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Alternating motion of liquid in catalyst pores in a liquid/liquid–gas reaction with heat or gas production

Leonid B. Datsevich

University of Bayreuth, LS CVT, Universitätstr. 30, D-95447 Bayreuth, Germany

Abstract

A theoretical analysis of liquid–gas reactions with heat or gas production on a porous catalyst shows the possibility of pulsating motion of liquid in pores caused by the formation of bubbles inside pores due to gas or vapor generation. The criterion number determining the conditions under which such behavior occurs is given. Since the mass transfer and chemical reaction in pores take place under forced, oscillating motion, the description of such a phenomenon cannot be made by the Thiele model. The approach to modeling for such processes is being developed.

Keywords: Oscillation model; Multiphase reaction; Kinetics; Effective diffusion

1. Introduction

Gas–liquid reactions with heat and gas production are mainly analyzed with the model suggested by Thiele [1]. In this model, the chemical reaction in the porous catalyst is considered together with mass and heat transfer, which is carried out by the molecular mechanism, i.e. liquid in pores has no forced convection. Such an approach, however, cannot be applied for some reactions during which considerable quantities of gas or heat are released.

Indeed, in the case of the reaction with gas production, a gaseous compound remains in a soluble state in liquid until the total pressure in a pore (equal to the sum of pressure in the reactor and pressure corresponding to a soluble gaseous compound) exceeds the maximum possible pressure, which can be defined as the sum of the outside and capillary pressures. If this occurs, a gas bubble will appear inside the pore.

In the case of exothermic gas–liquid reactions, if the heat released in the pore is sufficient for a temperature increase at which the vapor pressure exceeds the capillary pressure, then the bubble consisting of the gas and vapor comes into existence.

In both cases, if the quantity of the generated gas and heat is considerable, the growing bubble pushes the liquid out of the pore and the reaction fades. Since the liquid is no longer in the pore, the pressure in the pore becomes equal to the outside pressure and a new portion of liquid occupies the pore again driven by capillary force, and the whole process repeats.

The author calls such behavior the *oscillation model*.

Here a simplified description is considered with the following model assumptions: (a) the reaction takes place only in the liquid phase; (b) the liquid surrounding a catalyst particle is saturated with gas; (c) the catalyst possesses a wetting quality.

Following are some examples of reactions that can demonstrate the features of the oscillation model. Reactions with gas production: H_2O_2 decomposition,

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E-mail address: ldatsevich@web.de (L.B. Datsevich).

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Nomenclature

A_{particle}	pores surface per particle volume (m^{-1})
C_{Dl}	concentration of gaseous reagent in liquid (mol/m^3)
C_{Dg}	concentration of gas reagent in gas phase (mol/m^3)
C_p	specific heat of liquid (J/(kg K))
C_{s}	concentration on outside particle surface (mol/m^3)
d_{particle}	diameter of catalyst particle (m)
d_{pore}	diameter of catalyst pore (m)
$D_{\text{eff oscillation}}$	effective diffusion coefficient at oscillation (m^2/s)
Da	criterion number defined by Eqs. (8) or (15)
Da_{pore}	criterion number Da based on y_{pore}
H	Henry coefficient
$-\Delta H$	heat of reaction (J/mol)
k_{V}	true rate constant related to particle volume (s^{-1})
M	molar mass of evaporated compound (kg/mol)
$\Delta p_{\text{capillary}}$	capillary pressure (N/m^2)
P_{gas}	partial pressure of gas (N/m^2)
P_{max}	maximum possible pressure inside pore (N/m^2)
P_{reactor}	pressure in system (N/m^2)
P_{vapor}	partial pressure of vapor (N/m^2)
$Q_{\text{diffusion}}$	diffusion flow through pore filled with liquid (mol/s)
$Q_{\text{diffusion max}}$	maximal possible diffusion flow through pore (mol/s)
$Q_{\text{generated}}$	heat generated in pore per unit time (W)
Q_{reaction}	molar rate of compound D formation (mol/s)
Q_{removed}	heat removed from pore per unit time (W)
r_{particle}	reaction rate on single particle (mol/s)
r_{s}	mean reaction rate related to pore surface (mol/(m^2 s))
r_{vapor}	heat of vaporization per mol (J/mol)
r_{V}	chemical reaction rate related to catalyst volume (mol/(m^3 s))
R	gas constant (8.314 J/(mol K))
T	current temperature in particle (K)
T_{s}	temperature on outer surface of the particle (K)
U_{displace}	velocity of displacement motion (m/s)
U_{fill}	velocity of filling motion (m/s)
y	length of pore from outer surface to center (m)
y_{cr}	length of pore at which oscillation appears (m)
y_{displace}	distance of displacement (m)
y_{pore}	length of pore (m)

