*Journal of Engineering Physics and Thermophysics, Vol. 73, No. 4, 2000*

# TRANSFER PROCESSES IN POROUS CATALYSTS IN A MICROWAVE-RADIATION FIELD

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UDC 541.124

*The influence of microwave (superhigh-frequency) radiation on transfer processes in a porous catalyst is investigated theoretically with allowance for a heterogeneous chemical reaction.*

Microwave (superhigh-frequency) radiation is known to be able to rapidly and selectively heat a substance occurring in a condensed phase. Here the so-called inverse gradient of temperature where its maximum value is observed in the central regions of the system is realized in a number of cases. This property is widely used in modern chemical technology [1-3], in particular, to increase the rates of heterogeneous chemical reactions in porous-catalyst particles that, in turn, contain small particle-inclusions (active centers) that are characterized by strong absorption of microwave radiation [4]. In the work proposed, consideration is given to some problems related to the mentioned process. It is shown that the increase in the rate of the chemical reaction is influenced not only by so-called "hot spots" related to the active centers but also by "hot spots" whose appearance is caused by the more intense heating of the central parts of the catalytic porous particles.

At first we consider the case of a heterogeneous chemical reaction in a microwave-radiation field for a quasihomogeneous model of a catalyst with active centers. The total number of molecules that have reacted in the system is determined as (in what follows, a first-order chemical reaction will be considered for simplicity)

$$J = j_1 + j_2 = S_{1g} k_{r1} n_r + S_{2g} k_{r2} n_r \, , \tag{1}$$

where $S_{1g}$ and $S_{2g}$ are the areas of the surfaces of the skeleton of the porous body and the active centers that contact the gas phase, respectively (values of parameters for the porous-body skeleton and the active centers will be denoted by the subscripts 1 and 2, respectively); $n_r$ is the number density of the molecules of the reacting substance; $k_{ri}$ is the rate constant of the heterogeneous chemical reaction for the corresponding surface, expressed as [5]

$$k_{ri} = k_{r0} \exp \left\{ - E_{ri}/kT_i \right\} , \quad i = 1, 2 \, , \tag{2}$$

where $E_{ri}$ is the activation energy of the heterogeneous chemical reaction on the corresponding surface; $k_{r0}$ is the pre-exponential factor, assumed to be constant.

As follows from Eqs. (1) and (2), an increase in $J$ with introduction of the active centers into the porous catalyst and on exposure to the microwave radiation can be due both to the fact that the values of $E_{ri}$ on the surface of the active centers are lower than on the surface of the skeleton of the porous catalyst and to the increase in the surface temperatures of the active centers and the skeleton of the porous body because of intense absorption of the microwaves by the active centers. The problem of calculation of $J$ leads to the neces-

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1062-0125/00/7304-0676$25.00

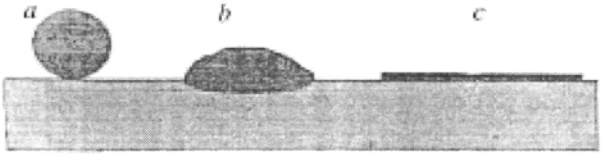

Fig. 1. Different shapes of particle-inclusions (active centers).

sity of finding $n_r$ and $T_i$. These values in the model of an ideal-mixing reactor can be found from a system of equations written for the mean values of the system parameters:

$$V_1 \rho_1 c_1 \frac{dT_1}{dt} = V_1 q_1 - h_{1g} S_{1g} (T_1 - T_g) - h_{12} S_{12} (T_1 - T_2) + n_r k_{r1} H_{r1} S_{1g} + Q_{12} , \tag{3}$$

$$V_2 \rho_2 c_2 \frac{dT_2}{dt} = V_2 q_2 - h_{2g} S_{2g} (T_2 - T_g) - h_{12} S_{12} (T_2 - T_1) + n_r k_{r2} H_{r2} S_{2g} + Q_{21} , \tag{4}$$

$$V_g \rho_g c_g \frac{dT_g}{dt} = h_{gs}^{e} (T_{g0} - T_g) - h_{1g} S_{1g} (T_g - T_1) - h_{2g} S_{2g} (T_g - T_2) , \tag{5}$$

$$V_g \frac{dn_r}{dt} = V_g \frac{n_{r0} - n_r}{\tau} - n_r (S_{1g} k_{r1} + S_{2g} k_{r2}) . \tag{6}$$

