IDENTIFICATION OF A MATHEMATICAL MODEL OF THE REDUCED SCHEME OF A-METHYLSTYRENE DIMERIZATION REACTION

Vaytiev V.A., Stepashina E.V., Mustafina S.A.
Bashkir State University, Ufa, e-mail: stepashinaev@ya.ru

Identification of a mathematical model of the reduced scheme of α-methylstyrene dimerization reaction has been held. The constants of rate stages and the values of activation energies have been defined. The obtained kinetic parameters allow to describe the dynamics of concentrations of target substances reaction scheme of a smaller dimension.

Keywords: an inverse problem, reduction of the kinetic schemes, reaction mechanism

Kinetic models based on the detailed mechanisms of complex chemical reactions, represent a systems of differential equations. In these systems the number of the unknowns equals the number of substances involved in the reaction. Hypothetical schemes of complex chemical reactions contain a large number of substances and reactions between them. However, direct measurement is available only for some of these substances. Precise description of the behavior of only a few substances are required for the analysis of the reaction mechanism. In this connection there is a need to replace an original system with a system of a smaller dimension, preserving the dynamics of concentrations of the selected substances. As a result of the reduction of the kinetic mechanism of the reaction scheme there would be defined by an equivalent scheme containing less substances and stages than an original one. Therefore, the construction of mathematical models of reduced reaction schemes results in solving the problem of an identification of a mathematical model of the reaction, i.e, solving the inverse problem of chemical kinetics.

Kinetic model of the reduced scheme of α-methylstyrene dimerization reaction

Let's construct the kinetic model of the reduced scheme of α-methylstyrene dimerization reaction. The products of this reaction (the linear and cyclic dimers) have been in practical use as plasticizers, polymer modifiers, rubber in the manufacture of synthetic lubricants, etc. A number of chemical reactions describing the same reaction, and the corresponding kinetic equations are as like [1]:

$$\begin{aligned}
2X_1 &\leftrightarrow X_2, & \omega_1(C,T) &= k_1C_1^2 - k_{10}C_2,\\
2X_1 &\leftrightarrow X_3, & \omega_2(C,T) &= k_2C_1^2 - k_{11}C_3,\\
2X_1 &\rightarrow X_4, & \omega_3(C,T) &= k_3C_1^2,\\
X_2 &\leftrightarrow X_3, & \omega_4(C,T) &= k_4C_2 - k_{12}C_3,\\
X_2 &\rightarrow X_4, & \omega_5(C,T) &= k_5C_3,\\
X_3 &\rightarrow X_4, & \omega_6(C,T) &= k_6C_2C_1,\\
X_1 + X_2 &\rightarrow X_5, & \omega_7(C,T) &= k_7C_1C_3,\\
X_1 + X_3 &\rightarrow X_5, & \omega_8(C,T) &= k_8C_1C_4,\\
X_1 + X_4 &\rightarrow X_5, & \omega_9(C,T) &= k_9C_2C_4,
\end{aligned} \qquad (1)$$

where the following designations were entered X_1 – α-methylstyrene; X_2 – α-dimer; X_3 – β- dimer; X_4 – cyclic dimer; X_5 – trimers, where $\omega_i(t, x)$ – velocity of the i-th stage (kmol/(m^3·h)) (i = 1,…,9); $\boldsymbol{C} = (C_1, \ldots, C_5)$ – vector of concentration of the components (kmol/m^3); $\boldsymbol{k} = (k_1,\ldots,k_{12})$ – vector of kinetic rate constants of the j-th reaction (m^3/(kmol·h)) (j = 1, …, 12).

The values of the kinetic constants and activation energies are shown in Table 1. The rate constant of the j-th reaction is calculated with the use of the selected basic temperature T_{base} = 373 K defined by the formula

$$k_j(T) = k_j(T_{on}) \exp\left(\frac{E_j}{RT_{on}}\left(1 - \frac{T_{on}}{T}\right)\right).$$

Table 1

Kinetic parameters of the process of α-methylstyrene dimerization in the presence of a catalyst NaHY of at a temperature 373 K

Number	k_i(373 K), m³/(kg$_{cat}$·h)	E_i, kJ/mol	Number	k_i(373 K), m³/(kg$_{cat}$·h)	E_i, kJ/mol
1	61,357	196	7	0,019308	247
2	8,9534	263	8	41,556	194
3	7,7916	259	9	0,03662	115
4	1,1693	238	10	0,04547	279
5	0,11922	275	11	0,0995	204
6	0,12041	127	12	0,05132	138

Kinetic model of α-methylstyrene dimerization with the changes in the number of moles in the course of a chemical reaction is a system [1]:

$$\frac{dx_i}{dt} = \frac{F_i(x,T) - x_i F_m(x,T)}{N};$$

$$F_i = \sum_{k=1}^{9} \nu_{ik} W_k; \quad \frac{dN}{dt} = F_n(x, T);$$

$$F_n = \sum_{j=1}^{9} W_j \sum_{i=1}^{5} \nu_{ij},$$

with initial conditions: $x_i(0) = x_i^0$, $i = 1, ..., 5$, $N(0) = 1$, where x_i – concentration of i-th component (mole fraction); $N = C/C_0$ – concentration of i-th component (mole fraction); C_0 – initial total concentration of reactants (kmol/m³); (ν_{ik}) – matrix of stoichiometric coefficients, $W_j = \omega_j/C_0$ – values of the chemical reaction rate ($j = 1,..,9$) (1/h).

