Mathematical modelling of thermal microexplosion in a catalyst granule with point sources of heat release

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Abstract. A mathematical model of heat and mass transfer in a spherical catalyst granule is proposed. Exothermic synthesis reactions are carried out on point active centres located inside a porous ceramic granule. From the surface of the granule the heat of catalytic reactions is removed into liquid synthesis products. The rate of a chemical reaction is modelled by a modified Arrhenius law. In contrast to the homogeneous model of a catalytic granule methods for calculating heat transfer processes in a system of point, active centres do not develop. An iterative procedure is suggested to calculate the unknown temperature and concentration of the reagent at the active centre. It is shown that the temperature of the active centres is significantly higher than in the volume of the granule. The results of modelling a thermal explosion with increasing granule size and reactor temperature are presented.

1. Introduction
Modern microtechnologies allow producing porous ceramic granules of catalysts with point active centers of the synthesis reaction [1, 2]. The synthesis processes are exothermic [3, 4]. The active centers on which the synthesis reactions occur are located in the volume for the thermal boundary layers around the microparticles not to overlap. In this case, the homogeneous model of the catalytic granule is incorrect [4 – 6]. Modeling of heat and mass transfer processes in a granule is complicated by the fact that the values of the temperature and concentration of the reagent are unknown. The paper proposes a self-consistent procedure for calculating the temperature and concentration at the active centers and in the volume of the granule. It is shown that when the thermal stability of the catalyst granule is lost, the temperature of the active centers is significantly higher than in the volume of the granule. Thermal microexplosion can lead to the destruction of the point centers of catalysis without visible damage to the catalyst granule. The thermal explosion of the granule as a whole, which leads to its destruction, is also investigated.

2. Problem statement

2.1. Basic equations
We consider a spherical catalyst granule with active microparticles on which synthesis reactions are taking place. The equation for the temperature of a granule with point active centers of heat release has the form
Here \( \rho_r, c_r, \lambda_r \) are the density, heat capacity and heat conduction of the granule; \( Q_0 \) is the heat of exothermic synthesis reaction; \( r_i^{(i)} \) are the position vectors of the \( i \)-th active centers; \( N_0 \) is the number of active centers in the granule; \( T_0^{(i)}, C_0^{(i)} \) are the temperature and concentration of reagent at the \( i \)-th active center; \( \delta ( \mathbf{r} ) = \delta (x) \delta (y) \delta (z) \) is Dirac delta-function, which is normalized as \( \int \delta ( \mathbf{r} ) \, d \mathbf{r} = 1 \).

Here \( dr = dx dy dz \) is the differential of the volume.

The boundary condition on the surface of the granule has the form

\[
-\lambda_r \frac{\partial T_{gr}}{\partial r} \bigg|_{r=d_{gr}/2} = \alpha_0 \left( T_{gr} \bigg|_{r=d_{gr}/2} - T_r \right)
\]

Here \( d_{gr} \) is the diameter of the granule; \( T_r \) is the temperature in the reactor tube outside the granule; \( \alpha_0 \) is the heat transfer coefficient between the granule surface and liquid products.

The equation for the concentration of gaseous regents \( C \) inside the granule is written as

\[
\frac{\partial C}{\partial t} = D_c \Delta C - \sum_{i=1}^{N_0} \Phi_0 \left( T_0^{(i)}, C_0^{(i)} \right) \delta \left( \mathbf{r} - r_i^{(i)} \right)
\]

Here \( D_c \) is the effective diffusion coefficient of the reagent inside the porous granule.

The boundary condition describes the mass exchange by reagent through the granule surface

\[
-\frac{\partial C}{\partial r} \bigg|_{r=d_{gr}/2} = \beta_c \left( C \bigg|_{r=d_{gr}/2} - C_R \right)
\]

Here \( C_R \) is the concentration of reagent outside the granule; and \( \beta_c \) is the mass transfer coefficient.

