

Scientific Foundations of the Theory of Catalytic Processes and Reactors

M. G. Slin'ko

Karpov Research Institute of Physical Chemistry (Russian State Scientific Center), Moscow, 103064 Russia

Received October 4, 1999

Abstract—The problems of the theory of heterogeneous catalysis are discussed based on mathematical modeling of catalytic reactions, processes, and reactors. The combination of actual and computational experiments are used to develop mathematical models. The role of mathematics and especially qualitative methods for the analysis of nonlinear mathematical models is discussed.

INTRODUCTION

Chemical, petrochemical, and petroleum refining industries are key economic areas. Catalysis forms the basis for the manufacturing of chemical products. In our country, the powerful industry of organic synthesis and production of fertilizers, polymers, detergents, petrochemical and other materials have been created on the basis of catalytic processes in the 1960–1970s. Many problems in the development of new technologies and defense engineering have been solved.

The scientific and technological progress in the chemical industry became possible due to the simultaneous development of theory and practice of catalysis and chemical technology. Two main sources of the foundation of the science of catalytic reactions, processes, and reactors can be distinguished. One is demand in the rapidly developing chemical industry. The other is the spontaneous development of the fundamental sciences of physics, chemistry, physical chemistry, and mathematics, and experimental methods of studying the surface and reactions at the molecular level.

The theory of catalytic reactions, processes, and reactors plays the most important role in industrial catalysis. This theory forms the basis for the construction and design of reactors and represents the fundamental science that relates the catalytic technology to natural and exact sciences and mathematics. The role of this theory increases due to a sharp decrease in the amount of industrially produced materials, aging of capital assets, personnel outflow, and the necessity of creating a competitive chemical industry in the market economy.

1. PROBLEMS OF THEORY

In 1930–1950s, the system for the application scientific achievements in catalysis to production assumed that laboratory-scale studies were followed by the multiple-stage studies on model, semi-pilot, and pilot

scales. Therefore, the creation of a new industrial process took over ten years. Many new processes became obsolete before seeing applications in industry. This created a demand in changing the system and developing scientific foundations of the theory of catalytic reactions, processes, and reactors that would make it possible to reduce the number of stages to pass from the laboratory scale to industry and shorten the period for putting the processes into operation. With this purpose, the following problems were stated:

(a) Creation of the scientific theory and methodology for the development of catalytic processes and reactors that combine the physicochemical basis with the strict accuracy of mathematics;

(b) Understanding of the mechanism of catalytic reactions and processes to establish the maximum possible yields of useful products and develop the procedure for finding optimum conditions;

(c) The optimization of technological schemes to save resources;

(d) The development of scaling methods for applying the results of laboratory-scale studies to industry. The difficulties of scaling are related to different effects of mass, heat, and pulse transfer processes in the reaction apparatus with different sizes;

(e) Safety of industrial processes, reactors, including environmental safety;

(f) The development of mathematical models for controlling catalytic processes and reactions;

(g) Solution of specific industrial problems based on the developed theory;

(h) The development of mathematical algorithms and programs for computational experiments in the field of catalysis.

2. METHODOLOGY OF STUDIES

Earlier, researchers had to study a catalytic process on laboratory, model, semi-pilot, and pilot scales. The

necessity for a gradual increase in the size of a setup was due to our inability to extrapolate the experimental data to unknown conditions without knowledge of actual process regularities. Every increase in the scale had to be checked experimentally and, hence, the conditions for an industrial process had to be found by a time-consuming trial-and-error method.

The methods of similarity theory were widely used for the modeling and scale transfer of various phenomena and structures in engineering. These methods made it possible to solve several practical problems in aerodynamics, heat technology, hydraulic engineering, and other areas. The similarity theory allowed researchers to avoid integrating differential equations and express experimental results in terms of similarity numbers. The results obtained were valid for all similar phenomena. However, the application of the methods of the similarity theory and physical modeling of chemical, including catalytic, processes was unsuccessful. The method of similarity theory did not reveal physicochemical regularities. Moreover, the influence of physical factors on the chemical reaction rate and on the real process depends on the scale of a reactor. Therefore, the similarity method does not allow the results of catalytic experiments to be generalized. Model and real catalytic process are similar when ten or more criteria are numerically equal. However, the simultaneous equality of these criteria is impossible. The influence of the physical factors on the reaction rate cannot be the same in a model installation and an industrial reactor. In practice, we often met the situation when the results obtained in laboratory experiments were irreproducible under industrial conditions, although the experiments were very careful. Serious errors impeded achievement in the designed capacity. This happened because the complete modeling of an industrial catalytic process on an experimental installation was impossible.

In some studies in the United States and Russia, instead of investigating the regularities of a catalytic process to determine optimum conditions for an industrial process, the authors used the multiple-correlation and black box methods to find a functional correlation between the parameters at the inlet and outlet of an industrial reactor. The results obtained did not reflect the objective regularities of the process in the apparatus. They were unable to serve as a basis for scaling and did not meet the requirements to scientific research.

Mathematical modeling of catalytic reactions, processes, and reactors is the only solutions to theoretical and practical problems in industrial catalysis. Catalytic reactions, processes, and reactors were studied by means of mathematical and computational techniques to predict the results of catalytic transformations in reactors with desired structures and sizes and with necessary conditions for the catalytic processes. Complexities of mathematical models for catalytic processes and nonintegrability of differential equations retarded the application of mathematical modeling in catalysis.

Simple models that were manually well solved did not meet the requirements of practice, and complex models that were appropriate for engineers and designers required much calculation.

In physics and engineering, mathematical models and the method of mathematical modeling have long been used with success. In our country, a traditionally high level of mathematical modeling is based on a high level of mathematics, many-years experience in solving important scientific and engineering problems, achievements in computational mathematics (the science of algorithms), and mathematical physics (the science of models).

The problems of atomic, space, aviation, and electronic technologies and other areas were studied by mathematical modeling. Physical phenomena were described by the fundamental conservation laws using the mathematical language in the form of equations forming a mathematical model. This article is a review of the studies devoted to solving the problems of industrial catalysis based on mathematical modeling.

3. MAIN PROPERTIES OF CATALYTIC SYSTEMS

Currently, the chemical industry produces 120000 materials. The conditions for their preparation vary over wide ranges of temperatures and pressures. Processes are carried out in various media and under different hydrodynamic conditions. Despite a great variety of substances and conditions, there are fewer physicochemical and chemical technological processes and their models.

Seemingly, different catalytic processes are often similar in their structures. This forms a basis for isomorphism and helps researchers and engineers to use the methods of catalytic technology and to overcome difficulties related to the diversity of materials. Chemical technological systems have a complicated multi-level structure beginning from the quantum, atomic-molecular, and supramolecular levels to the scale of the apparatus of the catalytic technology. The spatial scale can vary from 10^{-10} to 10 m. The time scale of particular steps is related to the spatial scale and varies from 10^{-5} to 10^8 s. The systems may contain several phases and components. In oil refining and hydrocarbon combustion, the number of components and reactions reaches several hundreds.

Active reaction media are diverse. They possess nonlinear properties and are represented, along with catalytic systems, by multiphase dispersion media, supercritical liquids, melts of polymers, systems with memory, media in which the properties are controlled by surface phenomena, regular and irregular porous media, fluidized beds, ascending transport currents, and others. The temperature in reactors ranges from 20 to 1700 K, and the pressure ranges from 10^{-6} to 3×10^3 atm.

