$$\mathbf{M} \begin{smallmatrix} \text{odeling} \\ \mathbf{MC} \\ \text{athematical} \end{smallmatrix} \begin{smallmatrix} \\ \text{omputing} \\ \end{smallmatrix}$$

Modeling of the effect of carbon dioxide desorption on carbon monoxide oxidation process on platinum catalyst surface

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A two-dimensional mathematical model for carbon monoxide (CO) oxidation on the platinum (Pt) catalyst surface is investigated according to the Langmuir–Hinshelwood (LH) mechanism. The effects of structural changes of the catalytic surface, the substrate temperature and desorption of the product of reaction (CO_2) are taken into account. It is shown that taking into account the finiteness of CO_2 desorption, both the course of oxidation reaction and the stability region are only slightly affected.

Keywords: *reaction of catalytic oxidation, reaction-diffusion model, mathematical modeling of reaction-diffusion processes.*

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1. Introduction

The catalytic carbon monoxide (CO) oxidation is one of reactions in surface chemistry that has led to new concepts in understanding of surface reactions and contributed significantly to the development of new advanced tools for studying surfaces [1].

It is known that the reaction of CO catalytic oxidation on the platinum (Pt) catalyst surface proceeds through the Langmuir–Ginshelwood (LH) mechanism [2]. Both reactants: CO and oxygen (O_2) have to adsorb on the catalyst surface before the reaction between adjacent adsorbate molecules can take place. Adsorbed oxygen atoms (which are produced by dissociation of O_2 molecule during adsorption) are strongly chemisorbed and remain immobile at temperatures below $550\,\mathrm{K}$. Adsorbed CO molecules chemisorb weakly and can diffuse along the Pt(110) surface [3]. The diffusion coefficient exhibits a strong anisotropy: the diffusion of CO molecules can be up to 10 times faster [4] along $[1\bar{1}0]$ direction, than along the perpendicular direction [001]. The clean Pt(110) surface is reconstructed and has a (1×2) structure [5]. The process of surface reconstruction into (1×1) bulk structure starts when CO coverage exceeds 0.2 [6] and is completed at CO coverage of 0.5 [7]. Such structural changes influence the rates of other elementary processes in particular, increase the oxygen sticking coefficient, which in turn leads to an increase in the reaction rate, and hence to a decrease in the CO coverage.

The desorption of reaction product (CO_2) is considered to be instantaneous in models of catalytic carbon monoxide oxidation proposed and investigated in [8–11]. CO_2 desorption coefficient significantly exceeds CO desorption coefficient, since the binding energy ΔE_{CO_2} of CO_2 molecule on the surface of a plate ($\Delta E_{CO_2} = 0.46\,\mathrm{kcal/mol}$ [12]) is much smaller that the binding energy ΔE_{CO} of CO molecule ($\Delta E_{CO} = 38\,\mathrm{kcal/mol}$ [8]). However, the rate of carbon dioxide desorption is, nevertheless, finite, and therefore the question of influence of this process on the reaction kinetics is relevant.

In present paper, a new kinetic model for description of time dynamics of CO oxidation on Pt(110) surface that accounts for CO_2 product desorption is developed. The effect of finiteness of CO_2 desorption on the course of reaction and the stability region is investigated.

2. Description of the mathematical model

We consider a model for catalytic CO oxidation that accounts for diffusion of CO molecules on Pt(110) surface and the finiteness of CO_2 desorption. The catalytic surface is assumed to be flat with a given Cartesian coordinate system XOY. The time evolution of CO (u) and O (v) surface coverages as well as the fraction of surface in the nonreconstructed (1×1) structure (W) are determined by the following kinetic equations [13]:

$$\frac{\partial u}{\partial t} = p_u \kappa_u s_u \left(1 - \left(\frac{u}{u_{sat}}\right)^3\right) - k_1 uv - k_2 u + D_x \frac{\partial^2 u}{\partial x^2} + D_y \frac{\partial^2 u}{\partial y^2}, \tag{1}$$

$$\frac{\partial v}{\partial t} = p_v \kappa_v \left[s_v^{1\times1} W + s_v^{1\times2}(1-W)\right] \left(1 - \frac{u}{u_{sat}} - \frac{v}{v_{sat}}\right)^2 - k_1 uv, \tag{2}$$

$$\frac{\partial W}{\partial t} = k_3 \left[1 + \exp\left(\frac{u_0 - \frac{u}{u_{sat}}}{\delta u}\right)\right]^{-1} - k_3 W. \tag{3}$$

