

Mathematical Modeling of Mesostructures on Modified Monocrystal Surface

GEORGII G. YELENIN, DMITRII S. NADOBENKO, MARIA G. YELENINA
 Department of Computational Mathematics and Cybernetics
 Lomonosov Moscow State University
 Leninskie gory, 119899, Moscow
 RUSSIA

Abstract: - The paper contains results of computational experiments with mathematical models of the catalytic carbon monoxide oxidation (CO+O₂)/Pt(111) and nitrogen monoxide reduction (NO+CO)/Pt(100) on modified monocrystal surfaces. The models are based on many-component systems of nonlinear differential equations and take into account lateral interactions among adsorbed atoms and molecules and surface imperfections. It has been shown that the spatiotemporal structures arise either spontaneously or due to the surface defects in the appropriate regions of the control parameters. The main attention is paid to the chemical turbulence and Turing's dissipative structures formation. The present results show the way how one can modify the catalyst to keep the system on the branch of high reactivity.

Key-Words: - Symmetry breaking, self-organization phenomena, catalysis, chemical turbulence, Turing's structure.

1 Introduction

The investigation of self-organization phenomena in non-ideal open systems is a very important problem of fundamental science and up-to-date industrial applications. Indeed, on the one hand it is not so easy to give the theoretical description of the condense state of non-ideal systems in wide range of spatial and temporal intervals. On the other hand the creation of free defects materials and materials with special organized spatial micro- and mesostructures opens new page in contemporary technologies.

The main goal of the paper is to show some results of computational experiments with mathematical models of the catalytic oxidation of carbon monoxide (CO) and the catalytic reduction of nitrogen monoxide (NO) and CO on the modified monocrystal surfaces of the noble metals.

Much experimental and theoretical effort has been devoted to elucidate the dynamical properties of the catalytic CO oxidation on the platinum metal surfaces [1]. Nevertheless, only part of the actual physical surface processes is really understood. The reason being that the elementary steps of the surface reactions are influenced by specific microscopic and mesoscopic "details" which are not very well known. In the paper we concentrate attention on the key "details" such as surface defects and the lateral interactions among chemisorbed atoms and molecules. The mathematical models and computational experiments give a good possibility to investigate the role of the non-ideality of the adsorbed layer and the surface imperfections in symmetry-breaking processes.

2 Problem Formulation

We consider the catalyst surface as the rectangular compartment $\Omega(I, J)$ of $2D$ lattice. A node of the lattice is a center of adsorption. The following nonlinear ordinary

differential equations form the basis of the class of the mathematical models of the systems under consideration.

$$\frac{dU_m}{dt} = F(U_m, P(t)) + \sum_{k \in O_1(m) \cap O_2(m)} W(U_k, U_m) - W(U_m, U_k)$$

$$U_m(t_0) = U_{m,0}, m \in \Omega(I, J)$$

where $U_m(t) = (u_m^1(t), \dots, u_m^s(t))$ is the vector of the coverage of catalyst center m ($m = 1, \dots, IJ$, $1 \ll IJ$) with adsorbed atoms and molecules, $u_m^i(t)$ is the coverage of center m with adsorbed particle of type i ($i = 1, \dots, s$), $U_{m,0}$ is the vector of the initial state of the system, $O_k(m)$ is the set of k -neighbors of the node m on the lattice, $F(U_m, P(t)) = (f^1, \dots, f^s)$ is the vector of the reaction rates at the center m , $W(U_k, U_m) = (w_{k,m}^1, \dots, w_{k,m}^s)$ is the vector of the mass flows between couple of the centers k and m , $P(t)$ is the vector of control parameters such as partial pressures in gas phase and catalyst temperature. The functions $F(U_m, P(t))$ and $W(U_k, U_m)$ depend on the mechanism of the reaction under consideration and the approximation of description of condense adsorbed layer state. Local surface defects are represented by the surface fragments $\omega_p(i, j, l_1, l_2)$, $p = 1, \dots$ with size l_1, l_2 , surrounding the center of heterogeneity with coordinates i, j in which the parameters of the model differ from the parameters of the rest surface.

