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Chaotic dynamics in the three-variable kinetic model of CO oxidation on platinum group metals

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ABSTRACT

The paper addresses the development of a simple three-variable kinetic model of CO oxidation on metallic catalysts under isothermal conditions and the numerical study of chaotic dynamics of the reaction rate. It is suggested that, at some concentrations of the adsorbed oxygen, a surface modification occurs and the reaction capability of adsorbed oxygen changes, so that the activation energy of the interaction between the adsorbed species increases sharply. Moreover, oxygen atoms can penetrate into the subsurface catalyst layer. At some critical values of the subsurface oxygen concentration, the catalyst surface reconstructs and the probability of oxygen adsorption decreases sharply. Based on these suggestions, a three-variable kinetic model of CO oxidation on the metals of the platinum group is developed, which has the hierarchy of characteristic times and one slow variable. For the purpose of studying the dynamics of the model, the one-parameter family of two-variable subsystems with fast variables is considered, and the steady states and periodic solutions of these subsystems were investigated. The conditions are described under which the dynamics of the model becomes chaotic by means of a cascade of period-doubling bifurcations or owing to complex multipeak oscillations.

1. Introduction

One of the most widely studied heterogeneous catalytic reactions is the CO oxidation on the platinum group metals. Observations of such critical phenomena as steady state multiplicity, relaxation oscillations, and chaotic dynamics help to determine a more reliable reaction mechanism and better understand the physical–chemical processes in the "reaction medium-catalyst" system. There are many efforts to explain theoretically the relaxation or complex irregular oscillations, involving different hypothesis such as dependence of the activation energy on the surface coverages [1], formation of the metal oxide or subsurface oxygen in the course of the oxidation reaction [2,3] and the adsorbate-induced reversible surface transformation [4,5,6].

Based on the experimental studies of the CO oxidation mechanism, which were carried out on the iridium surface at ultra high vacuum conditions, it was shown that, due to the reconstructive properties of the open and stepwise faces of the platinum metals, some oxygen atoms can penetrate into the subsurface layers and cause both structural and chemical modification of the adsorption sites [7,8]. The kinetic model suggested in Ref. [8] accounts for the dynamical behavior of the concentrations of CO and oxygen adsorbed on the initial and oxidized metallic surfaces as well as the behavior of the subsurface oxygen concentration. The model was able to describe some experimental data and predict the multiplicity of steady states and the harmonic oscillations of the reaction rate near the Andronov–Hopf bifurcation points.

Following Ref. [9], we now develop a simpler kinetic model of CO oxidation on platinum group metals under isothermal conditions, which describes both the relaxation and complex irregular oscillations. To study the dynamics of this nonlinear kinetic model, we use the hierarchical approach suggested in Refs. [10,11,12], where a three-variable kinetic model with fast, intermediate and slow variables for heterogeneous hydrogen oxidation over metallic catalysts was considered, and it was shown that if the one-parameter family of subsystems of the fast and intermediate variables has a hysteresis on the curve of steady states and some maximal families of stable limit cycles then the corresponding three-variable system can have the multipeak or complex irregular oscillations.

2. Kinetic model

Consider the kinetic scheme of CO oxidation on the platinum group metals based on the Langmuir–Hinshelwood mechanism:

$$\mathrm{CO} + \mathrm{Z} \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} \mathrm{ZCO}, \tag{1}$$

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$$O_2 + 2Z \xrightarrow{K_2} 2ZO, \tag{2}$$

$$ZCO + ZO \xrightarrow{K_3} CO_2 + 2Z. \tag{3}$$

The processes of subsurface oxygen formation and its reduction during the reaction are determined as follows [7,8]:

$$ZO + Z_V \xrightarrow{K_4} Z_VO + Z, \tag{4}$$

$$Z_VO + ZCO \xrightarrow{K_5} CO_2 + Z_V + Z. \tag{5}$$

Here ZCO and ZO are the intermediate compounds of CO and oxygen on the metallic surface, Z and Z_V are the active sites on the surface and in the subsurface layer of the catalyst, Z_VO is the intermediate compound of oxygen penetrated into the subsurface layer.

Basing on the mechanism (1)–(5), we consider the kinetic model that describes the behavior of the dimensionless concentrations of CO and oxygen adsorbed on the surface (x and y, correspondingly) and also the dimensionless concentration of subsurface oxygen (z):

$$x' = K_1(1 - x - y) - K_{-1}x - K_3xy, \tag{6}$$

$$y' = 2K_2(1 - x - y)^2 - K_3xy, \tag{7}$$

$$z' = K_4y(1 - z) - K_5xz \equiv \varepsilon(\alpha y(1 - z) - xz). \tag{8}$$

The rate of CO_2 production is given by the formula

$$R_{CO_2} = K_3xy + K_5xz.$$

The rate constants of the elementary reactions depend on the partial pressures P_{O_2} and P_{CO} (Torr) of oxygen and carbon oxide in the gas phase and on the temperature T (K) as follows [7,8]:

$$K_1 = 3.6 \times 10^5 P_{CO},\ K_{-1} = 10^{13} \times \exp\left(-\frac{E_1}{(RT)}\right),$$

$$K_2 = K_{20}P_{O_2},\ K_3 = 10^{13} \times \exp\left(-\frac{E_3}{(RT)}\right),$$

where R is the universal gas constant.

