stationary solution for an excitable medium, the stochastic model may exhibit internal-fluctuation-induced oscillations of the reaction rate and of the concentrations of adsorbed species. Below, we consider the mechanism of oscillatory dynamics that is realized in the region of two or more stationary solutions in the deterministic model.

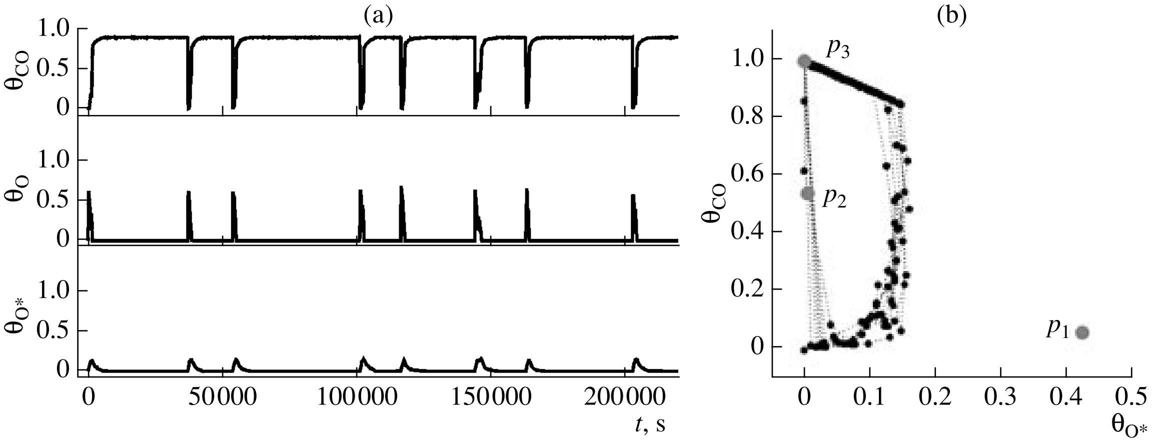

Fig. 8. Fluctuation-induced phase transitions. $P_{CO} = 0.9 \times 10^{-7}$ Torr. (a) $\theta_{CO}(t)$, $\theta_O(t)$, and $\theta_{O*}(t)$ curves obtained by the Monte Carlo method ($h = 0$ s^{-1}; 20 × 20 lattice). (b) Projections of the stable stationary solutions p_1, p_2, and p_3 of the ODE set (2) on the phase plane (θ_{O*}, θ_{CO}) (gray points). Monte Carlo data are plotted as black points and are connected with dotted lines.

Fluctuation-Induced Phase Transitions

Suppose that the phase portrait of the point model has two or more attractors. It is expected in this case that, if the fluctuations are sufficiently strong, the dynamic behavior of the reaction system deduced by Monte Carlo modeling will appear as reversible random transitions from the vicinity of one attractor to the vicinity of another. A behavior pattern typical of CO oxidation by the TSM mechanism on platinum-group metal catalysts is presented in Fig. 8a. The following parameters are used here: $k_1 = \bar{k}_1 P_{CO} = 0.9$ s^{-1} at $P_{CO} = 0.9 \times 10^{-7}$ Torr, $k_{-1} = 0.002$ s^{-1}, $k_2 = 0.5$ s^{-1}, $k_3 = 10^2$ s^{-1}, $k_4 = 0.0003$ s^{-1}, $k_5 = 0.0002$ s^{-1}, and $h = 0$ s^{-1} [29].

It is clear from Fig. 8 that, most of the time, the surface is mainly covered with adsorbed CO molecules. The evolution of the reaction system consists of random transitions from the state in which the surface is dominated by CO_{ads} to the state in which the surface is dominated by oxygen and vice versa. At the same rate constants of the elementary steps, the macromodel has three stationary states, two of which are stable.