Greek letters

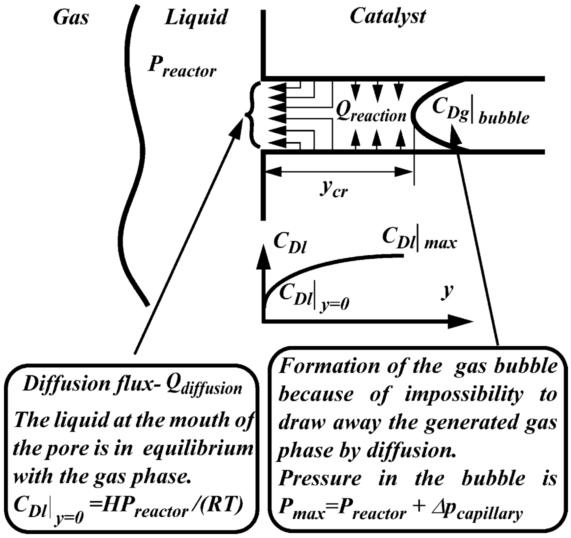
δ	tortuosity factor of catalyst
Δ	thickness of layer generating gas or heat into macropores (m)
λ_{liquid}	thermal conductivity of liquid (W/(m K))
ν	stoichiometric coefficient
ρ_{liquid}	density of liquid (kg/m^3)
σ	liquid surface tension (N/m)
$\Delta\tau_{\text{displace}}$	time of displacement (s)
$\Delta\tau_{\text{fill}}$	time of pore filling (s)
$\Delta\tau_{\text{warm}}$	time of liquid warming (s)

leaching processes (e.g. Al leaching in Ni-Reney catalyst), decarbonization (e.g. furfurol to furan). Exothermic reactions: hydrogenation and oxidation of organic compounds. There are also reactions with simultaneous gas and heat production, e.g. hydrogenation of furfurol to furfuril alcohol or H_2O_2 decomposition (at high H_2O_2 concentrations).

2. Mass and heat equilibrium in the pore in reactions with gas and heat production

2.1. Reactions with gas production: $A(liquid) \rightarrow B(liquid) + \nu D(gas)$

Let us consider an isothermal pore that is initially empty and then filled with liquid by means of capillary



Diffusion flux- $Q_{diffusion}$
The liquid at the mouth of the pore is in equilibrium with the gas phase.
$C_{Dl}|_{y=0}=HP_{reactor}/(RT)$

Formation of the gas bubble because of impossibility to draw away the generated gas phase by diffusion.
Pressure in the bubble is $P_{max}=P_{reactor}+\Delta p_{capillary}$

Fig. 1. Representation of a catalyst pore in the reaction with gas production.

force. The time necessary to fill the pore depends on the pore diameter and physical properties of the liquid [2] and is nearly always far less than the characteristic reaction time. This means that the concentration of the reacting compound as well as the reaction rate related to the pore surface are the same throughout the pore length at given time.

During the reaction (see Fig. 1) the gas is generated at the pore wall at the rate:

$$Q_{\text{reaction}} = \pi d_{\text{pore}} y r_{\text{s}} \nu \tag{1}$$

Two possibilities can occur: either gas remains in the liquid, in the saturated state or, alternatively, part of the gas, which cannot be removed by molecular diffusion, forms the gas bubble. The latter happens if the concentration of the gas compound D saturated in the liquid—C_{Dl} is equal to its equilibrium concentration, which corresponds to the maximum pressure in the capillary.

