

# Stability of carbon monoxide oxidation process on gold nanoparticles

Kostrobij P. P., Ryzha I. A.

*Lviv Polytechnic National University,  
12 S. Bandera Str., 79013, Lviv, Ukraine*

(Received 16 October 2020; Revised 1 February 2021; Accepted 4 February 2021)

The stability conditions for mathematical models of carbon monoxide oxidation on the surface of gold nanoparticles are investigated. The cases of reaction mechanisms of one-step and step-by-step transformation of reagents are consecutively considered. Using the stability analysis by Lyapunov method, it is shown that models which take into account the possibility of structural changes of the catalyst surface can predict the occurrence of oscillatory mode in the system as a result of Hopf instability.

**Keywords:** *reaction of catalytic oxidation, modeling of CO oxidation, gold nanoparticles.*

**2010 MSC:** 82C05, 82C70

**DOI:** 10.23939/mmc2021.01.116

## 1. Introduction

Studies of catalytic carbon monoxide (CO) oxidation is one of the most important problems in modern science [1]. On the one hand, this process is essential for environmental and industrial applications such as automotive emissions control, air purification, carbon dioxide lasers, CO sensors etc. On the other hand, it is one the simplest catalytic reaction and is often used as a model system in development of new catalysts.

Mathematical modeling of CO oxidation reaction on the surfaces of heterogeneous catalysts became the subject of many theoretical studies after the discovery of rate oscillations in this reaction on the surface of platinum (Pt) group catalysts. However, Pt catalysts are expensive and temperatures at which reaction of CO oxidation takes place are high (~500 K). These disadvantages led to the study of new structural elements of the catalyst surface, in particular from the group of noble metals.

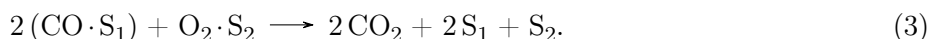
In the late 1980s, Haruta and co-workers first showed that small particles of gold (Au) can be active catalysts for the low-temperature CO oxidation [3]. Initially, the high activity of gold-based catalysts was considered to be caused by the type of composite substrate — the metal oxides (reducible: TiO<sub>2</sub>, NiO, Fe<sub>2</sub>O<sub>3</sub> or irreducible: Al<sub>2</sub>O<sub>3</sub>, MgAl<sub>2</sub>O<sub>4</sub>). However, after detailed investigations, it was found that the very active catalysts were small gold nanoparticles of about 2-4 nm in size [4], dispersed on these oxides.

The purpose of this work is to investigate the stability conditions for mathematical models of CO catalytic oxidation on the surface of gold nanoparticles. A similar problem was solved for some mathematical models of CO oxidation on the Pt-catalyst surface [5, 6], for which the stability regions of reaction and conditions for Hopf [7] and Turing [8] instabilities to arise were investigated.

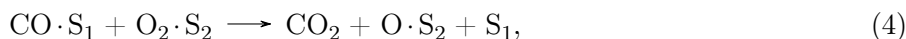
By analogy with Pt, we assume that oxidation reaction occurs according to the Langmuir-Hinshelwood mechanism [9]. That is, interaction between the reactants is possible only in the adsorbed layer, where there are free active sites of two different types (S<sub>1</sub> and S<sub>2</sub>). The reaction scheme consists of two elementary steps: the reversible molecular adsorption of CO and oxygen (O<sub>2</sub>) on the catalyst surface:



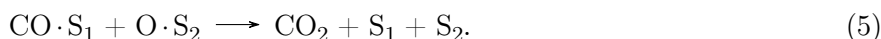
and the surface reaction between adsorbed CO and O<sub>2</sub> molecules to form the reaction product carbon dioxide (CO<sub>2</sub>)



Sometimes, instead of a concerted (one-step) reaction (3), a step-by-step transformation of reagents is considered. First a surface reaction between adsorbed CO and O<sub>2</sub> molecules occurs to form CO<sub>2</sub> and the intermediate — adsorbed O atoms:



then adsorbed CO and O interact with each other:



It is considered that CO molecules adsorb only on the free active sites of the first type (S<sub>1</sub>), whereas O<sub>2</sub> and O — only on the active sites of the second type (S<sub>2</sub>).

