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The influence of oxygen mobility in solid catalyst on transient regimes of catalytic reaction

N.M. Ostrovskii[a], S.I. Reshetnikov[b,*]

[a] *Hemijska Industrija HIPOL, Odžaci, Serbia and Montenegro*
[b] *Boreskov Institute of Catalysis RAS, Novosibirsk, Russia*

Abstract

Mathematical modeling of the influence of oxygen mobility in solid catalyst on transient regimes of catalytic reaction has been carried out. The region of Thiele modulus Ψ in which the diffusion of oxygen in solid catalyst effect on the transient regime of reaction was determined. These values of Ψ lies in the interval of 0.7–7. The diffusion coefficient corresponding to these values of Thiele modulus lies in the interval of 10^{-17}–10^{-13} cm^2/s.

Keywords: Mathematical modeling; Catalyst oxygen mobility; Catalytic reaction

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1. Introduction

The diffusion of ions and atoms in solid catalysts is widely observed and can influence significantly the catalytic processes. First of all it concerns the diffusion of oxygen in metal oxides. The rate of reaction is determined by both catalytic steps, including the formation of active complexes and various secondary processes such as a diffusion of oxygen in a catalyst, which affects the state of the catalyst. Each of these processes is characterized by a definite duration, i.e. relaxation time. For this reason changing in reaction conditions for different catalysts may have different effects on its state and, consequently, on the reaction rate, thus causing complex transient behavior of the catalytic system. The transient regimes of reactor operation may be significantly influenced by oxygen mobility in solid catalyst [1]. The investigation of the influence of oxygen mobility on the transient regimes of a reactors performance is important, first of all, for unsteady state processes, which can run in the absence of oxygen in gas phase [2] or in presence of gas phase oxygen [3].

The participation of oxygen of the catalyst occurs due to it diffusion into the bulk of the crystalline lattice. For example, in propylene oxidation over bismuth molybdate catalyst approximately 500 layers of oxide ions from the catalyst crystallite participate in product formation [4]. At the same time, on the catalyst with low oxygen mobility (phosphorus–vanadium and iron–antimony oxide) only 2–3 subsurface layers participate in the reaction [5,6].

The diffusion in crystalline lattice of metal oxides occurs due to displacement of point defects. This process can proceed by different mechanisms depending on the type of defect: exchange of atom of crystalline structure with its vacancy, simultaneous cycling replacement of several atoms and others [7]. However, the identification of individual process is not easy. The study of isotope mass effect is one of the approaches. Such a work is beyond the scope of the present publication and the detailed mechanism of diffusion is not considered here.

The aim of this work is the theoretical study of the effect of oxygen mobility in solid catalyst on transient regimes of catalytic reaction, which runs at presence oxygen in gas phase.

2. Formulation of model

Let us consider two reactions—a partial and deep oxidation:

$$A + nO_2 = P, \qquad A + mO_2 = D, \tag{1}$$

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* Corresponding author.
E-mail addresses: ostrovski@hipol.com (N.M. Ostrovskii), reshet@catalysis.nsk.su (S.I. Reshetnikov).

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Nomenclature

b_p, b_d	adsorption equilibrium constants
D	diffusion coefficient of oxygen in catalyst crystallite (cm^2/s)
D_0	pre-exponential factor in (17) (cm^2/s)
L	half-thickness of catalyst crystallite (cm)
Q	activation energy (kJ/mol)
X	conversion of reagent
Y_A, Y_O	molar fractions of A and O_2, respectively
Greek symbols	
θ_O, θ_R	fraction of oxidized (Z_O) and reduced (Z_R) active sites
$\xi = l/L$	dimensionless coordinate
$\sigma(\xi)$	oxidation level inside crystallite
$\langle\sigma\rangle = \int_0^1 \sigma(t, \xi)\, d\xi$	average oxidation level
σ_s	oxidation level of the crystallite surface
$\tau = k_s t$	dimensionless time
τ_r	contact time in reactor (s)
$\Psi^2 = L^2 k_s/D$	analogue of Thiele modulus

which proceed according to the following simplified scheme:

- Partial oxidation:

$$O_2 + 2Z \leftrightarrow 2ZO \quad (p1), \tag{2a}$$

$$A + ZO \rightarrow P + Z \quad (p2). \tag{2b}$$

- Deep oxidation:

$$O_2 + Z \leftrightarrow ZO_2 \quad (d1), \tag{3a}$$

$$A + ZO_2 \rightarrow D + Z \quad (d2). \tag{3b}$$

It is assumed in this scheme that for partial oxidation it is necessary the dissociative adsorption of oxygen (the strongly bonded oxygen), and for deep oxidation the oxygen is necessary to be adsorbed in molecular state (the weakly bonded oxygen).