As long as the distance y from the pore mouth is short, the diffusion of the generated gas, which remains in soluble state, is sufficient in order to remove the formed gas. The rate of diffusion is

$$Q_{\text{diffusion}} = \frac{\pi d_{\text{pore}}^2}{4} D_{\text{Dl}} \frac{C_{\text{Dl}}|_y - C_{\text{Dl}}|_{y=0}}{y} \tag{2}$$

Since the maximum pressure that ever can be achieved in the pore is

$$P_{\max} = P_{\text{reactor}} + \Delta p_{\text{capillary}} \tag{3}$$

one can express the maximum possible concentration of compound D in liquid as

$$C_{\text{Dl}}|_{\max} = HC_{\text{Dg}}|_{\text{bubble}} = \frac{H(P_{\text{reactor}} + \Delta p_{\text{capillary}})}{RT} \tag{4}$$

Taking into account

$$C_{\text{Dg}}|_{y=0} = \frac{P_{\text{reactor}}}{RT} \tag{5}$$

and

$$\Delta p_{\text{capillary}} = \frac{4\sigma}{d_{\text{pore}}} \tag{6}$$

[3], the maximum possible mass flux through the pore can be obtained as

$$Q_{\text{diffusion max}} = \frac{\pi d_{\text{pore}} D_{\text{Dl}} \sigma H}{RTy} \tag{7}$$

Let us designate the ratio of the rate of gas generation on the part of the pore y to the maximum possible quantity of gas that can be removed from the same part of the pore y as a criterion number:

$$Da = \frac{Q_{\text{reaction}}}{Q_{\text{diffusion max}}} = \frac{y^2 r_{\text{s}} \nu RT}{D_{\text{Dl}} \sigma H} \tag{8}$$

2.2. Exothermic reactions

As in the case of reactions with gas production, let us consider a pore that is initially empty and is then filled with liquid. Since the time for filling the pore is very short in comparison with the reaction time, the concentration of the reacting substances and the reaction rate related to the pore surface are the same along the pore length occupied by liquid.

The pore filled with liquid is shown in Fig. 2. In the process of the reaction on the pore wall, the released heat increases the temperature. The heat equilibrium in the pore can be defined, on the one hand, by the rate of the reaction and, on the other hand, by the heat removal from the reaction zone by means of molecular thermal conductivity. The heat generated per unit time on the pore length y is

$$Q_{\text{generated}} = r_{\text{s}} \pi d_{\text{pore}} y(-\Delta H) \tag{9}$$

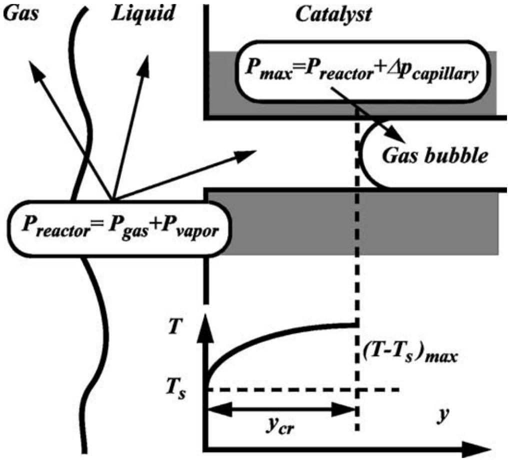


Fig. 2. Representation of a catalyst pore in the exothermic reaction.

The heat that can be led away from the same part y is

$$Q_{\text{removed}} = \frac{\pi d_{\text{pore}}^2}{4}\frac{\lambda_{\text{liquid}}(T - T_{\text{s}})}{y} \tag{10}$$

Let us introduce the ratio of both values as

$$Da = \frac{Q_{\text{generated}}}{Q_{\text{removed}}} = \frac{4r_{\text{s}}y^2(-\Delta H)}{\lambda_{\text{liquid}}d_{\text{pore}}(T - T_{\text{s}})} \tag{11}$$

In order to retain the equilibrium in the pore, number Da should be equal to unity. That means that as the pore length y increases, the difference $T - T_{\text{s}}$ should also increase. However, an increase in temperature leads to an increase in the partial pressure of the liquid vapor. The total pressure of saturated gas and vapor increases and, if it grows to the maximum possible pressure in the pore (Eq. (3)), a bubble consisting of the gas and vapor will appear [3].