Reactors also differ in the intensity of reactions. However, as indicated above, the number of mathematical models of the steps of catalytic processes are lim-

ited. This allows one to develop the theory of catalytic technology in a clear and compact form. Analysis of the process structure is significant for the development of theory [1, 2]. The structure determines the functional properties of the processes and reactors. The deeper and more detailed the data on the process structure, the more reliable are the research strategies and the structure of a mathematical model. Morphology (the science of structure) of a process and a reactor determines and relates the structural organization of particular parts beginning from the molecular level. The determination of the catalytic process structure forms the basis for analog inference and is the most important stage of investigation. This is defined by many properties: the stoichiometry and reaction mechanism, thermodynamic parameters, the number and properties of phases, the state of the catalyst in the reactor, the method of the organization of the catalyst layer, hydraulic parameters of the motion of the catalyst and reaction mixture, specific features of reactor design, heat exchange, the properties and evolution of the active reaction medium, and other technological parameters.

Catalytic reactors are very diverse and used in many industries. However, the number of mathematical models of catalytic reactors is much smaller. An analogy between different types of reactors exists. First, all structures have spatial and time hierarchy. By representing a reactor as a hierarchical multilevel model and determining the spectrum of the relaxation times of particular steps, we can decompose a complex process into simpler processes, study them using methods specific for these components, and determine cause-and-effect relations between the components. Depending on the purpose of a study, different methods for isolating of scale levels and components of the complex process in the reactor can be applied. Three main levels should be distinguished: the atomic–molecular or microlevel (1–1000 Å), mesolevel (1–1000 μm, and macrolevel (>1000 μm). Additional intermediate scale levels can reasonably be distinguished in practice. For example, the structure of a fixed-bed reactor has five scale levels, the structure of a fermenter has six levels, the structure of a cracking reactor has five levels, and the structure of the block polymerization of vinyl chloride has five levels. The atomic–molecular level is of special importance for solving the problems of industrial catalysis. The processes at the atomic–molecular level determine the selectivity and activity of a catalyst. Therefore, the study of processes in a chemical reactor starts from the atomic–molecular level. Based on detailed experimental data, researchers determine the mechanism of chemical reactions and parameters of the reaction system, calculate the rates of the separate steps of chemical transformations, and determine them as functions of the state and properties of the system. The model of a catalytic process at the atomic–molecular level helps us to understand the process and provides mathematical description necessary for the modeling of a catalytic

process at other levels. This stage of modeling is the most critical and science-intensive.

The representation of a catalytic reactor as the space–time hierarchical structure gives us the following possibilities:

(1) To study a complex catalytic process divided into its components and apply component-specific precision methods. This substantially reduces experimental and theoretical work, makes the sequence of particular mathematical models more complete and reliable, and makes it possible to obtain mathematical models detailing the process to various degrees.

(2) To determine the relationships between component processes and their role in the overall catalytic process inside a reactor and to study the influence of processes of mass, heat, and pulse transfer on the rate of a catalytic transformation.

(3) To compress information and reduce the dimension of models under study when switching from one level to another.

(4) To use knowledge and experience in the modeling of various reactors more completely.

(5) To solve the problem of transition from laboratory to industrial-scale conditions.

(6) To develop mathematical models for the dynamics of catalytic reactions, processes, and reactors and to study them by qualitative methods of mathematical analysis.

(7) To determine the optimal conditions for catalytic reactions, processes, and reactors at all scale levels.

4. ACTUAL AND COMPUTATIONAL EXPERIMENTS

Mathematical modeling based on the optimum ratio of the natural and computational experiments started when the Institute of Catalysis (Siberian Division, Russian Academy of Sciences) in Novosibirsk was founded. This marked a development of a new methodology in solving the problems of industrial catalysis. It combined the problems of searching for new catalysts, chemical kinetics, physics, mathematics, and engineering. This new methodology changed our knowledge and understanding of the catalytic process and the way make inference when studying catalytic processes. This methodology has been developed by Academician A.A. Samarskii, who had a many-year experience in the mathematical modeling of complex physical systems [3]. The combination of actual and computational experiments is actualized through a sequence of cycles where each next cycle brings us to a problem solution. The cycle starts from the preliminary development of a model based on the whole body of prior information on the catalytic process. Then, algorithms and programs are developed to analyze the mathematical model. Based on the results obtained, experimental studies are planned, and a new experiment begins only after this prior work. Every subsequent measurement is per-

formed after the real-time processing of the previous one. This approach implies an enhanced intellectual activity and overcomes the conservatism of empirical study. The labor productivity of a researcher and the quality of experimental results increase due to an optimum combination of actual and computational experiments. Direct measurements reflect only specific facts, but only the mathematical description gives us the complete picture of a process.

The cycles of actual and computational experiments make it possible to create a sequence of mathematical models that describe experimental data with more or less details. The conditions for the applicability of different models in various ranges of model parameters are found, and the parametric sensitivity is studied. Based on the models built, the parameters can be extrapolated to the ranges where an actual experiment is difficult or impossible to perform. The new unique results of computational experiments motivate new actual experiments. Thus, we have a natural combination of an actual experiment, theoretical methods of physics, physical chemistry, and mathematical and computational experiment. The advantages of computers and mathematics are completely revealed only in the combination of the listed areas.

5. MATHEMATICAL BASES

Mathematics in the theory and engineering of catalysis is related to experimental catalysis in the same way as mathematical physics is related to experimental physics. Mathematical methods apply to catalytic systems in several stages:

(1) The development of a preliminary mathematical model based on the idealized simplified understanding of a catalytic process, the choice of variables and parameters of the system, and the transformation of the equation of the mathematical model to a dimensionless form.

(2) The study of this model by qualitative methods and computational methods to plan further experiments.

(3) The development of methods to identify and analyze experimental observations, and solving the problems of process simulation and parameter estimation.

Mathematical problems that appear in the qualitative analysis of the equations of the models are as follows:

(a) Study of the mathematical correctness of the problem: the solution must exist, it must be the only one, and it must be continuously dependent on the initial and boundary conditions;

(b) Determination of the number of stationary solutions, which depend on the parameters, specifically, the conditions for the uniqueness and multiplicity of these solutions;

(c) Study of the stability of stationary solutions;

(d) Bifurcation analysis with the aim of determining bifurcation points and periodical solutions;

(e) Mathematical proof of the limiting transitions in time and parameters of the problem; and

(f) Study of possible model reduction while preserving the main qualitative properties and the model prediction strength.

The superficial clearness of a catalytic process, which was important in the first half of the 20th century, has been gradually losing its heuristic importance in the modern theory of catalysis and technology of catalytic processes. Many parameters are inaccessible for direct measurements and the mathematics extends our capabilities. It now allows us to describe and explain a process at quantum and microscopic scales. The importance of mathematics for research and engineering practice is due to the possibility of penetrating into the structure and dynamics of catalytic reactions, processes, and reactors. The main concepts of the kinetics and dynamics of catalytic reactions are also mathematical concepts. The concepts of the quasistationary approximation, stability, phase transitions, regular and chaotic oscillations of reaction rates, and others are based on mathematics. Therefore, mathematics is a powerful tool for knowledge acquisition rather than simply a means for calculation.

