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Mathematical Simulation of the Oxidation of *ortho*-Xylene to Phthalic Anhydride in a Fluidized Catalyst Bed

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Received March 28, 2008

Abstract—The oxidation of *ortho*-xylene to phthalic anhydride in a catalytic fluidized-bed reactor was simulated. The mathematical model implied that the reactor was separated into two temperature zones throughout the height of the bed and the catalyst circulated between these zones. The parameters responsible for the regulation of the catalyst state and, correspondingly, the process selectivity, were analyzed. It was found that the temperatures in the zones and the rate of catalyst circulation between them affected the selectivity of the reaction.

DOI: [10.1134/S0023158409020244](https://doi.org/10.1134/S0023158409020244)

INTRODUCTION

Phthalic anhydride is one of the most important products of organic synthesis. The commercial production of phthalic anhydride, which started in the 1920s, was performed initially by the oxidation of naphthalene with air in catalytic fixed-bed reactors; since the mid-1940s, the gas-phase oxidation of *ortho*-xylene in a fluidized-bed reactor has been used. Recently, phthalic anhydride has been mainly prepared from *ortho*-xylene in multitube reactors (about 40 000 tubes). The V_2O_5 – TiO_2 system is commonly used as a catalyst.

Many laboratories around the world have studied this reaction extensively. The main goal is to increase the selectivity of target product formation and to decrease the yield of carbon oxides and other compounds the removal of which makes the process more expensive. A serious effort was made to increase the selectivity of catalysts [1] and to optimize process conditions [2–4]. The current yield of phthalic anhydride in commercial reactors is as high as 82%.

A great number of studies have been devoted to the mathematical simulation of the process. Based on one- and two-dimensional mathematical models, many aspects of the operation of reactors designed for this purpose have been studied. Nikolov et al. [5] summarized the results in a review. The studies have been devoted primarily to the optimization of the performance characteristics of reactors that operate under steady-state conditions.

Experimental and theoretical studies demonstrated that the efficiency of catalytic processes can be increased using an unsteady state of the catalyst. The ratio between adsorbed complexes on the catalyst surface can be regulated by changing reaction conditions;

this allows one to increase the yield of the target product in a number of cases [6].

Ivanov et al. [7] reported experimental data on *ortho*-xylene oxidation to phthalic anhydride in a laboratory nonisothermal fluidized-bed reactor. Nonisothermal conditions were produced using a spiral packing placed in the reactor. The system was maintained in an unsteady state because of spontaneous catalyst transfer throughout the height of the reactor and temperature profile regulation. This improved the selectivity and increased the yield of phthalic anhydride to 97%. Under isothermal conditions, the yield was only 77%. It was found that the catalyst became more selective at the bottom of the bed at a lower temperature and the conversion of *ortho*-xylene mainly occurred at the top of the bed at an elevated temperature.

Note that, as a rule, kinetic models based on experimental data obtained under steady-state conditions (i.e., at the steady state of a catalyst with respect to a gas phase) are used to simulate catalytic processes in fluidized-bed reactors. However, catalyst particles continuously travel in the variable fields of reactant concentrations and temperature in fluidized-bed reactors. The reaction atmosphere affects the particles to change their catalytic properties. The rate of this change can be insufficiently high to consider the state of the catalyst to be steady with respect to the reaction atmosphere and temperature at any instant. A catalyst particle that has not managed to reach a steady state at a point in the reaction space immediately arrives at another point. The catalyst, which travels chaotically in the reactor, continuously changes its catalytic properties; that is, it occurs in an unsteady state. In this case, although the fluidized-bed reactor as a whole operates under steady-state conditions, the output parameters of the reactor and the concentration profiles throughout the height of

the reactor calculated from steady-state rate equations can differ from the experimentally determined characteristics.

Evidently, information on the motion of particles should be available and the relaxation of the catalytic system under conditions of a transition from one steady state to another should be taken into consideration for the simulation of catalytic reactions in a fluidized-bed reactor. To develop a non-steady-state model, the kinetics of not only catalytic steps but also a number of side processes that affect the state of a catalyst (the formation of active sites, diffusion phenomena, structure and phase transformations, etc.) should be studied in detail.