The maximum possible increment of temperature $T - T_{\text{s}}$, which causes an increase of the vapor pressure corresponding to $\Delta p_{\text{capillary}}$ and, consequently, the appearance of a bubble can be found by taking into account the dependence of the vapor pressure on temperature and density as

$$P_{\text{vapor}} = P_0 \exp\left(-\frac{r_{\text{vapor}}}{RT}\right) \tag{12}$$

and

$$P_{\text{vapor}} = \frac{\rho_{\text{vapor}}RT}{M} \tag{13}$$

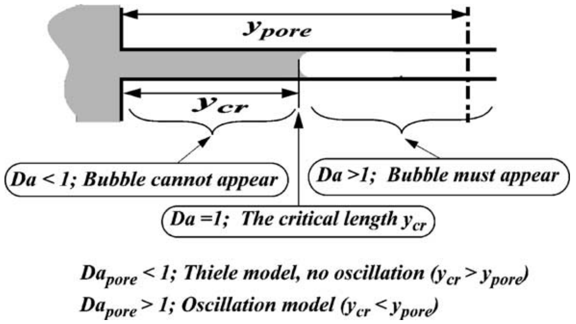


Fig. 3. Conditions of oscillation appearance.

This maximum increment is

$$(T - T_{\text{s}})_{\text{max}} = \frac{4\sigma TM}{d_{\text{pore}}r_{\text{vapor}}\rho_{\text{vapor}}} \tag{14}$$

By inserting it in Eq. (11), one can obtain

$$Da = \frac{y^2 r_{\text{s}} r_{\text{vapor}}\rho_{\text{vapor}}(-\Delta H)}{\lambda_{\text{liquid}}\sigma TM} \tag{15}$$

As can be seen for both types of reactions, the higher is the pore length y, the higher is the number Da. At the part of the pore y where Da becomes equal to unity, the bubble—either consisting of gas (gas production) or consisting of vapor and gas (heat production)—is created because generated gas and heat cannot be taken away by the molecular mechanism (see Fig. 3). Depending on the rate of bubble growth and its size, the liquid in the pore can be replaced completely or partially. If the bubble pushes the liquid from the pore completely, the pressure in the pore becomes equal to the pressure in the reactor P_{reactor} (no liquid and, therefore, no capillary pressure), and the liquid outside the pore, forced by the capillary effect, begins to fill the pore again and the whole process of oscillations recurs. If only part of the liquid is pushed out of the pore, the process of oscillation still takes place but with less intensity.

3. Conditions for the occurrence of oscillation and distance of oscillation penetration

Introducing the length of the pore as $y_{\text{pore}} = d_{\text{particle}}\delta/2$ and calculating number Da with it, the Da_{pore} number, which shows if the bubble has appeared or not, is obtained. When $Da_{\text{pore}} > 1$, the possibility of gas or heat removal by means of molecular diffusion or thermal conductivity is less than gas or heat generation.

We can determine co-ordinate y from the pore mouth at which the bubble should appear—the distance of oscillation penetration y_{cr}—equating Da in Eqs. (8) and (15) to unity. Interpreting the formation of the bubble from the point of view of this distance, we can conclude that if y_{cr} is less than y_{pore}, then $Da_{pore} > 1$ and oscillatory behavior must occur (see Fig. 3).

4. Reaction rate r_s related to the surface of micropores and macropores

Since the real catalyst particle has a complex network of micropores and macropores of different diameters (see Fig. 4), it is important to estimate r_s proceeding from an experimental study which gives the chemical reaction rate related to the volume of a catalyst particle r_v, taking into account that micropores branching out of the macropore bring significant contribution of heat and gas production. This approach to such an estimation is shown in Fig. 4.

5. Elementary steps of oscillatory motions in pores

At first, the pore is empty (or partially empty), and then due to the capillary force, liquid begins to fill the pore (time: $\Delta\tau_{fill}$; velocity: U_{fill}). In the case of exothermic reactions, the second step is warming of the liquid until a vapor-gas bubble appears (time: $\Delta\tau_{warm}$). The third step is the vaporization of the liquid in the pore and its displacement out of the pore (displacement distance: $y_{displace}$; time: $\Delta\tau_{displace}$; velocity: $U_{displace}$). In the case of reactions with gas production, the second step is the displacement of liquid out of the pore due to the growth of the bubble in the course of the reaction. A detailed description of all these steps will be published later [4,5].