### 2.2. Equations in dimensionless form

We rewrite the equations of heat balance, concentration and boundary conditions in a dimensionless form. We define the dimensionless temperature and concentration as

\[
\Theta = \left( T_{gr} - T_r \right) / T_r,
\]

\[
\Psi_C = \left( C_R - C \right) / C_R.
\]

The dimensionless time is

\[
\xi = t \lambda_{gr} / (d_{gr} / 2)^2 \quad (\chi_{gr} = \lambda_{gr} / (\rho_c c_{gr}) \text{ is the thermal diffusivity of the granule}); \text{ dimensionless coordinate is } \eta = 2r / d_{gr}.
\]

The equation and the boundary condition for the dimensionless granule temperature take dimensionless form

\[
\frac{\partial \Theta}{\partial \xi} = \Delta \Theta + 4\pi \sum_{i=1}^{N_0} \Xi_{gr}^{(i)} \delta \left( \eta - \eta_i^{(i)} \right) \left( \frac{\partial \Theta}{\partial \eta} + \alpha_0' \Theta \right) \bigg|_{\eta^{(i)}+1} = 0
\]

(1)

Here \( \alpha_0' = \alpha_0 \left( d_{gr} / 2 \right) / \lambda_{gr} \) is the dimensionless coefficient of heat transfer; and \( \Xi_{gr}^{(i)} \) is the dimensionless heat release during the synthesis reactions (see, for example, [3])

\[
4\pi \Xi_{gr}^{(i)} = \Omega_{gr}^{(i)} \Gamma \left( \Theta_0^{(i)} \right), \quad \Gamma (\Theta) = \exp \left[ E_c^* / (1 + \Theta) \right] \left[ 1 + b_0 \exp \left[ E_c^* / (1 + \Theta) \right] \right]^{-2}
\]

Here \( E_c^* = E_c^*/(R_t T_r) \), \( E_c^* = E_c^*/(R_t T_r) \) are the dimensionless activation energy; \( R_u \) is the universal gas constant; \( \Omega_{gr}^{(i)} = Q_0 d_0 \exp \left( -E_c^*/(\rho_{gr} T_r (d_{gr} / 2)) \right) \) is the dimensionless thermal effect of the reaction; and \( d_0, b_0 \) is the empirical function that depends on the concentration of the reagent.

Equation and boundary condition for the dimensionless concentration are

\[
\frac{\partial C}{\partial \xi} = \Delta C - \sum_{i=1}^{N_0} \Phi_0 \left( T_0^{(i)}, C_0^{(i)} \right) \delta \left( \eta - \eta_i^{(i)} \right)
\]
Here $\beta_C = \beta_C (d_C / 2) / D_c$ is the dimensionless coefficient of mass transfer; $\text{Le}_c = \chi_{gs} / D_c$ is the Lewis number; and the dimensionless rate of reagent consumption is equal to

$$4\pi \Xi^{(i)}_C = \Omega^{(i)}_C \Gamma (\Theta^{(i)}_\theta) \quad \Omega^{(i)}_C = a_0 \exp (-E_a^\prime) / D_c C_r (d_{gs} / 2)$$

3. Stationary distribution of temperature and reagent concentration in the granule

The loss of the thermal stability of the granule occurs as a result of random fluctuations near the stationary state. The temperature and concentration of the reagent on the active centers are unknown. The calculation of these parameters is carried out in a self-consistent manner. At the first stage, we find an analytical solution for a given power of heat release at the point centers of synthesis. At the next stage, we perform an iterative refinement of the temperature and concentration of the reagent at the active centers.