Slin'ko et al. [8] were among the first who studied the unsteady state of a catalyst in a fluidized-bed reactor. They considered a model reaction scheme of partial oxidation by a redox mechanism. The state of the catalyst was characterized by one variable, the fraction of reduced surface sites. According to calculated data, the selectivity of the reaction at the unsteady state of a catalyst can be considerably different from the value found with the use of steady-state rate equations.

The aim of this work was to develop a non-steady-state kinetic model for *ortho*-xylene oxidation to phthalic anhydride in a two-zone catalytic fluidized-bed reactor with catalyst circulation between zones. Attention was focused on the effect of the unsteady state of a catalyst on the selectivity of the process.

MATHEMATICAL MODEL

Let us consider a process in a fluidized-bed reactor. Assume that the states of the catalyst particles are characterized by $\theta_1, \dots, \theta_m$. Under conditions of the convective diffusion of catalyst particles in the fluidized-bed reactor, an equation for the concentration of active complexes, which determine the state of the catalyst, can be written in the following form [9]:

$$\frac{D}{L^2} \frac{\partial^2 \theta_i^n}{\partial \xi^2} - \frac{u_c}{L} \frac{\partial \theta_i^n}{\partial \xi} - \sum_{j=1}^m \beta_{ji} r_j(c, \theta, T) = 0. \quad (1)$$

Boundary conditions:

$$\text{at } \xi = 0: \frac{D \partial \theta_i^1}{L \partial \xi} = u_c (\theta_i^1(0) - \theta_i^2(1));$$

$$\text{at } \xi = \xi_1, \frac{D \partial \theta_i^1}{L \partial \xi} = 0, \text{ in the first zone and}$$

$$\frac{D \partial \theta_i^2}{L \partial \xi} = u_c (\theta_i^2(\xi_1) - \theta_i^1(\xi_1)); \text{ in the second zone;}$$

$$\text{at } \xi = 1, \frac{D \partial \theta_i^2}{L \partial \xi} = 0.$$

Here, r_j is the rate of the j th step, θ_i is the concentration of the i th intermediate complex, L is the catalyst bed height, $\xi = 1/L$ is the dimensionless coordinate of the

bed height, D is the apparent diffusion coefficient of particles, u_c is the circulation rate of catalyst particles, β_{ji} are stoichiometric coefficients, and T is temperature.

The first and second terms in Eq. (1) take into account changes in the concentration of active complexes because of the diffusion of catalyst particles and the occurrence of the reaction, respectively.

To describe reactant concentration changes in the gas phase, we use a two-phase model [10], which reflects the main peculiarities of a fluidized bed—the occurrence of two phases (the dense phase and the bubble phase) and mass exchange between them:

$$\begin{aligned} \frac{1-q}{fL} \frac{d(C_i^b U)}{d\xi} &= -\beta(C_i^b - C_i^d), \\ \frac{q}{fL} \frac{d(C_i^d)}{d\xi} &= \beta(C_i^b - C_i^d) + \sum_{j=1}^m \alpha_{ji} r_j(C, \theta, T). \end{aligned} \quad (2)$$

Boundary conditions:

$$\text{at } \xi = 0, C_i^b = C_i^d = 0 \text{ and } U = U^0; i = 1, \dots, n.$$

Here, β is the phase-exchange coefficient per unit volume of a dense phase; q is the gas fraction passed through the dense phase; f is the ratio between the heights of a packed bed and a fluidized bed; U and U^0 are the linear velocity and the initial velocity of a gas in the reactor, respectively; α_{ij} is the stoichiometric coefficient; and r_j is the rate of the j th step.

Standard finite-difference methods can be used for the numerical solution of a set of differential Eqs. (1) and (2), which describes a process in the fluidized-bed reactor with consideration for the unsteady state of the catalyst.