Here p_u, p_v are the partial pressures of CO and O, respectively; κ_u, κ_v are the impingement rates; s_u, s_v are the sticking coefficients; u_{sat}, v_{sat} refer to the maximum coverages, namely the saturation coverages; k_1, k_2, k_3 are the rates of oxidation reaction, CO desorption and structural phase transition on the Pt(110) surface; D_x, D_y are CO diffusion coefficients in x and y directions, respectively; u_0, δu are the parameters of structural phase transition.

The rates of reaction, desorption and phase transition are temperature T dependent and are determined by the Arrhenius equations [14]:

$$k_i = k_i(T) = k_i^0 \exp\left(-\frac{E_i}{RT}\right), \quad i = \overline{1,3}. \tag{4}$$

Here k_i^0 are the temperature independent coefficients; E_i are the activation energies; R is the universal gas constant.

The time evolution of carbon dioxide surface coverage is modeled by the following equation:

$$\frac{\partial \theta}{\partial t} = f(\theta)(k_1 uv - k_4 \theta), \tag{5}$$

where variable θ denotes CO_2 surface coverage; $f(\theta)$ is a non-decreasing smooth function of the interval $[0; 1]$; coefficient k_4 is a rate of CO_2 desorption. The function $f(\theta)$ is modeled as follows:

$$f(\theta) = 1 - \frac{1}{1 + \exp\left\{-a\left(\frac{\theta}{\theta_{max}} - b\right)\right\}}, \tag{6}$$

where parameter a determines the steepness of $f(\theta)$ curve and b is the x-value of the curves midpoint. The value θ_{max} refers to the maximum coverage of carbon dioxide. Since the CO_2 product formation requires adsorbed CO and O, we assume that $\theta_{max} = u_{sat} v_{sat}$.

Using reaction stoichiometry constraints (the sum of surface coverages of adsorbed species, namely CO_{ads}, O_{ads}, CO_2^{ads}, and the fraction of empty adsorption sites is constant), equation (2) is modified in the following way:

$$\frac{\partial v}{\partial t} = p_v \kappa_v \left[s_v^{1\times1} W + s_v^{1\times2}(1-W)\right] \left(1 - \frac{u}{u_{sat}} - \frac{v}{v_{sat}} - \frac{\theta}{\theta_{max}}\right)^2 - k_1 uv. \tag{7}$$

The equations (1), (3), (5), (7) compose proposed mathematical model for carbon monoxide oxidation process on the platinum catalyst surface that accounts for the finite rate of carbon dioxide desorption.

3. Numerical analysis of the mathematical model

The equations (1), (3), (5), (7) are transformed into dimensionless form by substituting:

$$u = u_{sat}U, \quad v = v_{sat}V, \quad \theta = \theta_{max}\Theta, \tag{8}$$

$$x = l_0\tilde{x}, \quad y = l_0\tilde{y}, \quad t = t_c\tilde{t}, \tag{9}$$

where

$$t_c = \frac{v_{sat}}{p_u\kappa_u s_u}. \tag{10}$$

The parameter l_0 is chosen according to experimental data for the size of Pt-crystal $l_0 \sim 10^{-3}$ cm [15].

In dimensionless form, the equations (1), (3), (5), (7) compose a mathematical model for reaction of CO oxidation on Pt surface:

$$\begin{cases} \dfrac{\partial U}{\partial \tilde{t}} = \dfrac{v_{sat}}{u_{sat}}\left(1 - U^3\right) - \tilde{k}_1 v_{sat}UV - \tilde{k}_2 U + \tilde{D}_x\left(\dfrac{\partial^2 U}{\partial \tilde{x}^2} + D_0\dfrac{\partial^2 U}{\partial \tilde{y}^2}\right), \\[2mm] \dfrac{\partial V}{\partial \tilde{t}} = \tilde{p}_v\left[s_v^{1\times 1}W + s_v^{1\times 2}\left(1 - W\right)\right]\left(1 - U - V - \Theta\right)^2 - \tilde{k}_1 u_{sat}UV, \\[2mm] \dfrac{\partial W}{\partial \tilde{t}} = \tilde{k}_3\left[1 + \exp\left(\dfrac{u_0 - U}{\delta u}\right)\right]^{-1} - \tilde{k}_3 W, \\[2mm] \dfrac{\partial \Theta}{\partial \tilde{t}} = \left(\tilde{k}_1\dfrac{u_{sat}v_{sat}}{\theta_{max}}UV - \tilde{k}_4\Theta\right)\dfrac{\exp\left\{a\left(b - \Theta\right)\right\}}{1 + \exp\left\{a\left(b - \Theta\right)\right\}}. \end{cases} \tag{11}$$

