

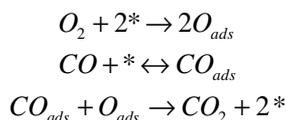
TWO-DIMENSIONAL MATHEMATICAL MODEL
FOR CARBON MONOXIDE OXIDATION PROCESS ON THE
PLATINUM CATALYST SURFACEPetro Kostrobii¹*, Iryna Ryzha¹<https://doi.org/10.23939/chcht12.04.451>

Abstract. The 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 and the substrate temperature are taken into account. It is shown that when two-dimensionality and structural changes are accounted for, both the dynamics of oxidation process and the stability region change.

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

1. Introduction

One of the mechanisms of catalytic carbon monoxide oxidation on platinum is the classical Langmuir-Hinshelwood (LH) mechanism [1]. In the LH mechanism the two reacting species CO and oxygen have to adsorb on the catalytic surface before the reaction takes place:



where “*” denotes an empty adsorption site on the catalytic surface and the subscript “ads” denotes an adsorbed state of respective species.

Oxygen desorption is neglected because it is very unlikely to occur in the range of temperatures at which experiments are conducted [2]. Since diffusion coefficient of adsorbed oxygen is 3-4 orders of magnitude smaller than CO diffusion coefficient [3], adsorbed oxygen is considered to be immobile.

The processes of surface reconstruction of the catalyst atoms play a crucial role in heterogeneous catalysis. The clean Pt(110) surface has a (1×2) structure [4]. During the reaction oxygen and carbon monoxide

adsorb on the Pt surface. If CO coverage exceeds specific critical value the surface reconstructs into (1×1) bulk structure [5]. When oxygen and CO react, carbon dioxide is formed, and the surface returns to its initial configuration. Such structural changes influence the rates of other elementary oxidation processes, therefore, it should be taken into account when developing a mathematical model of reaction.

For the temperature ~500 K further structural changes of the Pt(110) surface are observed for ongoing reaction, namely, the formation of new crystal planes (faceting) [6]. It substantially changes the adsorption properties of the crystal, in particular with respect to oxygen.

For thin plate catalysts the heat generated in the chemical processes may dynamically change the temperature T of the catalyst surface. Even small changes of T may alter the CO oxidation dynamics dramatically. It is therefore also relevant to analyze the heat balance conditions which make it possible to understand the characteristic time and space scales of the temperature field that may influence the chemical reaction.

In the present paper a new kinetic model for the description of time dynamics of CO oxidation on Pt(110) surface is developed. The effect of two-dimensionality, faceting and temperature on the dynamics of the reaction is investigated.

2. Theory

We consider a model for catalytic CO oxidation that accounts for diffusion of molecules of CO on Pt(110) surface. Unlike existing models [6, 7], 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 are determined by the following kinetic equations [8]:

$$\begin{aligned} \frac{\partial u}{\partial t} = & p_u k_u s_u (1 - (u/u_{sat})^q) - k_{des} u - k_r u v + \\ & + D_x \frac{\partial^2 u}{\partial x^2} + D_y \frac{\partial^2 u}{\partial y^2} \end{aligned} \quad (1)$$

¹ Lviv Polytechnic National University
12, S. Bandera St., 79013 Lviv, Ukraine
* ira.saj@gmail.com

© Kostrobii P., Ryzha I., 2019

$$\frac{\partial v}{\partial t} = p_u k_u s_v (1 - u/u_{sat} - v/v_{sat})^2 - k_r uv \quad (2)$$

where p_u and p_v are the partial pressures of respective species; k_u and k_v are the impingement rates; s_u and s_v are the sticking coefficients; u_{sat} and v_{sat} refer to the maximum coverages, namely the saturation coverages; k_r and k_{des} are the rates of oxidation reaction and CO desorption; D_x and D_y are CO diffusion coefficients in x and y directions, respectively. The factor $q=3$ models the asymmetric inhibition of CO and O₂ adsorption since the adsorbed CO blocks oxygen adsorption stronger [9].

The structural phase transition $(1 \times 2) \leftrightarrow (1 \times 1)$ on the Pt(110) surface is modeled by the following equation [10]:

$$\frac{\partial W}{\partial t} = k_{ph} (f(u) - W) \quad (3)$$

where variable W denotes the fraction of the surface in the non-reconstructed structure (surface of type (1×1)); $f(u)$ is a non-decreasing smooth function of the interval $[0;1]$; coefficient k_{ph} is a rate of structural phase transition.