KINETIC MODEL

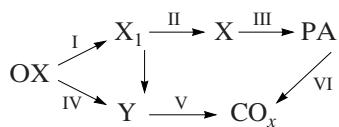
A great number of studies have been devoted to the mechanism of *ortho*-xylene oxidation to phthalic anhydride on V-Ti-O catalysts. In particular, the nature of active sites [11] and the types of reactions occurring at these sites [12] were determined. It was found [13, 14] that the reaction proceeds by an associative mechanism. Oxidized compounds tightly bound to the surface were formed by the interaction of *ortho*-xylene with the catalyst. Reaction products released as a result of the interaction of these compounds with gaseous oxygen. The reaction paths of the formation of complete oxidation products were studied, and it was found that strongly adsorbed compounds, which were slowly oxidized to CO and CO₂, were formed on the catalyst in the course of the reaction [14–16].

In a kinetic study of *ortho*-xylene oxidation to phthalic anhydride, two types of active sites were detected on the surface of the V-Ti-O catalyst. Partial oxidation mainly occurred at sites as associated tetrahedral complexes of V with the OH group (ZOOH). Sites containing vanadium bound to the surface through

three oxygen atoms (Z_2O_3) were responsible for deep oxidation reactions [17].

The formation mechanism of reaction products involves the chemisorption of *ortho*-xylene, a number of consecutive steps of the removal of hydrogen atoms from the *ortho*-xylene molecule with the formation of water, surface dehydration, and the release of carbon-containing products into a gas phase. The main role of oxygen consists in the oxidation of reduced sites formed upon the consecutive transformations of *ortho*-xylene into oxidized surface structures. As a result of the oxidation of reduced sites, the bond energy between products and the surface decreases and the products are released into the gas phase.

In terms of the current concepts, the mechanism of the test reaction [18] can be represented as the following scheme [19]:



where OX is *ortho*-xylene; PA is phthalic anhydride; and X, X_1 , and Y are various surface structures.

The above scheme corresponds to the following stoichiometric equations of reaction steps:

- (1) $OX + 3[ZO] \rightarrow [X_1]$;
- (2) $[X_1] \rightarrow [X] + [ZO] + 2H_2O$;
- (3) $[X] + 3O_2 \rightarrow PA + 2[ZO] + H_2O$;
- (4) $[X_1] + 2[ZO] \rightarrow [Y] + 2H_2O$;
- (5) $[Y] + 9O_2 \rightarrow 8CO_x + 5[ZO] + 3H_2O$;
- (6) $PA + 7.5O_2 \rightarrow 8CO_x + 2H_2O$.

At the first step, the adsorption of *ortho*-xylene occurs and the resulting water enters into the composition of adsorption complexes X_1 . The interaction with oxygen and the formation of phthalic anhydride (step 3) can occur only after the dehydration of complex X_1 and the release of water (step 2). A portion of surface structures X_1 bound to ZOOH sites through methyl groups reacts with adjacent Z_2O_3 sites to form more oxidized compounds Y (step 4). These compounds interact with oxygen from the gas phase to release CO, CO_2 , and water (step 5). Step 6 describes the oxidation of phthalic anhydride.

In the proposed mechanism, H_2O molecules, which are adsorbed on the surface from the gas phase, and undehydrated complexes X_1 (partially Y), which contain from one to three water molecules, play the main role. The concentration ratio between active sites on the catalyst surface changes depending on the temperature and composition of the environment. At a temperature of 350°C or higher, Z_2O_3 sites (they are among ZO sites) predominate on the surface, whereas ZOOH predominates at a low temperature. This allows us to conclude that the conversion of sites into others can occur:



This step is a side process with respect to the catalytic reaction because it does not enter into the catalytic cycle. Under steady-state conditions, step 7 is an equilibrium step and the ratio between the sites of selective and deep *ortho*-xylene oxidation depends on this equilibrium state. Transforming the catalyst into a nonequilibrium state by transferring it in a concentration and temperature field can shift the above equilibrium; because of this, the reaction selectivity can be increased.

