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FLEXIBLE LABORATORY SYSTEM FOR INVESTIGATION OF CATALYTIC PROCESSES

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Abstract

A new method for determining of reaction mechanism and kinetics, catalyst pellet model and adsorption kinetics was developed on the basis of a computer analysis of parametric sensitivity of models for various types of experimental equipments. For solving these problems the following elements of investigation are to variate:

1. the combination and number of laboratory reactors,
2. the character of the input signals supplied into each reactor,
3. the methods of parameter estimation and algorithm of numerical integration of the model equations.

Using this method it is possible to decrease the parameter errors connected with the selection of the 'best' model.

Keywords: reaction mechanism and kinetics, catalyst pellet model, adsorption kinetics, parametric sensitivity, heterogeneous-catalyst processes.

Introduction

Detailed information on adsorption and kinetic models for porous catalyst pellets and numerical values of the model parameters are necessary for the synthesis of effective design for a reactor and its control. However, a general statistics has not yet been developed for verifying the adequacy of similar models or for guiding corrections to them, nor a theory for planning precise and discriminating experiments with the objective of selecting, from among a set of concurrent ones, those models which best reflect the experimental data. This is naturally a definite restraining factor in the implementation of scientific developments in industry. A new method of solving this problem was developed on the basis of a computer analysis of parametric sensitivity of model parameter for various types of experimental reactor arrangements.

Model

In estimating the macrokinetic model constants for pellets on the basis of adsorption measurements, the influence of external diffusion cannot be neglected because of the frequent occurrence in many processes of adsorption. A mathematical description of the diffusion and adsorption in catalyst pellets, assuming the model for the porous structure as quasi homogeneous, will then have the following form:

$$(V_R - V_K)\frac{\partial c_a}{\partial t} = v_e c_e - v_a c_a + S_k K_m[c_a - (c_n)_R], \tag{1}$$

$$\varepsilon\frac{\partial c_n}{\partial t} = D_{\text{eff}}\left(\frac{\partial^2 c_n}{\partial r^2} + \frac{2}{r}\frac{\partial c_n}{\partial r}\right) - N^{(i)},\ i = 1,2,3, \tag{2}$$

$$N^{(1)} = k_a\left(c_n - \frac{n}{K_a}\right) = \frac{\partial n}{\partial t}, \tag{3}$$

$$N^{(2)} = k_a\left[\left(1 - \frac{n}{n_{\max}}\right)c_n - \frac{n}{n_{\max}}K_a^{-1}\right], \tag{4}$$

$$N^{(3)} = k_a\left[c_n e^{-gn} - n e^{\frac{kn}{K_a}}\right]. \tag{5}$$

The initial conditions are

$$0 \le r \le R;\ t = 0, \tag{6}$$

$$c_a = \overset{0}{c_a} = 0 : c_n = \overset{0}{c_n} = 0;\ n = \overset{0}{n} = 0.$$

The boundary conditions are

$$t > 0;\ \frac{\partial c_n}{\partial r} = 0 : r = 0, \tag{7}$$

$$t > 0 : D_{\text{eff}}\frac{\partial c_n}{\partial r}\bigg|_R = K_m\Big(C_a - C_n(R)\Big). \tag{8}$$

where c_a and c_n are the tracer concentrations in the reactor bulk and in the pores of the catalyst, respectively; c_e is the concentration of the indicator at the inlet to the reactor; R and r are the radius of the particle and the variable of particle radius, respectively; n is the concentration of adsorbed indicator at the surface of the pores; D_{eff} the effective diffusion coefficient; k_a the rate constant and K_a the adsorption/desorption equilibrium constant; K_m the mass transfer coefficient; S_K the surface area of the catalyst per unit volume in the catalyst bed; ε is the porosity of a catalyst granule; $N^{(1)}$, $N^{(2)}$, $N^{(3)}$ are models for adsorption kinetics, where $N^{(2)}$ is the Langmuir model, and $N^{(3)}$ is the Zel'dovich-Roginskii model for energetically heterogeneous catalytic surfaces.

The system of Equations (1) to (8) was integrated numerically. Preliminary calculations performed by using the method of least squares showed that the accuracy of evaluating the macrokinetic constants, obtained from an experimental curve in response to only one unit impulse perturbation was not great but increased substantially as an effect of several successively imposed perturbations of standard indicators over time. The need for sequential planning of precise experiments is thus evident. The possibility of numerical construction of the response curves as functions of the type of input signal $c_c(t)$ and values of the control variables $u = (v_e, T, P, c_c)$ is also postulated.