3.1. The solution for the specified heat releases on active centres

We describe the solution for temperature, because for concentration the calculations are carried out similarly. The stationary temperature distribution is the solution of the following problem

$$\Delta \Theta + 4\pi \sum_{i=1}^{N_i} \Xi^{(i)}_\psi \delta (\eta - \eta^{(i)}_\psi) = 0 \quad (\partial \Theta / \partial \eta + \alpha \Theta)_{|\eta=0} = 0 \quad (2)$$

At the first stage, we set the heat generation capacity $\Xi^{(i)}_\psi = \text{const}. \quad \text{The temperature distribution inside the granule (Equation 2) consists of two components}$

$$\Theta(\eta) = \Theta'(\eta) + \Theta''(\eta)$$

The $\Theta'(\eta)$ component describes the solution of an inhomogeneous Equation 2 in an infinite medium. The component $\Theta''(\eta)$ is the solution of the Laplace equation in a spherical coordinate system. The stationary temperature distribution inside the granule has the form

$$\Theta(\eta) = \sum_{i=1}^{N_i} \Xi^{(i)}_\psi \left[ \frac{1}{(\eta - \eta^{(i)}_\psi)} + \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} C^{(i)}_{m,n} \eta^n \cos \left[ m(\varphi - \varphi^{(i)}_\theta) \right] P_n^m (\cos \theta) \right]$$

(3)

Here $P_n^m (x)$ are the associated Legendre polynomials [7]; the coefficients $C^{(i)}_{m,n}$ are found from the boundary condition in Equation 2.

3.2. Iterative calculation of temperatures and concentrations at active centres

The next step in the self-consistent method consists in averaging the obtained temperature distribution in the granule over the volume of the active center. We perform the integration of the granule temperature (Equation 3) over the volume of the selected active center

$$\Theta^{(i)}_\theta = \frac{1}{V_0} \int_{V_0} \Theta(\eta^{(i)}_\psi + \eta) \, d\eta$$

Here $V_0$ is the volume of the active reaction center; $d\eta$ is the differential of the volume of the center. As a result of calculations, we obtain a system of transcendental algebraic equations for self-consistent calculation of the temperature of active centers

$$\Theta^{(i)}_\theta = \sum_{i=1}^{N_i} \Xi^{(i)}_{\psi_0} \left[ \frac{1}{(\eta^{(i)}_\psi - \eta^{(i)}_\psi)} + \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} C^{(i)}_{m,n} \cos \left[ m(\varphi^{(i)}_\theta - \varphi^{(i)}_\theta) \right] P_n^m (\cos \theta) \right]$$

(4)
Equation 4 takes into account both the boundary conditions on the surface of the granule and the mutual influence of all active centers inside the granule. The solution of the equation for the concentration of the reagent inside the granule is found in a similar way. A system of equations for the concentration of the reagent on the active centers is obtained in a self-consistent manner. For the iterative solution of Equation 4, we use an effective method of finding a stable solution by solving a system of ordinary differential equations [8]

\[
\tau_0 \frac{d\Theta^{(j)}}{dt} = \sum_{j=1}^{N} \frac{\Xi^{(j)}}{\tau_0} + \frac{3\Xi^{(j)}}{\delta_0} - \sum_{\ell=1}^{N} \epsilon_n \sum_{n=0}^{N} \sum_{m=0}^{N} C^{(j)} \cos(m(\varphi^{(j)} - \varphi^{(j)})) P_n \cos(\Theta^{(j)}) (\Theta^{(j)} - \Theta^{(j)})
\]

Here \( \tau_0 \) is the relaxation parameter selected from the stability condition of the solution.

The stationary solution of the system of equations \( \frac{d\Theta^{(j)}}{dt} = 0 \) presented above leads to the desired values of the temperature of the active reaction centers (see Equation 4).

3.3. The average temperature of the granule with localized reaction centres

The thermal explosion of the granule as a whole is investigated on the basis of the dynamics of changes in the average temperature of the granule

\[
\bar{\Theta}(\bar{\tau}) = \frac{1}{V^*_{gr}} \int \Theta(\bar{\tau}, \eta) d\eta
\]

Here \( V^*_{gr} \) is the volume of the granule in dimensionless variables.