The sites Z are the ions of metal in optimal oxidation state which are able to activate the oxygen. These sites can be reduced by reagent up to inactive state Z_R:

$$Z + A \rightarrow Z_R \quad (r). \tag{4}$$

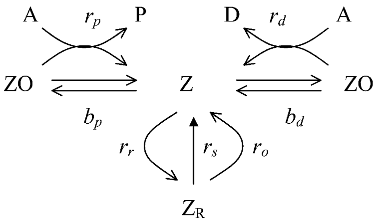
The reduced sites can be oxidized again by the oxygen from gas phase:

$$Z_R + O_2 \rightarrow Z \quad (o) \tag{5}$$

or by lattice oxygen from the bulk of catalyst:

$$Z_R + [O]_S \rightarrow Z \quad (s). \tag{6}$$

This mechanism can be represented by the following schema:



(7)

The chemisorption steps (2a) and (3a) are assumed to be in equilibrium, therefore $\Theta_{Z_O} = (b_p Y_O)^{1/2}\Theta_Z$ and $\Theta_{Z_{O_2}} = b_d Y_O \Theta_Z$. The stoichiometric coefficients of lumped stages (2b) and (3b) depend on concrete reaction, but for our analysis the pseudo-first order may be assumed.

Under these assumptions, the rate of reactions (1) and steps (4–6) can be written as:

$$r_p = k_p (b_p Y_O)^{1/2} Y_A \Theta_Z, \qquad r_d = k_d b_d Y_O Y_A \Theta_Z, \tag{8}$$

$$r_r = k_r Y_A \Theta_Z, \qquad r_o = k_o Y_O \Theta_R, \qquad r_s = k_s \Theta_R \sigma_s, \tag{9}$$

where the rate constants k_p, k_d ($l/l_{cat}s$) and k_s, k_o, k_r ($l_{cat}/l_{cat}s$) have different dimensions.

It should be noted, that the stage (*s*) is named “reaction” only formally, since actually this is the substitution of surface oxygen vacancy by oxygen from the catalyst bulk.

Let us consider now the process in quasi-steady state, when the rate of steps (4)–(6) are much slower than the rate of steps (2) and (3). Than, at the beginning of process ($t = 0$):

$$\sum \Theta_j^o = \Theta_Z^o + \Theta_{Z_O}^o + \Theta_{Z_{O_2}}^o, \qquad \sum \Theta_j^o = 1$$

and consequently:

$$\Theta_Z^o = \frac{1}{1 + (b_p Y_O)^{1/2} + b_d Y_O}. \tag{10}$$

During the reaction ($t > 0$) under quasi-steady state condition, the following equations are valid [1]:

$$\sum \Theta_j = 1 - \Theta_R, \qquad \Theta_Z = \Theta_Z^o (1 - \Theta_R),$$
$$\Theta_R = 1 - \frac{\Theta_Z}{\Theta_Z^o}. \tag{11}$$

Then, taking into account (8), (9) and (11), we can write the following equation for active site dynamics:

$$\frac{d\Theta_Z}{dt} = (k_s \sigma_s + k_o Y_O)\left(1 - \frac{\Theta_Z}{\Theta_Z^o}\right) - k_r Y_A \Theta_Z,$$
$$t = 0, \quad \Theta_Z = \Theta_Z^o. \tag{12}$$

Let us define the “oxidation level” of crystallite (σ) as the ratio of oxygen concentration in crystalline lattice to its maximal concentration. The oxidation level of catalyst surface (σ_s) is determined by diffusion of oxygen ions in catalyst bulk, and by reduction of the surface. Thus, for (σ) and (σ_s) the diffusion model can be used [1]:

$$\frac{\partial \sigma}{\partial \tau} = \frac{1}{\Psi^2} \frac{\partial^2 \sigma}{\partial \xi^2} \tag{13}$$

with the initial ($t = 0$, $\sigma(\xi) = \sigma_o$) and boundary conditions:

$$\xi = 0: \quad \frac{d\sigma}{d\xi} = 0, \qquad \xi = 1: \quad \frac{d\sigma}{d\xi} = -\Psi^2 \Theta_R \sigma_s. \tag{14}$$

The boundary condition on the crystallite surface depicts the fact that surface oxygen on the one hand, is consumed in reaction, and on the other hand, is generated owing to diffusion of oxygen ions from the bulk to the surface.