The function $f(u)$ is modeled [7]:

$$f(u) = \frac{1}{1 + \exp\left(\frac{u_0 - u/u_{sat}}{du}\right)} \quad (4)$$

where parameter u_0 determines the threshold value above which adsorbed CO molecules significantly influence the structure of the surface and du is the steepness of this threshold.

The oxygen sticking coefficient s_v is modified in Eq. (2) and can be rewritten as a linear combination of the values for the (1×2) and (1×1) structures:

$$s_v = s_v^{(1)}W + s_v^{(2)}(1 - W) \quad (5)$$

where $s_v^{(1)}$ and $s_v^{(2)}$ are oxygen sticking coefficients in (1×1) and (1×2) phases, respectively.

To complete the model thermal processes generated in chemical reactions should be taken into account. In phenomenological definition [11] the heat balance equation includes the catalyst surface thermal conduction and the heat of oxidation reaction:

$$c_p r \frac{\partial T}{\partial t} = k_{cond} \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) - 2n_{sites} \Delta H_{u,ads} p_u k_u s_u (1 - (u/u_{sat})^3) - 2n_{sites} \Delta H_{v,ads} p_v k_v s_v (1 - u/u_{sat} - v/v_{sat})^2 - 2n_{sites} \Delta H_{des} k_{des} u - 2n_{sites} \Delta H_r k_r uv \quad (6)$$

where c_p is the heat capacity, r is the density, k_{cond} is the thermal conductivity of the catalyst; n_{sites} is the number of active sites in 1 cm² of Pt(110) surface [11]; $\Delta H_{u,ads}$ and $\Delta H_{v,ads}$ are the heats of adsorption of respective species; ΔH_{des} is CO desorption activation energy; ΔH_r is the enthalpy of oxidation reaction.

The degree of faceting Z is a consequence of a competition between the formation of facets, with the free energy of the reaction as a driving force, and thermal annealing, for which the flat surface is thermodynamically favored. It is modeled by the following equation [6]:

$$\frac{\partial Z}{\partial t} = k_f uvw(1 - Z) - k_i Z(1 - u) \quad (7)$$

where k_f and k_i are the rates of facet formation and thermal annealing, respectively.

The oxygen sticking coefficient s_v is significantly enhanced on a faceted surface, so (5) is modified:

$$s_v = s_v^{(1)}W + s_v^{(2)}(1 - W) + s_v^{(3)}Z \quad (8)$$

where $s_v^{(3)}$ is an increase of s_v for maximum faceting ($Z=1$).

The rates of the reaction, desorption, phase transition and thermal annealing are dependent on temperature T and are determined by the Arrhenius equations [12]:

$$k = k^0 \exp(-E/RT) \quad (9)$$

where k^0 is the temperature independent coefficient; E is the activation energy; R is the universal gas constant. The effect of the existing near-surface electric field on activation energies was investigated in papers [13, 14]. It was shown there that the effect of near-surface electric fields can be neglected.

Eqs. (1)-(3), (6), (7) compose proposed a two-dimensional mathematical model for CO oxidation process on the platinum catalyst surface.

3. Results and Discussions

For numerical analysis Eqs. (1)-(3), (6), (7) are transformed into dimensionless form by substituting:

$$u = u_{sat} U, \quad v = v_{sat} V, \quad T = T_0 \theta, \quad (10)$$

$$x = l_0 \xi, \quad y = l_0 \eta, \quad t = t_c \tau \quad (11)$$

where

$$t_c = v_{sat} / p_u k_u s_u \quad (12)$$

Parameter l_0 is chosen according to experimental data for the size of Pt-crystal $l_0 \sim 10^{-3}$ cm [15]. $T_0 = 540$ K is the temperature at which the reaction of CO oxidation has the maximum CO₂ output.