To carry out the computational experiments the special software has been created. The computer program PROMETHEUS is used for the modeling of evolution of the reaction-diffusion type systems [2]. The code PATH is intended for bifurcation analysis of solutions of nonlinear equations (steady states) and boundary value problems for nonlinear ordinary differential equations (self-oscillations, auto waves, Turing's structures) [3].

The main question is “How does local surface defect influent on the reactivity of the system under investigation?”

Running forward let us announce the main results. In the case of (CO+O₂)/Pt(111) system local defects may assist the nucleation of new non-equilibrium state with low or high reaction rate. Under appropriate conditions the group of the same defects can stabilize the metastable state of high reactivity due to the pinning-effect. In the case of (NO+CO)/Pt(100) system the inhomogeneous of catalyst surface can induce the regime of chemical turbulence which gives the high reaction rates or may stimulate the non-equilibrium transition from self-oscillations of reaction rates to steady state dissipative Turing’s structures.

The theoretical predictions and the results of the laboratory experiments [4] are in a complete qualitative agreement (with the exception of the transition “self-oscillations-Turing’s structures” which is not yet observed in laboratory experiment as far as we know).

2.1 CO-oxidation on modified Pt(111) surface

The results of detailed experimental analysis of the system (CO+O₂)/Pt(111) were published in [4]. The existence of hysteresis of the reaction rate, the branches of low and high reactivity, the regions of assisted nucleation of CO and oxygen islands, the pinning-effect in vicinity of the point of equistability was shown. The mesoscopic nature of hysteresis was also investigated with the help of the photoelectron emission microscopy and clear shown, for example, that the sharp transition from the branch of high reactivity to the branch of low reactivity was the result of assisted nucleation and growth of CO islands.

To give the theoretical explanation of the experimental results the mesoscopic mathematical model of the reaction on modified catalyst surface has been developed. The model belongs to the above mentioned class of lattice models with $s = 2$,

$$\begin{aligned} f_m^1 &= k_1^+ P_{co} (1 - u_m^1 - u_m^2) - k_1^- u_m^1 - k_3^+ u_m^1 u_m^2, \\ f_m^2 &= k_2^+ P_{o_2} (1 - u_m^1 - u_m^2)^2 - k_2^- (u_m^2)^2 - k_3^+ u_m^1 u_m^2, \\ w_{k,m}^1 &= k_4 u_k^1 (1 - u_m^1 - u_m^2), w_{k,m}^2 = k_5 u_k^2 (1 - u_m^1 - u_m^2), \\ k_d^{+,-} &= K_d^{+,-} \exp(-\beta E_d^{+,-}), E_d^{+,-} = E_{d,0}^{+,-} + \varepsilon_{d,1}^{+,-} u_m^1 + \varepsilon_{d,2}^{+,-} u_m^2, \\ \beta &= (RT)^{-1}, \end{aligned}$$

where u_m^1, u_m^2 are surface covers of the center m with CO molecules and oxygen atoms, k_4, k_5 are the diffusion coefficients of CO and oxygen, P_{co}, P_{o_2} are CO and oxygen partial pressures, T is the catalyst temperature.

Two types of defects are distinguished. An O-type defect is active in oxygen island formation and CO-type defect induces nucleation of CO-island. The defect may be intrinsic or artificial.

2.2 NO-reduction on modified Pt(100) surface

The simplest mathematical model of (NO+CO)/Pt(100) system belongs the same class of lattice model with $s = 3$ and [5]

$$\begin{aligned} f_m^1 &= k_1^+ P_{co} (1 - u_m^1 - u_m^2) - k_1^- u_m^1 - k_5^+ u_m^1 u_m^3, \\ f_m^2 &= k_2^+ P_{no} (1 - u_m^1 - u_m^2) - k_2^- u_m^2 - k_3^+ u_m^1 u_m^*, \\ f_m^3 &= k_3^+ u_m^1 u_m^* - k_5^+ u_m^1 u_m^3, \\ w_{k,m}^1 &= k_6 u_k^1 (1 - u_m^1 - u_m^2), w_{k,m}^2 = k_7 u_k^2 (1 - u_m^1 - u_m^2), \end{aligned}$$

where u_m^1, u_m^2, u_m^3 are surface covers of the center m with CO molecules, NO molecules and oxygen atoms, k_6, k_7 are the diffusion coefficients of CO and NO, P_{co}, P_{o_2} are CO and NO partial pressures. It is assumed that on the local surface defects the rate of NO dissociation is higher.