In Eqs. (3)-(6) $V_i$ and $V_g$ are the volumes of the solid phases and the gas, respectively; $T_i$ and $T_g$ are the mean temperatures of the solid phases and the gas; $\rho_i$ and $c_i$ are the mass density and the specific heat of the corresponding component; $t$ is the time; $h_{ig}$ is the coefficient of heat transfer between the solid and gas phases; $h_{12}$ is the coefficient of heat transfer between the solid phases; $h_{gs}^{e}$ is the effective coefficient that allows for heat transfer with the surrounding medium, including heat removal by the outgoing flow [6]; $H_{ri}$ is the thermal effect of the chemical reaction (it can be both positive and negative depending on the type of reaction); the quantities $Q_{12}$ and $Q_{21}$ characterize the radiative heat transfer between the solid phases (the gas is assumed to be transparent relative to the incident radiation and not radiative); $\tau$ is the time of gas detention in the volume; $n_r$ is the number density of the reacting molecules; $T_{g0}$ and $n_{r0}$ are the gas temperature and the number density of the reacting molecules in the surrounding medium (at the inlet to the reactor), respectively. We have the following expression for $q_i$ [1]:

$$q_i = \frac{1}{2} \varepsilon_{ei}'' \omega \varepsilon_0 \, |E|^2 . \tag{7}$$

The model considered enables one to understand the general regularities of transfer processes in the system investigated. The coefficients present in it must be determined from a more detailed study of the individual elements of the system. The shape of the particle-inclusions (active centers) (see Fig. 1) can be important. The most complicated is case *b*, analysis of which is possible only by numerical methods that require solving a three-dimensional problem of heat transfer.

First we examine case *a*, where a spherical particle is on a smooth surface. We assume for simplicity that the following conditions are fulfilled: $S_{12}$, $h_{12} \to 0$, $\tau \to 0$, $n_r = n_{r0}$, and $T_g = T_{g0} = T_1$. The thermal conductivity of the small spherical particle is assumed to be rather large, so that uniform heating of it can be studied. We can write the following equation for the particle temperature $T_2$:

$$\rho_2 c_2 \frac{dT_2}{dt} = q_2 - \frac{3}{R} h_{2g} (T_2 - T_1) - \frac{3}{R} \varepsilon_2 \sigma (T_2^4 - T_1^4) + \frac{3}{R} n_{r0} k_r H_{r2} . \tag{8}$$

The value of $\varepsilon''_{ei}$ is known to increase with the temperature [1]. Furthermore, we assume that the temperature dependence of $\varepsilon''_{e2}$ has the form

$$\varepsilon''_{e2} = \varepsilon''_{e2}(T_1) + \varepsilon''_{B2}\left(1 - \exp\left\{-\frac{\chi_2 (T_2 - T_1)}{T_1}\right\}\right), \tag{9}$$

where $\varepsilon''_{B2}$ and $\chi_2$ are constants that allow one to approximate the actual dependence $\varepsilon''_{e2}(T)$.