In the system (11): $\tilde{k}_i = k_i t_c$, $i = \overline{1, 4}$, $\tilde{p}_v = \frac{p_v\kappa_v t_c}{v_{sat}}$, $\tilde{D}_x = \frac{D_x t_c}{l_0^2}$, $D_0 = \frac{D_y}{D_x}$.

The partial pressures p_u and p_v and the temperature T play a role of control parameters of a model. Explanation and parameter values used in numerical calculations are given in Table 1 [13].

Table 1. Parameters of mathematical model

CO	Partial pressure	p_u	
	Impingement rate	κ_u	4.2×10^5 1/(s Torr)
	Sticking coefficient	s_u	1
	Saturation coverage	u_{sat}	1
	Diffusion coefficient	D_x	1.2×10^{-7} cm^2/s
O$_2$	Partial pressure	p_v	
	Impingement rate	κ_v	7.8×10^5 1/(s Torr)
	Sticking coefficient	$s_v^{1\times 1}$; $s_v^{1\times 2}$	0.6; 0.4
	Saturation coverage	v_{sat}	0.8
Rates	Reaction	k_1^0	3×10^6 1/s
		E_1	10 kcal/mol
	Desorption of CO	k_2^0	2×10^{16} 1/s
		E_2	38 kcal/mol
	Phase transition	k_3^0	2×10^{-2} 1/s
		E_3	7 kcal/mol
Other	Temperature	T	540 K
	Gas constant	R	0.001987 kcal/(mol K)
	Model parameter of diffusion	D_0	0.1
	Parameters of structural phase transition	u_0; δu	0.35; 0.05
	Parameters of CO$_2$ coverage	a; b	80; 0.01