The mass balance of reagent A in CSTR is defined by equation:

$$Y_A^o - Y_A = \tau_r [k_p (b_p Y_O)^{1/2} Y_A \Theta_Z + k_d b_d Y_O Y_A \Theta_Z]. \tag{15}$$

The conversion (X) and selectivity (S) toward the product of partial oxidation P may be calculated by the following relations obtained from (15):

$$X = \frac{D_a \Theta_Z}{1 + D_a \Theta_Z}, \qquad S = \frac{1}{1 + B_s}, \qquad D_a = A_x k_p \tau_r,$$

$$A_x = (b_p Y_O)^{1/2} + \frac{b_d Y_O k_d}{k_p}, \quad B_s = \left(\frac{k_d b_d}{k_p b_p^{1/2}} \right) Y_O^{1/2}. \tag{16}$$

It is seen from (13) and (14) that the oxidation level inside the crystallite depends only on the parameter Ψ, but the conversion of reagent depend also on the active sites concentration in accordance with Eq. (12).

The mathematical model (12)–(16) was used for the modeling of transient regimes of catalytic reaction in the continuous stirred tank reactor (CSTR), taking into account the influence of oxygen mobility in solid catalyst. The semi-implicit method was used to solve this system of nonlinear differential equations. We should note that this model describes the reaction run in the reactor in the presence of oxygen in gas phase. In the case of separate periods of reaction and catalyst oxidation, the only reaction rate expressions are changed $r_p = k_p^* Y_A \Theta_Z$, $r_d = k_d^* Y_A \Theta_Z$,, together with the corresponding parameters.

3. Results and discussion

Let us define the parameters of model. Suppose that at $t = 0$, $X = 0.8$, $S = 0.9$, $\Theta_Z^o = 0.7$. Than, for $k_p = 1\,c^{-1}$, the remaining kinetic parameters should be the following: $k_d = 1.8\,c^{-1}$, $b_p = 0.2$, $b_d = 0.03$. In order to satisfy the quasi-steady state condition, the oxygen diffusion in catalyst should be much slower in comparison with the reaction, for example, $r_s = (10^{-2}$ to $10^{-3})r_p$. In our calculations we have used $k_s = 0.004\,c^{-1}$. The rate constant values of steps (o) and (r) were chosen arbitrarily, but so that the decline of Θ_Z in time was significant, for instance, $k_o = 0.0001\,c^{-1}$, $k_r = 0.1\,c^{-1}$.