We suggest that the processes of adsorption, desorption and reaction between adsorbed species are faster than the oxygen penetration and the interaction between subsurface oxygen and adsorbed CO. Therefore, the elementary reaction rate constants K_4 and K_5 are much smaller than K_i, $i = 1, -1, 2, 3$; and we consider the model (6)–(8) with parameters

$$\varepsilon = K_5 \ll 1, \quad \alpha = \frac{K_4}{K_5}.$$

In order to describe the influence of the reaction medium on the properties of the metal surface, we assume that there exist some critical values of the surface coverage with oxygen at which a surface modification occurs and the reaction ability of the catalyst changes strongly, i.e., E_3 sharply increases [9]. The activation energy E_3 of interaction between the adsorbed species depends on the concentration y of adsorbed oxygen and it is described by the following smooth function:

$$E_3(y) = \begin{cases} E_{31}, & y \le y_c - \delta, \\ \tilde{E}_3, & |y - y_c| < \delta, \\ E_{32}, & y \ge y_c + \delta, \end{cases} \tag{9}$$

where

$$\tilde{E}_3(y_c - \delta) = E_{31},\ \tilde{E}_3(y_c) = \frac{E_{31} + E_{32}}{2}, \quad \tilde{E}_3(y_c + \delta) = E_{32}.$$

The parameters y_c and $0 < \delta \ll 1$ determine the middle and the width of the interval of y values over which E_3 increases (see Fig. 1a).

Moreover, due to the oxygen penetration into the subsurface layer, a reconstruction of the metallic surface can occur, changing the adsorption properties of the catalyst. For some critical values of the concentration of subsurface oxygen, K_{20} sharply decreases. We use a similar smooth function to describe the dependence of K_{20} on z:

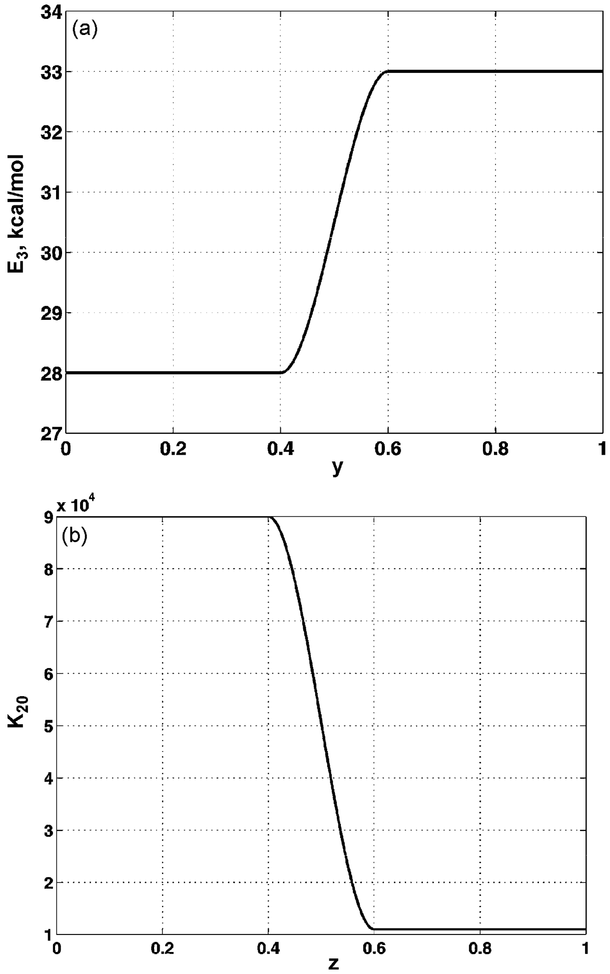

Fig. 1. Dependences of E_3 on y (a) and K_{20} on z (b) for $y_c = z_c = 0.5$, and $\delta = \delta_z = 0.1$.

$$K_{20}(z) = \begin{cases} K_{21}, & z \le z_c - \delta_z, \\ \tilde{K}_{20}, & |z - z_c| < \delta_z, \\ K_{22}, & z \ge z_c + \delta_z, \end{cases} \tag{10}$$

where

$$\tilde{K}_{20}(z_c - \delta_z) = K_{21}, \quad \tilde{K}_{20}(z_c) = \frac{K_{21} + K_{22}}{2}, \quad \tilde{K}_{20}(z_c + \delta_z) = K_{22}.$$

The parameters z_c and $0 < \delta_z \ll 1$ determine the middle and the width of the z-interval over which K_{20} decreases (see. Fig. 1b).