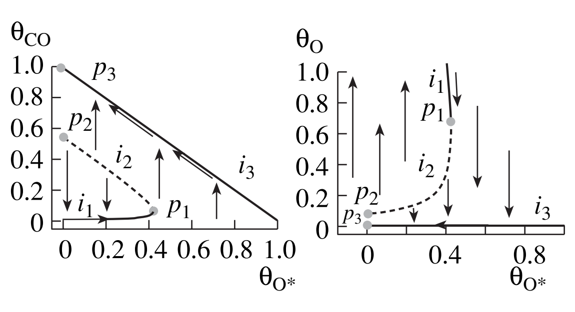

Fig. 9. Projections of the isoclines of the variables θ_{CO} and θ_O of the ODE set (2) on the phase planes (θ_{O*}, θ_{CO}) and (θ_{O*}, θ_O) at $P_{CO} = 0.9 \times 10^{-7}$ Torr. The solid lines are the attractive isocline branches i_1 and i_3, the dashed line is the repulsive isocline branch i_2, and ● are stationary points. The arrows show trajectory directions.

Let us plot the isoclines and phase trajectories of the ODE set (2). Figure 9 shows the projections of the phase portrait of the system on the planes (θ_{O*}, θ_{CO}) and (θ_{O*}, θ_O) at $P_{CO} = 0.9 \times 10^{-7}$ Torr. The zero isocline of the first two equations consists of three branches. The branches i_1 and i_2 constitute one line, and the branch i_3 is another line. The branches i_3 and i_1 are stable and attract trajectories, and the branch i_2 is unstable. The points are the isoclines of the third equation. These isoclines intersect the isoclines i_3, i_1, and i_2 at the stationary points p_3, p_1, and p_2. The stable stationary point p_1, which represents the state with a low CO_{ads} coverage of the surface and high concentration of subsurface oxygen, is situated near the turning point of the zero isocline, at which the stable and unstable branches merge. The domain of attraction of the point p_1 is very small in some directions. It is clear from Fig. 9 that, in a small neighborhood of the stationary point p_1, there are trajectories that recede from this point. A slight increase in θ_{CO} or θ_{O*} will take the system from the domain of attraction of the point p_1 and bring it to the stable state p_3, with a high CO_{ads} coverage of the surface. To return the system into the state p_1, it is necessary to increase θ_O and considerably decrease θ_{CO} so as to "step over" the unstable branch i_2. The resulting trajectories will be attracted to the stable branch i_1 and will run along this isocline up to the point p_1.

Let us describe the behavior of this system subject to fluctuations. Return to Fig. 8. Small fluctuations of the concentrations of adsorbed species do not allow the system to stay in the state p_1, with a low θ_{CO} and a high θ_O. The new state, which is represented by the stationary point p_3 and is characterized by a high CO_{ads} coverage of the surface, arises as islets of adsorbed CO mol-

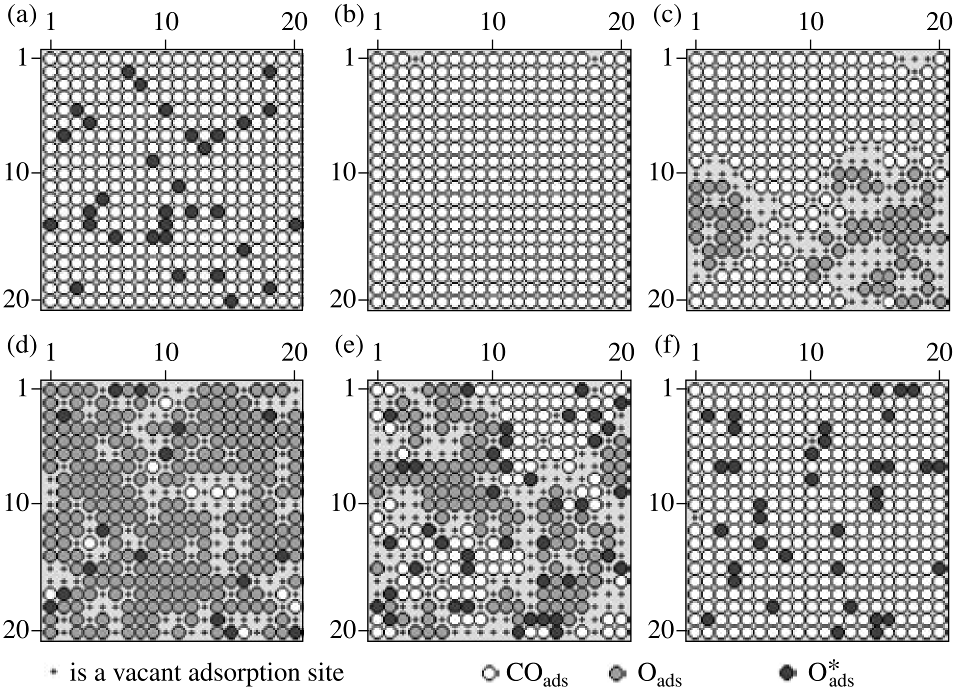

Fig. 10. Microstate portraits of a lattice fragment obtained during one phase-transition cycle (Monte Carlo method, 20 × 20 lattice).

