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Modeling the complex dynamics of heterogeneous catalytic reactions with fast, intermediate, and slow variables

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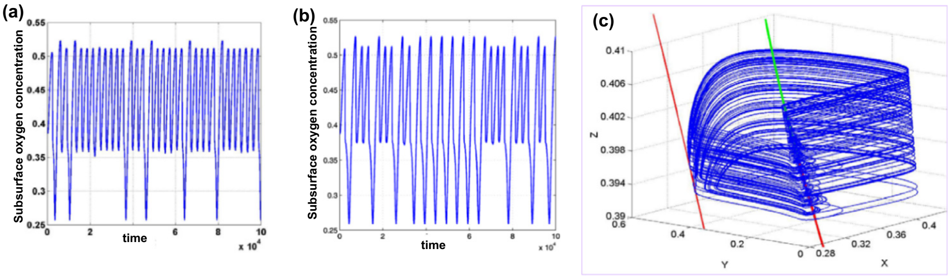
HIGHLIGHTS

- Scenario for complex behavior generation in a nonlinear dynamical system is proposed.
- Three-variable kinetic model with fast, intermediate, and slow variables is studied.
- We assume kinetic parameters to depend on surface coverage by intermediate substances.
- Different types of kinetic multi-peak oscillations are shown for catalytic reaction.
- Numerical simulation of chaotic behavior uses special methods of high accuracy.

GRAPHICAL ABSTRACT

Two-mode *multi-peak oscillations* (a) and (b) with different concentrations of lower peaks and some *chaotic dynamics* (c) in heterogeneous catalytic reaction of hydrogen oxidation.



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ABSTRACT

The paper presents some results of studying different types of the multi-peak oscillations and the chaotic behavior in the low-dimensional dynamical systems with a hierarchy of characteristic times. Under study is a kinetic model which consists of three nonlinear ordinary differential equations with fast, intermediate, and slow variables and illustrates that the influence of adsorbed species on the rate of catalytic reaction may lead to multi-peak oscillations and even to chaotic behavior under isothermal conditions. Such a situation occurs, for example, when the surface heterogeneity of the catalytic sites causes the activation energy of some reaction stage (or stages) to change with the surface coverage by one of the intermediate substances. Numerical simulations are used to demonstrate different types of the multi-peak oscillations and chaos in the kinetic model of hydrogen oxidation on nickel catalyst.

1. Introduction

The discovery of the self-oscillations in the heterogeneous reactions of CO oxidation on Pt catalyst and hydrogen oxidation on metallic Ni and Pt catalysts [1–3] initiated the application of the theory of nonlinear dynamics in catalysis. In spite of a wide variety of oscillating catalytic systems [4], up to now there is no common theoretical explanation of multi-peak oscillations and aperiodic behavior of heterogeneous catalytic reactions.

One of the approaches that serves to theoretical study of the complex dynamics of a heterogeneous catalytic reaction consists in the development of a mathematical model as some system of nonlinear ordinary differential equations to describe the temporal

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changes of the concentrations of the individual intermediates on the catalyst surface. Note that some "additional" processes should be taken into account which can reveal the changes of catalyst properties under reaction conditions. For example, it can be the oxygen diffusion into the subsurface layers of metallic catalyst which causes some surface modification [5,18]. Such systems can have periodic and multi-peak oscillations and even chaotic dynamics. The authors of the article [6] considered the mathematical models in which a feedback in a heterogeneous system was presented by the action of reactants on the catalyst properties. Note that, without taking the feedback relations into account, there are neither self-oscillations nor chaotic dynamics in the low-dimensional models under consideration.

This paper is devoted to studying chaotic behavior in the three-variable dynamical systems with a hierarchy of characteristic times, i.e., with fast, intermediate and slow variables. In particular, we deal with modeling the two-mode multi-peak oscillations with different concentrations of the lower peaks with respect to the total number of peaks in dependence on the system parameters.

2. Mathematical model

Consider the mathematical model of the heterogeneous reaction of hydrogen oxidation on metallic catalysts [10,7]. The model is based upon the mechanism of the heterogeneous reaction of hydrogen oxidation on nickel catalysts:

$$H_2 + 2[\mathrm{Me}] \leftrightarrow 2[\mathrm{H\,Me}], \tag{1}$$

$$O_2 + 2[\mathrm{Me}] \leftrightarrow 2[\mathrm{O\,Me}], \tag{2}$$

$$2[\mathrm{H\,Me}] + [\mathrm{O\,Me}] \rightarrow 3[\mathrm{Me}] + H_2O, \tag{3}$$

$$H_2 + [\mathrm{O\,Me}] \rightarrow [\mathrm{Me}] + H_2O, \tag{4}$$

$$[\mathrm{Me_v}] + [\mathrm{O\,Me}] \leftrightarrow [\mathrm{O\,Me_v}] + [\mathrm{Me}]. \tag{5}$$

Here [Me] denotes a vacant active site on the catalyst surface and $[\mathrm{Me_v}]$ is an atom in the subsurface layer; [H Me], [O Me] and $[\mathrm{O\,Me_v}]$ are hydrogen and oxygen atoms adsorbed on the surface and "dissolved" into the subsurface layer of the catalyst. In addition to the law of existing surfaces the activation energies of the third and fourth reaction steps are assumed to depend linearly upon the oxygen concentrations in the subsurface layer and on the catalyst surface [6,10,15].