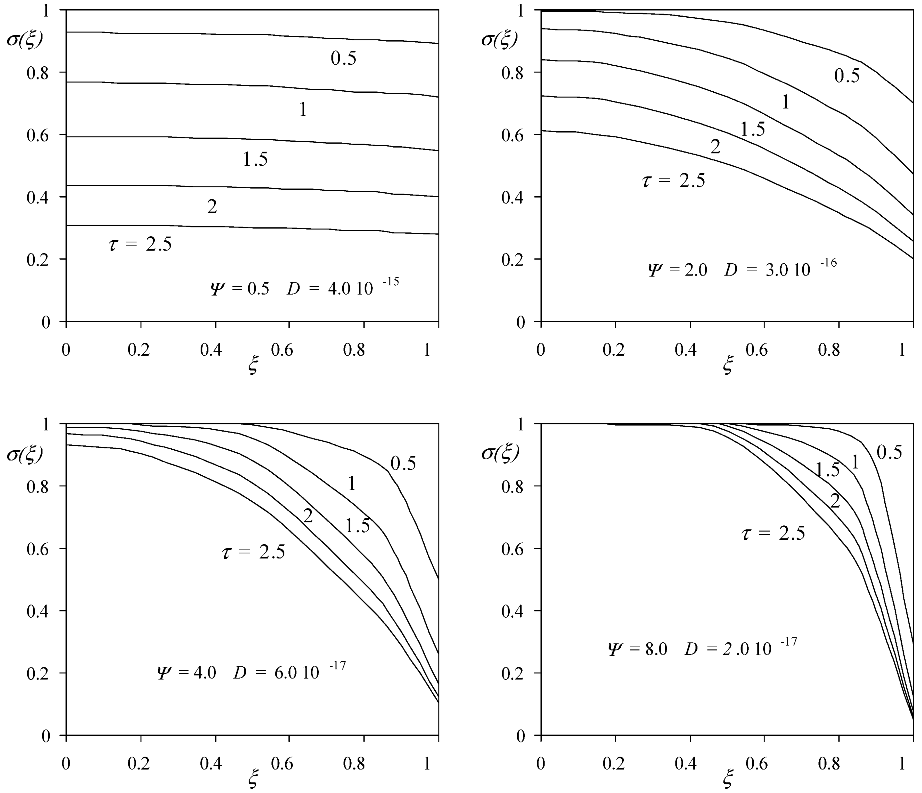


Fig. 1. Profiles of oxidation level of crystallite along its depth (ξ) at the different times and Thiele modulus. $L = 5$ nm, $k_s = 0.004\,s^{-1}$, D (cm^2/s).

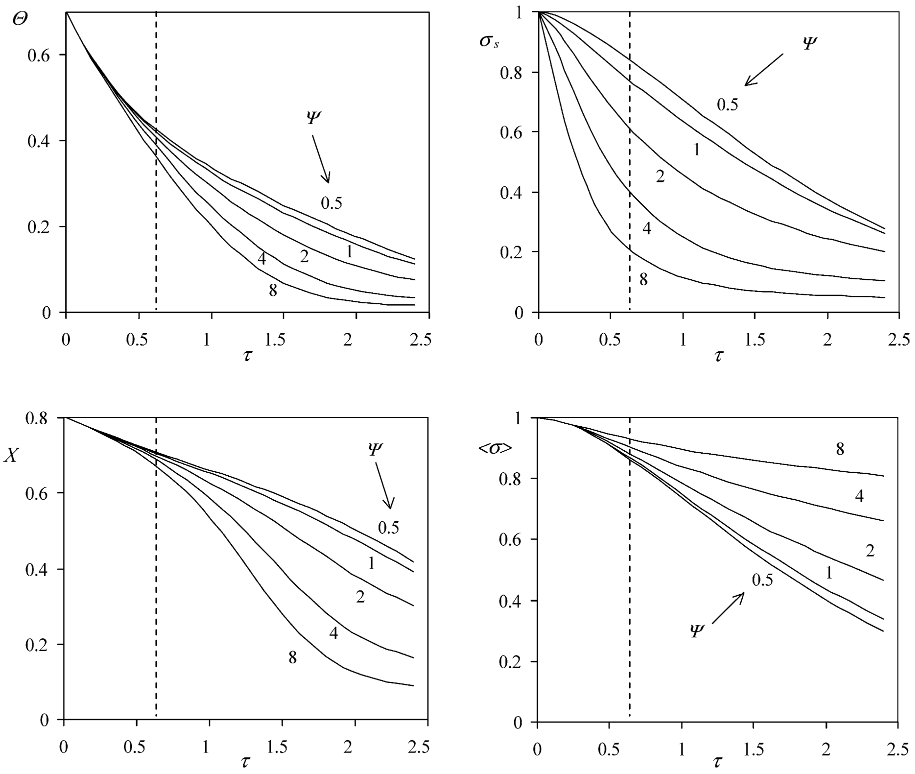


Fig. 2. Time dependencies of fraction of active sites (Θ_Z), oxidation level of the catalyst surfaces (σ_s), conversion of reagent (X) and average oxidation level $\langle\sigma\rangle$ at different Thiele modulus.

Fig. 1 shows the dependence of oxidation level of crystallite along its depth at different time and Thiele modulus. At the initial time, only the oxygen from subsurface catalyst layers takes part in surface oxidation, and than the oxygen from the bulk diffused. At low Ψ (fast diffusion) the uniform reduction of the catalyst crystallite occurs. At high Ψ (slow diffusion) the mobility of oxygen is insufficient for reoxidation of catalyst surface. In this case, the only subsurface oxygen layers take part in surface oxidation. That is why the σ_s, Θ_Z and X are decreased drastically in time at high Ψ (Fig. 2), since the average oxidation level $\langle\sigma\rangle$ decreases more slower than at low Ψ.

It is seen from Fig. 2, that at the beginning of the process ($\tau \leq 0.7$, at $k_s = 0.004\,\mathrm{s}^{-1}$, $t \leq 3\,\mathrm{min}$) the oxygen mobility practically does not influence the number of active sites (Θ_o), conversion (X) and average oxidation state of crystallite $\langle\sigma\rangle$. On the contrary, the oxidation level of surface (σ_s) decreases maximally just in this interval. It is clear from Fig. 2, that for the process efficiency the high oxygen mobility (low Ψ) is preferable.