Mathematical models of catalytic systems in the general form are rather sophisticated. Often, they consist of nonlinear systems of differential equations containing both conventional equations and equations with partial derivatives of parabolic, hyperbolic, and other forms. Efficient simulation is only possible if a well-developed qualitative theory of differential equations (mainly, equations with partial derivatives) and high-performance programs for computational experiments exist.

The qualitative theory of differential equations studies the properties of solutions of differential equations without the finding of the solutions. The fundamentals of the qualitative theory of standard differential equations were founded at the end of the XIX century by Poincaré and Lyapunov. However, despite the relative completeness of the classical qualitative theory of ordinary differential equations, early simulation studies in 1960 revealed the absence of a satisfactory theory for the systems with distributed parameters. Only some results were known, which were insufficient for the mathematical modeling of catalytic processes. Therefore, an exigency to study the qualitative theory of evolution equations with partial derivatives appeared.

Studies along these lines have been carried out since 1958 and at the Institute of Mathematics (Siberian Division, Russian Academy of Sciences) in Novosibirsk by Professor T.I. Zelenyak and his disciples. Academician S.L. Sobolev actively supported early studies at the institute. Important results for the theories of ordinary differential equations and equations in partial derivatives and the theory of catalytic processes were

obtained due to a series of studies [4–10]. The time behavior of solutions to the differential equations of mathematical models in general, the existence and number of periodical and stationary solutions, their stability and maximally acceptable deviations, the stabilization of solutions to unsteady problems, the behavior of parabolic systems in the vicinity of unstable solutions, and the determination of special points, including branching points, were studied. The regions of the attraction of stable stationary solutions were described. Convenient stability criteria in the first approximation of stationary solutions of parabolic nonlinear equations of the second order were found. The first steps in the development of optimum control theory with distributed parameters that generalizes the classical principle of maximum introduced by Academician L.S. Pontryagin were made.

The strength of qualitative methods for studying mathematical models is based on the depth of mathematical ideas and their general nature. The bifurcation analysis of the mathematical models of catalytic systems is of both theoretical and practical interest. Bifurcation analysis helps to understand processes deeper than traditional methods. The distinctive feature of bifurcation analysis is the consideration of all possible solutions at all possible parameters. Therefore, the results of the analysis allow us to explain and predict the behavior of catalytic systems.

In the modeling of catalytic reactions at the molecular level, the stochastic approach is also fruitful along with the simulation based on equations (the deterministic approach). Stochastic simulations (the dynamic Monte Carlo method) makes it possible to penetrate into the microlevel, monitor detailed changes in the adsorption layer, and explain the observed phenomena. The comparison of the results of the calculation by the stochastic and deterministic models for the thermal desorption of CO from Ru(001) performed in [11] shows their coincidence with a acceptable accuracy.

6. KINETIC MODEL

The kinetics of a catalytic reaction should be studied in detail to understand the physicochemical basis of the catalytic reaction, to model a catalytic process and a reactor, and determine the conditions for its industrial application. Kinetics forms the basis of the quantitative characteristics of the selectivity and activity of the catalyst.

The kinetic mathematical model includes the mechanism, consisting of elementary steps of the reaction, the rate laws of each elementary step, and kinetic parameters of the steps as functions of temperature and reactant composition on the surface and in the near-surface layer. In addition, depending on the purpose of the description and specific conditions, a kinetic model contains several additional physicochemical assumptions. These are assumption of reversible and equilib-

rium steps, the coverages of surface and near-surface layer with reactants, the stationary or unsteady composition of the surface with respect to the reaction medium, and others. Depending on the approximation, different kinetic models in different ranges of conditions and parameters can correspond to the same mechanism. The knowledge of the behavior of the nonlinear dependences of the reaction rates on variables at the macroscopic level is especially important. The nonlinearity of macroscopic rate laws is due to the participation of more than one species in an elementary act and the complex cooperative interaction of adsorbed atoms and molecules with each other and with the catalyst surface. The nonlinearity of macroscopic rate laws is also due to the phase transitions in the adsorption layer, surface restructuring during the process, catalyst surface nonuniformity, the influence of mass, heat, and pulse transfer processes on the reaction rate due to the delay in the feedback.

The following problems can be solved using the kinetic model:

(a) Choosing the catalyst and comparison of the selectivity and activity of catalysts and their performance under optimum conditions for each catalyst;

(b) The determination of the optimum sizes and structure of catalyst grains and the necessary amount of the catalyst to achieve the specified values of the selectivity of the process and conversion of the starting products;

(c) The determination of the composition of all by-products formed during the process;

(d) The determination of the stability of steady states and parametric sensitivity; that is, the influence of deviations of all parameters on the steady-state regime and the behavior of the reactor under unsteady-state conditions;

(e) The study of the dynamics of the process and deciding if the process should be carried out under unsteady-state conditions;

(f) The study of the influence of mass and heat transfer processes on the chemical reaction rate and the determination of the kinetic region of the process; and

(g) Choosing the type of a reactor and structure of the contact unit that provide the best approximations to the optimum conditions.

Kinetic models for unsteady-state and pseudo-steady-state conditions for the catalytic reaction should be distinguished.

6.1. Kinetic Model for Unsteady-State Conditions

Unsteady-state catalytic processes are those during which the composition of reactants adsorbed on the surface or dissolved in the near-surface catalyst layer changes with time. These are starting regimes, processes in the fluidized-bed and ascending catalyst layers, unsteady-state physical processes coupled with cat-

alytic conversion, catalytic cracking, cleaning of exhaust from internal combustion engines, and other processes and conditions. The development of a kinetic model for unsteady-state conditions is difficult in experiment and theory. It is necessary to measure the concentrations of reactants in the gas phase and determine *in situ* the composition of the surface and near-surface catalyst layers. Mathematical difficulties also appear because the relation between the mechanism and kinetics of the reaction is determined by a system of nonlinear differential equations. The development of the kinetic model for unsteady-state conditions begins with the detailed experimental studies and the simulation of a catalytic transformation at the molecular level [12–14].

The transition to the modeling of catalytic processes at the molecular level during the simulation of an unsteady-state process is necessary for the understanding and provision of the meso- and macroscopic levels with regular dependences of the chemical reaction rates on the composition of the reaction medium, transfer coefficient, and reaction surface properties. To interpret the results of experimental studies and determine the constants of elementary steps and parameters of the model, it is also necessary to develop models of the microlevel.

The most complete mathematical model of a non-uniform adsorbed layer is the distributed model, which takes into account interactions of adsorbed species, their mobility, and a possibility of phase transitions under the action of adsorbed species. The layer of adsorbed species corresponds to the two-dimensional model of the lattice gas, which is a characteristic model of statistical mechanics. Currently, it is widely used in the modeling of elementary processes on the catalyst surface. The energies of the lateral interaction between species localized in different lattice cells are the main parameters of the model. In the case of the chemisorption of simple species, each species occupies one unit cell. The catalytic process consists of a set of elementary steps of adsorption, desorption, and diffusion and an elementary act of reaction, which occur on some set of cells (nodes) of the lattice.