The characteristic time of the reaction is an important property of step 7. Ivanov et al. [7] estimated this time at >10 min. Note that deep oxidation sites are transformed into selective oxidation sites with the participation of *ortho*-xylene molecules. Therefore, in the simulation of *ortho*-xylene oxidation, we assumed that the formation of selective sites should occur in the bottom zone of the reactor at a lower temperature. The main reaction occurs in the top zone at an elevated temperature.

The rate equations of the corresponding steps can be represented in the following forms [19]:

$$\begin{aligned}
 r_1 &= k_1 C_{OX} \theta_{ZO}^4, & r_4 &= k_4 \theta_{X_1} (1 + 3\theta_{ZO}) \alpha, \\
 r_2 &= k_2 \theta_{X_1}, & r_5 &= k_5 \theta_Y C_{O_2}, \\
 r_3 &= k_3 \theta_X C_{O_2}, & r_6 &= k_6 C_{PA} \theta_{ZO}^4.
 \end{aligned}$$

Here, α denotes the fraction of deep oxidation sites Z_2O_3 among all of the active sites ZO.

The balance of intermediate concentrations is given by the relation

$$\theta_{ZO} + 3\theta_{X_1} + 2\theta_X + 5\theta_Y = 1.$$

Assuming that the reaction is first-order with respect to the concentration of active sites for selective oxidation and ignoring the dependence of the rate of reaction on water concentration, we obtain the following equation:

$$d\alpha/dt = -k_7 \alpha + k_8 (1 - \alpha), \quad (3)$$

where k_7 and k_8 are the rate constants of the mutual transformation of sites in the forward and backward directions, respectively.

In this scheme, we assume that sites of both types (Z_2O_3 and ZOOH) are uniformly distributed over the catalyst surface and, in general, they form ZO sites at which *ortho*-xylene is adsorbed. The rate of adsorption does not depend on the type of sites. The ratio between the rates of transformation of X_1 into X and Y depends on the probability of a certain number of free sites occurring in the close vicinity of an adsorption site. In the above kinetic scheme, the adsorption of *ortho*-xylene at Z_2O_3 sites was taken into consideration as the factor α in an expression for the rate r_4 .

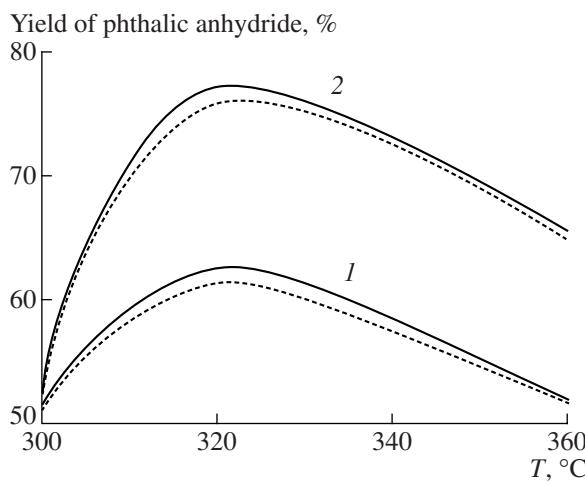


Fig. 1. The temperature dependence of the yield of phthalic anhydride in an isothermal fluidized catalyst bed at the particle diffusion coefficients $D =$ (dashed line) 0 and (solid line) $0.01 \text{ m}^2/\text{s}$ and the interphase exchange coefficients $\beta =$ (1) 0.6 and (2) 3.0 s^{-1} .

RESULTS AND DISCUSSION

Let us consider the occurrence of the process in a fluidized-bed reactor separated into two zones with different temperatures under conditions of catalyst circulation between the zones. In the simulation of the process, we use a kinetic model that includes steps 1–6.

To determine conditions under which a maximum yield of phthalic anhydride is reached, we consider first the case of a constant temperature over the entire reactor. Figures 1 and 2 show the temperature dependences of the yield of phthalic anhydride at $C_{\text{OX}} = 1\text{--}3\%$, $C_{\text{O}_2} = 20\%$, $U^0 = 1.0 \text{ m/s}$, $q = 0.2$, $f = 0.5$, and $D = 0.001 \text{ m}^2/\text{s}$. The mass exchange coefficient was taken equal to 3 s^{-1} , which corresponds to a real value for an organized fluidized bed [20], that is, a bed with various packings (Rashig rings, Berl saddles, etc.) inserted for destroying bubbles [21].