ecules in many places at a time. At the same time, much larger concentration fluctuations in the adsorption layer are necessary for the system to pass from the state in which the surface is dominated by CO_{ads} to the state in which the surface is mainly covered by oxygen. Such fluctuations are comparatively unlikely, and the system is in the state p_3 most of the time. The forming phase propagates as an oxygen wave throughout the surface. Paradoxically, this wave propagates not through oxygen migration but because of the absence of oxygen migration.

Figure 10 illustrates this oscillatory behavior of the reaction system.

(1) Let the system be in a low-reactivity state with a high θ_{CO} and low θ_O and θ_{O*} (Figs. 10a, 10b).

(2) A fairly large, accidentally formed, oxygen-dominated island is surrounded by a buffer of vacant sites, which have resulted from the fast reaction between O_{ads} and CO_{ads} (Fig. 10c). A pair of neighboring active sites, vacated owing to the reaction at the boundary of the new phase, adsorbs a dioxygen molecule by a dissociative mechanism, because oxygen is adsorbed by a clean surface at a higher rate than CO. The adsorbed oxygen atoms react with the nearest CO_{ads} molecules, displacing the buffer zone and moving apart the boundaries of the new phase until the old, CO_{ads}-dominated phase disappears.

(3) Part of the oxygen atoms that are inside the islet of the new phase and are far from CO_{ads} turn into oxide oxygen (Fig. 10d). As θ_{O*} grows, the probability of islets of the old phase reappearing on the surface increases. The CO_{ads} molecules and islets situated near oxidized active sites (O^*_{ads}) are the most stable. On the one hand, the surface oxide prevents the adsorption of oxygen molecules from the gas phase and, accordingly, the reaction between oxygen and CO_{ads}. On the other hand, the reaction between CO_{ads} and O^*_{ads} (step (V)) is much slower than the reaction between CO_{ads} and oxygen on the surface (step (III)).

(4) As oxygen is removed from the catalyst surface, the interaction between CO_{ads} and O^*_{ads} becomes the main reaction pathway. Thus, the surface oxide, which at first initiates the formation of islets of the CO_{ads}-dominated phase, is then entirely annihilated by this phase (step (V)). The cycle is thus closed.

The observed oscillatory processes will be analyzed in terms of the amplitude Fourier spectrum and the autocorrelation function for the solution $\theta_{CO}(t)$ of the stochastic model (Fig. 11). The continuous spectrum and the correlation function, which decreases rapidly to zero, are typical of random noise perturbations. Thus, the spontaneous phase transitions in the stochastic model cannot be assigned to periodic oscillations.

Further investigation demonstrated that taking into account the mobility of the adsorbed species may lead to a qualitatively different behavior pattern: the oscillation period increases, finally resulting in the complete disappearance of phase transitions, and the system comes to the stationary state p_3, with a high CO_{ads} coverage of the surface.