With the mentioned conditions, Eqs. (8) and (9) yield the following equation for the stationary particle temperature:

$$\frac{1}{2}\omega\varepsilon_0 |E|^2 \left[\varepsilon''_{e2}(T_1) + \varepsilon''_{B2}\left(1 - \exp\left\{-\chi_2 \frac{T_2 - T_1}{T_1}\right\}\right)\right] R + 3n_{r0}k_{r0}\exp\left\{-\frac{E_{r2}}{kT_2}\right\} H_{r2} =$$

$$= 3h_{2g}(T_2 - T_1) + 3\varepsilon_2\sigma(T_2^4 - T_1^4). \tag{10}$$

The existence of a stationary temperature (i.e., of a solution of Eq. (10)) is related to the possibility of heat removal from the particle. In the case where heat generation in the system is not compensated by heat removal, a stationary temperature for the system (for the considered shape of the particle and the special features of the particle-surface contact) cannot be realized and the particle can melt. Its shape will change, and the contact with the surface and, correspondingly, the heat-transfer coefficient $h_{12}$ will increase. Furthermore, the surface area of the thin film formed from the particles can exceed the surface area of the initial particles.

We consider the case where a stationary particle temperature exists and the following inequalities are fulfilled:

$$\frac{\Delta T}{T_1} << 1, \quad \frac{E_{r2}\Delta T}{kT_1^2} << 1, \quad \frac{\chi_2 \Delta T}{T_1} << 1, \quad \text{where } \Delta T = T_2 - T_1.$$

In what follows we assume for simplicity that radiative heat transfer can be neglected. Then Eq. (8) yields the following expression for $\Delta T$:

$$\Delta T = \frac{F}{G}(1 - \exp\{-Gt\}), \tag{11}$$

where

$$F = \frac{1}{2}\frac{\omega\varepsilon_0 |E|^2 \varepsilon''_{e2}(T_1)}{\rho_2 c_2} + \frac{3n_{r0}k_{r0}H_{r2}}{R\rho_2 c_2}\exp\left\{-\frac{E_{r2}}{kT_1}\right\};$$

$$G = \frac{3h_{2g}}{R\rho_2 c_2} - \frac{1}{2}\frac{\omega\varepsilon_0 |E|^2 \varepsilon''_{B2}\chi_2}{\rho_2 c_2 T_1} - \frac{3n_{r0}k_{r0}E_{r2}H_{r2}}{R\rho_2 c_2 k T_1^2}\exp\left\{-\frac{E_{r2}}{kT_1}\right\}.$$

It is seen from Eq. (11) that the value of $\Delta T$ is substantially affected by the increase in $\varepsilon''_{ei}$ with the temperature and by the heat source related to the chemical reaction.

We note that metallic particles are often used as the active centers introduced into porous catalytic particles [4]. It is shown in [7] that the electrical conductivity in metallic particles with a diameter less than 1 μm can decrease sharply due to the manifestation of a dimensional effect related to the metal-insulator transition. As is noted in [7], this effect is observed only in a three-dimensional object, and the mobility of a two-dimensional electron gas does not change substantially as the dimension decreases in just one direction. The noted phenomenon can lead to a reduction of absorption of microwaves by small spherical particles. Taking account of the above, we can assume that in some cases it is expedient, for better microwave absorption, to cover the internal surface of the porous catalyst with a thin film of a substance that absorbs microwave radiation well (case $c$ in Fig. 1). This can be carried out by the method of chemical deposition of this substance from the gas phase. The question of the conditions that are necessary for realization of a uniform course of the heterogeneous chemical reaction (including chemical deposition) over the volume of the porous spherical particle will be considered below.

Let us consider the case of heating of a system that is a base (the skeleton of a porous body) that does not absorb microwaves with a deposited thin layer (a film on the porous-body surface) of a substance that absorbs microwave radiation using as an example a one-dimensional two-layer system: two plane-parallel layers that are infinite in one direction. Here one layer is a plate of thickness $L_1$ of a substance that does not absorb microwaves, and the second layer is a plate of an absorbing substance of thickness $L_2$ (in what follows, the parameters of these layers will be denoted by subscripts 1 and 2, respectively). The gas temperature $T_g$ on both sides of the system is assumed to be the same.