Using the approach of quasi-stationary concentrations [8,9], we proved that the original dynamical system can be reduced to the following three-variable kinetic model with respect to the dimensionless concentrations of the reaction intermediates [H Me], [O Me] and $[\mathrm{O\,Me_v}]$:

$$\begin{aligned} \tfrac{dx}{dt} &= k_1(1-x-y)^2 - k_{-1}x^2 - 2k_3(y)\cdot x^2y = P(x,y), \\ \tfrac{dy}{dt} &= k_2(1-x-y)^2 - k_{-2}y^2 - k_4(y,z)\cdot y - k_3(y)\cdot x^2y = Q(x,y,z), \\ \tfrac{dz}{dt} &= \varepsilon[y(1-z) - \alpha z(1-x-y)] = F(x,y,z), \end{aligned} \tag{6}$$

where x and y are the catalyst surface coverages by hydrogen and oxygen adsorbed, while z is the concentration of oxygen dissolved into the subsurface layer, and t is the time. Due to the assumption that the reaction activation energies depend linearly upon the oxygen concentrations, the rate constants of the third and fourth reaction steps are the functions of y and z [10]:

$$k_3(y) = k_{30}\exp(-\mu_3 y), \quad k_4(y,z) = k_{40}\exp(-\mu_4 y + \mu_5 z). \tag{7}$$

Moreover, k_1, k_2, and k_{40} in (6) and (7) are linear functions of the oxygen and hydrogen partial pressures P_{O_2} and P_{H_2} so that $k_1 = k_{10}P_{H_2}$, $k_2 = k_{20}P_{O_2}$, and $k_{40} = K_{40}P_{H_2}$. Here k_{10}, k_{-1}, k_{20}, k_{-2}, k_{30}, K_{40} and $k_{\pm5}$ stand for the reaction rate constants of the mechanism stages (1)–(5), $\varepsilon = k_5$, and $\alpha = k_{-5}/k_5$, while μ_3, μ_4, and μ_5 represent the influence of the reaction conditions onto the catalyst activity, and all parameters are non-negative.

In general form, the kinetic model (6) looks as follows:

$$x' = f(x,y), \quad \mu y' = g(x,y,z), \quad z' = \varepsilon h(x,y,z), \tag{8}$$

where we use the ratio $\mu = k_1/k_2$ and the notation:

$$\begin{aligned} &f(x,y) = P(x,y), \quad h(x,y,z) = y(1-z) - \alpha z(1-x-y), \\ &g(x,y,z) = k_1\left[(1-x-y)^2 - \tfrac{k_{-2}}{k_2}y^2 - \tfrac{k_4(y,z)}{k_2}y - \tfrac{k_3(y)}{k_2}x^2y\right]. \end{aligned}$$

There are two small parameters $\varepsilon \ll 1$ and $\mu \ll 1$ in (8) since the dissolution into the subsurface layer is the rather slow process as compared with the reversible adsorption or the catalytic stages and, moreover, μ is also small if $k_1 \ll k_2$ and y is separated from zero. Hence, we have the kinetic model with a hierarchy of timescales, and the concentrations x, y, and z are identified as intermediate, fast, and slow variables. Such a situation is typical for catalytic reactions and, therefore, it enables us to hope that the developed approach is rather general. For example, a model of the self-oscillating reaction of hydrogen with oxygen on platinum catalysts [15] has the form (8) for the values of the parameters for which it describes the experimental oscillations. Note that some model of the reaction of CO oxidation on PdO/Al_2O_3 catalysts studied in [16] also has the form (8) and describes the multi-peak oscillations of the reaction rate though it takes into account some other feedback mechanism.

In what follows, we show that some relaxation oscillations, multi-peak oscillations, and chaotic attractors can be obtained in the kinetic model (6). Note that the introduction of the feedback mechanism (7) ensures the existence of oscillations in the model (8) for $\varepsilon = 0$ and multi-peak oscillations if $\varepsilon > 0$, while without these dependencies there are no periodic solutions for $\varepsilon = 0$ and no two-dimensional invariant tori when $\varepsilon > 0$. Introduction of some other types of feedback mechanisms in kinetic models can be found in [6] and [14].

3. Geometric description of self-oscillations in dynamical system (8)

Let us give some geometric description of the different types of self-oscillations in the three-variable autonomous system (8) with two small parameters ε and μ. This approach is based upon the examination of global dynamics of the one-parameter family of the two-variable subsystems with intermediate and fast variables:

$$x' = f(x,y), \quad \mu y' = g(x,y,z) \tag{9}$$

with parameter z, $0 < z < 1$. This system is the limit case of system (8) as $\varepsilon \to 0$.

A scheme that allows us to generate the multi-peak oscillations is shown in Fig. 1. The presented scheme for one slow and two fast variables was first proposed by Chumakov, Slin'ko, and Belyaev in [10] for the kinetic models of heterogeneous catalytic reactions. The geometric way of thinking helps us to understand the mechanism of complex dynamics (in particular, the transition from relaxation oscillations to the multi-peak oscillations) observed in different catalytic reactions and explain some unpredictable behavior of the reaction rate:

(a) Relaxation oscillations (see Fig. 1a)

To obtain relaxation oscillations in the (x,y,z) phase space of system (8) we first need some S-shaped curve ABCD that

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