In dimensionless form Eqs. (1)-(3), (6), (7) compose a mathematical model for reaction of CO oxidation on Pt surface:

$$\begin{cases}
 \frac{\partial U}{\partial \theta} = \frac{v_{sat}}{u_{sat}}(1-U^3) - k_{des}^0 U - k_r^0 v_{sat} UV + \\
 \quad + D_x^0 \left(\frac{\partial^2 U}{\partial \bar{x}^2} + D_0 \frac{\partial^2 U}{\partial \bar{y}^2} \right) \\
 \frac{\partial V}{\partial \theta} = k_{s_v}^0 (1-U-V)^2 - k_r^0 u_{sat} UV \\
 \frac{\partial W}{\partial \theta} = k_{ph}^0 \left[1 + \exp\left(\frac{u_0 - U}{du}\right) \right]^{-1} - k_{ph}^0 W \\
 \frac{\partial Z}{\partial \theta} = k_{cond}^0 \left(\frac{\partial^2 Z}{\partial \bar{x}^2} + \frac{\partial^2 Z}{\partial \bar{y}^2} \right) - \\
 \quad - \Delta H_{u,ads}^0 v_{sat} (1-U^3) - \\
 \quad - \Delta H_{v,ads}^0 k_{s_v}^0 v_{sat} (1-U-V)^2 - \\
 \quad - \Delta H_{des}^0 k_{des}^0 u_{sat} U - \Delta H_r^0 k_r^0 u_{sat} v_{sat} UV \\
 \frac{\partial Z}{\partial \theta} = k_f^0 u_{sat} v_{sat} UVW (1-Z) - \\
 \quad - k_r^0 Z (1-u_{sat} U)
 \end{cases} \tag{13}$$

where $k_{des}^0 = k_{des} t_c$, $k_r^0 = k_r t_c$, $k_{ph}^0 = k_{ph} t_c$, $k_f^0 = k_f t_c$,

$$k_i^0 = k_i t_c, \quad k_v^0 = \frac{p_v k_v t_c}{v_{sat}}, \quad k_{cond}^0 = \frac{k_{cond} t_c}{c_p r l_0^2}, \quad D_x^0 = \frac{D_x t_c}{l_0^2},$$

$$D_0 = \frac{D_y}{D_x}, \quad \Delta H_{u,ads}^0 = \frac{2n_{sites}}{c_p r T_0} \Delta H_{u,ads}, \quad \Delta H_{v,ads}^0 = \frac{2n_{sites}}{c_p r T_0} \Delta H_{v,ads},$$

$$\Delta H_{des}^0 = \frac{2n_{sites}}{c_p r T_0} \Delta H_{des}, \quad \Delta H_r^0 = \frac{2n_{sites}}{c_p r T_0} \Delta H_r.$$

Parameter values used in numerical calculations are given in [8] and Table 1 [6].

The results of numerical analysis of model (13) are presented in Figs. 1 and 2.

Figs. 1-2 show that the dependence dynamics of surface coverages $U(x,y,t)$ and $V(x,y,t)$ and the fraction of the surface in the non-reconstructed structure (1×1) $W(x,y,t)$ exhibits clear oscillatory behavior. The period of oscillations has a weak dependence on y -coordinate. At the same time the amplitude of oscillations changes with a change of y . This shows the effect of CO diffusion along OY -axis despite the fact that $D_y \sim 0,1D_x$ [3, 15].

In contrast to the one-dimensional model [16], the dynamics of surface coverages dependency we have calculated demonstrates mixed-mode oscillations (MMO) which were observed experimentally on Pt(110) [17].

Table 1

Parameters of mathematical model

k_f	Rate of facet formation	$k_f = 0.03$ 1/s
k_i	Rate of thermal annealing	$k_i^0 = 2.65 \cdot 10^5$ 1/s $E_i = 83.72$ kJ/mol
$s_v^{(3)}$	Increase of s_v for maximum faceting ($Z = 1$)	$s_v^{(3)} = 0.2$