The solution of the stationary heat-conduction equation for the indicated system with heat exchange with the gas phase by Newton's law under the assumption of a constant microwave-radiation power $q_2$ absorbed in one of the layers considered gives the following values of the dimensionless temperatures (relative to the gas temperature) of the system surfaces contacting the gas phase:

$$\bar{T}_{1s} = \frac{T_{1s}}{T_g} = 1 + \beta_1 \frac{\dfrac{L_1}{L_2}\dfrac{\lambda_2}{\lambda_1}\left(\dfrac{1}{2\alpha} + \dfrac{\beta_2}{\alpha}\right)}{\beta_2 + 1 + \dfrac{L_1}{L_2}\dfrac{\lambda_2}{\lambda_1}(1 + \beta_1)}, \tag{12}$$

$$\bar{T}_{2s} = \frac{T_{2s}}{T_g} = 1 + \beta_2 \frac{\dfrac{1}{2\alpha} + (1 + \beta_1)\dfrac{1}{\alpha}\dfrac{L_1}{L_2}\dfrac{\lambda_2}{\lambda_1}}{\beta_2 + 1 + \dfrac{L_1}{L_2}\dfrac{\lambda_2}{\lambda_1}(1 + \beta_1)}, \tag{13}$$

where $\alpha = \lambda_2 T_g / L_2^2 q_2$; $\beta_i = \lambda_i / L_i h_{ig}$; $\lambda_i$ is the thermal conductivity of the corresponding phase.

As follows from Eqs. (12) and (13), with absorption of microwave radiation by one of the layers, the temperatures of both system surfaces, which determine the heterogeneous-reaction rates on these surfaces, exceed the gas temperature and increase with decrease in the parameter $\alpha$, i.e., with increase in the thickness of the absorbing layer and the radiation power absorbed by unit volume and with decrease in the thermal conductivity of the absorbing layer. The dimensionless temperature difference of the external surfaces $\Delta \bar{T}_s = \bar{T}_{2s}(1) - \bar{T}_{1s}(0)$ for the two-layer system considered also increases with decrease in the parameter $\alpha$.

We note that the considered two-layer system in the gas phase will be affected by the force related to the uncompensated recoil momentum of the gas molecules that escape from opposite surfaces (this effect is analogous to the case of exposure of the system to resonance laser radiation [8]). If the system considered can move in the gas phase, the microwave energy is capable of transforming into mechanical energy in this manner.

Above, we considered a quasihomogeneous model of a porous catalyst and heating of particle-inclusions of different shapes. It should, however, be noted, that the use of the model mentioned to describe actual processes can be found to be insufficiently correct. Frequently utilized spherical particles of a porous catalyst that are located in a gas phase can be given as an example [4]. Here it is necessary to distinguish between the overall porosity of the system and the porosity within an individual catalytic particle, since the regimes of the gas flow within the particles and between them can be different. Furthermore, a low thermal conductivity of the porous particles and the volumetric absorption of microwave radiation lead to a nonuniform temperature distribution inside the porous-catalyst particles (the temperature of the central parts of the particles will be higher). Thus, "hot spots" that are caused by nonuniform heating of the porous catalytic particles can occur. We note that this effect was not considered in [4].

The following equation for the distribution of the temperature $T_p$ in a spherical porous particle of radius $R_p$ can be written by analogy with [5]:

$$\rho_p c_p \frac{\partial T_p}{\partial t} = \frac{\lambda_p}{R_p^2 \bar{r}^2} \frac{\partial}{\partial \bar{r}} \left( \bar{r}^2 \frac{\partial T_p}{\partial \bar{r}} \right) + q_p + H_r s_p k_{r0} \exp \left\{ - \frac{E_{rp}}{k T_p(\bar{r})} \right\} n_{rp}(\bar{r}) , \tag{14}$$

where $\bar{r} = r/R_p$; $q_p$ is the microwave-radiation power absorbed in unit volume of the porous particle, assumed to be constant; $r$ is the radial coordinate; $E_{rp}$ is the activation energy of the heterogeneous chemical reaction in the porous particle; $\rho_p$ and $c_p$ are the mass density and the specific heat of the porous particle, respectively; $s_p$ is the specific surface per unit volume; $n_{rp}(\bar{r})$ is the number density of the reacting molecules in the porous particle, which is determined from the diffusion equation for the molecules of the reacting substance in the particle [5]. The last term in Eq. (14) is related to the heat source due to the chemical reaction.