The values of the activation energies E_1, E_{31}, and E_{32}, as well as the constants for the oxygen adsorption rate are given in Table 1. We will consider the model (6)–(8) at the real experimental conditions:

$$P_{CO} = 1.1 \times 10^{-7}\,\text{Torr}, \quad P_{O_2} = 9 \times 10^{-7}\text{Torr}, \quad T = 500\,\text{K}.$$

Table 1
Values of the activation energies and the rate constants.

E_1 (kcal/mol)	E_{31} (kcal/mol)	E_{32} (kcal/mol)	K_{21} (s^{-1} $Torr^{-1}$)	K_{22} (s^{-1} $Torr^{-1}$)
35	28	33	0.9×10^5	0.11×10^5

The model (6)–(8) is considered in the region

$$\Omega = \{(x,\ y,\ z) :\ x,\ y,\ z \geq 0,\ x+y \leq 1,\ z \leq 1\},$$

which corresponds to the nonnegative and bounded values of the concentrations. Let Γ denote the surface in Ω, in which the rate of z-coordinate change is equal to zero:

$$\Gamma = \{(x, y, z) \in \Omega :\ h(x, y, z) \equiv \alpha y(1-z) - xz = 0\} \quad (11)$$

The system (6)–(8) of autonomous differential equations generates a vector field (and a phase flow) in the phase space (x, y, z). Let us describe some important properties of this field which are satisfied for every set of values of the parameters under consideration.

There exists a hyperbolic steady state at the point (0,1,1) such that one of its stable separatrices $(0, 1, z(t))$ lies on the boundary surface of the region Ω, while the leading unstable separatrix is directed into inside of Ω. If we consider a cross-section of Ω with a plane z = const then there always exists a saddle steady state of the subsystem (6)–(7) at the point $(x_s, y_s) = (0,1)$, whose local stable manifold does not belong to Ω, however one of the unstable separatrices lies inside Ω. Studying the structure of the null-clines of the two-variable subsystems (with parameter z) of the dynamical system (6)–(8) allows us, for an arbitrarily small $\theta > 0$, to construct a subregion $\Omega_\theta \subset \Omega$ such that the vector field of (6)–(8) at the boundary $\partial\Omega_\theta$ is transversal and directed inside the region. Hence, the region Ω is invariant with respect to the phase flow; i.e., if a point (x_0, y_0, z_0) is taken in Ω then the solution $(x(t), y(t), z(t))$ of (6)–(8) with the initial condition (x_0, y_0, z_0) at $t = 0$ belongs to Ω for all $t > 0$.

Since z is the only slow variable ($\varepsilon \ll 1$) in the three-variable autonomous dynamical system, the dynamics of the model (6)–(8) is determined by the structure of two sets of solutions (the steady states and the periodic solutions) of the one-parameter family of two-variable subsystems (6)–(7) with parameter $z \in [0,1]$ (see [10,11]). Our purpose is to clarify whether the kinetic model (6)–(8) describes some complex and irregular oscillations under assumption of isothermal conditions.

3. Two-variable model

In Ref. [9], we studied the dynamics of the two-variable model (6)–(7) at a constant value of the oxygen adsorption rate constant $K_{20} = 0.9 \times 10^5\ \mathrm{s}^{-1}\ \mathrm{Torr}^{-1}$. In the case E_3 = const, this kinetic model qualitatively describes the steady state multiplicity and does not exhibit oscillatory behavior. We showed that if the activation energy E_3 depends on y due to (9) then the system (6)–(7) has relaxation oscillations in the case of the oxygen excess in the gas phase. Moreover, as $\delta \to 0$, the variables $x+y$ and $x-y$ are correspondingly fast and slow near the stable limit cycle, i.e.,

$$|x' + y'| \gg |x' - y'|.$$

We studied the effect of the parameters y_c and δ which determine the interval of y values, where the activation energy E_3 changes; and we showed that, for small values of y_c and δ at some fixed T and P_{CO}, there are two $P_{\mathrm{O_2}}$ values at which the bifurcation of a periodic solution from a homoclinic trajectory (a saddle loop separatrix in our case) occurs in (6)–(7).

Now let $K_{20} \neq$ const and depend on z due to (10). Consider the case when the set of steady states of the one-parameter family of systems (6)–(7) has a hysteresis. For example, put $z_c = y_c = 0.5$ and $\delta_z = \delta = 0.1$. Then there is an interval (z_B, z_C) of z-values for which the system (6)–(7) has three steady states. Outside of this interval, at $0 \leq z < z_B$ and $z_C < z \leq 1$, a single steady state exists for every z. Therefore, the set of the steady states forms a curve *ABCD*, which consists of the three branches: *AB*, *BC*, and *CD*. The branch *AB* is stable, while *BC* is unstable and consists of the saddle points of (6)–(7).

