SIMPLE TYPES OF KINETIC OSCILLATORS
IN HETEROGENEOUS CATALYSIS

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We consider kinetic oscillators in heterogeneous catalysis with the most common types of feedback. We determine simple abstract schemes for the mechanisms of reactions which can occur in the isothermal self-excited oscillation regime. These schemes are a component of the mechanisms for specific heterogeneous catalytic reactions which are characterized by self-excited oscillations.

At the present time, a rather larger number of heterogeneous catalytic reactions are known in which self-excited oscillations have been observed in laboratory experiments [1-5]. We cannot exclude the possibility, as Schmidt and Aris suggested [1], that self-excited oscillations may also occur in industrial reactors, which so far have been studied little with respect to observation of oscillations.

Self-excited oscillations have been observed most often in reactions catalyzed by noble metals. Oscillatory regimes have been investigated in particular detail in reactions between CO and O2 [3, 4, 6-23] and CO and NO [1, 24-28] in the presence of platinum or palladium catalysts.

The reasons for self-excited oscillations are rather diverse. They may be due to physical factors such as heat and mass transfer, rearrangement of the surface of the catalyst under the action of the reaction mixture, and phase transitions, including within the surface layer of the catalyst. Such self-excited oscillations will not be considered below, except for cases when the reaction mechanism includes a stage of diffusion exchange of reagents between the surface of the catalyst and its volume and the rate of this stage can be described by an equation similar to the law of surface action. In this review, we will restrict ourselves to self-excited oscillations which occur mainly due to chemical factors. We consider kinetic (chemical) oscillators, i.e., systems in which self-excited oscillations are determined especially by the mechanism of the process. In order for self-excited oscillations to arise, the kinetic model of the reactions should, for example, allow for the existence of a single but unstable stationary state.

However, let us first briefly analyze the cases when self-excited oscillations arise in a system with several stationary states, but in a gradient-free reactor only one of these states is realized: the unstable one.

In this connection, let us consider a simple hypothetical mechanism consisting of two stages:

1) \( A + Z \rightarrow ZA \)
2) \( ZA \rightarrow Z + B \)

\[ A = B \] (1)

assuming that the activation energy for the reactions of desorption and conversion of ZA particles to product B depends linearly on the coating of the surface by ZA particles:

\[ E_{-1} = E_{-1}^0 + \alpha_{-1}RT[ZA] \] (2)
Fig. 1. Dependence of $r$ on $C_A$ (mechanism (1)) for $k_1 = 50; k_2 = 1; k_{-1.0} = 50; \alpha_{-1} = 6; \alpha_2 = 0$. The line $U(C_A^0 - C_A)$ is calculated for $U = 8; C_A^0 = 0.12$.

Fig. 2. Dependence of the surface concentration of ZA particles (mechanism (1)) on time for $k_1 = 1; k_{2.0} = 0.5; k_{-1.0} = 50; \alpha_2 = 1; \alpha_{-1} = 6; U = 0.02; C_A^0 = 10$.

$$E_2 = E_2^0 + \alpha_2 RT[Z_A]$$

Under steady-state conditions, the reaction rate in a gradient-free reactor is determined by the expression

$$r_A = k_1 C_A (1 - [Z_A]) - k_{-1.0} \exp(-\alpha_{-1}[Z_A])[Z_A] = k_2 \alpha \exp(-\alpha_2[Z_A])[Z_A]$$

We note that a mechanism similar to scheme (1) is used in [29] to explain the kinetic characteristics of the reaction of hydrogenation of CO with formation of methane on a nickel catalyst. In the same paper, it is shown that for certain values of $\alpha_2$ (it was assumed that $k_{-1} = 0$), there may be three internal stationary states in the considered system. In this case, "counterclockwise" hysteresis is possible in the system for certain values of the kinetic parameters [30], as illustrated by Fig. 1. It can be shown [30] that the intermediate stationary state is unstable.

In a gradient-free reactor, the reaction rate can also be expressed as the difference between the rate of addition of reagent A to the reactor and the rate of its exit from the reactor:

$$r_A = \nu(C_A^0 - C_A),$$

where $\nu$ is the flow rate of the reaction mixture; $C_A^0$ and $C_A$ are the concentrations of A and at the inlet and outlet from the reactor respectively. The intersection of the linear dependence of $r_A$ on $C_A$ expressed by Eq. (5) and the dependence of $r_A$ on $C_A$ found from the steady-state Eq. (4) corresponds to a stationary state of the system. For some values of the parameters, the stationary state may correspond to the point of intersection of a straight line with the unstable stationary state. This may lead to the appearance of a self-excited oscillation regime, as illustrated by Fig. 2, where we present the dependence of the concentration of intermediate particles on the reaction time. The indicated dependence, having the character of stable oscillations, is found by solution of the nonstationary kinetic model, consisting of two differential equations:

$$d[Z_A]/dt = k_1 C_A (1 - [Z_A]) - k_{-1.0} \exp(-\alpha_{-1}[Z_A]) - k_2 [Z_A]$$

$$dC_A/dt = \nu(C_A^0 - C_A) - (k_1 C_A (1 - [Z_A]) - k_{-1.0} \exp(-\alpha_{-1}[Z_A]))$$

(for simplicity of the analysis, we assume $\alpha_2 = 0$, i.e., $k_{2.0} = k_2$).