The stationary solution of Eq. (14) with neglect of the last term on its right-hand side in the case of heat transfer with the surrounding medium by Newton's law and a constant value of $q_p$ over the particle volume has the form

$$T_p = T_g + \frac{Q_p}{4\pi R_p^2 h_{gp}} + \frac{Q_p}{8\pi R_p \lambda_p} (1 - \bar{r}^2) , \tag{15}$$

where $T_g$ is the gas temperature; $h_{gp}$ is the coefficient of heat transfer of the porous particle with the surrounding medium; $Q_p$ is the total power of the microwave radiation absorbed by the particle: $Q_p = \frac{4}{3} \pi R_p^3 q_p$.

It follows from Eq. (15) that the porous-particle temperature increases from the periphery to the center of the particle; the difference between the temperatures at $r = R_p$ and $r = 0$ is determined as

$$\Delta T_p = T_p(0) - T_p(1) = \frac{Q_p}{8\pi R_p \lambda_p} . \tag{16}$$

It is seen from Eq. (16) that $\Delta T_p$ increases with increase in $R_p$ and $q_p$ and decrease in $\lambda_p$. It should be noted that the increase in $Q_p$ upon introduction of microparticle-inclusions (active centers) with a high loss factor into the porous particle will lead to an increase in $\Delta T_p$.

The solution of the stationary heat-conduction equation with energy supply through the particle surface, the same law of heat transfer with the surrounding medium, and the same radiation power absorbed by the particle gives the following value for the particle temperature:

$$T_p = T_g + \frac{Q_p}{4\pi R_p^2 h_{gp}} . \tag{17}$$

It follows from Eqs. (15) and (17) that the particle-surface temperature is identical for the two considered variants of heating and identical values of $Q_p$, but the mean stationary temperature of the particle for volumetric absorption of radiation (for example, in microwave heating of the particle) is higher than the stationary temperature of the particle for surface absorption of radiation (for the same character of heat exchange with the surrounding medium). This results in a larger number of reacting molecules in the porous particle in the first case than in the second. Furthermore, in accordance with the above, with volumetric absorption the rate constant of the heterogeneous chemical reaction at the center of the particle will be larger than on its surface. On the other hand, due to diffusion resistance, it is more difficult for the molecule-reactant to reach the center of the particle than a point that is closer to the external surface of the particle. Because of the simultaneous manifestation of the indicated factors, the course of the chemical reaction over the particle volume in particle heating by microwave radiation can be more uniform than for an isothermal particle, or a situation can be realized where the reaction rate at the center of the particle is maximum. The latter case (especially with an increase in the effective loss factor with the temperature, which is often observed in practice [1]) can lead to initiation of a combustion process inside the porous particle or to its explosion. According to the theory of thermal explosion [6], the condition for its onset corresponds to parameters for which the stationary solution of Eq. (14) ceases to exist; this depends on both the heat release related to the chemical reaction and the porous-particle heating by the microwave radiation.

The increase in the reaction rate within the porous catalytic particle can also be substantial when the reaction products block access of the reactant to the internal part of the particle. Such a case can be realized in the process of pyrolytic chemical deposition of a substance when molecules form a solid layer on the surface that decreases the permeability of the pores and, in principle, is capable of completely blocking access of the reactant to the internal part of the porous particle. This will decrease the effectiveness of the porous catalytic particle.