3 The results of computational experiments

The results of computational experiments concerning evolution of the systems under investigation have been arranged as the computer movies.

3.1 (CO+O₂)/Pt(111) system

The results of bifurcation analysis show the existence of the region of bistability in the control parameters space (P_{co}, P_{o_2}, T) . The region of bistability contains regions of assisted nucleation of the states with low and high reactivity (CO-state and O-state). The mathematical model of the reaction gives a possibility to investigate the mesoscopic nature of hysteresis of reaction rate, the nucleation of the stable nonequilibrium states and the stabilization of metastable states.

3.1.1 Assisted nucleation

The computational experiments show that a local surface defect may be a center of assisted nucleation of new stable non-equilibrium state. Remark that not any defect can initiate the phase transition. Only “well-off” defect produces growing nuclei of new stable state of the same type. The boundary movement of growing island of new state looks like a diffusion-reaction wave of phase transition. The wave spreads through a metastable state leaving new stable state behind. The induction time is required for the formation of the phase transition wave in a neighborhood of a “well-off” defect. The value of induction time depends on control parameters, type and size of defect and can appear great. “Insolvent” defect creates a stable stationary gem with limited size and can not initiate wave of phase transition. The computer movies show the peculiarities of the phase transition “metastable stable – stable state” initiated by local surface defects.

3.1.2 Pinning-effect

The local surface defect may pin up the auto wave of the phase transition. As a result the group of a certain type defects for example O-type can stabilize the metastable O-state in the case of subcritical distances among them. The computer movies demonstrate the evolution of the system in the cases of subcritical and supercritical distances.

3.1.3 Wettability and nonwettability

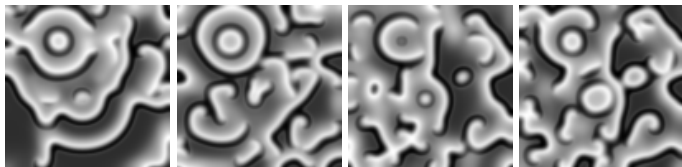
It is interesting to note that the interaction of the phase transition auto wave with lengthy defects looks like as the wettability or nonwettability in the capillarity. The computer movies demonstrate these effects.

3.2 (NO+CO)/Pt(100) system

The system (NO+CO)/Pt(100) is very rich in nontrivial phenomena [5]. The self-oscillation of the reaction rate has been investigated in [5]. It is interesting to study the regimes of chemical turbulence and Turing's structures formation.

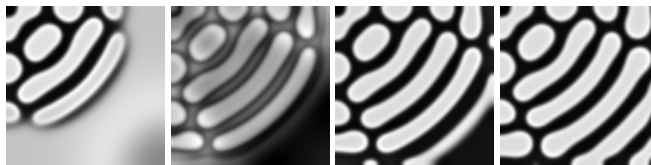
3.2.1 Chemical turbulence

The local defects can initiate the regime of chemical turbulence under certain conditions. The scenario of the phenomenon is the following. The defects with lower activation energy of NO dissociation play the role of pacemakers and give the sets of solitary waves. The interactions among the solitons led to arising of spiral wave germs. The growth of germs and interactions (with partial annihilation) give birth to new germs of spiral waves and so on. The following set of frames of computer movie shows the developed stage of the regime.



3.2.2 Phase transition "self-oscillation – Turing's structure"

The next set of computer movie frames show how the local defects located in left upper corner of the surface compartment initiates the extrusion of self-oscillatory regime by steady state Turing's structure.



So the temporal periodicity transforms into spatial "periodicity" due to the local surface defects.

4 Conclusion

1. In the case of the CO oxidation on modified Pt(111) surface the local defects play two faced role in the region of instability. On the one hand they may initiate the growth of islands of new stable state of low or high reactivity. On the other hand subcritical group of local defects can stabilize metastable state of low or high reactivity.
2. In the case of NO and CO reduction the local defects may initiate the regime of chemical turbulence with high reaction rate or the non-equilibrium transition "self-oscillations of reaction rate \rightarrow Turing's dissipative structure".

The results show the way how one can modify the catalyst to keep the system on the branch of high reactivity.

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