We integrate Equation 1 by the volume of the granule

\[
\frac{d\bar{\Theta}}{d\bar{\tau}} = \frac{1}{V^*_{gr}} \int \Delta \Theta d\eta + \frac{4\pi}{V^*_{gr}} \sum_{j=1}^{N} \Xi^{(j)}
\]

Using the Ostrogradsky - Gauss theorem, we obtain

\[
\frac{d\bar{\Theta}}{d\bar{\tau}} = -\alpha_0 \frac{S^*_{gr}}{V^*_{gr}} \bar{\Theta} + \frac{4\pi}{V^*_{gr}} \sum_{j=1}^{N} \Xi^{(j)}
\]

Here \( \bar{\Theta}(\bar{\tau}) \) is the temperature averaged over the granules surface area \( S^*_{gr} \)

\[
\bar{\Theta}(\bar{\tau}) = \frac{1}{S^*_{gr}} \int \Theta(\eta, \bar{\tau}) dS^*_{gr}
\]

For a spherical granule we have the equation for the average temperature of the granule

\[
\frac{d\bar{\Theta}}{d\bar{\tau}} = -3\alpha_0 \bar{\Theta} + 3 \sum_{j=1}^{N} \Xi^{(j)}
\]

The mean temperature of the granule surface and mean temperature of active centers are calculated by the formulas

\[
\bar{T}_{gr} = (1 + \bar{\Theta}) T_R \quad T_0 = (1 + \bar{\Theta}_0) T_R
\]

4. Calculation results

The rate constants of chemical reactions and the thermal effect correspond to the synthesis of artificial oil by the Fischer-Tropsch method [9, 10]. An increase in the reactor temperature leads to a thermal explosion. There are two scenarios that can be distinguished. Microthermal explosion inside the granule and loss of thermal stability of the granule as a whole. Figure 1 shows the overheating of the active centers in relation to the average temperature of the granule.
It can be seen that during thermal microexplosion, the temperatures of the active centers significantly exceed the surface temperature of the granule. Significant overheating can lead to the destruction of the reaction centers. At the same time, the surface temperature of the granule does not reflect the real thermal situation inside the granule with point active centers. Modern microtechnologies allow us to place active centers inside the granule according to a certain law. Figure 2 shows a granule with random uniformly distributed point centers of the reaction. In this case, the temperature distribution inside the granule is significantly inhomogeneous either.

Using different densities of microparticles inside the granule, it is possible to control the temperature distribution in the granule volume. Figure 3 shows that an increase in the concentration of active microparticles in the center of the granule leads to a noticeable increase in the temperature in the center compared to the periphery of the granule.

The loss of thermal stability of the granule as a whole is determined by the diameter of the granule and the temperature of the reactor. Increasing the diameter of the granule reduces the critical temperature of the reactor, after which a thermal explosion occurs. With a fixed diameter of the catalyst granules, there is a critical temperature of the reactor, exceeding which will always lead to a thermal explosion.
Figure 4 shows the dependences of the average temperature of the granule and the average temperature of the active centers with the loss of thermal stability of the granule. It can be seen that the temperature of the active centers is always higher than the surface temperature of the granule.

5. Conclusions
The method for calculating the heat and mass transfer in porous granules of a synthesis catalyst with point reaction centers has been proposed. The rate of an exothermic chemical reaction has been described by a modified Arrhenius law. The unknown temperature and concentration of the reagent at the active reaction centers has been calculated in a self-consistent iterative way. For the catalyst granule, we distinguish two types of thermal explosion. During a microexplosion, the active point centers of the synthesis reaction are significantly overheated. At the same time, the temperature of the granule volume and its surface is significantly lower than the temperature of the active centers. The thermal explosion of the catalyst granule as a whole is accompanied by a sharp increase in the average temperature of the granule. At a given reactor temperature, there is a critical granule size, the excess of which entails a thermal explosion. An increase in the reactor temperature also contributes to the onset of a thermal explosion.

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