It is known that reaction of catalytic CO oxidation can significantly influence the structure of the catalyst surface. For platinum group metals, structural changes in the course of reaction (for example, 1×1→1×2 structural transition on Pt(110) [10]) lead to appearance of an oscillatory mode [2], when the self-sustained (undamped) rate oscillations arise in a system without any external periodic forces acting on it [11]. In some cases, such non-steady-state conditions may lead to higher reaction rate or better average process performance [12].

On the surface of gold nanoparticles CO and oxygen can cause their restructuring [13]. At higher CO pressures Au nanoparticles are faceted (the structure of “type 1”), whereas at lower CO pressures they become rounded (the structure of “type 2”) (see [13]). Such reconstruction of the catalyst surface may cause changes in its characteristics, especially with respect to the adsorption and desorption properties.

In order to establish regularities of the influence of such changes on the course of reaction processes, we consider mathematical models of catalytic CO oxidation on the surface of gold nanoparticles for the cases of one-step (scheme (1)–(3)) and step-by-step (scheme (1)–(2), (4)–(5)) reactions. Using the Lyapunov method [14], the stability analysis of solutions of the respective systems is carried out. It is established that structural changes of the catalyst surface have a significant influence on the process of CO oxidation, in particular the presence of rate oscillations.

## 2. Mathematical models

### 2.1. One-step reaction

First we consider a mathematical model of catalytic CO oxidation on the surface of gold nanoparticles according to the reaction mechanism (1)–(3). The system of kinetic equations that describe the temporal change of surface coverages of adsorbed CO ( $u$ ) molecules on the sites of the first type S<sub>1</sub> and O<sub>2</sub> ( $v$ ) molecules on the sites of the second type S<sub>2</sub> is proposed in [15] and has the following form:

$$\frac{du}{dt} = P_u I_u s_u (1 - u) - d_u u - 2ru^2 v, \quad (6)$$

$$\frac{dv}{dt} = P_v I_v s_v (1 - v) - d_v v - ru^2 v. \quad (7)$$

Here  $P_u$ ,  $P_v$  are the partial pressures of CO and O<sub>2</sub>, respectively;  $I_u$ ,  $I_v$  are the impingement rates;  $s_u$ ,  $s_v$  are the sticking coefficients (probabilities);  $d_u$ ,  $d_v$  are the desorption rate coefficients;  $r$  is the rate coefficient of reaction (3).

By introducing a dimensionless time variable:

$$\tilde{t} = \frac{t}{t_c}, \quad t_c = \frac{1}{P_u I_u} \quad (8)$$

we rewrite equations (6)–(7) in the dimensionless form:

$$\frac{du}{d\tilde{t}} = s_u(1-u) - \tilde{d}_u u - 2\tilde{r}u^2v \equiv A(u, v), \quad (9)$$

$$\frac{dv}{d\tilde{t}} = \tilde{P}_v s_v(1-v) - \tilde{d}_v v - \tilde{r}u^2v \equiv B(u, v), \quad (10)$$

where

$$\tilde{P}_v = \frac{P_v I_v}{P_u I_u}, \quad \tilde{r} = t_c r, \quad \tilde{d}_{u,v} = t_c d_{u,v}. \quad (11)$$

System (9)–(10) can have steady-state solutions  $(u^s, v^s)$  satisfying the system of algebraic equations:

$$A(u^s, v^s) = 0, \quad B(u^s, v^s) = 0.$$

Note that  $(u^s, v^s)$  must have physical values, in other words, they must satisfy constraints on the values of surface coverages of adsorbed species:

$$0 \leq u^s \leq 1, \quad 0 \leq v^s \leq 1. \quad (12)$$

The steady-state solutions of (9)–(10) can be easily found analytically (see [15]). But in [15] the issue of system stability was not considered, therefore we analyze the stability of steady-state solutions  $(u^s, v^s)$  by the Lyapunov method.