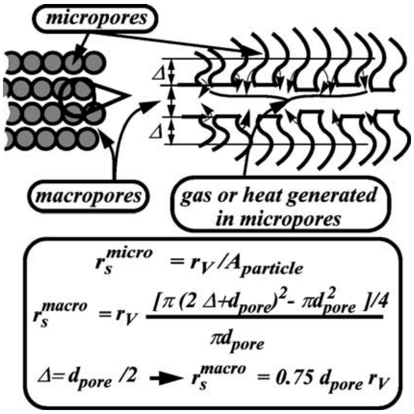


Fig. 4. Definition of r_s related to the surface of the macropore (the catalyst consists of a pressed powder with the fine porous structure).

The oscillation process is illustrated with the reactions described in [6,7]: H_2O_2 decomposition, the reaction with gas production, and hydrogenation of dinitrotoluene (DNT), the reaction with heat production. The reaction conditions are listed in Table 1.

Values of Da_{pore} and the temporal characteristics of oscillatory motion are given in Tables 2 and 3. For both reactions, since $Da_{pore} > 1$, the oscillatory motion of

Table 1
Experimental data and physical properties

	Reference	
	[6]	[7]
Reaction	$H_2O_2 \rightarrow H_2O + 0.5O_2$	2,4-DNT + $6H_2 \rightarrow$ 2,4-TDA + $4H_2O$
Catalyst	CuCr (Engelhard), $d_{particle} = 1.6 \times 10^{-3}$ m, $\rho_p = 1.05 \times 10^3$ kg/m^3, $\delta = 3$ (assumption), $A = 126 \times 10^6$ m^{-1}	5% Pd on Al_2O_3, $d_{particle} = 2 \times 10^{-3}$ m, $\rho_p = 1.8 \times 10^3$ kg/m^3, $\delta = 7.5$, $A = 360 \times 10^6$ m^{-1} (assumption)
Experimental conditions	$P = 1$–13.8 bar, $T = 295$ K, $C_{H_2O_2} = 2\%$	$P = 30$ bar, $T = 328$ K, $C_{DNT} = 500$ mol/m^3, $C^*_{H_2} = 268$ mol/m^3
Reaction rate	$r_v = 2.1 \times 10^6\, e^{-44100/(RT)} C_{H_2O_2}$ (true)	$r_{obs,v} = 20$ mol$_{DNT}$/(m^3 s) (observed)
Physical data	$H = 2.92 \times 10^{-2}$, $D_{O_2 l} = 2.41 \times 10^{-9}$ m^2/s, $\sigma = 72.8 \times 10^{-3}$ N/m, $\mu = 0.96 \times 10^{-3}$ Ns/m^2	$r_{vapor} = 3.2 \times 10^{-4}$ J/mol, $\lambda_{liquid} = 0.102$ W/(mK), $\sigma = 19.8 \times 10^{-3}$ N/m, $\mu = 0.31 \times 10^{-3}$ Ns/m^2

Table 2
The main characteristics of oscillation process at H_2O_2 decomposition

d_{pore} (m)	Da_{pore}	$U_{displace}$ (m/s)	$\Delta\tau_{displace}$ (s)	U_{fill} (m/s)	$\Delta\tau_{fill}$ (s)
10^{-8}	109	1.28×10^{-11}	78	3×10^{-7}	3.2×10^{-3}
2×10^{-8}	109	2.6×10^{-11}	160	3×10^{-7}	1.3×10^{-3}
4×10^{-8}	109	5.1×10^{-11}	310	3×10^{-7}	5.2×10^{-2}
10^{-6}	10^4	1.2×10^{-7}	83	0.4×10^{-5}	2.8
1.42×10^{-6}[a]	1.44×10^4	1.9×10^{-6}	83	1.5	1.34×10^{-5}
2×10^{-6}	2.0×10^4	4.84×10^{-7}	35	2.5	0.7×10^{-5}
3×10^{-6}	2.9×10^4	1.1×10^{-6}	13	4.5	0.3×10^{-5}
4×10^{-6}	4.0×10^4	1.9×10^{-6}	6.3	7.0	0.17×10^{-5}
5×10^{-6}	4.7×10^4	3×10^{-6}	3.6	9.6	0.11×10^{-5}
10^{-5}	10^5	1.2×10^{-5}	0.9	28	0.27×10^{-6}

[a] At this diameter $y_{cr} = y_{displace}$.