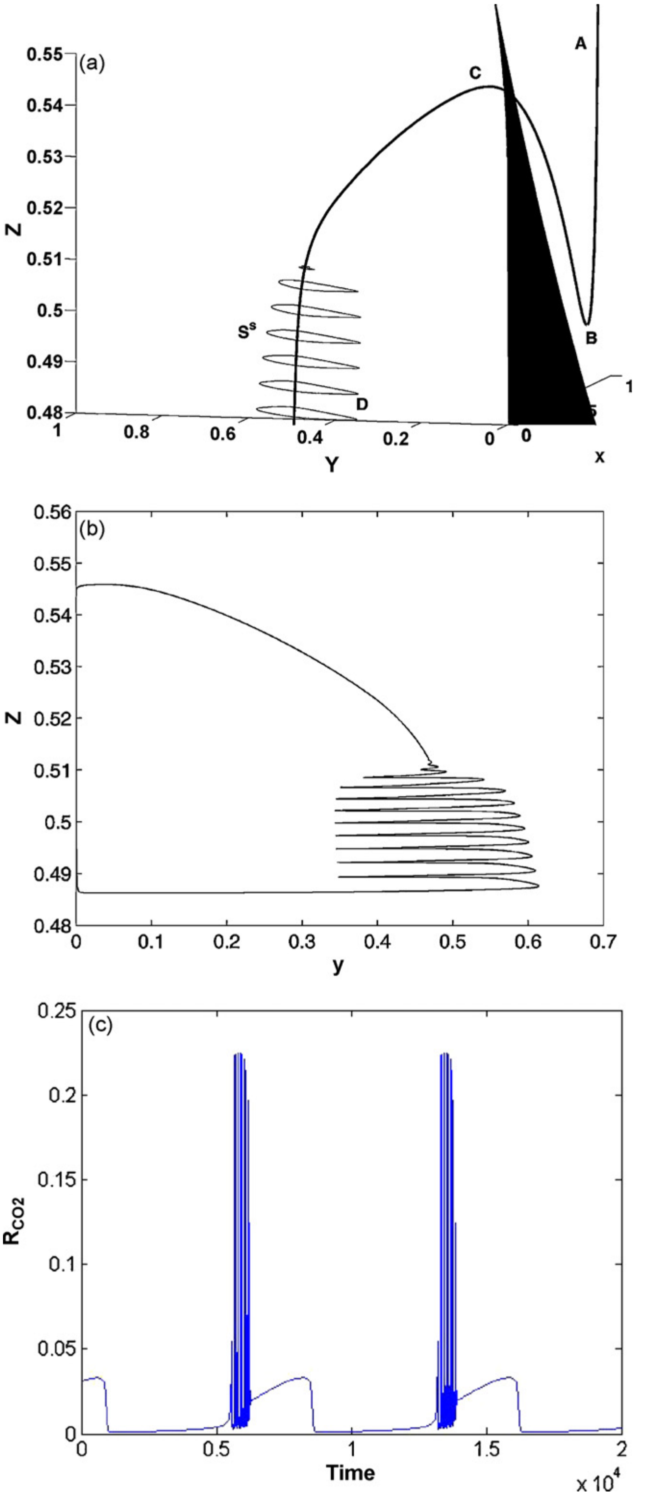

Fig. 2. The maximal families *ABCD* and S^s of the steady states and the periodic solutions of the system (6)–(7) and the surface Γ (a); the multipeak oscillations of (6)–(8) (b); and the rate of $\mathrm{CO_2}$ production (c). The parameters are as follows: $y_c = z_c = 0.5$, $\delta = \delta_z = 0.1$, $\alpha = 4.65$, and $\varepsilon = 3 \times 10^{-5}$.

Moreover, at $z^{\max} = 0.5096$, the stable periodic solution appears in (6)–(7) in result of the Andronov–Hopf bifurcation. So, the steady states on the branch *CD* are stable for $z \in [z^{\max}, z_C)$ and unstable for $z \in [0, z^{\max})$. The system (6)–(7) has a maximal family S^s of stable periodic solutions for z in the interval $[0, z^{\max})$ (see Fig. 2a). Note that we compute the maximal family of the periodic solutions to (6)–(7) with parameter z by using the efficient algorithm developed in Ref. [13].