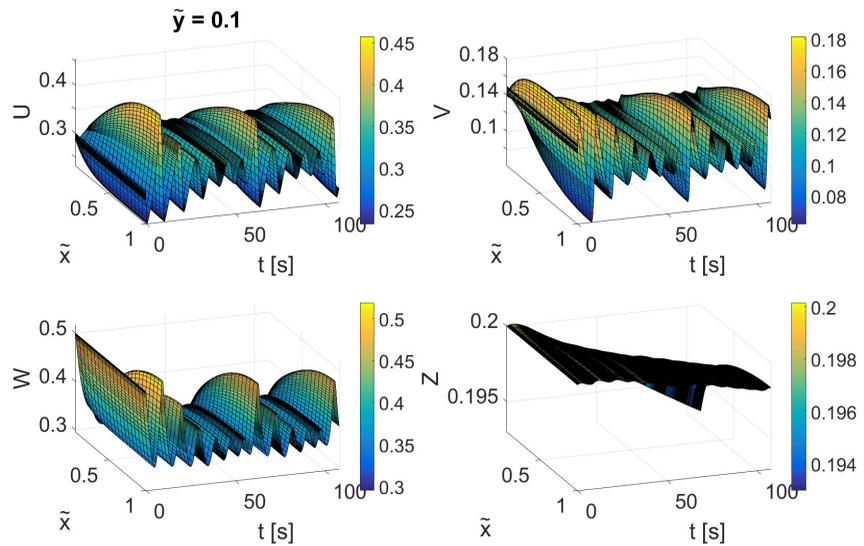


Fig. 1. Dependency of CO $U(x,y,t)$ and O $V(x,y,t)$ surface coverages and fraction of the surface in the non-reconstructed structure (1×1) $W(x,y,t)$ and degree of faceting $Z(x,y,t)$ for $D_x/D_y = 10$, $p_u = 3.53 \cdot 10^{-3}$ Pa, $p_v = 8.53 \cdot 10^{-3}$ Pa and certain value of coordinate $y = 0.1$

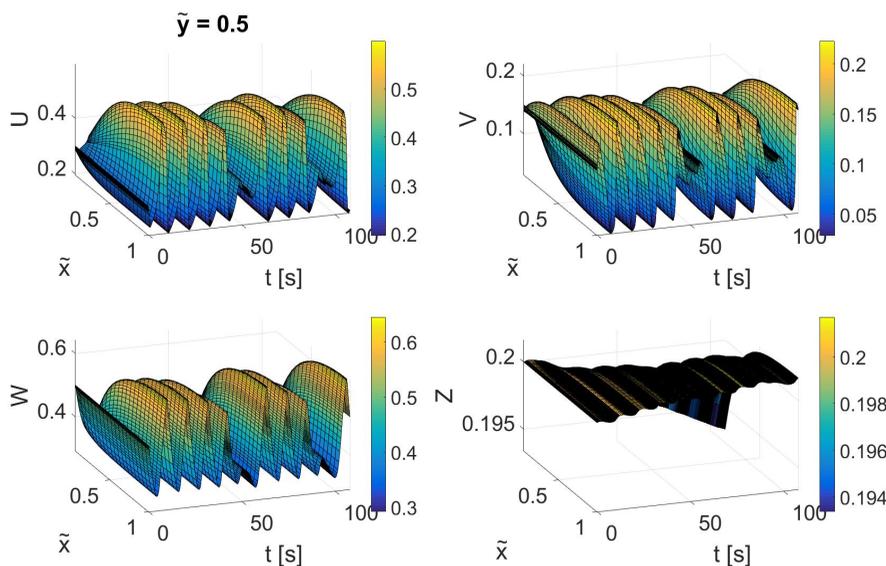


Fig. 2. Dependency of CO $U(x,y,t)$ and O $V(x,y,t)$ surface coverages and fraction of the surface in the non-reconstructed structure (1×1) $W(x,y,t)$ and degree of faceting $Z(x,y,t)$ for $D_x/D_y = 10$, $p_u = 3.53 \cdot 10^{-3}$ Pa, $p_v = 8.53 \cdot 10^{-3}$ Pa and certain value of coordinate $y = 0.5$

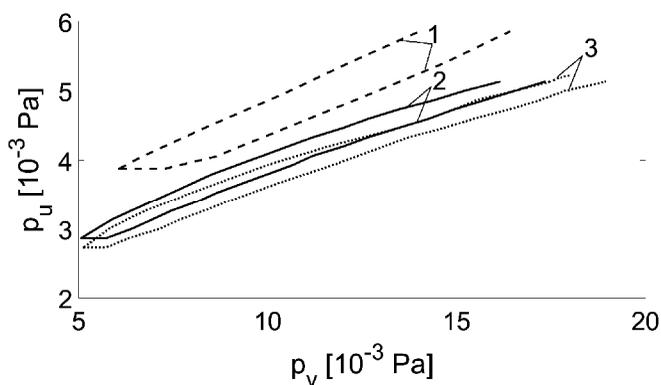


Fig. 3. Stability diagram for reaction of CO oxidation in the partial pressures (p_u, p_v)-parameter plane for two-dimensional model (13) (line 2), two-dimensional model without taking faceting into account [8] (line 3) and one-dimensional model [16] (line 1)

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 behaviors) for model (13) and one-dimensional model [16] and two-dimensional model without taking an equation for faceting into account [8] is depicted in Fig. 3. It can be seen that the stability region for reaction of CO oxidation on the catalyst surface in two-dimensional case is narrower than the stability region for the one-dimensional model and shifts to the region of small CO and O₂ partial pressures.