Table 3
Characteristics of the oscillation process in macropores at hydrogenation of DNT

d_{pore} (m)	Da_{pore}	$U_{displace}$ (m/s)	$\Delta\tau_{displace}$ (s)	U_{fill} (m/s)	$\Delta\tau_{fill}$ (s)	$\Delta\tau_{warm}$[a] (s)
5×10^{-8}	33	360	5.5×10^{-7}	0.7×10^{-3}	2.0	30.0
10^{-7}	66	180	1.1×10^{-6}	2×10^{-3}	0.5	14.6
5×10^{-7}	330	36	5.5×10^{-6}	2.3×10^{-2}	1.6×10^{-2}	3.0
10^{-6}	660	18	1.1×10^{-5}	6.4×10^{-2}	0.52×10^{-2}	1.5
2×10^{-6}[b]	1300	9.5	2.2×10^{-5}	17.5×10^{-2}	0.12×10^{-2}	0.7
5×10^{-6}	3300	2.4	5.5×10^{-5}	0.7	0.2×10^{-3}	0.3

[a] $\Delta\tau_{warm}$ is the characteristic time of the reaction in the pore.
[b] At this pore diameter$y_{cr} = y_{displace}$.

liquid occurs in all pores. The velocity of liquid motion in macropores (filling process) can reach values of more than 10 m/s.

The dependence of y_{cr} and $y_{displace}$ on pore diameter is shown in Figs. 5 and 6. The displacement distance $y_{displace}$ is more than y_{cr} in pores bigger than 1.42 μm at H_2O_2 decomposition and in pores bigger than 2.0 μm at DNT hydrogenation. That means that bubbles formed in these pores remove liquid out of pores completely. For these pores, the appearance of small

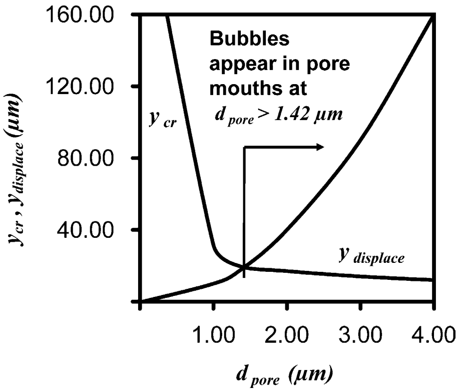


Fig. 5. y_{cr} and $y_{displace}$ at H_2O_2 decomposition. $y_{pore} = 2400$ μm.

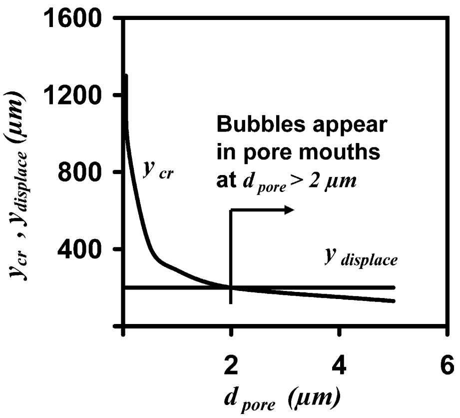


Fig. 6. y_{cr} and $y_{displace}$ at hydrogenation of DNT. $y_{pore} = 7500$ μm.

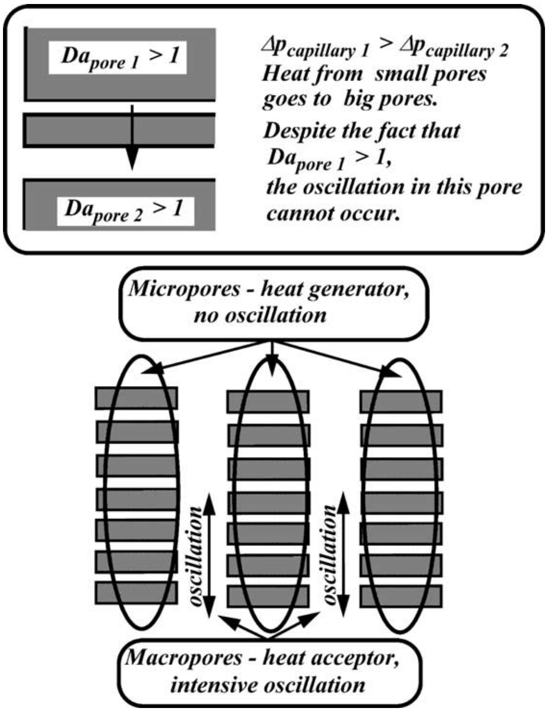


Fig. 7. Oscillations and dissipation of heat in pores of different diameters.

bubbles on the outer surface of the catalyst particle can be observed in experiments.