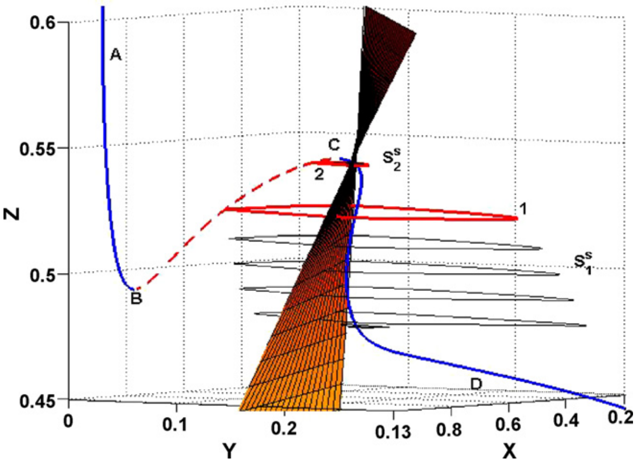

Fig. 3. The maximal set *ABCD* of steady states, the maximal families S_1^s and S_2^s of stable periodic solutions of the system (6)–(7) and the surface Γ for $\alpha = 4.65$. Here 1 and 2 are the saddle loop separatrices, $z_1{}^{\min} = 0.4776$, $z_1{}^{\max} = 0.521452$, $z_2{}^{\min} = 0.538367$, $z_2{}^{\max} = 0.5385$, $z_c = 0.5$, $\delta_z = \delta = 0.1$, and $y_c = 0.101$.

4. Multipeak oscillations

Let the value of α be such that the surface Γ determined by (11) intersects the curve *ABCD* at only one point on the branch *BC* and does not intersect the surface S^s of periodic solutions of (6)–(7). Then, on the curve *AB* the rate of change of z is negative, while $z' > 0$ on the curve *CD* and surface S^s.

In this case the model (6)–(8) has the only unstable steady state and a stable limit cycle describing multipeak oscillations at some sufficiently small ε (see Fig. 2b,c). If the initial point (x, y, z) is near *AB* in the phase space of (6)–(8), then this point moves down along the trajectory near *AB* while $z > z_B$. At some z just under z_B, the point "jumps" to the neighborhood of the surface S^s, turns several times around S^s, moves up along the branch *CD*, and "jumps" back to *AB* at z near z_C. If the parameter ε decreases, then the number of turns around S^s increases. Thus, the number of peaks of the reaction rate increases with decreasing the rate constant $K_5 = \varepsilon$ of the subsurface oxygen formation.

5. Cascade of period doubling bifurcations and chaotic dynamics

Consider the case when the family S^s of stable periodic solutions bifurcates, so that the system (6)–(7) has two maximal families S_1^s and S_2^s. Note that this situation is similar to the one studied in Ref. [11] for the hydrogen oxidation reaction. In this case, the periodic solutions of (6)–(7) exist for z in the intervals $(z_1{}^{\min}, z_1{}^{\max})$ and $(z_2{}^{\min}, z_2{}^{\max})$, where $z_1{}^{\max} < z_2{}^{\min}$. At $z = z_1{}^{\min}$ and $z = z_2{}^{\max}$, the Andronov–Hopf bifurcations occur in the system (6)–(7). At $z = z_1{}^{\max}$ and $z = z_2{}^{\min}$, the periodic solutions degenerate into the saddle loop separatrices; i.e., there exist two saddle loop separatrices in the phase space. Near these homoclinic bifurcations,

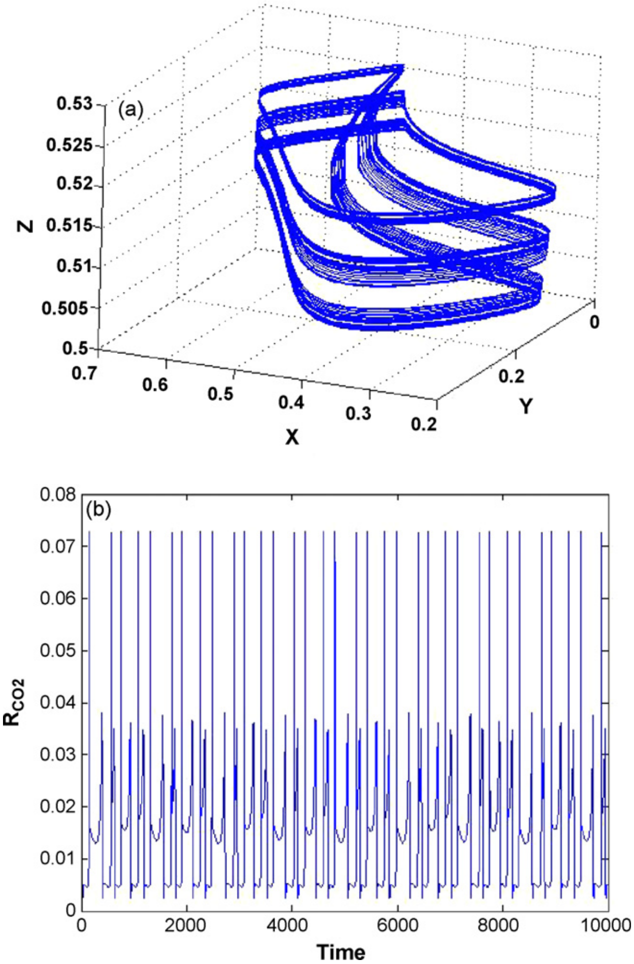

Fig. 4. The attracting set *A* (a) and the chaotic oscillations of the reaction rate (b) at $\alpha = 4.65$ and $\varepsilon = 0.00038$.