4. Conclusions

In the present paper the two-dimensional mathematical model for carbon monoxide oxidation according to the Langmuir-Hinshelwood mechanism is developed and investigated. It is shown that when faceting

and two-dimensionality of the catalyst surface are accounted for, the stability region of CO oxidation reaction changes. The reaction of CO oxidation on Pt-catalyst surface has an oscillating character in the stability region. Moreover mixed mode oscillations are obtained, which could not be predicted by the one-dimensional model [16] when equation for degree of faceting is not accounted for [6].

References

- [1] Baxter R., Hu P.: J. Chem. Phys., 2002, **116**, 4379. <https://doi.org/10.1063/1.1458938>
- [2] Wilf M., Dawson P.: Surf. Sci., 1977, **65**, 399. [https://doi.org/10.1016/0039-6028\(77\)90456-3](https://doi.org/10.1016/0039-6028(77)90456-3)
- [3] Gomer R.: Rep. Prog. Phys., 1990, **53**, 917. <https://doi.org/10.1088/0034-4885/53/7/002>
- [4] Kellogg G.: Phys. Rev. Lett., 1985, **55**, 2168. <https://doi.org/10.1103/PhysRevLett.55.2168>

- [5] Gritsch T., Coulman D., Behm R., Ertl G.: Phys. Rev. Lett., 1989, **63**, 1086. <https://doi.org/10.1103/PhysRevLett.63.1086>
- [6] Krischer K., Eiswirth M., Ertl G.: J. Chem. Phys., 1992, **96**, 9161. <https://doi.org/10.1063/1.462226>
- [7] Bzovska I., Mryglod I.: Condens. Matter. Phys., 2010, **13**, 34801. <https://doi.org/10.5488/CMP.13.34801>
- [8] Kostrobij P., Ryzha I.: Math. Model. Comput., 2016, **3**, 146. <https://doi.org/10.23939/mmc2016.02.146>
- [9] Gasser R., Smith. E.: Phys. Lett., 1967, **1**, 457.
- [10] Bertram M., Mikhailov A.: Phys. Rev. E., 2003, **67**, 036207. <https://doi.org/10.1103/PhysRevE.67.036207>
- [11] Cisternas Y., Holmes P., Kevrekidis I., Li X.: J. Chem. Phys., 2003, **118**, 3312. <https://doi.org/10.1063/1.1531070>
- [12] Connors K.: Chemical Kinetics. The Study of Reaction Rates in Solution. VCH Publishers, New York 1990.
- [13] Kostrobij P., Markovych B., Suchorski Y.: Solid State Phenom., 2007, **128**, 219. <https://doi.org/10.4028/www.scientific.net/SSP.128.219>
- [14] Holst B., Piskur J., Kostrobij P. *et al.*: Ultramicroscopy, 2009, **109**, 413. <https://doi.org/10.1016/j.ultramic.2008.11.021>
- [15] Suchorski Y.: private communication.
- [16] Bzovska I., Mryglod I.: Ukr. Phys. J., 2016, **61**, 140. <https://doi.org/10.15407/ujpe61.02.0134>

- [17] Eiswirth M., Krischer K., Ertl G.: Appl. Phys. A., 1990, **51**, 79. <https://doi.org/10.1007/BF00324269>

Received: February 20, 2018 / Revised: March 13, 2018 / Accepted: June 12, 2018

ДВОВИМІРНА МАТЕМАТИЧНА МОДЕЛЬ ПРОЦЕСУ ОКСИДАЦІЇ КАРБОН (II) ОКСИДУ НА ПОВЕРХНІ ПЛАТИНОВОГО КАТАЛІЗАТОРА

Анотація. Досліджено двовимірну математичну модель оксидації карбон (II) оксиду (CO) на поверхні платиного каталізатора (Pt) згідно механізму Лангмюра-Гіншелвуда. Враховано впливи структурних змін каталітичної поверхні та температури підложки. Показано, що врахування двовимірності структурних змін веде до зміни як динаміки процесу оксидації, так і області стійкості.

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