As the reactor temperature was increased, the conversion of *ortho*-xylene increased, whereas the selectivity of phthalic anhydride formation decreased. Therefore, the yield of phthalic anhydride formation as a function of temperature passed through the maximum (Fig. 1). According to calculated data, this yield depends only slightly on the diffusion coefficient of catalyst particles in the isothermal fluidized-bed reactor (solid and dashed lines). The temperature at which the yield of phthalic anhydride reached the maximum depends on many factors. The main factors are the following: the initial concentration of *ortho*-xylene, the contact time, and the intensity of mass exchange between the dense phase and the bubble phase, which is specified by the factor β . Figure 1 shows the temperature dependence of the yield of phthalic anhydride in an isothermal reactor with a fluidized catalyst bed at dif-

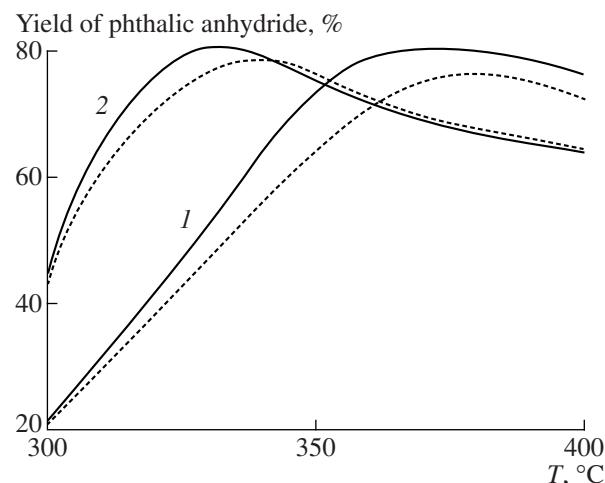


Fig. 2. The temperature dependence of the yield of phthalic anhydride in an isothermal reactor at the contact times $\tau =$ (1) 3 and (2) 7 s and the catalyst particle diffusion coefficients $D =$ (dashed line) 0 and (solid line) $0.01 \text{ m}^2/\text{s}$.

ferent diffusion coefficients of particles and interphase exchange factors β .

As the contact time (τ) and the intensity of mass exchange were decreased, the maximum yield of phthalic anhydride was reached at a higher temperature in the bed (Fig. 2). The calculations demonstrated that the optimum temperature, that is, the temperature at which the maximum yield of the product was observed, also increased as the concentration of the starting reagent was increased. Thus, as the concentration of *ortho*-xylene was increased from 1 to 3%, this temperature increased from 330 to 370°C. Thus, each initial *ortho*-xylene concentration and each contact time corresponded to a certain temperature at which a maximum yield of phthalic anhydride was reached.

Figure 3 shows the dependence of the yield of phthalic anhydride on the ratio between the volume of the hot zone and the total catalyst volume in the reactor at various temperatures in the hot zone and various catalyst circulation ratios. The temperature in the cold zone was taken equal to 270°C. In Fig. 3, it can be seen that the yield of the product passed through the maximum. This can be explained by the fact that the selectivity of the reaction decreases with temperature. If the process is performed at a low temperature, the selectivity of the formation of the product can be high but the product yield is low because of the low conversion of the starting reagent. On the contrary, a high degree of conversion is reached at a high temperature but the selectivity decreases. Thus, it is reasonable to separate the fluidized-bed reactor into two zones in which different temperatures are maintained. In the first zone, a high temperature should be kept to increase the rate of reaction, whereas a lower temperature should be maintained in the second zone to provide higher selectivity and, correspondingly, a higher yield of the target prod-