It is necessary to point out that in exothermic reactions pores of different diameters behave differently. Liquid in macropores can undergo oscillation with far greater intensity than liquid in micropores since the slight overheating of the liquid in macropores is enough to create the gas–vapor bubble due to low capillary pressure. On the other hand, the capillary pressure is significant in micropores and cannot be exceeded since heat dissipation goes in the direction of makropores (see Fig. 7).

6. Some main consequences of the oscillation model

6.1. Concentration profile

At $Da_{\text{pore}} \gg 1$ for the catalyst particle of parallel pores of equal diameters there are two zones. The first is the zone of intensive reaction and is near the particle shell where oscillations take place (difference in the concentration is insignificant). The second is the stagnation zone on which oscillations have a little influence.

6.2. Reaction rate on a single particle r_{particle}

For reactions with gas production with true kinetics $r_{\text{V}} = K_{\text{V}}C$ at $Da_{\text{pore}} > 1$, $r_{\text{particle}} \sim C_{\text{s}}^{0.5}$ (Thiele model: $r_{\text{particle}} \sim C_{\text{s}}^{1}$). For exothermic reactions of two reagents (e.g. hydrogenation) with true kinetics $r_{\text{V}} = K_{\text{V}}C_{\text{A}}C_{\text{B}}$, $r_{\text{particle}} \sim (C_{\text{As}}C_{\text{Bs}})^{0.5}$ at $Da_{\text{pore}} > 1$ (Thiele model: $r_{\text{particle}} \sim C_{\text{As}}^{0.5}C_{\text{Bs}}$, when compound B is in deficiency, e.g. as H_2 in hydrogenation reactions, at Thiele module $\phi > 3$ [8]).

6.3. Intensification of outer mass and heat transfer and effective diffusion in pores

It is to be expected that forced motion of liquid in pores, especially when the bubble leaves the pore mouth, will create a strong disturbance around the particle, intensifying outer mass and heat transfer and increasing the effective diffusion in pores. For exothermic reactions, if $\Delta\tau_{\text{warm}}$ is more than $\Delta\tau_{\text{fill}} + \Delta\tau_{\text{displace}}$, the effective diffusion coefficient in the pore is calculated as

$$D_{\text{eff oscillation}} = \frac{\lambda_{\text{liquid}}}{\rho_{\text{liquid}}C_p} \qquad (16)$$

This gives a value which is several times greater than a molecular diffusion coefficient. Considering the appearance of gas bubbles at the outer catalyst surface, an analogy can be made between the oscillation model and the boiling theory permitting a better understanding as well as providing some quantity estimations of a reaction's influence on both outer mass and heat transfer.

6.4. Possible loss of catalyst activity in reactions with non-evaporating substance

In exothermic reactions with a non-evaporating substance, on the part of the pore where the bubble appears, a non-evaporating substance can leave a deposit which deactivates the pore. This can lead to the loss of catalyst activity (often encountered in hydrogenation of nitrocompounds).

7. Conclusion

The oscillation model under consideration provides an explanation—not only observed in some experiments—of a high grade of mass transfer [9], a lack of correspondence in estimation of non-isothermality in a particle made by Prater's formula [10], and an interpretation in some cases of the observed dependence of the reaction rate on the reagent concentration. It also indicates the way of process intensification and catalyst development (which solvent to choose; how to optimize the pore structure; how to provoke oscillation behavior (when there is no oscillation) by means of additional heat or gas generation, or by means of pressure pulsation).

The author has described here a simplified approach to the phenomenon of oscillation. The real picture is more complex involving both statistical and non-steady features and some other physical effects (e.g. cavitation and pumping effects in pores) that can have an additional influence on catalyst behavior.

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