The interatomic and intermolecular interactions of adsorbed species and their state on the catalyst surface are the basis of all elementary steps of the catalytic process. The importance and reliability of the results depend on the correct choice of the potential of the interatomic interaction. The question about the type and nature of interatomic forces between adsorbed species is the focus. Interatomic forces are diverse and usually anisotropic. Adsorbed species do not form structures at low coverages. When the number of adsorbed species and the rate of their surface diffusion increase, the probabilities of their interaction and formation of surface polyatomic structures increase. These structures can be rather stable and they form islands of adsorbed species.

The theory of interatomic interactions on the catalyst surface is far from being complete. Only some specific mechanisms for the formation of interatomic forces are known. Exchange forces act at short distances and result in repulsion. Long-distance dispersion forces always result in attraction between surface species. Therefore, the repulsive interactions between nearest neighbors and attractive interactions between next-nearest neighbors are considered in the modeling. Taking into account a critical effect of interaction parameters on the rates of elementary steps and the fact that it is currently impossible to theoretically determine the true interaction parameters, their apparent values are obtained from the whole set of experimental data on adsorption, desorption, and thermal desorption, including the analysis of TPR spectra. The assumption of the perfect mixing of adsorbed species makes it possible to develop rather simple models for complex reactions. These simplified models nevertheless do take into account lateral interactions in the adsorbed layer. The model of this type provided acceptable mathematical description for various experimental data on the reaction of NO and CO on the Pt(100) surface [14]. This reaction is important from the viewpoint of environmental catalysis because the starting reactants are the toxic components of exhaust from internal combustion engines. The development of efficient afterburning agents for exhaust seems possible only if physicochemical processes at the gas–catalyst interface are well understood and if a kinetic model for the unsteady-state conditions is available. The reaction of NO and CO on the Pt(100) surface has the complex dynamic behavior. The multiplicity of steady states, the explosive nature of the reaction, and the reaction oscillations were observed [14].

A search for analytical macroscopic rate laws based on microscopic mathematical models is difficult. Therefore, the derivation of exact macroscopic rate laws can be abandoned from the knowledge of elementary processes of the molecular level in the further development of mathematical modeling. Instead, the corresponding algorithms and programs for computational experiments can be created that would determine the numerical values of reaction rates.

6.2. Kinetic Model for Pseudo-Steady-State Conditions

Pseudo-steady-state processes with a catalytic activity that changes slowly should be described by a kinetic model with autonomous equations, where the right-hand side does not contain the astronomical time in an explicit form. This means that the rate values of all reactions are unambiguously determined by the concentrations, temperature, and the state of the catalyst at a certain moment. The structure of the model has the form

$$\mathbf{W} = f(\mathbf{k}, \mathbf{a}, \mathbf{c}), \quad (1)$$

$$d\mathbf{a}/dt = f_a(\mathbf{k}_a, \mathbf{a}, \mathbf{c}), \quad (2)$$

where \mathbf{W} is the vector of reaction rates, \mathbf{c} is the vector of the concentrations, \mathbf{a} is the vector of the states of a catalyst, and \mathbf{k} and \mathbf{k}_a are the corresponding matrices of the rate constants with equal numbers of rows and columns.

Equations (1) and (2) can conveniently be represented in the dimensionless form, and the parameter μ , which characterizes the ratio of the relaxation times of the formation of the target product and reactions that change the catalyst activity, can be isolated. The parameter $\mu = \varphi(\mathbf{k}/\mathbf{k}_a)$ (the function implied the ratio between the corresponding elements of the matrices \mathbf{k} and \mathbf{k}_a) for pseudo-steady-state processes is low (usually lower than 0.05). This simplifies the analysis of a kinetic model and the determination of the optimum regimes.

A change in the activity is determined by a change in the properties of the catalyst, its phase and chemical composition, surface, and porous structure. This change is not necessarily a decrease in the catalytic activity. Often, a change in the activity is due to the action of various foreign substances (admixture) rather than main reactants. The shielding of the catalyst surface by adsorbed admixtures and the chemical interaction of active sites with them can change the rate of the catalytic process.

Note that, in several papers devoted to the study of catalytic processes with a variable activity, astronomic time is on the right-hand side of the rate laws in the explicit form. In this case, the kinetic model reflects the kinetic dependences characteristic of the specific setup used in the kinetic study. Therefore, these data cannot be used for the simulation and optimization of chemical reactors.

Complex catalytic reactions accompanied by the fast deactivation can be considered as unsteady-state processes during which both the number and nature of catalytic sites change. As mentioned above, the models of the molecular level that make it possible to predict the behavior of the process in the space and time should be used for the simulation of reactions in which complex unsteady-state processes occur.

6.3. Kinetic Models for Steady-State Conditions

When the knowledge of the reaction rate is only required for steady-state conditions, we may use the steady-state condition for reactants on the catalyst surface. This makes it possible to determine the concentrations of reactants on the surface as functions of the concentrations of reactants and temperature in the volume of the reactor and exclude the concentrations of the surface substances from the equations that describe a change in the concentrations of the reactants in the reactor.

In most cases under industrial conditions, catalytic processes are steady-state. The experimental study of the reaction rate under steady-state conditions in a gradient-free reactor simplifies obtaining information on

the relation between the reaction mechanism and kinetics, which is determined by a system of nonlinear algebraic equations.

The theory of steady-state complex reactions was developed by M.I. Temkin [15]. The theory can be applied to both heterogeneous and homogeneous reactions. According to this theory, elementary reactions that compose a complex reaction are grouped in steps. The resulting chemical equations of the complex reaction are obtained by adding up the chemical equations of steps multiplied by so-called stoichiometric numbers. The latter are selected to exclude intermediate species upon adding equations up. Every set of stoichiometric numbers of steps determines a reaction route.

M.I. Temkin with co-workers studied the kinetics of several most important industrial catalytic processes, such as ammonia synthesis, ethylene epoxidation, methane reforming, carbon monoxide conversion, and others [15]. These works favored the creation of the scientific foundations for the modeling of industrial catalytic processes. Further developments in the theory of steady-state reactions of the organic catalysis on surfaces with induced nonuniformity was presented in [16].

6.4. Research Strategy

It is reasonable to experimentally determine the rates of elementary steps of the whole reaction under the gradient-free conditions. However, an actual experiment only to determine the reaction rate is often insufficient because many parameters are inaccessible for direct measurements. Special experimental studies and computational experiments are necessary. This approach in kinetic studies was used by V.B. Skomorokhov and B.S. Bal'zhinimaev from the early days of the Institute of Catalysis. The studies of ethylene polymerization on the high-activity titanium-magnesium catalysts [17–20] is an example of the use of a procedure that combines the actual and computational experiments.

The kinetics of olefin polymerization on the Ziegler–Natta catalysts has been under study since the 1960s. The polymer chain growth was found to occur via the insertion of an olefin into the active titanium–alkyl bond (on the catalyst surface) and to have the first order with respect to the monomer. This process differs from other heterogeneous catalytic processes in that the polymer formed on the catalyst surface is not removed from it. Therefore, the particle size of the catalyst with the polymer gradually increases. All polymerization steps from the beginning to the end occur in this particle. This feature of the process impedes the study because it prevents other steps from isolation. The only information accessible to researchers during polymerization is the monomer concentration as a function of the time of the experiment (a kinetic curve). As a rule, it has three regions: an increase in the reaction rate, a more or less pronounced region with a constant rate,

and a decrease in the rate. The following main steps of the polymerization capable of affecting the shape of the kinetic curve are also known:

- (1) Diffusion of the monomer to the catalyst surface;
- (2) Formation of active sites during the interaction of the co-catalyst with the transition metal compound; and
- (3) Chain growth.

