



THE DERIVATION OF THE GENERALIZED DEACTIVATION KINETICS EQUATION FOR A NONLINEAR REACTION MECHANISM

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ABSTRACT

In this paper, the model the kinetics of deactivation of the catalyst on the basis of stage machinery in a quasi-stationary, namely, in the nonlinear mechanism of the reaction has been developed. The model reflects the simultaneous effects of the processes of decontamination and self-regeneration of the catalyst.

Key words: Modeling and simulation, Quasi-stationary, The linear mechanism of the reaction, Nonlinear mechanism of the reaction.

INTRODUCTION

The processes affecting the decrease in activity of the catalyst occur slowly enough, so the corresponding mathematical models are chemical kinetics equations with the quasi-stationary subsystem, describing the change in activity of the catalyst. The method of the quasi-stationary concentration is based on the fact that the velocity difference in the formation of an intermediate substance and its consumption is low compared to the rates by the formation and consumption of the intermediates and may be set to zero¹. With regard to the deactivation of the concept of quasi-stationary means that to meet the quasi-stationary conditions are intermediates involved in the catalytic cycle of the reaction, and the intermediates of the reaction that are switched off due to the deactivation of the *i*-type, will not satisfy the condition of the quasi-stationary.

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EXPERIMENTAL

The justification of the quasi-stationary hypothesis is based on the presence in the original system of differential equations of the small parameter ε , which stands in front of some derivatives. By varying the time scale, and introducing a replacement, you can go from the source system to a system of differential equations in partial derivatives. Then the conditions of the quasi-stationary based on the deactivation of the catalyst can be written as follows:

$$\frac{\partial \Theta_j}{\partial \tau} = f(\Theta_j, \Theta_p) \approx 0, j = 1, \dots, n, \quad \dots(1)$$

$$\frac{\partial \Theta_p}{\partial t} = \frac{1}{\varepsilon} g(\Theta_j, \Theta_p) \neq 0, \quad \dots(2)$$

where Θ_j - the intermediates involved in the catalytic cycle of the reaction; Θ_p - intermediates excluded from the reaction as a result of deactivation; ε - a small parameter; τ - contact time (the time of one catalytic cycle reaction); t - astronomical time (the time work of the catalyst). Then for each fixed Θ_j can be investigated the system of fast movements (2). From the quasi-stationary conditions will imply that the sum of all intermediates will be equal to the difference between the unit and the proportion of the deactivated parts of the active centers, i.e. it will be true ratio:

$$\sum_{j=1}^n \Theta_j = 1 - \Theta_p \quad \dots(3)$$

To display the reaction rate equations and deactivation, which take place on the linear and nonlinear mechanisms, it is necessary to use the following assumptions: the equilibrium of adsorption stage; the presence of one limiting stage; the implementation of quasi-stationary conditions. The reaction rate at the initial time (on the fresh catalyst) is written according to certain rules, based on the theory of stationary reactions. Then, in a stationary mode (on the fresh catalyst) the reaction rate r^0 is equal to any of the stages of the mechanism r_j^0 and for the linear mechanism it takes the form:

$$r^0 = r_j^0 = w_j \Theta_j^0 - w_{-j} \Theta_{j+1}^0, \quad \dots(4)$$

wherein w_j , w_{-j} - the weight of the selected stage in the forward and backward directions.

For the non-linear mechanism

$$r^0 = r_j^0 = w_j \Theta_j^0 \Theta_i^0 - w_{-j} \Theta_{j+1}^0 \Theta_{i+1}^0 \quad \dots(5)$$

In the case of the non-linear mechanism reaction can be assumed that the order of steps for intermediates above the second is impossible. In this case there are only binary interactions. Then, taking into account the input assumptions the following ratio will be faithful^{2,3}:

$$a(t) = (1 - \Theta_p(t))^2, \quad r(t) = r^0 \cdot a(t), \quad d\Theta_p = -\frac{da}{2\sqrt{a}} \quad \dots(6)$$

To derive the deactivation equations generally must be considered self-regeneration processes leading to the restoration of the active centers under the influence of the components of the reaction mixture, not in a separate regeneration period. Thus, generally the deactivation is regarded as a partially reversible process.

RESULTS AND DISCUSSION

In the work⁴, it is shown that the reactions occurring on linear mechanisms, taking into account the input assumptions, the generalized equation of the deactivation rates for reactions occurring on the linear mechanisms if the conditions of the quasistationarity are reduced to separable kinetics of the following type:

$$\frac{da}{dt} \approx -f_0(C, T) f_c(C, T) f_a(a), \quad \dots(7)$$

where $f_0(C, T) = r^0/w_j$ - a function that depends only on kinetics of the main reaction; w_j - a weight j of stages of reaction mechanism; $f_c(C, T) = \sum w_p$ - a function determined by the kinetics of the deactivation stage; $f_a(a) = (a - a_s)/(1 - a_s)$ - a function that depends on the activity of the catalyst. In the case of the nonlinear base reaction mechanism the rate reaction is described by equation (5). In this case, because of the quasi-stationary conditions is true the ratio $\Theta_j = \Theta_j^0(1 - \Theta_p)$. Then any intermediate involved in the reaction can be expressed in terms of the speed and weight of the j -th and i -th stages $\Theta_j^0 = \frac{r^0}{w_j \Theta_i^0}$.

Designating $f(r^0) = r^0/w_j \Theta_i^0$, which will be determined in the concrete case of the reaction mechanism, we can write the equation of the deactivation of the catalyst:

$$\frac{d\Theta_P}{dt} = w_P f(r^0)(1 - \Theta_P) - w_R \Theta_P \quad \dots(8)$$

By relations (6), the equation (8) can be rewritten in terms of relative activity:

$$\frac{da}{dt} = -2w_P f(r^0)a + 2w_R(\sqrt{a} - a) \quad \dots(9)$$

We derive an expression for the steady activity of the catalyst, by equating the right-hand side of equation (9) to zero:

$$2w_P f(r^0)a_s = 2w_R(\sqrt{a_s} - a_s), \quad \frac{w_P f(r^0)}{w_R} = \frac{(\sqrt{a_s} - a_s)}{a_s}$$

From this we can derive an expression for a_s :

$$a_s = \left[1 + \frac{w_P f(r^0)}{w_R} \right]^{-2} \quad \dots(10)$$

From the relation (10), we express w_R in terms of a_s :

$$w_R = \frac{w_P f(r^0)a_s}{\sqrt{a_s} - a_s}, \quad \dots(11)$$

And substituting it into the equation (9), we obtain a generalized equation for the deactivation rate of reactions that occur in the nonlinear mechanism with the linear deactivation mechanism under the conditions of the quasi-stationary. Type The equation reduces to the type (7):

$$\frac{da}{dt} \approx -2f(r^0)w_P \left[a - a_s \frac{\sqrt{a} - a}{\sqrt{a_s} - a_s} \right], \quad \dots(12)$$

where $2f(r^0) = f_0(C, T)$ - a function that depends only on the kinetics of the main reaction; $w_P = f_C(C, T)$ - a function defined by the kinetics of stages of deactivation;

$\left(a - a_s \frac{\sqrt{a} - a}{\sqrt{a_s} - a_s} \right) = f_a(a)$ - a function that depends on the activity of the catalyst.

This confirms that the deactivation equation is not arbitrary, which is to be determined through experimental data and recorded on the basis of rate stages of the mechanism.

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Accepted : 30.11.2016