The results of numerical analysis of two-dimensional mathematical model (11) for CO oxidation on Pt catalyst surface are presented in Figs. 1, 2. Although the finiteness of CO_2 desorption is accounted for (in case of $\tilde{k}_4/\tilde{k}_2 \sim 10^2$), it can be seen that the dependence dynamics of surface coverages $U(\tilde{x}, \tilde{y}, \tilde{t})$, $V(\tilde{x}, \tilde{y}, \tilde{t})$ and fraction of the surface in the nonreconstructed (1×1) structure $W(\tilde{x}, \tilde{y}, \tilde{t})$ retains clear oscillatory behaviour. The amplitudes of oscillations change with a change of y-coordinate, which shows the influence of CO diffusion along OY-axis, despite the fact that $D_y \sim 0.1 D_x$.
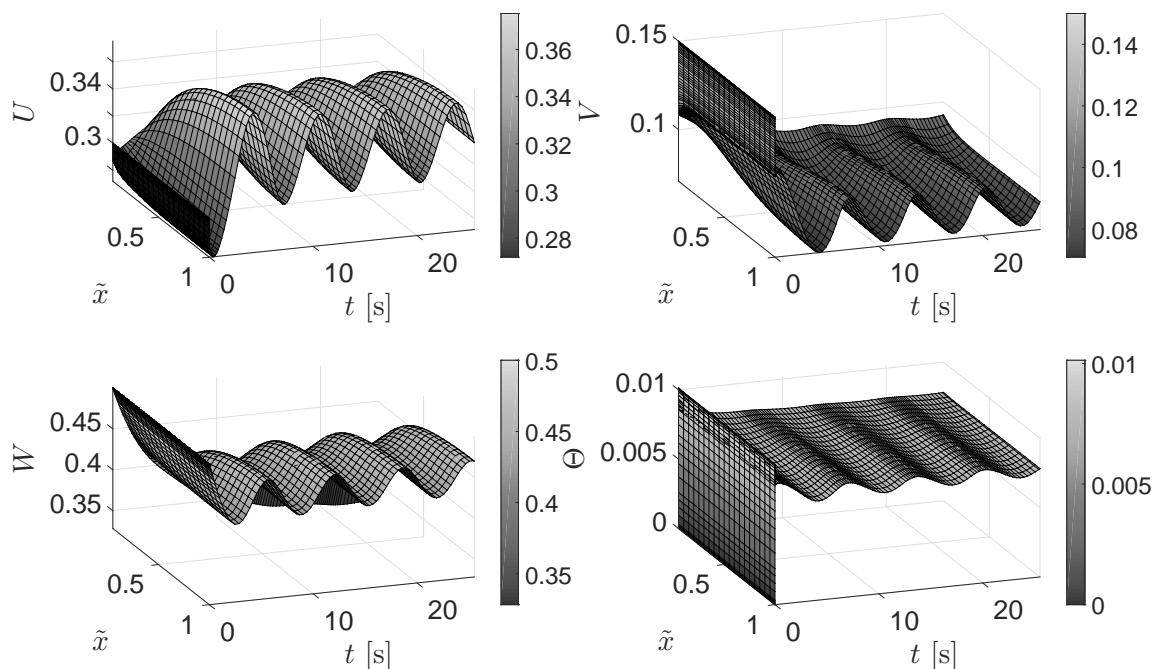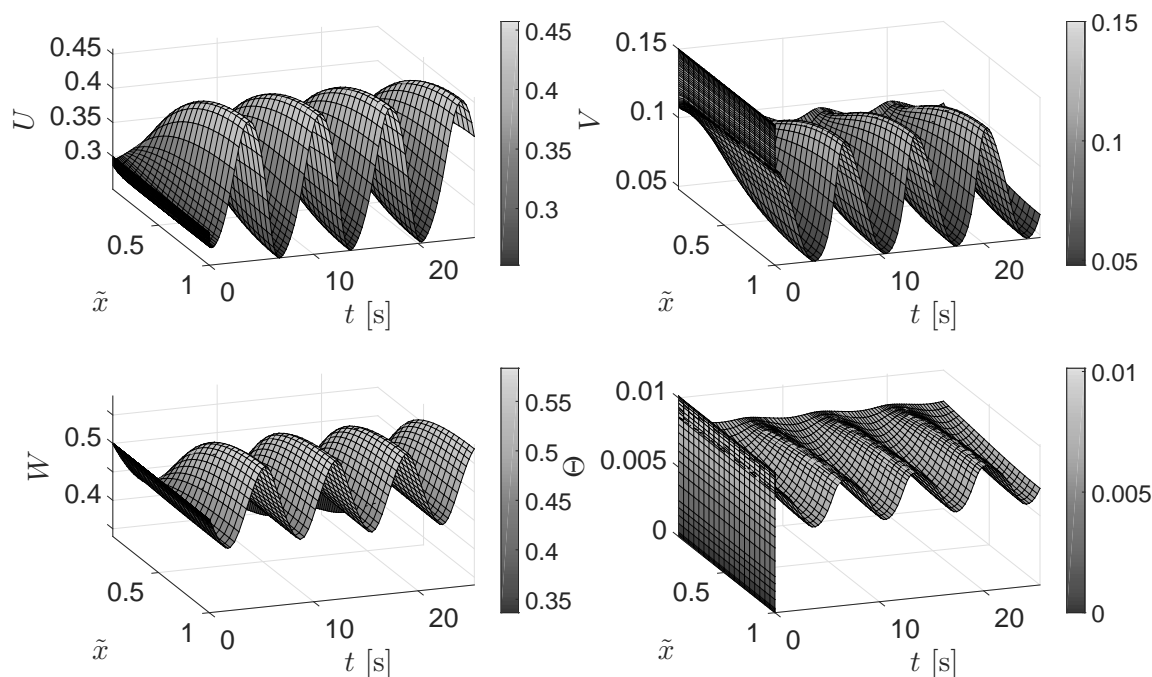

Fig. 1. Example of oscillations of CO, O, CO_2 surface coverages and fraction of the surface in the nonreconstructed (1×1) structure for model (11) at pressures $p_u = 2.25 \times 10^{-5}$ Torr, $p_v = 5.0 \times 10^{-5}$ Torr and certain value of coordinate $\tilde{y} = 0.1$.

