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Conditions required to maximise the productivity of porous catalyst granules with a controlled activity profile

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The possibility of increasing the effectiveness of a porous catalyst granule with an artificially changing activity profile in the case of a simple catalytic reaction proceeding under non-steady-state conditions is shown.

Let us analyse a reaction of the following form:

$$\mathrm{A}_1 \xrightarrow{r_1} \text{products} \tag{1}$$

The reaction exhibits arbitrary kinetics r_1 and proceeds on porous catalyst granules of spherical, cylindrical or plate form.

For a catalytic reaction of form (1) it is shown[1] that the theoretical effectiveness of the porous catalyst granule reaches a maximum when the active centres on the internal surface are distributed not uniformly, but when the same quantity of centres is arranged as a δ-function at a certain depth from the granule centre. In a real case the δ-function can be approximated[6] by a rectangular distribution of an active layer of thickness *ca.* $0.04R_\mathrm{S}$ (R_S is the granule radius). In the case of a uniform distribution of active centres on the internal surface of the catalyst granule the possibility of increasing the effectiveness of reaction (1) under non-steady-state conditions in comparison with steady-state ones is shown.[2,3] In this connection an analysis of the possibility of increasing the effectiveness of a porous catalyst granule is important when a catalytic reaction is realised under non-steady-state conditions on a porous catalyst with an artificially changing activity profile on its internal surface. Such management of activity profile can be achieved with the help of an electromagnetic field, for example, and also with the help of other methods which will provide the basis of a separate article.

Let the concentration C_1 of the substance A_1 and the temperature T in the nucleus of the external reaction mixture stream change with time as follows:

$$C_{01}(t) = \tilde{C}_{01} + \hat{C}_{01}(t), \quad \int_0^{\tau_1} \hat{C}_{01}(t)\,\mathrm{d}t = 0,$$

$$T_0(t) = \tilde{T}_0 + \hat{T}_0(t), \quad \int_0^{\tau_2} \hat{T}_0(t)\,\mathrm{d}t = 0, \quad p_1\tau_1 = p_2\tau_2 = \tau \tag{2}$$

where $\tilde{C}_{01}$ and $\tilde{T}_0$ do not depend on time, p_1 and p_2 are arbitrary whole positive numbers; and τ_1 and τ_2 are the periods of change for the functions $\hat{C}_{01}(t)$ and $\hat{T}_{01}(t)$. To simplify the analysis, let us assume[2,3] that the values τ_1 and τ_2 are significantly larger in comparison with the characteristic times of the process proceeding in the porous catalyst granule (quasi-steady-state conditions). In this case, for a description of reaction (1) proceeding on a porous catalyst granule the steady-state quasi-homogeneous model[4] can be used.[2,3] The proposed model for reaction (1) has the following form:

$$x^{-\alpha}\frac{\mathrm{d}}{\mathrm{d}x}\left(x^{\alpha}\frac{\mathrm{d}C_1}{\mathrm{d}x}\right) - g(x)R_\mathrm{S}^2\, r_1(C_1, T)/D_1^* = 0$$

$$x^{-\alpha}\frac{\mathrm{d}}{\mathrm{d}x}\left(x^{\alpha}\frac{\mathrm{d}T}{\mathrm{d}x}\right) + g(x)R_\mathrm{S}^2\, Qr_1(C_1, T)/\lambda^* = 0 \tag{3}$$

with boundary conditions:

$$x = 0:\ \frac{\mathrm{d}C_1}{\mathrm{d}x} = \frac{\mathrm{d}T}{\mathrm{d}x} = 0; \quad x = 1:\ D_1^*\frac{\mathrm{d}C_1}{\mathrm{d}x} = R_\mathrm{S}\beta_1[C_{01}(t) - C_{\mathrm{S}1}],$$

$$\lambda^*\frac{\mathrm{d}T}{\mathrm{d}x} = R_\mathrm{S}\beta_\mathrm{T}[T_0(t) - T_\mathrm{S}] \tag{4}$$