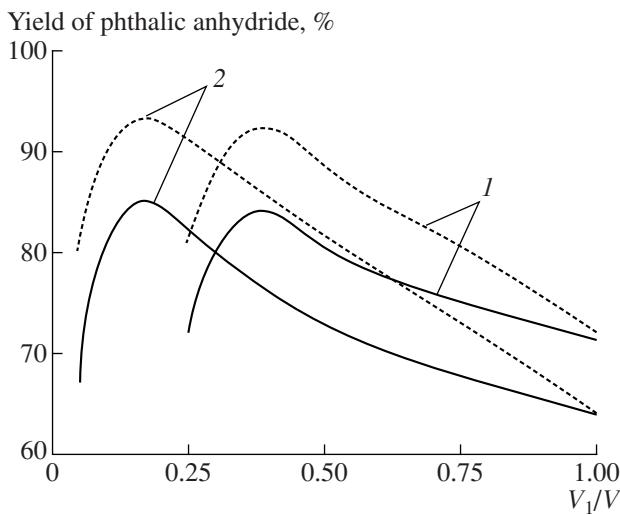


Fig. 3. Dependence of the yield of phthalic anhydride on the ratio between the volume of the hot zone and the total reactor volume at hot-zone temperatures of (1) 360 and (2) 400°C and the catalyst circulation rates U_c = (solid line) 0 and (dashed line) 4.5 h^{-1} . $\tau = 6.9$ s; $C_{\text{OX}} = 3\%$.

uct. In this case, the control parameters are the temperature in the first zone, the catalyst fraction that occurs in this zone, and the catalyst circulation ratio.

Figure 3 shows the effects of the above parameters on the yield of phthalic anhydride. The temperature at which the yield of the target product reached a maximum depended on the catalyst fraction that occurred in the first zone. As this fraction was increased from 0.15 to 0.35, the optimum temperature decreased from 400 to 360°C. In this case, the yield of phthalic anhydride varied within the range of 81.5–82.3% (solid lines); that is, taken alone, the separation of the reactor into two zones with different temperatures did not increase considerably the yield of the product. A dramatic increase in the yield resulted from catalyst circulation between the zones. The catalyst moved from top to bottom; that is, it arrived at the inlet of the first zone upon leaving the second zone. Because catalyst circulation between zones in a traditional fluidized-bed reactor is difficult to control, we considered a reactor design with forced circulation. Figure 3 shows data calculated at a circulation rate of 4.5 h^{-1} as dashed lines. In this case, we designate the ratio of the catalyst volume circulating for 1 h to the total catalyst volume in the reactor as the circulation rate U_c (or the turnover number of the catalyst). In other words, this quantity indicates how many times the catalyst was renewed in the reactor in 1 h. As a result of catalyst circulation, the yield of phthalic anhydride increased by 10–12%, as compared with the yield in the two-zone reactor without circulation (solid lines).

Calculated data showed that the reaction selectivity (S) also increased because of enhanced circulation at other concentrations and temperatures in the first zone.

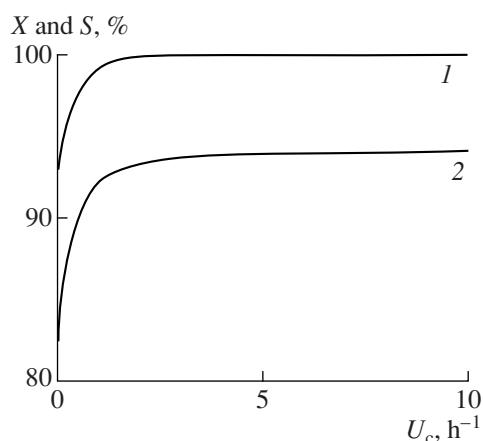


Fig. 4. Dependence of (1) the conversion of *ortho*-xylene and (2) the selectivity of phthalic anhydride formation on the circulation rate. $C_{\text{OX}} = 3\%$; $\tau = 6.9$ s; $T = 380^\circ\text{C}$.

Note that the maximum yield of phthalic anhydride (X) was reached even at the circulation rate $U_c = 1 \text{ h}^{-1}$ (Fig. 4).