Of these, only step 3 is reliably known. However, the time function of the reaction rate $w(t)$, that is, the kinetic curve directly accessible to detection depends on the unknown time functions ($C_{as}(t)$ (the concentration of active sites) and $C(t)$ (the concentration of the monomer) determined by the regularities of the first and second steps. Since the kinetic curve reflects the total effect of the steps under consideration, they cannot be separated in one experiment. The iteration procedure of the actual and computational experiments made it possible to build a kinetic model and determine the rate constants of active site formation, their activation energies, and the activation energy of the polymerization for the catalysts $TiCl_4/MgCl_2$ and $TiCl_4/MgCl_2 \cdot nD$, where D is butyl ether [20].

To construct a kinetic model, the reliability analysis becomes an integral part of the problem of identifying and determining the properties of kinetic models. Identifiers are designed to process kinetic experiments described by a system of differential and algebraic equations [21–23]. An identifier contains a set of statistical criteria, and mathematical algorithms for parameter estimation. These identifiers are supplemented by the methods for the control of unstable estimates and by the methods for the empirical analysis of their reliability. These methods must improve the structure of the model and serve for the discrimination of various hypotheses.

The developed methods are now available as computer programs. The accumulated experience in studies using new software makes it possible to recommend them for research groups that study the kinetics of complex one-phase (gas-phase, liquid-phase) catalytic reactions and the reaction kinetics in binary gas–liquid systems where the chemical reaction is accompanied by phase transformations.

The most important stage in the study of a kinetic model is qualitative analysis and, more importantly, the bifurcation analysis of a system of equations of the kinetic model to determine the phase and parametric portraits. The conditions for the existence of spatially nonuniform stationary solutions that characterize dissipative structures and the conditions for the appearance of oscillations and autowave states should also be determined [14, 24, 25].

7. DETERMINATION OF OPTIMUM CONDITIONS

The optimization of catalytic processes should be performed in two stages: (1) theoretical optimization and (2) choosing the reactor type that makes it possible to find the optimum conditions of the processes and control the contact unit. Theoretical optimization is performed on the basis of a kinetic model in the absence of the influence of any factors (transfer processes, hydrodynamics, and others) that decrease the efficiency of the catalytic process. At this stage, the best conditions (in a sense of a chosen optimum criterion) are determined regardless of the possibility of meeting them. The theoretically optimal regime is often determined from the condition of the maximum intensity of the process at a specified yield of the target product or from the requirement of the maximum yield of the target product. For example, the optimum temperature regime, pressure, and the initial composition of a reaction mixture are found in the theoretical optimization of the process. After the calculation of the optimum values of these parameters, the best reactor and technological scheme of the contact unit are chosen, which allow approaching to the theoretically optimum regime in the most suitable way.

Inequality-type constraints on the controlling parameters and the concentration and temperature values are important for the optimization of a catalytic process with a decreasing activity. For example, the optimum temperature regime is determined by the maximal/minimal allowable temperatures during the whole cycle (one-step dehydrogenation of butane) or during its part (synthesis of vinyl acetate or cyanogen chloride trimerization). The constraint on the product quality is important for the selective hydrogenation of acetylene. In the case of a continuous decrease in the catalyst activity, the regime of monotonically increasing temperature until approaching its limit is recommended during the working period. In some cases of the optimal regime, the temperature reaches the maximum acceptable value immediately. Therefore, the principle of maximum introduced by L.S. Pontryagin is used for the formulation of the necessary optimal conditions [26–30].

8. NONLINEAR DYNAMICS

A heterogeneous catalytic system is an open, nonlinear, dissipative, distributed, and multiparametric medium. It exhibits many nonlinear phenomena: the multiplicity of steady states (stable and unstable), hysteresis phenomena, the ignition and extinction of the process, critical phenomena, phase transitions, a high sensitivity of the process to changes in the parameters, oscillations and wave phenomena, chaotic regimes, the formation of dissipative structures, and self-organization phenomena. These specific features have been observed by specialists in the history of catalysis. How-

ever, nonlinear phenomena have received special attention only after the discovery of regular and chaotic oscillations of the reaction rate [31–33]. The discovery of the reaction rate oscillations in the heterogeneous catalysis played the same role in the development of the nonlinear theory of catalytic processes as the general theory of nonlinear oscillations and waves in modern nonlinear physics.

Nonlinear dynamics is the part of dynamics that studies the systems whose processes do not satisfy the superposition principle. The mathematical models of these systems consist of nonlinear equations of mathematical physics. Currently, nonlinear dynamics is an interdisciplinary science that combines physics, mathematics, and many other natural sciences and engineering. The special place of nonlinear dynamics is determined by the general nature of objective laws regardless of the specific nature of a system. Therefore, a unified approach to the study of nonlinear systems was developed, which made it possible to distinguish basic models, general concepts, and definitions and formulate mathematical ideas, approaches, and mathematical apparatus for analysis and simulation.

The nonlinear dynamics of catalytic reactions, processes, and reactors forms the basis for the development of theory and practice of catalysis. The study of the nonlinear dynamics of heterogeneous catalytic reactions, processes, and reactors at all scales is important in the studies and understanding of the mechanism of a catalytic reaction and the methods for its industrial development and determination of the optimum operating conditions. The dynamic properties of reaction systems depend (to a greater extent than the equilibrium and stationary properties) on the nature of interactions between molecules. This requires the development of microscopic models that allow self-consistent description at different scales and for different characteristic times and for the cases when the reactant concentrations undergo substantial changes. Models at the molecular level make it possible to substantiate the structure of equations for macroscopic variables and parameters used in the mathematical modeling of catalytic processes.

The high sensitivity of the catalytic process to nonlinear properties and parameters poses the problem of the physicochemical substantiation of nonlinear functions at the micro- and mesolevels. The development of the functional structure of dynamical equations will allow one to understand the physical nature and nature of nonlinearity of the equations, which will provide the explanation of the nature of nonlinear phenomena from the viewpoint of lateral interactions.

The penetration of the ideas and methods of nonlinear dynamics and modern mathematical methods into the theory of catalytic processes helped to understand the physicochemical essence of catalysis [2, 25, 34–36]. In particular, the development of the nonlinear dynamics of het-

erogeneous catalytic reactions, processes, and reactors made it possible to realize the following ideas:

(1) The mechanism of catalytic processes near and far from the equilibrium of the reaction differs. Linear models are valid only within a narrow range of conditions near equilibrium. The rate constants as functions of the concentration of the reactants and temperature found near the equilibrium can be unsuitable for the description of the reaction far from equilibrium.

(2) Coverages of adsorbed species substantially affect the properties of a catalytic surface. The multiplicity of steady states, their stability, the ordering of adsorbed species, and catalyst surface reconstruction under the influence of adsorbed species also depend on the surface coverage.

(3) Nonlinear phenomena at the atomic–molecular level strongly affect the rate and selectivity of a heterogeneous catalytic reaction. Under dynamic (unsteady-state) conditions, conclusions on the processes on the catalyst surface cannot be drawn only from the data on changes in the concentrations of the reactants in the gas phase.