The condition of a uniform course of the first-order heterogeneous chemical reaction over the volume of the spherical catalytic particle consists in the constancy of the quantity $J_p$:

$$J_p = s_p k_{rp} n_{rp} = \text{const}\,, \tag{18}$$

where $k_{rp}$ is the rate constant of the heterogeneous chemical reaction in the porous particle. Solution of the diffusion equation for the molecules of the reacting substance in a porous particle with account for Eq. (18) and the expression for the rate constant of the heterogeneous chemical reaction leads to the following relation for the temperature distribution, which ensures a uniform course of the reaction over the particle volume:

$$T_p = \frac{E_{rp}}{k \ln \dfrac{k_{r0}}{J_p}\left[ n_{rp0} - \dfrac{s_p J_p}{6D_e}\left(R_p^2 - r^2\right)\right]}\,, \tag{19}$$

where $D_e$ is the effective diffusivity of the reactant molecules in the porous particle (assumed to be constant); $n_{rp0}$ is the number density of the molecules of the reacting substance at $r = R_p$; $E_{rp}$ is the activation energy of the heterogeneous chemical reaction in the porous particle.

As follows from Eq. (19), fulfillment of the condition $J_p$ = const is possible only for $n_{rp0} > s_p J_p R_p^2/6D_e$, i.e., $n_{rp0}$ must increase with increase in $R_p$ and decrease in $D_e$ at this value of the reaction rate $J_p$. The temperature of the porous particle must increase toward its center (in particular, this condition occurs in particle heating by microwave radiation).

This case is analogous to the case considered in [9], where the problem of a uniform course of a heterogeneous chemical reaction in a single cylindrical capillary with a free-molecular regime of gas flow was investigated and it was shown that the temperature of the internal surface of the capillary must be higher at its center for a uniform course of the reaction.

Microwave radiation is also capable of affecting particle conglomerates that can be formed in a humid atmosphere with capillary condensation of water vapor in the area of contact of the particles [10]. The presence of the indicated conglomerates, as is noted in [10], often turns out to be undesirable. Application of microwave radiation can be useful for separation of the particles that form the conglomerates due to rather strong absorption of the microwave radiation by water. We consider briefly the effects arising in this action. With increase in the system temperature due to absorption of the microwave radiation, the surface tension of the capillary-condensed liquid will decrease, which will decrease the force necessary for particle separation. The high heating of the internal parts of the conglomerate by the microwave radiation increases the pressure of the water vapor in them, which promotes separation of the particles forming the conglomerate. The system heating also increases the evaporation of the capillary-condensed liquid between the particles.

Thus, it is shown in the work that the increase in the effectiveness of a porous catalyst in a microwave-radiation field can be related to both heating of the active centers that are present in the porous catalytic particles by the microwave radiation and higher heating of the internal parts of the system. Questions of the influence of microwave radiation on the course of heterogeneous chemical reactions (in particular, chemical deposition) over the volume of the porous particles are analyzed. The temperature distribution in a spherical porous particle that ensures the condition of a uniform course of a heterogeneous chemical reaction over the particle volume is obtained. The possibility of using microwave radiation to affect conglomerates of particles connected by a capillary-condensed liquid with the aim of separating the particles is discussed.

## NOTATION

$E_r$, activation energy of the heterogeneous chemical reaction; $k$, Boltzmann constant; $T_i$, surface temperature of the corresponding phase; $q_i$, power of microwave radiation absorbed in unit volume of the corresponding substance; $\varepsilon''_{ei}$, effective loss factor; $\varepsilon_0$, permittivity of the vacuum; $\omega$, angular frequency; $|E|$, electric-field strength; $R$, radius of the particle-inclusion (active center); $\sigma$, Stefan–Boltzmann constant; $\varepsilon$, emissivity; $R_p$, radius of the porous particle; $\lambda_p$, effective thermal conductivity of the porous particle; $D_e$, effective diffusivity of the reactant molecules in the porous particle; the subscript p refers to the porous catalytic particle.

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