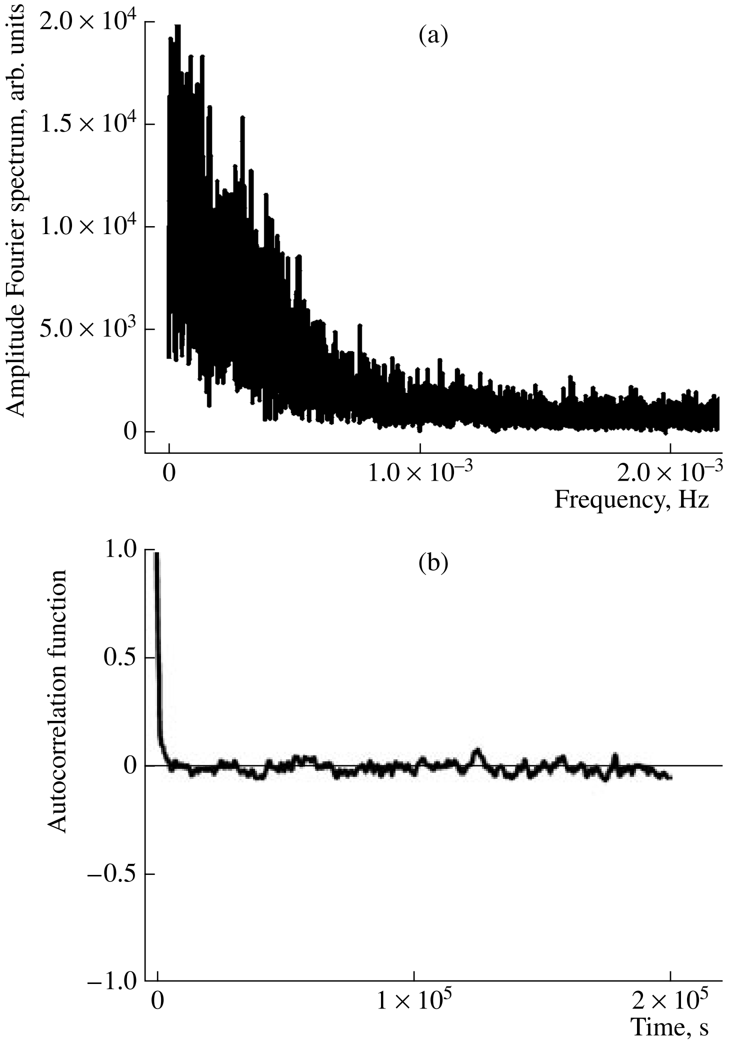

Fig. 11. (a) Amplitude Fourier spectrum and (b) autocorrelation function for the $\theta_{CO}(t)$ relationships calculated using the Monte Carlo method (see Fig. 8a).

CONCLUSION

Three types of oscillatory dynamics were discovered in the microscopic stochastic model and were studied by mathematical modeling using heterogeneous CO oxidation as the model reaction. Two consistent models were considered, namely, the stochastic model based on the Monte Carlo method and the point deterministic model in the ideal adsorption layer approximation.

Two types of the oscillatory behavior of the stochastic model can be viewed as kinetic oscillations, and the third type is random phase transitions from one phase state to another.

Two types of kinetic oscillations were discovered, one occurring in the oscillating medium of the point model and the other in an excitable medium. Oscillations of the first type can be observed in a near-ideal adsorption layer on a face of a single crystal of macroscopic size. This behavior of the reaction system is described by a set of ODEs. In smaller systems, these oscillations do not always take place, because they may be prevented by internal fluctuations.

Kinetic oscillations of the second type, which are oscillations in an excitable medium, should most often be observed on faces of single crystals in experiments using instruments with a high space resolution, capable of detecting helical waves and other spatiotemporal phenomena. Catalyst particles are usually rather large, and species diffusion on their surface should be taken into account in modeling. It is helical or plane waves, which usually appear spontaneously on defect sites, that are responsible for the experimentally observed macroscopic oscillations. The concentration waves forming on the catalyst surface can be adequately described using sets of partial differential equations of the reaction–diffusion type. In the stochastic model, these kinetic oscillations are induced by internal fluctuations. Note that they will not occur in an ideal adsorption layer. The corresponding ODE set implies a single, stable, excitable, stationary state.

The third type of oscillatory dynamic can be observed only in an adsorption layer in which the formation of separate islets of a distinct phase is possible. For a nucleus of a new phase to begin to grow, it is necessary that the reaction kinetics have several stable stationary states. If this is the case, spontaneous transitions between states at the atomic level are induced by fluctuations caused by the nucleation and growth of islets of different phases. Examination of the amplitude Fourier spectra and the correlation matrix of the corresponding time series demonstrated that these phase transitions can be treated as kinetic oscillations.

The classification suggested here for the oscillatory regimes of heterogeneous catalytic reactions is obviously not exhaustive. If the point deterministic model is characterized by a more sophisticated bifurcation diagram (for example, there are solutions as both a limit cycle and an excitable stable stationary point), then other nontrivial oscillatory behavior patterns will be possible for the microscopic stochastic model.

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