(4) The instability of steady states is the most important property of heterogeneous catalytic systems. Instability and nonlinearity result in oscillations of the reaction rate, autowaves with different structures, ordered structures, chaotic regimes (chemical turbulence) at all levels of catalytic systems.

9. CATALYTIC REACTORS

In catalytic reactors, chemical transformations occur simultaneously with physical processes of mass and heat transfer (that affect the transformations) under various hydrodynamic conditions. Diversity of catalytic reactors is due to the nature and physical properties of substances participating in the transformations and various combinations of steps. The analysis of the structure of the process and the reactor makes it possible to classify reactors and create a system of mathematical models based on this classification. Too many studies of catalytic reactors have been performed recently to cover all of them in this review. I only briefly consider the main reactor types.

9.1. Fixed-Bed Reactors

The majority of catalytic processes occur in the fixed bed of a catalyst. Two types of mathematical models are possible in this case: quasihomogeneous (based on the continuous-media mechanics) and discrete, in which a body of well-stirred cells with certain linkages between them is considered. The models of the first type are the most abundant and simplest. Sixteen mathematical models of the fixed bed taking into account specific features of mass and heat transfer over the layer and their relations are presented in [37]. Based on these mod-

els, many industrial processes were simulated and high-performance reactors were developed [1, 2, 38–45].

9.2. Reactors with Honeycomb Catalysts

Honeycomb block catalysts with a high porosity (50–80%) and a large hydraulic diameter of channels make it possible to clean exhaust with high linear rates of gas filtration (5–10 m/s) and an insignificant hydraulic resistance of the contact apparatus. However, to create compact catalytic reactors, several specific features inherent in honeycomb catalysts should be taken into account. The theoretical basis of the simulation of these processes are presented in [46]. These reactors are especially useful for processes with short contact times. The theoretical foundations for the simulation of catalytic processes on the honeycomb catalysts were applied for the development of the mathematical model of ammonia oxidation in the production of nitric acid on the oxide catalysts. The reactor for this process was a two-step system where a package of platinoid networks appears first on the way of a gas flow and then a layer of the honeycomb oxide catalyst is placed. Three catalytic reactions on the honeycomb catalyst are taken into account for the development of the model: the oxidation of ammonia to nitrogen monoxide and nitrogen, the decomposition of nitrogen monoxide, and one homogeneous reaction, the interaction of ammonia and nitrogen monoxide. The system of equations for these processes on the honeycomb catalyst is supplemented by the system of equations describing the processes on the surface of platinoid networks. The oxidation of ammonia to nitrogen monoxide on the platinoid networks and the interaction of platinum with oxygen, which was accompanied by the removal of platinum, were also taken into account. Based on the model developed, the influence of the geometric parameters of honeycomb blocks on the efficiency of ammonia oxidation to nitrogen monoxide was examined in detail. The optimum sizes of channels in honeycomb catalysts at different pressures used in the process were determined. The theoretical calculations created the scientific basis for the large-scale use of honeycomb catalysts in the nitrogen industry [47].

9.3 Reactors with Catalysts in the Unsteady State

Periodical changes in the composition and/or temperature of the reaction mixture at the inlet of the catalyst layer result in a change in the state of the catalyst surface and its adjustment to new conditions. The time of a transition process can vary from several seconds to the tens of minutes for different types of catalytic reactions, catalysts and reaction conditions. These properties make it possible to develop new technological solutions that provide purposeful maintenance of the catalyst at the required level of activity [45, 48, 49]. The use of unsteady-state catalyst surface can increase the selectivity of the process, reduce energy expenses, and

provide the stability of the catalytic processes during variations in the initial composition of the reaction mixture.

9.4. Fluidized-Bed Reactors

A fluidized bed possesses several unique properties that provide numerous applications: high thermal conductivity, convective heat transfer to the cooling surface, low internal-diffusion resistance when working with fine grains, efficient use of the reactor volume, a simple structure of large apparatus, ease of introduction and removal of species, and others. A fluidized bed is especially attractive for catalytic processes due to these advantages.

The studies of fluidization performed during the last decade made it clear the essence of the main phenomena occurred in the bed and described satisfactorily the mechanism of heat and mass transfer. However, these studies have not resulted in the development of a sufficiently general and uniform mathematical model that could provide a basis for the reactor design [50–55].

The regularities of particles motion in the fluidized bed play an important role in the analysis of thermal regimes of strongly exothermic process, the analysis of phenomena related to the chemical unsteady state of the catalyst, etc. The models based on the concepts of the diffusion stirring of particles and the circulation nature of particle motion with the exchange between the ascending and descending flows are the most popular. The experiments with heat-labeled particles and their subsequent treatment by the diffusion and circulation models allowed one to conclude that the last model describes transition processes more exactly [55]. The catalyst changes under the influence of variable-composition reaction medium. Physical processes on the surface occur along with chemical steps of reactant interaction. The unsteady state of the catalyst composition with respect to the reaction medium is uniquely manifested in the fluidized bed where particles constantly move in the field of variable concentrations. Each particle continuously changes its catalytic properties and never reaches equilibrium with the reaction medium, although the properties of the catalyst averaged over a sufficiently long time period remain unchanged and the reactor as a whole works in a steady-state regime, its output parameters may differ substantially from the values calculated using steady-state rate laws. The parameters of the catalyst state determining the reaction rate and the laws of their change under the action of a reaction mixture should be found to develop the unsteady-state kinetics of the catalytic process. The mass transfer between compact and noncompact parts of the bed is the rate-limiting step of the catalytic process, which decreases the selectivity and activity. Small-volume packing in the bed makes it possible to control the catalyst circulation, increase the intensity of mass exchange, and substantially enhance both the selectivity and activity of the catalyst. The

results of the studies of organized fluidized bed [52, 53, 55] were used in the development and use of reactors of the dehydrogenation of butane to butylene, the oxidative ammonolysis of propylene and aromatic hydrocarbons, the oxidation of naphthalene to phthalic anhydride, the oxidation of sulfur dioxide to sulfur trioxide, and other reactions.

9.5. Reactors with an Ascending Catalyst Flow [56]

Intensive processes occurring within short contact times are associated with problems of mass and heat exchange. These problems can be largely solved in reactors with an ascending flow consisting of the gas and solid catalysts. The contact of the catalyst grains with the reaction mixture is improved in this reactor. The preliminary treatment of the catalyst allows one to perform the process at an optimum unsteady state of the surface catalyst. The kinetic model for unsteady-state conditions should be used in simulations.

9.6. Reactors for Three-Phase Processes

Processes involving gas, liquid, and solid catalysts are widely used in oil refining, organic synthesis, and in environmental chemistry. Reactors for these processes are characterized by several interacting phases, chemical and phase transformations, and changes of various parameters over the length of the apparatus (temperature, concentration, flow rates, fractions of participating phases, and pressure). Of course, the existence of several interacting phases, interfaces between them both in the free volume of the layer and inside the porous grain, and nonlinear interactions between the phases complicate the general procedure for the development of the mathematical model of a multiphase reactor, although the main principles remain the same.

For-fixed bed reactors, the active surface of the catalyst grain on which the chemical reaction occurs in the liquid or gas phase is used as a first-level mathematical model for the multiphase process. The outcome of this level, is the kinetic model of a chemical reaction that occurs on the wetted catalyst surface and, for the partially immersed grain, nonwetted catalyst surface.