The calculated data are consistent with experimental data [7]. The yield of phthalic anhydride in a laboratory nonisothermal reactor was 92–97% [7]. The temperatures in the hot and cold zones varied over the ranges from 300 to 400°C and from 250 to 270°C, respectively.

The effect of catalyst circulation on the selectivity of the process was due to the unsteady state of the catalyst. Let us consider the reasons responsible for the increase in the selectivity.

It is well known that a catalyst in the unsteady state changes its properties under the action of the reaction atmosphere. A time referred to as relaxation time is required for reaching a steady state. It depends on the slowest steps of side processes. In the test system, the redistribution of ZOOH and Z_2O_3 sites is the slowest process. According to Eq. (3), the concentration of Z_2O_3 sites, at which the reaction of deep oxidation occurs, is changed as follows:

$$\alpha = \alpha_{\text{ss}}(1 - e^{-t/\tau_r}).$$

Here, $\tau_r = 1/(k_7 + k_8)$ is the relaxation time, that is, the time it takes for α to reach the steady-state value of $\alpha_{\text{ss}} = k_8/(k_7 + k_8)$. Data on the constants suggest that the rate of redistribution of ZOOH and Z_2O_3 sites is much lower than the rates of catalytic cycle steps.

The state of the catalyst at each section through the height of the bed depends on the concentration of intermediate substances θ_i . If the values of θ_i correspond to the ambient reaction atmosphere (that is, the time derivative of θ_i is zero), we assume that the catalyst occurs in a steady state; otherwise, it occurs in an unsteady state.

Figure 5 shows changes in the concentrations of intermediate substances θ_i (X , Y , ZO , and α) through-

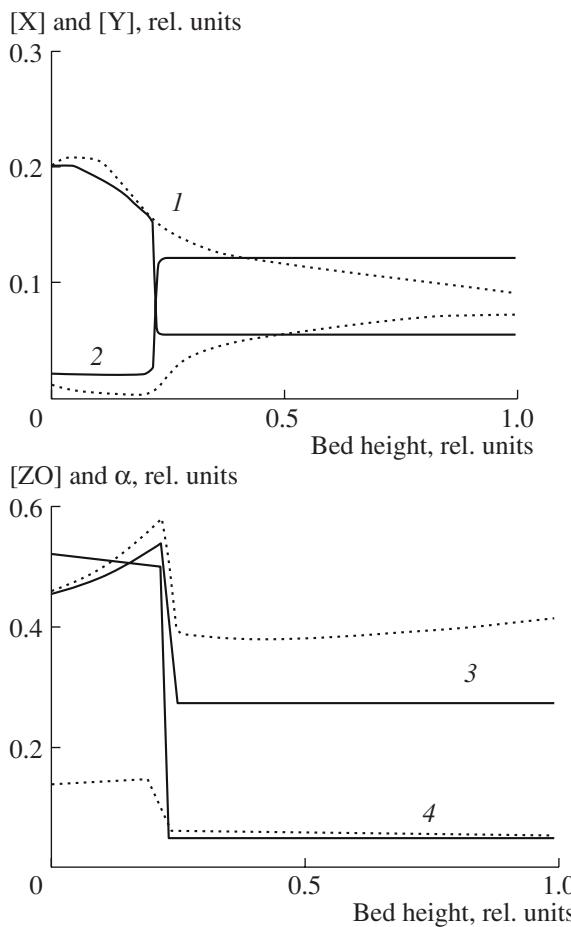


Fig. 5. Changes in the surface concentrations of the intermediate substances (1) X, (2) Y, (3) ZO, and (4) α throughout the height of the catalyst bed at U_c = (solid line) 0 and (dashed line) 1.0 h^{-1} . $C_{\text{OX}} = 2\%$; $\tau = 6.9 \text{ s}$; $T = 380^\circ\text{C}$.

out the height of the two-phase reactor in the absence of circulation (solid lines) and at a circulation rate of 0.9 h^{-1} (dashed lines). Figure 6 shows the corresponding dependences of the values of X and S . The temperatures in the first and second zones were taken equal to 380 and 270°C , respectively. Differences between the values of θ_i with and without circulation suggest that, under circulation conditions, the catalyst occurred in an unsteady state with respect to the ambient reaction atmosphere.