Here x is the dimensionless distance from the centre of a granule of radius R_S; $C_{\mathrm{S}1}$ is the concentration of substance A_1 near the external surface of a granule; T_S is the temperature at the external surface of a granule; D_1^* is the effective coefficient of diffusion of substance A_1 in the pores; λ^* is the effective coefficient of a granule's heat conductivity; Q is the heat effect of the reaction; β_1 and β_T are, respectively, coefficients of mass exchange on substance A_1 and heat exchange between a granule and external reaction mixture stream; α is a parameter which is determined by a granule geometric form ($\alpha = 0$ for a plate, $\alpha = 1$ for a cylinder, $\alpha = 2$ for a sphere) and $g(x)$ is the density function of the catalyst distribution on a porous granule which satisfies the condition:

$$\int_0^1 g(x)x^{\alpha}\mathrm{d}x = \frac{g_0}{\alpha + 1} \tag{5}$$

Here g_0 is the catalyst density when it is distributed uniformly on a porous granule. The maximum of the porous catalyst effectiveness can be reached[1] when the following form of function $g(x)$ holds:

$$g(x) = \frac{g_0\delta(x - x_1)}{(\alpha + 1)x^{\alpha}}, \quad 0 \le x_1 \le 1 \tag{6}$$

Here the value x_1 is the optimal position of the δ-function in the porous catalyst granule at which the maximum of its effectiveness is reached. This function satisfies relation (5).

The productivity of a porous catalyst granule is determined by an equation:

$$J(t) = -FR_\mathrm{S}^{\alpha-1}\, D_1^*\tilde{C}_{01}\left.\frac{\mathrm{d}U_1}{\mathrm{d}x}\right|_{x=1} \tag{7}$$

where $U_1 = C_1/\tilde{C}_{01}$, $F = 4$ for $\alpha = 2$, $F = 2\ h$ for $\alpha = 1$ (h is the cylinder height) and $F = 2S$ for $\alpha = 0$ (S is the square of the plate surface perpendicular to the x axis). The average value of quantity $J(t)$ during the period τ is calculated by the equation:

$$J = \frac{1}{\tau}\int_0^{\tau} J(t)\,\mathrm{d}t \tag{8}$$

Solution of the model (2)–(6) gi ves the following equations for the determination of δ-function position in a porous granule:

$$\frac{J(t)}{\tilde{J}_0} = \frac{r_1(U_{11}, \theta_1)}{\tilde{r}_{01}} = \frac{1 + \hat{C}_{01}(t)/\tilde{C}_{01} - U_{11}}{\varphi^2 + \sigma I_1}, \tag{9}$$

$$\theta_1 = \frac{T_1}{\tilde{T}_0} = 1 + \frac{\hat{T}_0(t)}{\tilde{T}_0} + \frac{\beta[\sigma(B_\mathrm{T}^{-1} - B_1^{-1}) + \varphi^2 + \sigma I_1]}{\varphi^2 + \sigma I_1}\left(1 + \frac{\hat{C}_{01}(t)}{\tilde{C}_{01}} - U_{11}\right), \tag{10}$$

$$U_{11} = C_{11}/\tilde{C}_{01},\ \sigma = \frac{\tilde{r}_{01}g_0R_\mathrm{S}^2}{(\alpha + 1)\tilde{C}_{01}D_1^*},\ \tilde{r}_{01} = \tilde{r}_1(\tilde{C}_{01}, \tilde{T}_0),\ \beta = \frac{D_1^*Q\tilde{C}_{01}}{\lambda^*\tilde{T}_0},$$

$$B_1 = \frac{R_\mathrm{S}\beta_1}{D_1^*},\ B_\mathrm{T} = \frac{R_\mathrm{S}\beta_\mathrm{T}}{\lambda^*},\ \varphi^2 = \sigma(I_0 + 1/B_1),\ I_0 = \int_{x_{01}}^{1} x^{-\alpha}\mathrm{d}x,\ I_1 = \int_{x_1}^{x_{01}} x^{-\alpha}\mathrm{d}x$$

Here $C_{11} = C_1(x_1)$ and $T_1 = T(x_1)$; x_{01} is the position of the δ-function in a granule in the case of reaction (1) proceeding under a steady-state regime [$C_{01}(t) = \tilde{C}_{01} =$ const., $T_0(t) = \tilde{T}_0 =$ = const.], x_1 is a function of time; and $\tilde{J}_0$ is the productivity under the steady-state conditions.