The scale of the porous catalyst grain surrounded by a liquid (for the completely wetted grain) or gas-liquid film (for the incompletely wetted grain) can be considered to be the second level of model building. The observed reaction rate in the liquid and vapor/gas phases and the rate of phase transformation on the catalyst grain are determined by the analysis of the processes at this level. However, this can be done only for extreme cases, for example, for a completely wetted or completely dried grain. The partially wetted catalyst does not allow one to solve this problem in the simple form because the fraction of wet surface may depend on the processes in the free volume of the bed, temperature of the grain, and the reaction rate.

The calculation of the concentration fields, phase temperatures, flow rates, phase fractions, and pressure distribution over the length of the reactor that determine its technological parameters is the result of the analysis of the processes in the catalyst bed (the third level of the model). The boundary conditions for solving these equations are specified for different types of the flow distribution at the inlet of the bed and at the outlet of the reactor and they are determined by the processes on the reactor scale.

The conditions of gas and liquid flow through the granular layer play a decisive role in the mass and heat transfer processes and phase composition. These factors substantially affect the general efficiency of the reactor. The regimes of weak and strong interactions are the main regimes of the gas and liquid flow for the descending concurrent flow. Changes in the viscosity of the liquid, gas density, reactor pressure, grain size, and layer porosity lead to changes in the boundary of the transition from the weak interaction regime to the strong one. Changes in the surface tension, grain wettability, and size of the apparatus also lead to changes in the position of the boundaries of the transition, but they do so in the opposite direction.

A chemical reaction with phase transformations of the liquid-gas type on the catalyst surface results in the formation of a poorly soluble gas, which oversaturates the near-surface liquid layer. A new phase is nucleated in potentially active sites when the critical oversaturation value is achieved on this surface. These nuclei give rise to the growth of bubbles. The growth occurs due to both the diffusion of the formed gaseous reaction products into the bubble and evaporation of the components of the liquid phase. Several parameters can barely be measured in the experimental study of catalytic processes involving the gas, liquid, and solid catalysts. Therefore, a combination of actual and computational experiments is especially helpful for reactors of this type. The general mathematical model of the reactor is cumbersome and complicated and, hence, specific features and details are very important for the simplification of the model. The theoretical problems of mathematical modeling and simulation of the processes of the liquid-phase oxidation of sulfur dioxide to sulfuric acid, hydrogenation of trinitrotoluene to triaminotoluene, and the decomposition of hydrogen peroxide and hydrazine were reported in [57–62].

CONCLUSION

The works reviewed here were performed at the Institute of Catalysis and the Institute of Mathematics of the Siberian Division of the Russian Academy of Sciences. They made the most important contribution to founding and developing the new scientific direction of the theory of catalysis in our country—the mathematical modeling of catalytic reactions, processes, and reactors. This direction formed scientific bases for the scaling transition from the laboratory to industrial stud-

ies, as well as for stable and safe work of the reactors under the optimum industrial conditions. Mathematical modeling made it possible to introduce into the industry many large-scale contact units for the processes of partial oxidation, oxidative ammonolysis of hydrocarbons and aromatic compounds, oxidative chlorination, dehydrogenation, and hydrogenation, ammonia synthesis, sulfur dioxide oxidation, and others.