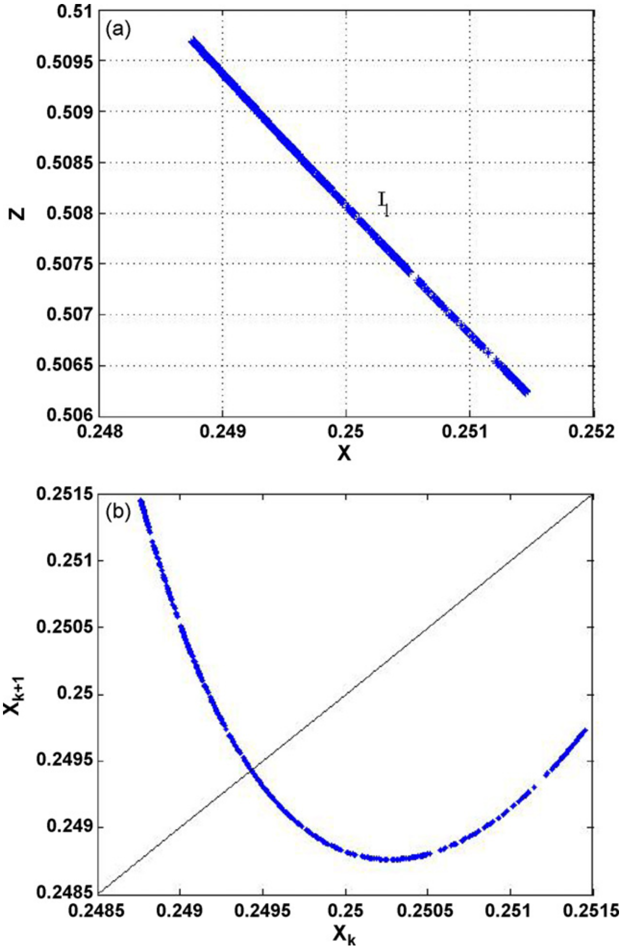

Fig. 5. The Poincare map *P* (a) and the one-dimensional map *F* (b) for the trajectory of Fig. 4a.