Functions $\hat{C}_{01}(t)$, $\hat{T}_{01}(t)$ and $x_1(t)$ maximising function (8) are determined from the Lagrange equations.[5] Taking into account formulae (9) and (10) they give the following conditions required to maximise the productivity of a porous catalyst granule.

$$\int_0^\tau \frac{(\beta R_{1\theta} - \psi)\hat{C}_{01}(t)}{\psi(\varphi^2 + \sigma I_1) + R_{1\theta}\beta\sigma(B_\mathrm{T}^{-1} - B_1^{-1}) - 1}\,\mathrm{d}t = 0, \quad {}_0^\tau\, \hat{C}_{01}(t)\,\mathrm{d}t = 0, \tag{11}$$

$$\int_0^\tau \frac{R_{1\theta}\hat{T}_0(t)}{\psi(\varphi^2 + \sigma I_1) + R_{1\theta}\beta\sigma(B_\mathrm{T}^{-1} - B_1^{-1}) - 1}\,\mathrm{d}t = 0, \quad {}_0^\tau\, \hat{T}_0(t)\,\mathrm{d}t = 0, \tag{12}$$

$$\left[\beta - \frac{\partial R_1}{\partial U_{11}}\left(\frac{\partial R_1}{\partial \theta_1}\right)^{-1}\right]\left[1 + \frac{\hat{C}_{01}(t)}{\tilde{C}_{01}} - U_{11}\right] = 0, \tag{13}$$

$$\theta_1 = 1 + \frac{\hat{T}_0(t)}{\tilde{T}_0} + \beta\left(1 + \frac{\hat{C}_{01}(t)}{\tilde{C}_{01}} - U_{11}\right) + R_1\beta\sigma(B_\mathrm{T}^{-1} - B_1^{-1}) \tag{14}$$

Here $R_1 = r_1(C_{11}, T_1)/\tilde{r}_0$, $R_{1\theta} = \partial R_1/\partial\theta_1$ and $\psi = \beta R_{1\theta} - \partial R_1/\partial U_{11}$. Obviously, in equations (11) and (12) $\psi = 0$, when for $R_\mathrm{S} \neq 0$ the equation (13) is fulfilled. In equation (13) the condition

$$\left[1 + \frac{\hat{C}_{01}(t)}{\tilde{C}_{01}} - U_{11}\right] = 0$$

corresponds to $R_\mathrm{S} = 0$.

The variation of δ-function position in a porous granule with time is determined by equations (15*a*)–(15 *c*):

$$\alpha = 0:\ x_1(t) = 1 - \ \ (t) \tag{15a}$$

$$\alpha = 1:\ x_1(t) = \exp[- \ \ (t)] \tag{15b}$$

$$\alpha = 2:\ x_1(t) = [1 + \ \ (t)]^{-1} \tag{15c}$$

$$(t) = \frac{1 + \hat{C}_{01}(t)/\tilde{C}_{01} - U_{11}}{\sigma R_1} - \frac{1}{B_1}$$

Equations (15) fail to give a physically meaningful x_1 when $(t) < 0$ or $(t) > 1$ for plate geometry and when $(t) < 0$ for cylindrical and spherical geometrical forms. In such cases one must set $x_1 = 0$ if equation (15*a*) gives a negative x_1 [$(t) > 1$] and $x_1 = 1$ if equations (15) result in a x_1 value greater than unity [$(t) < 0$]. The optimal values U_{11} and θ_1 are then defined as the values of concentration and temperature that maximise J and satisfy the constraints

$$\frac{1 + \hat{C}_{01}(t)/\tilde{C}_{01} - U_{11}}{R_1} \leq \sigma(1 + 1/B_1) \tag{16}$$

for $\alpha = 0$ and

$$\frac{1 + \hat{C}_{01}(t)/\tilde{C}_{01} - U_{11}}{R_1} \geq \sigma/B_1 \tag{17}$$

for $\alpha = 0$–2. These constraints ensure that $x_1 \in [0,1]$. This was shown previously[1] for the case $C_{01}(t) = \tilde{C}_{01}$, $T_0(t) = \tilde{T}_0$ (steady-state regime).

When $x_1 \in [0,1]$ the equation (13) has no solution when $R_\mathrm{S} \neq 0$, then in these cases it is necessary to use equation (18) for a determination of the maximum porous catalyst granule productivity instead of equation (13) and here the value R_1 is maximised.

$$\frac{\sigma R_1}{B_1} = 1 + \hat{C}_{01}(t)/\tilde{C}_{01} - U_{11} \tag{18}$$

It follows clearly from equation (13) that if, *e.g.*, the derivatives $\partial R_1/\partial U_{11}$ and $\partial R_1/\partial\theta_1$ are positive when $\beta \leq 0$, the function $J(t, \varphi_1)$ has no local maximum. In this case a necessary requirement to maximise the productivity of the porous catalyst granule is an exothermic process. Otherwise, the greatest productivity involves catalysts which have an active component localised on an external surface of the granule.

Thus, the results obtained provide a basis for controlling the catalytic processes proceeding on porous catalyst granules with the aim of maximising their productivity.

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