Fig. 3 shows the results of numerical analysis of two-dimensional model (1)–(3) [13] without taking an equation for carbon dioxide surface coverage into account (instantaneous desorption of CO_2). The amplitude values of coverages U_{max}, U_{min}, V_{max}, V_{min} and the period of oscillations τ_0 for the two models differ little: the deviation is no more than 6% (see Table 2), that does not exceed the model accuracy.

Table 2. Comparison of numerical analysis results for model (11) and model (1)–(3) [13] ($p_u = 2.25 \times 10^{-5}$ Torr, $p_v = 5.0 \times 10^{-5}$ Torr, $\tilde{y} = 0.5$).

	with equation for CO_2	without equation for CO_2
U_{max}	0.4406	0.4122
U_{min}	0.2557	0.2530
V_{max}	0.1300	0.1317
V_{min}	0.0516	0.0596
τ_0	3.39	3.48

The oscillatory character has a strong dependency on the initial values of the partial pressures p_u and p_v. A comparison of stability regions (oscillatory behaviours) for model (11), model (1)–(3) (instantaneous desorption of CO_2) [13] and one-dimensional model [11] is depicted in Fig. 4. It can be

Fig. 2. Example of oscillations of CO, O, CO_2 surface coverages and fraction of the surface in the nonreconstructed (1×1) structure for model (11) at pressures $p_u = 2.25 \times 10^{-5}$ Torr, $p_v = 5.0 \times 10^{-5}$ Torr and certain value of coordinate $\tilde{y} = 0.5$.
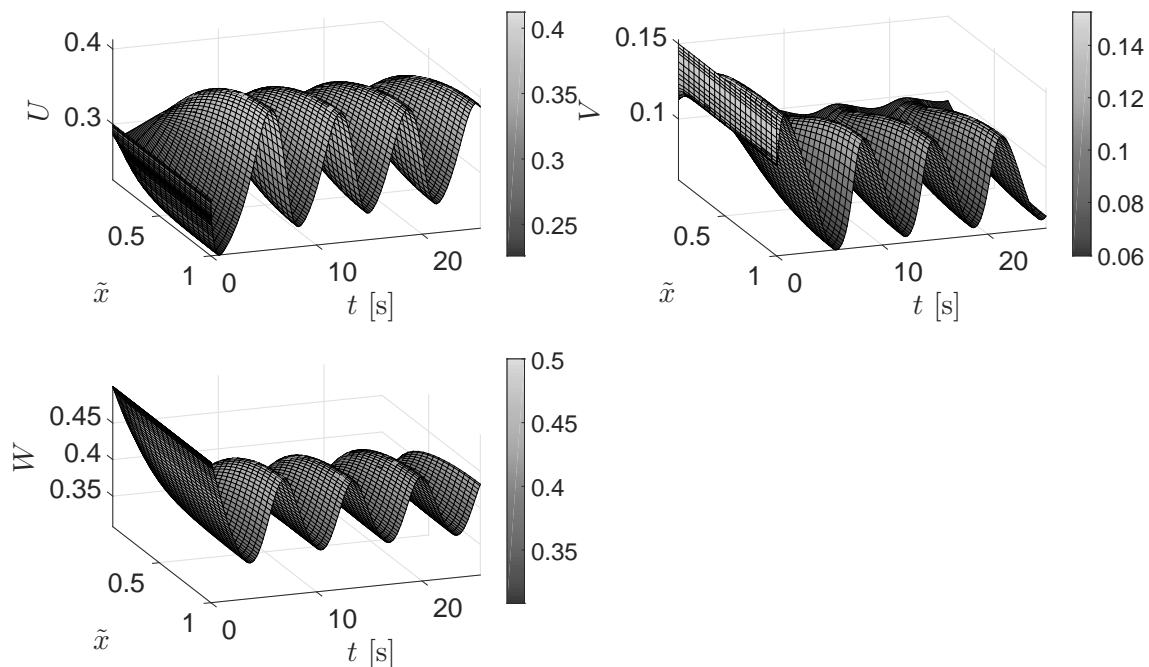
Fig. 3. Example of oscillations of CO, O surface coverages and fraction of the surface in the nonreconstructed structure (1×1) for model (1)–(3) (instantaneous desorption of CO_2) [13] at pressures $p_u = 2.25 \times 10^{-5}$ Torr, $p_v = 5.0 \times 10^{-5}$ Torr and certain value of coordinate $\tilde{y} = 0.5$.