REFERENCES

- Slin'ko, M.G., *Modelirovanie khimicheskikh reaktorov* (Modeling of Chemical Reactors), Novosibirsk: Nauka, 1968.
- Slin'ko, M.G., *Plenarnye lektsii konferentsii po khimicheskim reaktoram Khimreaktor-1–Khimreaktor-13* (Plenary Lectures of the Conferences on Chemical Reactors ChemReactor-1–ChemReactor-13), Novosibirsk: Institute of Catalysis, 1996.
- Samarskii, A.A., *Vestn. Akad. Nauk SSSR*, 1979, p. 38.
- Zelyanyak, T.I., Rudenko, E.A., Ivanov, E.A., and Belonosov, V.S., *Modelirovanie khimicheskikh protsessov i reaktorov* (Modeling of Chemical Processes and Reactors), Novosibirsk: Siberian Division, USSR Acad. of Sciences, 1972, vol. 4, p. 5.
- Zelenyak, T.I. and Slin'ko, M.G., *Kinet. Katal.*, 1977, vol. 18, no. 5, p. 1235.
- Zelenyak, T.I. and Slin'ko, M.G., *Kinet. Katal.*, 1977, vol. 18, no. 6, p. 1548.
- Slin'ko, M.G., Zelenyak, T.I., Akramov, T.A., et al., *Matem. Model.*, 1997, vol. 9, no. 12, p. 87.
- Zelenyak, T.I., *Matem. Sb.*, 1977, no. 3, p. 480.
- Zelenyak, T.I., *Dinamika reaktorov* (Dynamics in Reactors), Novosibirsk: Nauka, 1984, p. 83.
- Zelenyak, T.I., Beskov, V.S., and Slin'ko, M.G., *Kinet. Katal.*, 1966, vol. 7, no. 5, p. 865.
- Makeev, A.G. and Semendyaeva, N.L., *Matem. Model.*, 1995, no. 7, p. 29.
- Elenin, G.G. and Slin'ko, M.G., *Matematicheskoe modelirovanie yavlenii na poverkhnosti* (Mathematical Modeling of Surface Phenomena), Moscow: Znanie, 1988, no. 8.
- Slin'ko, M.G., *Khim. Prom-st'*, 1993, nos. 1–2, p. 1.
- Samarskii, A.A. and Slin'ko, M.G., *Izv. Akad. Nauk, Ser. Khim.*, 1998, no. 10, p. 1895.
- Temkin, M.I., *Adv. Catal.*, 1979, vol. 28, p. 173.
- Murzin, D.Yu., *Doctoral (Chem.) Dissertation*, Moscow: Karpov Research Inst. of Phys. Chem., 1999.
- Skomorokhov, V.B., Zakharov, V.A., Kirillov, V.A., and Sergeev, S.A., *Kinet. Katal.*, 1994, vol. 35, no. 3, p. 464.
- Skomorokhov, V.B., Zakharov, V.A., and Kirillov, V.A., *Vysokomol. Soedin. A*, 1993, vol. 35, no. 7, p. 777.
- Skomorokhov, V.B., Zakharov, V.A., and Kirillov, V.A., *Macromol. Chem. Phys.*, 1996, vol. 197, no. 5, p. 1615.
- Skomorokhov, V.B., Zakharov, V.A., and Kirillov, V.A., *Vysokomol. Soedin. A*, 1998, vol. 39, no. 5, p. 757.
- Ermakova, A., *Matematicheskoe modelirovanie kataliticheskikh reaktorov* (Mathematical Modeling of Chemical Reactors), Novosibirsk: Nauka, 1989, p. 120.
- Ermakova, A., Gudkov, A.V., Anikeev, V.I., and Bobrin, A.S., *Teor. Osn. Khim. Tekhnol.*, 1995, no. 1, p. 1.
- Ermakova, A., Gudkov, A.V., and Anikeev, V.I., *Kinet. Katal.*, 1997, vol. 38, no. 2, p. 309.
- Bykov, V.I., *Modelirovanie kriticheskikh yavlenii v khimicheskoi kinetike* (Modeling of Critical Phenomena in Chemical Kinetics), Moscow: Nauka, 1988.
- Slin'ko, M.G., *Khim. Prom-st'*, 1996, no. 8, p. 3.
- Slin'ko, M.G., *Kinet. Katal.*, 1969, vol. 10, no. 5, p. 957.
- Yablonskii, G.S. and Slin'ko, M.G., *Teor. Osn. Khim. Tekhnol.*, 1973, vol. 7, no. 5, p. 698, *Teor. Osn. Khim. Tekhnol.*, 1974, vol. 8, no. 1, p. 30.
- Bykov, V.I. and Fedotov, A.V., *Teor. Osn. Khim. Tekhnol.*, 1974, vol. 8, no. 3, p. 378.
- Bykov, V.I. and Fedotov, A.V., *Optimizatsiya reaktorov s padayushchei aktivnost'yu katalizatora* (Optimization of Reactors with a Decreasing Catalyst Activity), Novosibirsk: Inst. of Catalysis, 1983.
- Fedotov, A.V., Volin, Yu.M., Ostrovskii, G.M., and Slin'ko, M.G., *Teor. Osn. Khim. Tekhnol.*, 1968, vol. 2, no. 1, p. 3.
- Wicke, E., Bensch, H., and Feguth, P., *ACS Symp. Ser.*, 1972, vol. 109, p. 615.
- Belyaev, V.D., Slin'ko, M.M., Timoshenko, V.I., and Slin'ko, M.G., *Kinet. Katal.*, 1973, vol. 14, no. 4, p. 810.
- Slinko, M.M. and Jaeger, N.L., *Oscillating Heterogeneous Catalytic Systems*, *Stud. Surf. Sci. Catal.*, 1994, vol. 86.
- Slin'ko, M.G., *Khim. Prom-st'*, 1992, no. 10, p. 574.
- Slin'ko, M.G., *Teor. Osn. Khim. Tekhnol.*, 1998, vol. 32, no. 4, p. 433.
- Slin'ko, M.G., *Teor. Osn. Khim. Tekhnol.*, 1999, vol. 33, no. 4, p. 380.
- Slin'ko, M.G., Dil'man, V.V., Markeev, B.M., and Kronberg, A.E., *Khim. Prom-st'*, 1980, no. 11, p. 22.
- Malinovskaya, O.A., Beskov, V.S., and Slin'ko, M.G., *Modelirovanie kataliticheskogo protsessa na poristykh zernakh* (Modeling of a Catalytic Process on the Porous Grains), Novosibirsk: Nauka, 1975.
- Badatov, E.V., Slin'ko, M.G., and Nakoryakov, V.E., *Teor. Osn. Khim. Tekhnol.*, 1970, vol. 4, no. 6, p. 868.
- Kirillov, V.A. and Slin'ko, M.G., *Modelirovanie khimicheskikh protsessov i reaktorov* (Modeling of Chemical Processes and Reactors), Novosibirsk: Inst of Catalysis, 1972, vol. 3, p. 62.
- Matros, Yu.S., Noskov, A.S., and Chumachenko, V.A., *Kataliticheskoe obezvrezhivanie otkhodyashchikh gazov promyshlennykh proizvodstv* (Catalytic Cleaning of Exhaust Gases from Industrial Processes), Novosibirsk: Nauka, 1991.
- Ostapenko, V.A. and Slin'ko, M.G., *Aerodinamika khimicheskikh reaktorov* (Aerodynamics of Chemical Reactors), Novosibirsk: Inst. of Catalysis, 1976, p. 5.
- Slin'ko, M.G. and Beskov, V.S., *Khim. Prom-st'*, 1979, no. 4, p. 34.
- Noskov, A.S. and Chumachenko, V.A., *Khim. Interes. Ust. Razv.*, 1994, vol. 2, nos. 2–3, p. 623.
- Noskov, A.S., *Fiz. Goreniya Vzryva*, 1997, no. 3, p. 49.
- Noskov, A.S. and Zagoruiko, A.N., *Blochnye nositeli i katalizatory sotovoi struktury. Trudy mezhdunar. semi-*

- nara (Monolithic Honeycomb Supports and Catalysts: Proc. of the Int. Seminar, Novosibirsk: Inst. of Catalysis, 1995, part 1, p. 57.
47. Sadykov, V.A., Brushtein, E.A., and Telyatnikova, T.V., *Khim. Prom-st'*, 1997, no. 12, p. 819.
 48. Noskov, A.S., Bobrova, L.N., and Borisova, E.S., *Catal. Today*, 1997, vol. 38, p. 97.
 49. Zagoruiko, A.N., Kostenko, O.V., and Noskov, A.S., *Chem. Eng. Sci.*, 1996, vol. 51, no. 11, p. 2989.
 50. Slin'ko, M.G. and Sheplev, V.S., *Kinet. Katal.*, 1970, vol. 11, no. 2, p. 531.
 51. Sheplev, V.S. and Slin'ko, M.G., *Modelirovanie khimicheskikh protsessov i reaktorov* (Modeling of Chemical Processes and Reactors), Novosibirsk: Inst. of Catalysis, 1971, vol. 2, p. 5.
 52. Slin'ko, M.G., Pokrovskaya, S.A., and Sheplev, V.S., *Dokl. Akad. Nauk SSSR*, 1975, vol. 221, no. 1, p. 157.
 53. Pokrovskaya, S.A., Sheplev, V.S., and Slin'ko, M.G., *Dokl. Akad. Nauk SSSR*, 1979, vol. 224, no. 3, p. 669.
 54. Kernerman, V.A., Kuznetsov, Yu.I., Oigenblik, A.A., and Slin'ko, M.G., *Khim. Prom-st'*, 1979, no. 11, p. 22.
 55. Sheplev, V.S. and Meshcheryakov, V.D., *Matematicheskoe modelirovanie khimicheskikh reaktorov* (Mathematical Modeling of Chemical Reactors), Novosibirsk: Nauka, 1984, p. 41.
 56. Doronin, V.P., Sheplev, V.S., Pokrovskaya, S.A., and Slin'ko, M.G., *Dokl. Akad. Nauk SSSR*, 1977, vol. 234, no. 4, p. 880.
 57. Stegasov, A.N. and Kirillov, V.A., *Teor. Osn. Khim. Tekhnol.*, 1993, vol. 27, no. 3, p. 340.
 58. Kirillov, V.A. and Stegasov, A.N., *Teor. Osn. Khim. Tekhnol.*, 1993, vol. 27, no. 3, p. 241.
 59. Kirillov, V.A., Kuz'min, V.A., and Kuzin, N.A., *Teor. Osn. Khim. Tekhnol.*, 1993, vol. 27, no. 5, p. 508.
 60. Kirillov, V.A. and Stegasov, A.N., *Khim. Prom-st'*, 1994, no. 3, p. 175.
 61. Kirillov, V.A., Kuzin, N.A., Gavrilin, V.N., and Kuz'min, V.A., *Kinet. Katal.*, 1995, vol. 36, no. 5, p. 674.
 62. Kirillov, V.A., *Reaktory s uchastiem gaza, zhidkosti i tverdogo nepodvizhnogo katalizatora* (Reactors with Gas, Liquid, and a Solid Fixed-Bed Catalyst), Novosibirsk: Nauka, 1997.