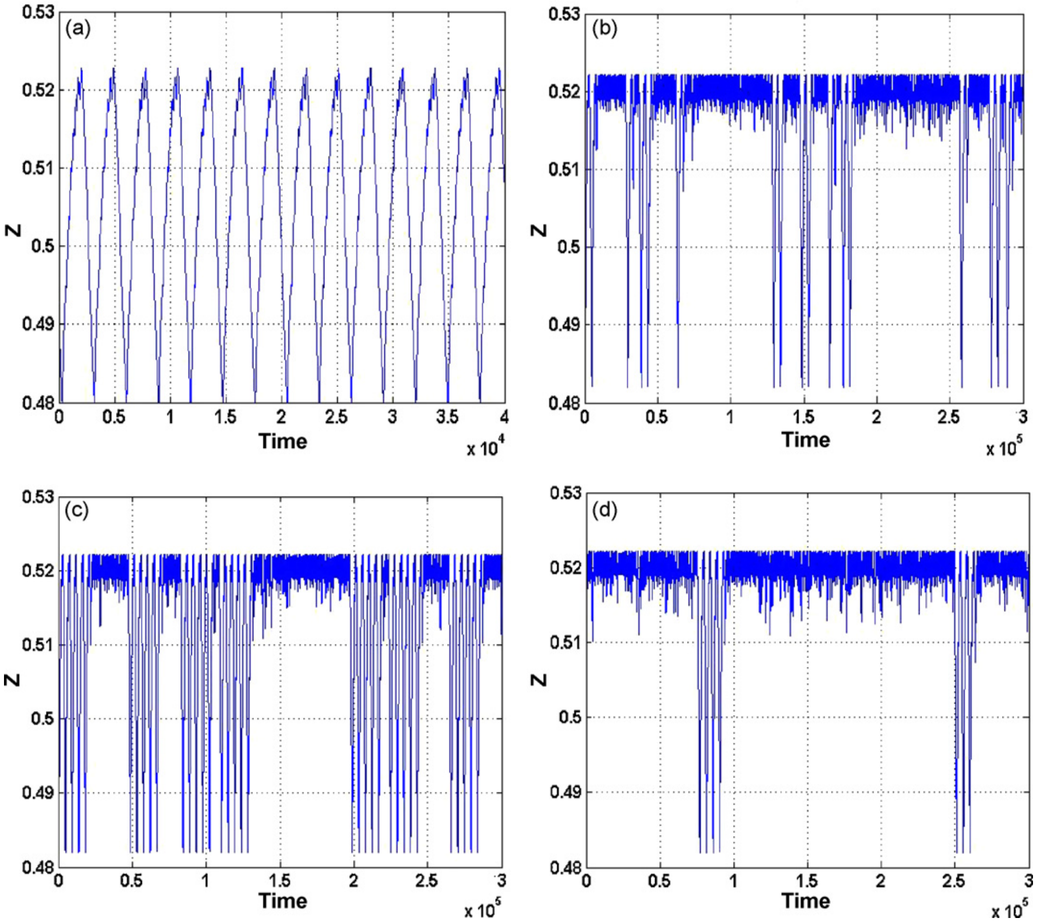

Fig. 6. Regular (a) and irregular (b–d) multipeak oscillations of the system (6)–(8) for $\varepsilon = 0.0001$ (a), 7.1965×10^{-5} (b), 7.1957×10^{-5} (c), 7.191×10^{-5} (d).

the solutions are highly sensitive to the small changes of parameters. If z approaches the bifurcation value (for example, $z = z_1{}^{\max}$), the period of oscillations increases to infinity, while the amplitude remains almost constant [14]. In this case, the system (6)–(7) stays near the saddle steady state located on the branch BC for a long time during the period. For $z_1{}^{\max} < z < z_2{}^{\min}$, the system (6)–(7) has three steady states inside Ω and no periodic solutions. In more detail, the first steady state in *CD* is unstable; the second, in *BC*, is a saddle point; and the third, on the curve *AB*, is a sink which attracts almost all trajectories. For example, such a structure of solutions of (6)–(7) exists at $z_c = 0.5$, $\delta_z = \delta = 0.1$, and $y_c = 0.101$ (see Fig. 3).

Let α be such that the surface Γ intersects $S_1{}^s$. The following theorem holds:

Theorem ([15,12]). *Let the three-variable system with a small parameter* $0 < \varepsilon \ll 1$:

$$x' = f(x, y, z), \quad y' = g(x, y, z), \quad z' = \varepsilon\, h(x, y, z),$$

be such that the one-parameter family of the two-variable subsystems with parameter z

$$x' = f(x, y, z),\ \ y' = g(x, y, z)$$

has a family of stable limit cycles $\gamma(z)$ *for z from an interval I. Consider the function*

$$\eta(z) = \int_0^{T(z)} h(\varphi_z(t), \psi_z(t), z)\mathrm{d}t,$$

where $T(z)$ *is the period of solution* $x = \varphi_z(t)$, $y = \psi_z(t)$ *that corresponds to the limit cycle* $\gamma(z)$. *Let* $z^* \in I$ *be such that* $\eta(z^*) = 0$ *and* $\eta'(z^*) < 0$. *Then the three-variable system has a stable limit cycle* γ_ε *with period* T_ε *such that* $\gamma_\varepsilon \to \gamma(z^*)$ *and* $T_\varepsilon \to T(z^*)$ *as* $\varepsilon \to 0$.

In the case under consideration, for $\alpha = 4.65$, there exists $z^* = 0.5207$ such that $\eta(z^*) = 0$ and $\eta'(z^*) < 0$ on the periodic solution $\gamma(z^*)$ of (6)–(7). Note that z^* is close to $z_1{}^{\max}$ and z^* increases as α increases. It follows from the theorem that there exists $\varepsilon_0 > 0$ such that, for $0 < \varepsilon < \varepsilon_0$, the model (6)–(8) has a stable limit cycle. Let us denote it by γ_ε.

Numerically we obtain that the *period-doubling bifurcation* occurs at $\varepsilon_1 = 2.079 \times 10^{-4} > \varepsilon_0$; i.e., the cycle γ_ε becomes unstable at $\varepsilon = \varepsilon_1$ (denote it by γ_1) and a stable limit cycle γ appears in a small neighborhood of γ_1. The cycle γ_1 corresponds to the T_p-periodic solution ($T_\mathrm{p} = 276.8948$ s); and γ, to the $2T_\mathrm{p}$-periodic solution. The consequent period-doubling bifurcations occur at $\varepsilon_2 = 3.075 \times 10^{-4}$, $\varepsilon_3 = 3.496 \times 10^{-4}$, and so on. The model (6)–(8) generates chaotic oscillations via the Feigenbaum cascade of period doubling bifurcations such that the sequence of $\varepsilon = \varepsilon_i$, $i = 1, 2, \ldots$, has a limit value $\tilde{\varepsilon} = \lim\limits_{i \to \infty} \varepsilon_i$. For some ε above $\tilde{\varepsilon}$, the model (6)–(8) has complex irregular oscillations.