seen that the finiteness of CO_2 desorption (in case of $\tilde{k}_4/\tilde{k}_2 \sim 10^2$) only slightly affects the stability region of oxidation reaction. This enables us to assert that desorption of reaction product (CO_2) can be considered instantaneous when modeling carbon monoxide oxidation on Pt catalyst surface.
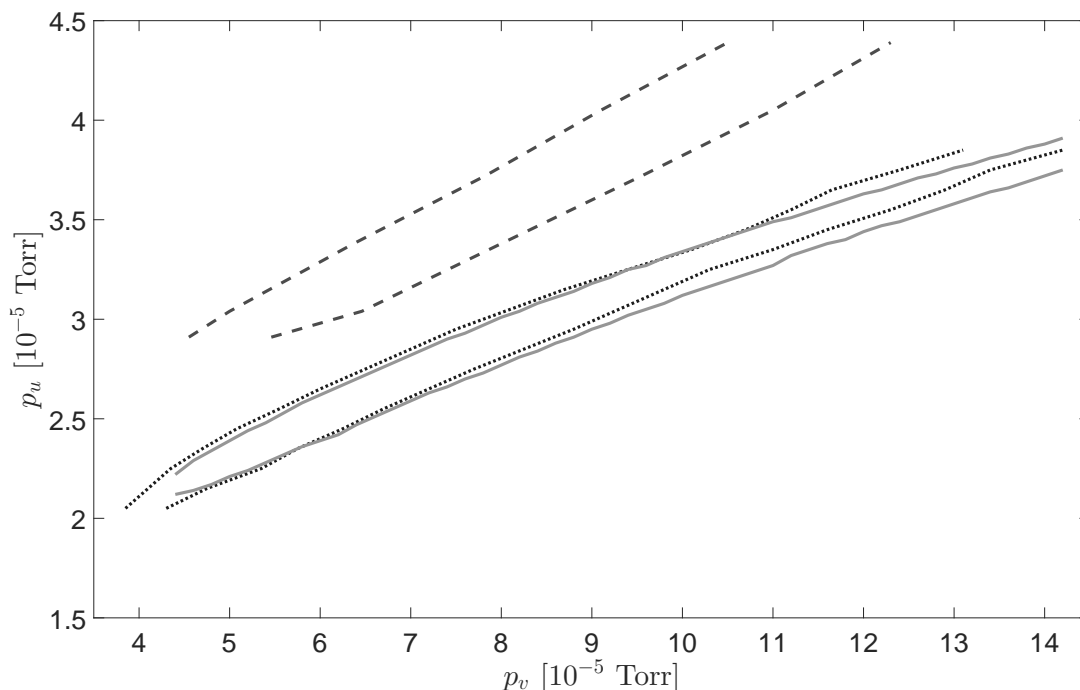
Fig. 4. Stability diagram for reaction of CO oxidation in the partial pressures (p_v, p_u)-parameter plane for model (11) (solid line), model (1)–(3) [13] (dotted line) and one-dimensional model [11] (dashed line).

4. Conclusions

In this paper, the two-dimensional mathematical model for carbon monoxide oxidation on the Pt catalyst surface is developed and investigated according to the Langmuir–Hinshelwood mechanism (when the rate of carbon dioxide desorption is finite). It is shown that when the finiteness of CO_2 desorption is accounted for, both the course of oxidation reaction and the stability region are only slightly affected. Therefore, the desorption of CO_2 can be considered instantaneous.

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Моделювання впливу десорбції діоксиду вуглецю на процес оксидації монооксиду вуглецю на поверхні Pt-каталізатора

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Досліджено двовимірну математичну модель окиснення монооксиду вуглецю (CO) на поверхні платинового каталізатора (Pt) згідно з механізмом Лангмюра–Гіншелвуда. Враховано впливи структурних змін каталітичної поверхні, температури підкладу та десорбції продукту реакції (CO$_2$). Показано, що врахування скінченності десорбції CO$_2$ незначно впливає як на хід реакції окиснення, так і на область стійкості реакції.

Ключові слова: *каталітична реакція окиснення, реакційно-дифузійна модель, математичне моделювання реакційно-дифузійних процесів.*

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