In accordance with the above reaction mechanism, the selectivity of phthalic anhydride formation depends on the concentration of complexes X, whereas the selectivity of by-product formation depends on the concentration of complexes Y. Under catalyst circulation conditions, the integral concentration of complexes X throughout the height of the reactor increased, whereas the concentration of Y decreased (Fig. 5). As a result, the selectivity and, consequently, the yield of the product increased (Fig. 6).

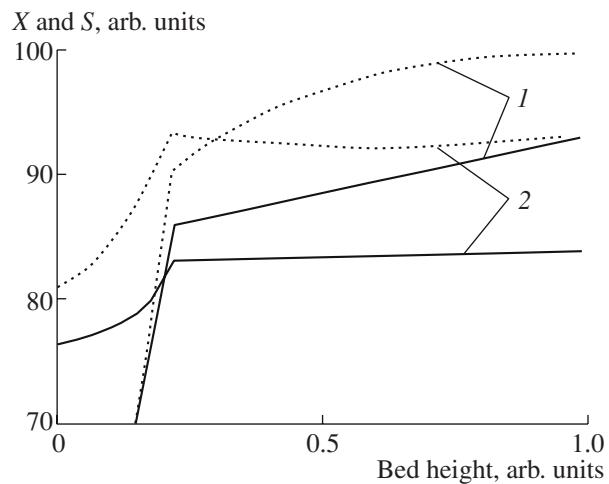


Fig. 6. Changes in (1) the conversion of *ortho*-xylene and (2) the selectivity of phthalic anhydride formation throughout the height of the catalyst bed at U_c = (solid line) 0 and (dashed line) 1.0 h^{-1} . $C_{\text{OX}} = 2\%$; $\tau = 6.9 \text{ s}$; $T = 380^\circ\text{C}$.

The concentrations of complexes X and Y depended on the step rates r_2 and r_4 . With no catalyst circulation, the rate ratio r_2/r_4 remained almost constant under changes in the reactor temperature. Because of this, the separation of the reactor into two zones with different temperatures did not cause a considerable increase in selectivity. The ratio r_2/r_4 increased as a result of catalyst circulation because the rate r_4 decreased. Therefore, the reaction shifted toward the formation of phthalic anhydride.

A change in α , that is, the concentration of $Z_2\text{O}_3$ sites, at which deep oxidation occurs, had the most considerable effect on the rate of the fourth step. As circulation was enhanced, the fraction of deep oxidation sites α decreased at $T = 380^\circ\text{C}$ from $\alpha_{\text{ss}} = 0.52$ to $\alpha_{\text{ss}} \approx 0.07$. Consequently, the fraction of the active sites of selective oxidation increased. The increase in α with temperature can be explained by the fact that the time it takes for the catalyst to reach a steady state (τ_r) is shorter than the residence time of the catalyst in the high-temperature zone. Thus, at $T = 380^\circ\text{C}$ $\tau_r = 30 \text{ min}$ and the residence time of the catalyst in the first zone at $U_c = 0.9 \text{ h}^{-1}$ is 13 min . Consequently, the catalyst has no time to adapt to the ambient reaction atmosphere. Therefore, $\alpha < \alpha_{\text{ss}}$, which leads to a decrease in the rate of the fourth step. As the circulation rate is increased, α approaches a steady-state value, which depends on the temperature in the second zone. Under these conditions, the reaction selectivity reaches a maximum.

Thus, based on the kinetic reaction scheme for *ortho*-xylene oxidation, which includes a side step of the mutual transformation of deep and selective oxidation sites, we simulated the process in a two-zone reactor with a fluidized catalyst bed. The main parameters affecting the state of the catalyst are the temperature; the ratio between the volume of the hot zone and the

total volume of the catalyst; and the rate of catalyst circulation between the zones, which depends on the slow steps of the mutual transformation of sites.

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