For example, consider the dynamics of (6)–(8) at $\varepsilon = 3.8 \times 10^{-4}$ (see Fig. 4). We obtain that there is an attracting set *A* in the phase space, which has a complex structure. To study the oscillations, we construct the Poincare map P: $S \to S$ of a planar region $S \subset \Omega$ into itself. Let S lie on the plain $y = 0.1$ so that the points on S have the coordinates $x \in (0.248, 0.252)$ and $z \in (0.505, 0.511)$. Note that the vector field (6)–(8) is such that, along every trajectory, the y-coordinate increases under crossing S. This means that S is transversal to the vector field. Consider some point $\xi_0 = (x_0, y_0, z_0)$ in section S near the attracting set A. Let $\xi_k = P^{(k)}(\xi_0)$, $k = 1, 2, \ldots$, be the images of ξ_0 obtained using k times the Poincare map P. Our simulations show that the points ξ_k, $k = 1, 2, \ldots$, fill up a set which can be approximated with a segment I_l of some curve l; and there is the one-to-one map ω of I_l onto a segment I_x on OX axis. In our case, $I_x = \{x{:}\ 0.2485 \le x \le 0.2514\}$ (see Fig. 5).○

Let us also plot the one-dimensional map $F = P \circ \omega$ from I_x to I_x. We have shown that F is unimodal and has unstable cycles of periods 2, 4, and so on. Thus, on the attracting set A there are infinitely many unstable periodic orbits with different periods. By the Sharkovsky theorem [16], we have a one-dimensional evidence for the existence of chaotic dynamics in the model (6)–(8).

6. Chaotic multipeak oscillations

The model (6)–(8) also exhibits chaotic dynamics for increasing values of α. Recall that the set of steady states and the two maximal families of periodic solutions of the subsystem (6)–(7) are shown in Fig. 3. For $\alpha = 5.5$ and $\varepsilon = 0.0001$, the model (6)–(8) exhibits regular multipeak oscillations (see Fig. 6a). If the initial point lies near the branch AB consisted of the stable steady states of (6)–(7), then the corresponding point in the phase space slowly moves down along AB until $z = z_B$, where it “jumps” to the surface S_1^s. Thereafter, the point turns several times around S_1^s, while $z < z_1{}^{\max}$, and then “jumps” back to the branch AB. Thus, this is a closed trajectory.

As the value of ε decreases, the oscillations become irregular. Indeed, consider the times $t = t_i$, when the z-coordinate is near z_B and is minimal. We obtain that the distribution of the time series $\{\mathrm{t}_i\}$ on a fixed long enough time interval is irregular (see Fig. 6b–d). In this case, for small enough changes of ε and the initial values of x, y and z, we can obtain different number of the minimal values of $z(t)$ with different distribution of $\{\mathrm{t}_i\}$ over the same time interval.

7. Conclusions

Studying complex dynamics of CO oxidation reaction on the platinum group metals under isothermal conditions, we proposed a simple three-variable kinetic model based on the Langmuir–Hinshelwood mechanism with two addition stages, which are the formation of the subsurface oxygen and its interaction with adsorbed CO. We proposed to describe the chemical effect of the surface modification under oxygen penetration into the subsurface layer as a strong change of the adsorption properties of the catalyst surface. Moreover, this model includes the sharp change of the catalyst activity at the certain values of the surface coverage with oxygen. As a result, this kinetic model takes into account the stepwise dependences of, first, the activation energy of interaction between adsorbed species on the surface coverage by adsorbed oxygen and, second, the constant of oxygen adsorption rate on the concentration of subsurface oxygen.

The processes of formation of the subsurface oxygen and its interaction with the adsorbed CO are slower than the adsorption, desorption, and interaction of adsorbed species. Therefore, the model has one slow variable z, i.e., the concentration of subsurface oxygen. The dynamics of this model is determined by the sets of steady states and periodic solutions of the one-parameter family of two-variable subsystems, which describe the behavior of the concentrations of CO and oxygen adsorbed on the surface for different possible values of the parameter z.

We have shown that, under oxygen excess in the gas phase, our two-variable system has a hysteresis of steady states, and the periodic solutions exist for z in two intervals described above. At one of the boundaries of each interval, the Andronov–Hopf bifurcation occurs; while, at the other boundaries, the periodic solutions degenerate into the saddle loop separatrix. In this case, we found the following two scenarios of chaotic oscillations generation in the three-variable kinetic model: through the cascade of period doubling bifurcations and via the irregular multipeak oscillations. Thus, the dynamics of the CO oxidation reaction can essentially change under some small variation of the catalyst properties that determine the ability for the subsurface oxygen formation.

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