In order to estimate the limiting values of Ψ, the dependence of $\langle\sigma\rangle$ versus $1/\Psi$ is used (Fig. 3). It is seen that there are two regions of Ψ in which the oxygen mobility does not affect the transient regime in catalyst crystallite. The first region is at $\Psi < 0.7$, where the oxygen mobility is faster in comparison with the rate of catalyst reduction. This value is in a good agreement with Ψ, obtained from the consideration of similar process on a catalyst pellet and in a fluidized bed reactor [1]. The second region is $\Psi > 7$, corresponding to low oxygen mobility. In other words, the region of Thiele moduli in which the diffusion of oxygen in solid catalyst affects the transient regime of catalytic reaction is $\Psi \in [0.7–7]$.

It is important to estimate the value of the diffusion coefficient of oxygen in the catalyst crystallite, which corresponds to this interval of $\Psi \in [0.7–7]$. Since the Thiele modulus is proportional to $L/D^{1/2}$, the certain set of L and D values correspond to obtained interval of Ψ (Fig. 4). The size of crystallite depends on pore structure of catalyst and is commensurable with the pore size. Schematically, within the framework of model (13) and (14), we can present the crystallite as a baffle between two neighbouring pores. For a

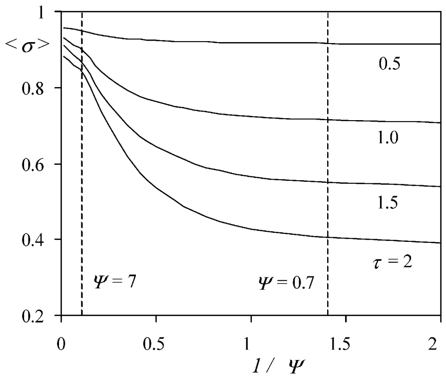


Fig. 3. Dependence of average oxidation level on Thiele modulus.

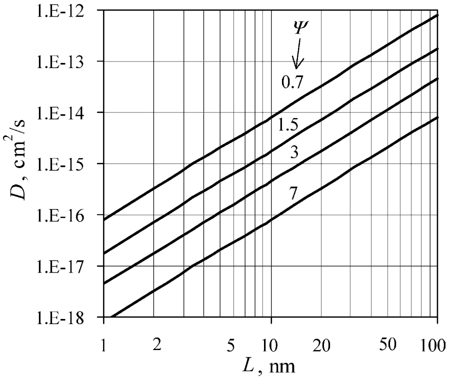


Fig. 4. Dependence of diffusion coefficient on crystallite size at $k_s = 0.004\,\mathrm{s}^{-1}$.

catalyst with mesopores the crystallite size L may vary in the interval of 2–30 nm. For these crystallite sizes the diffusion coefficients lies in the interval of 10^{-17}–10^{-13} cm^2/s (Fig. 4). These values are typical for oxygen diffusivity in some metal oxides [7].

The diffusivity of any species D depends on temperature according to Arrhenius equation: $D = D_0 \exp(-Q/RT)$. Fig. 5 shows the temperature dependence of oxygen diffusivity in some oxides. Solid lines correspond to the data calculated from the values of D_0 and Q in the temperature range of experiments. The dash lines are extrapolation. It is seen that in temperature range of 300–500 °C, which is typical for oxidative catalysis, there are some oxides with $D \in [10^{-17}$ to $10^{-13}]$ cm^2/s. In [12] for $CoCr_2O_4$ the diffusion coefficient equal to 10^{-17} to 10^{-16} cm^2/s was obtained in temperature range of 400–600 °C.

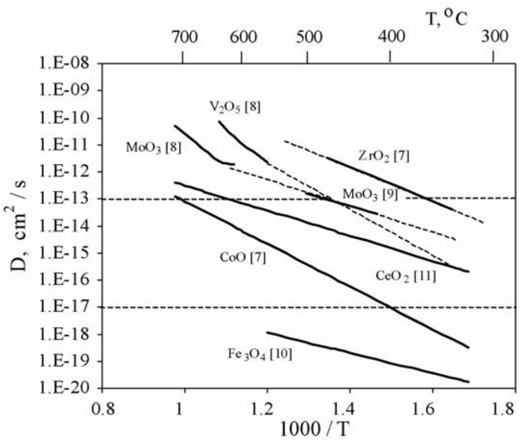


Fig. 5. Coefficients of diffusion of oxygen in oxides. In brackets are references. Dashed lines are extrapolation. *Sources*: [7–11].