The reduced scheme of this reaction, obtained in [2, 3] based on the combined algorithm of reduction of the reaction scheme in the time and temperature range of the reaction course, and its kinetic equations have the following form:

$$\begin{aligned}
&2X_1 \leftrightarrow X_2, && \omega_1(C,T) = k_1 C_1^2 - k_7 C_2,\\
&2X_1 \leftrightarrow X_3, && \omega_2(C,T) = k_2 C_1^2 - k_8 C_3,\\
&2X_1 \rightarrow X_4, && \omega_3(C,T) = k_3 C_1^2,\\
&X_2 \leftrightarrow X_3, && \omega_4(C,T) = k_4 C_2 - k_9 C_3,\\
&X_2 \rightarrow X_4, && \omega_5(C,T) = k_5 C_2,\\
&X_3 \rightarrow X_4. && \omega_6(C,T) = k_6 C_3,
\end{aligned} \qquad (2)$$

where $C = (C_1, C_2, C_3, C_4)$ – vector of concentration of components, $k = (k_1, \ldots, k_9)$ – vector of kinetic rate constants of the reaction stages (2).

Solution of the inverse kinetic problem for the reduced reaction scheme

An inverse kinetic problem is a problem of minimizing the functional deviations between the calculated and experimental data:

$$Q = \sum_{i=1}^{l} \sum_{j=1}^{n} \left| x_{ij}^P - x_{ij}^E \right| \rightarrow \min, \qquad (3)$$

where x_{ij}^P, x_{ij}^E – calculated and experimental values for substances respectively; l – number of measurements; n – number of substances.

To solve the problem of identification of a mathematical model of the reduced reaction scheme it is necessary to calculate the values of kinetic constants k_{0j}, minimizing the functional (3), and the values of activation energies E_j.

With the application of the algorithm for solving the inverse problem of chemical kinetics, constructed in [2] on the basis of Hooke-Jeeves' method, kinetic parameters of the reduced scheme of α-methylstyrene dimerization reaction have been calculated (Table 2).

Results and Discussion

As a result of solving the inverse kinetic problem the values of activation energies E_j and kinetic constants k_{0j} ($j = 1, \ldots, 9$) for the reduced scheme of α-methylstyrene dimerization reaction have been calculated. On the basis of the obtained values a direct kinetic problem has been solved. The relative difference between the calculated and experimen-

tal values of the concentration of substances has been more than 11 %, which is within the measurement error in the experiment. The reduction of the reaction scheme (1) has not changed the overall dynamics of changes in the concentrations of substances with time. Relative error vectors concentrations of substances X_1, X_2, X_3, X_4 for the reduced scheme of α-methylstyrene dimerization reaction amounted: $\delta(x'_1) = 1{,}35\,\%$, $\delta(x'_2) = 1{,}68\,\%$, $\delta(x'_3) = 10{,}24\,\%$, $\delta(x'_4) = 7{,}93\,\%$. This shows that the accuracy of the description of the dynamics of concentrations of target substances of the reduced scheme of α-methylstyrene dimerization reaction is within the error limits of quantitative analysis. Therefore, the reduced scheme of α-methylstyrene dimerization reaction (2) can be used to solve other problems based on the analysis of the kinetic model of the reaction scheme.

Table 2

Kinetic parameters of the reduced scheme of α-methylstyrene dimerization reaction in the presence of a catalyst NaHY at a temperature of 373 K

Number	k_i(373 K), $m^3/(kg_{cat}\cdot h)$	E_i, kJ/mol	Number	k_i(373 K), $m^3/(kg_{cat}\cdot h)$	E_i, kJ/mol
1	62,788	197,6	6	0,70168	320,9
2	6,037	231,4	7	0,00121	301,3
3	9,055	263,3	8	0,00847	242,4
4	1,092	311,9	9	0,00468	184,0
5	0,0012	573,3			

References

1. Mustafina S.A. Optimization of Catalytic Processes and Reactors / S.A. Mustafina, Yu.A. Valieva, R.S. Davletshin, A.V. Balaev, S.I.Spivak // Kinetics and Catalyses. – 2013. – Vol. 46, № 5. – P. 705–711.

2. Vaytiev V.A. Identification of Mathematical Models of Reduced Reaction Schemes / V.A. Vaytiev, E.V. Stepashina, S.A. Mustafina // Tomsk Polytechnic University News. – Tomsk, 2013. – Vol. 323, № 3. – P. 10–14.

3. Stepashina E.V. Graph-Theoretic Methods for the Reduction of Complex Kinetic Schemes / E.V. Stepashina, S.A. Mustafina – Sterlitamak: Sterlitamak Branch of Bashkir State University, 2013. – 97 p.

4. Stepashina E.V. Graph Approach for Modeling of Catalytic Processes with Varying Reaction Volume / E.V. Stepashina, S.A. Mustafina // Control Systems and Information Technology. – Voronezh, 2012. – Vol. 47, № 1. – P. 14–19.

5. Baytimerova A.I. Search for the Optimal Control in a Reactor Cascade Processes with Varying Reaction Volume / A.I. Baytimerova, S.A. Mustafina, S.I. Spivak // Control Systems and Information Technology. – Voronezh, 2008. – № 2 (32). – P. 38–42.

6. Vaytiev V.A. Numerical Research of Processes with Stable and Variable Reaction Volume in Uncertainty of Kinetic Data / V.A. Vaytiev, S.A. Mustafina // Bashkir Chemistry Journal. – Ufa, 2013. – Vol. 20, № 2. – P. 45–48.