MODELING OF STEADY STATES MULTIPLICITY IN CATALYTIC REACTIONS

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ABSTRACT

This review discuss the modern approaches for studies of critical phenomena of multiplicity steady states (MSS) type in catalytic reactions kinetics. The analytical and numerical methods of the analysis of MSS, number and coordinates of internal and boundary steady states (SS), stability of SS, establishment of linear and nonlinear conservation laws are considered. The classes of mechanims describing MSS in form of S-shape histeresises, self-crossing, breakdown, izola and mushroom on kinetic dependences are carried out. The main result of this review is the development of mathematical methods for research of MSS and various forms of its appearing, number and coordinates of SS in kinetics of catalytic reactions and also computerisation of these studies by development of the appropriate softwares.

Annotation on review
«Modeling of steady states multiplicity in catalytic reactions»

Nowadays the problem of investigation of critical phenomena like multiplicity of steady states (MSS) attracts attention of chemists and mathematicians. In this review the investigation and modeling of catalytic reactions with MSS and different forms of its realization took a great part. This investigation demands special analytic and numerical methods, the implementation of which is impossible without modern computer techniques. The development of mathematical modeling methods in kinetics of catalytic processes is one of promising and still developing directions. Such notions as number and stability of steady states, bifurcation etc. are widely used today in the investigation of catalytic reactions. Therefore, the development of mathematical methods in chemistry, or «mathematical chemistry» became natural and reflects a general tendency of expanding exact sciences to various fields. This is confirmed by great research in this direction, by many publications and reports in journals and at conferences.

The aim of the review is the analysis of existing approaches and developing mathematical methods and computer programs of MSS type critical phenomena in catalytic reactions kinetics, their application in studing kinetic dependencies for concrete reactions. The review consists of 7 chapters and the appendix. In the first chapter the basic stages of MSS investigation for catalytic reactions are described. In particular, the first stage was a period of collecting experimental data about MSS existence in concrete heterogeneous catalytic reactions. Further these phenomena were described by means of heat transfer and diffusion effects. Other factors were used also for this purpose, such as changing catalyst surface structure or enlarging chain and homogeneous/heterogeneous character of reaction proceeding. Discovering MSS for some reactions in a pure kinetic region became a starting point for developing the third stage, based on the description of a critical phenomena by model mechanisms, such as Langmuir-Hinshelwood mechanism. The fourth stage is a modern period of the investigation of analytic methods and mathematical models which permit to describe complex kinetic behaviour of catalytic reactions in MSS region. The results achieved in this direction by a number of research groups and by the authors constitutes a main topic of this review.

In the second chapter the main approaches described in publications on MSS investigation in model and real catalytic reactions are analyzed. In particular: 1) the classes of mechanisms without MSS are collected and characterized (linear schemes; schemes without interaction of different intermediates; complex balanced systems; «quasilinear» schemes); 2) the necessary condition for the MSS existence is established - the presence of stages of different intermediates interaction; 3) the sufficient conditions for the MSS are formulated for particular classes of mechanisms; 4) it is shown that the most common type of MSS realization is a S-shape hysteresis, characterized by three internal steady states, two of which are stable, and one is unstable; 5) a criterion is constructed, which permits via stoichiometry of a stage scheme in a concrete reaction to decide whether it is possible to use this reaction for describing MSS.

In the third chapter mathematical methods of MSS investigation are developed and the criteria of MSS and singular points degeneration are stated and proved. The criteria are formulated in terms of stochiometry for a general case of a one-route stage scheme of catalytic reaction. On the base of these criteria for a class of catalytic reactions, characterized by homogeneous schemes, it is found that they could be characterized not only by S-shape hysteresis, but also by self-crossing kinetic dependencies. The suggested methods simplify the MSS analysis by means of simple analytical calculations. In addition, these methods are easy for computer implementation, helping their usage for the multi-stage catalytic reactions.

In the fourth chapter the estimates of the number of internal steady states for various classes of reaction stage schemes are given, and procedures for finding the number and coordinates of boundary steady states are described. Using the methods, given in this chapter, simplifies significantly the determination of an amount and coordinates of all possible steady states for catalytic reactions, characterized by various complex mechanisms.

In a fifth chapter various forms of MSS realization (self-crossing, breakdown, isola and mushroom) are analyzed and new results connecting these forms with the stochiometry of reactions stage scheme, are established. The stochiometric conditions for such kinetic dependencies are found and the examples of two-stage schemes, characterized by these dependencies, are given. It is shown that kinetic curves of self-crossing, isolated and mushroom forms could be described by simple nonlinear two- and three-stage schemes. These forms are transformed one into another after changing

reaction conditions. In the same chapter the notion of a full portrait is given, which permits to do a deeper the check of correctness of the stage scheme for the reaction by means of determining whether such scheme has or has no positive or negative S-shape hysteresis. Thus, in this chapter the existing methods of MSS investigation are systematized and new methods are developed. The main attention was given to the investigatigation analytic approaches, which allow, on the base of the analysis of a stochiometric matrix of reactions stage schemes, the determination possible forms of MSS and to estimate the values of kinetic parameters at which such MSS forms are realized for concrete reactions.

In the sixth chapter the existing approaches and new methods of the analysis of linear and non-linear conservation laws (CL) in kinetics of catalytic reactions are described. Under general assumptions the method of finding stochiometric and kinetic linear CL is developed. Concrete examples illustrate the approaches. New information on the existence of nonlinear CL for some particular classes of stage schemes of catalytic reactions is given. The obtained CL permit to decrease the dimension of the system of differential equations, describing the dynamics of catalytic reactions, and to simplify the qualitative and numeric analysis of such systems, which is especially important for reactions, characterized by critical phenomena.

The seventh chapter is devoted to the description of algorithms and computer programs of MSS analysis, calculation of the number and coordinates of boundary steady states, parametric analysis of internal steady states, their stability and the number and forms of linear conservation laws. Hence, algorithms and methods described in this chapter permit to evaluate the number, coordinates and determine the stability of all possible steady states, and also to find the region of kinetic parameters, at which MSS is realized for one-route catalytic reactions. Some examples are given, illustrating the effectiveness of these methods for the investigation of concrete reaction mechanisms.

The appendix contains the texts of five computer programs: MSS analysis, Sturma sequence construction, linear conservation laws finding, the number and coordinates of boundary steady states determining, the stoichiometric conditions of stability of steady states. The programs were implemented using the Maple V system of mathematical programming and the Qbasic language. These programs help on the base of the given stage scheme to simplify the analysis of the possibility of MSS arising or to prove the

MSS absence, to determine the region of kinetic parameters at which such multiplicity is realized.

The review contains many examples illustrating the effectiveness of described mathematical methods of investigation of MSS and various forms of MSS realization for different classes of stage schemes of catalytic reactions, as well as for concrete reactions of carbon monoxide oxidation and the interaction between carbon monoxide and nitride on platinum metals.

Thus, the main result of this review is the development of the mathematical methods of MSS investigation and forms of its realization, estimation of number and evaluation of coordinates of steady states in catalytic reaction kinetics, as well as in automation of these investigations by means of developing corresponding computer programs. Using the methods and programs shows their effectiveness for MSS investigation and modeling in concrete reactions. The methods and programs given in the review can be also adopted and used for the investigation of a wider class of catalytic reactions.

The review will be useful for persons who are involved in «mathematical chemistry» and for readers interested in problems of mathematical modeling of critical phenomena in various processes.

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