It is useful to present some dependencies in terms of dimension time $t = \tau/k_s$ (in Fig. 6, at $k_s = 0.004\,\mathrm{s}^{-1}$). With the increasing of time and Thiele modulus, the difference between the oxidation level of crystallite $\langle\sigma\rangle$ and its surface (σ_s) is increased. Thus, low oxygen mobility hinders its supply toward the surface and re-oxidation of active

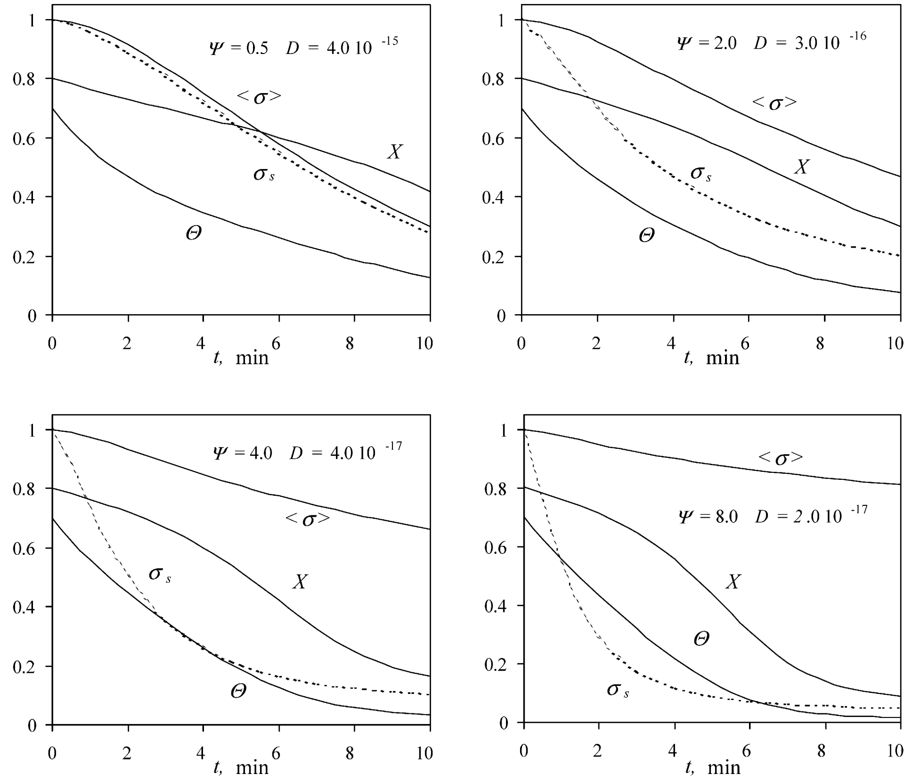


Fig. 6. Influence of oxygen mobility on dynamics of catalyst surface.

centers. This leads to the rapid drop in conversion and reduces the working period of process. On the contrary, high oxygen mobility allows to prolong the working period, which may continue for 5–15 min upon the investigated ratio of parameters.

4. Conclusion

On the base oxidation–reduction scheme, theoretical study of the influence of oxygen mobility in solid catalyst on transient regimes of catalytic reactions has been carried out. It was shown that there are two regions of Thiele modulus Ψ in which the diffusion of oxygen in the catalyst does not affect the transient regime of the reaction. The first region is at $\Psi < 0.7$, where the oxygen mobility is faster in comparison with the rate of surface reduction, and the second one is at $\Psi > 7$, where the oxygen mobility is low. Thus, the region of Thiele modulus in which the diffusion of oxygen in solid catalyst affects the transient regime of catalytic reaction is $\Psi \in [0.7–7]$. The diffusion coefficient corresponding to these values of Thiele modulus lies in the interval of $10^{-17}–10^{-13}$ cm^2/s.

At the temperature 400–600 °C, which is the typical for the oxidative catalysis, in correspondence with published data, Fe_3O_4 has the low oxygen mobility and Cr_2O_3 is oxide with the high oxygen mobility. The following oxides: CoO, CeO_2, MoO_3, V_2O_5 can be considered as the catalysts in which the diffusion of oxygen affects the transient regime of catalytic reaction.

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