Experimental Method

Equations (1) to (8) are then supplemented by the following expressions for mathematical description of the measurement system:

$$\frac{dc_a}{dt} = f(c_a, c_c\Theta, u), \tag{9}$$

$$Z(t) = H(C_a, \Theta) + v(t);\ t \in [O, T], \tag{10}$$

where Θ is a vector of parameters; T the fixed time over which the measurements are taken; and $v(t)$ the error in the measurement with the following properties:

$$M[v(t)] = 0;\ D[v(t), v(\tau)] = M[v(t)v(\tau)] = D(t)\delta(t-\tau), \tag{11}$$

where by $M.[...]$ and $D[...]$ the mean value and covariance operator are denoted.

The dosing system must clearly admit the possibility of input impulses of the indicator with volumes of $v^{(1)}, v^{(2)}, \ldots, v^{(N)}$ discretely over identical time intervals of Δt independently of the volumetric flow rate of the carrier gas feed. For a given overall time of the experiment, the vector of control variables u and the input times of the impulses of indicator $t, (\Delta t, \ldots, N\Delta t = T)$ determine the sequence of volumes of input impulses, $v^{(1)}, v^{(2)}, \ldots, v^{(N)}$, which ensure maximization of a certain functional Φ of the information matrix $M(\varepsilon)$ with $\varepsilon = v$:

$$M(v) = \int_0^T F(v, \Theta) D^{-1}(t) F(v, \Theta)^T dt, \tag{12}$$

where

$$F(v,\Theta) = \frac{\partial H(v)}{\partial c_a} \cdot \frac{\partial c_a}{\partial \Theta} + \frac{\partial H(v)}{\partial \Theta}. \tag{13}$$

The solution to this problem in this framework is achieved by nonlinear programming methods. Thus, the system of *Eqs.* (9), (10) is first transformed into the following form:

$$\begin{aligned} & c_a(t_{k+1}) = \int F[c_a(t), c_e(t_k), \Theta, u]dt + c_a(t_k) \\ & = \Psi[c_a(t_k), c_e(t_k), \Theta, u]; \\ & t \in [0, T - \Delta t], \\ & c_e(t_k) \in v = [v^{(1)}, v^{(2)}, \ldots, v^{(N)}]. \end{aligned} \tag{14}$$

It is required to find the sequence of stepwise perturbations of the indicator $v^{(1)}, v^{(2)}, \ldots, v^{(N)}$, the volumes of the input impulses, which maximize

$$J(V) = \Psi[M(V), T].$$

During this procedure the following elements of investigation are to variate:
1. the combination and number of laboratory reactors,
2. the character of the input signals supplied into each reactor,
3. the method of parameter estimation and algorithm of numerical integration of the model equations.

Results

It was shown that by such an approach to the study of adsorbents and catalysts the evaluation of models for adsorbents and of the constants therein with an acceptable accuracy was made possible (see *Table 1*).

So, this new universal procedure gives the opportunity to estimate with the necessary accuracy the parameters of a wide class of models of heterogeneous-catalyst processes for the limited time intervals.

Table 1

Parameters k_a, K_a, D_{eff} accuracy estimation characteristics, dependent on reactor system scheme and input signal form ($d_p = 0.5$ cm, $w = 1.3$ ml/sec, o f – optimal form, s f – standard form)

Reactor system scheme	Impulse form	Normal standard deviation k_a	$K_a 10^4$	D_{eff}	Determinant for the information matrix
1 reactor	o f	1.07	10.5	1.38	$1.59 \cdot 10^{-10}$
	s f	10.09	10.9	12.90	$4.83 \cdot 10^{-13}$
2 reactors in series	o f	0.84	5.55	1.09	$1.93 \cdot 10^{-9}$
	s f	4.87	5.40	6.24	$2.86 \cdot 10^{-11}$
3 reactors in series	o f	0.10	3.7	0.11	$2.36 \cdot 10^{-6}$
	s f	3.52	3.55	4.52	$2.55 \cdot 10^{-10}$
3 reactors, 2 in parallel	o f	0.74	5.19	0.95	$3.52 \cdot 10^{-9}$
	s f	4.61	5.10	5.90	$4.09 \cdot 10^{-11}$
2 reactors in parallel	o f	1.27	9.86	1.64	$0.74 \cdot 10^{-10}$
	s f	2.55	9.65	3.28	$0.76 \cdot 10^{-11}$

References

1. KAFAROV, V. V. (1993): Methoden zur Entwicklung industrieller katalytischer Prozesse, Thesis, Merseburg.
2. KAFAROV, V. V. – TUREK, F. (1989): Möglichkeiten der Nutzung flexibler automatisierter Systeme zur Erarbeitung reaktionskinetischer Modelle. *Vortrag zur 9. Arbeitstagung über chemische Reaktionskinetik*, Leipzig.
3. PISARENKO, V. N. – KAFAROV, V. V. (1991): Problems of Industrial Catalysis in a Fixed Bed Reactor. *International Chemical Engineering*, Vol. 31, N. 2, pp. 213–263.