Let  $\delta u(\tilde{t})$ ,  $\delta v(\tilde{t})$  be the time-dependent small deviations from the steady states  $(u^s, v^s)$

$$u(\tilde{t}) = u^s + \delta u(\tilde{t}), \quad v(\tilde{t}) = v^s + \delta v(\tilde{t}).$$

Then the linearized system (9)–(10) near  $(u^s, v^s)$  looks as follows:

$$\frac{d}{d\tilde{t}} \begin{pmatrix} \delta u \\ \delta v \end{pmatrix} = \mathbf{J} \cdot \begin{pmatrix} \delta u \\ \delta v \end{pmatrix}, \quad (13)$$

where

$$\mathbf{J} = \begin{pmatrix} A'_u & B'_v \\ A'_v & B'_u \end{pmatrix} \quad (14)$$

is the Jacobian matrix [17] for the system of functions (9)–(10), with all partial derivatives calculated at a steady-state point  $(u^s, v^s)$ :

$$A_u = -s_u - \tilde{d}_u - 2\tilde{r}uv, \quad A'_v = -2\tilde{r}u^2, \\ B'_u = -2\tilde{r}uv, \quad B'_v = -\tilde{P}_v s_v - \tilde{d}_v - \tilde{r}u^2.$$

We look for solutions  $(\delta u, \delta v)$  of system (13) proportional to  $\exp(\lambda \tilde{t})$ , where  $\lambda$  are the eigenvalues of matrix  $\mathbf{J}$ . Calculation of eigenvalues  $\lambda$  is reduced to solving the following quadratic equation:

$$\lambda^2 - \lambda \operatorname{tr} \mathbf{J} + \det \mathbf{J} = 0, \quad (15)$$

where  $\operatorname{tr} \mathbf{J}$ ,  $\det \mathbf{J}$  are the trace and determinant of matrix  $\mathbf{J}$ , respectively.

We know, that solutions  $(u^s, v^s)$  are stable when  $\operatorname{Re}(\lambda_{1,2}) < 0$ . Since the discriminant of equation (15) is non-negative for any physical parameters of the model:

$$\Delta = \operatorname{tr}^2 \mathbf{J} - 4 \det \mathbf{J} = (A'_u - B'_v)^2 + 4A'_v B'_u \geq 0,$$

the roots

$$\lambda_{1,2} = \frac{1}{2} \left( \text{tr } \mathbf{J} \pm \sqrt{\text{tr}^2 \mathbf{J} - 4 \det \mathbf{J}} \right)$$

are real and have negative values if

$$\det \mathbf{J} > 0. \quad (16)$$

We see, that for any physical values of model parameters ( $P_{u,v}$ ,  $I_{u,v}$ ,  $s_{u,v}$ ,  $d_{u,v}$ ,  $r$ ) condition (16) is never violated, therefore system (9)–(10) is always stable.

Now, in order to establish regularities of the influence of structural changes of the catalyst surface, we add to mathematical model (6)–(7) the third equation. It describes the possibility of reconstruction of the catalyst surface from the structure of “type 1” (faceted gold nanoparticles) to another structure of “type 2” (rounded gold nanoparticles). For simplicity, we assume that this reconstruction is stimulated only by the presence of adsorbed CO molecules on the surface (in general, it can also be caused by adsorbed O<sub>2</sub> molecules or other factors).

Let variable  $z$  denote the fraction of the catalyst surface in the structure of “type 1”. Then the temporal change of  $z$  is determined by equation:

$$\frac{dz}{dt} = k_z [f(u)(1-z) - (1-f(u)z)],$$

or

$$\frac{dz}{dt} = k_z [f(u) - z], \quad (17)$$

where  $k_z$  is the rate coefficient of structural transition;  $f(u)$  is a function, that takes on values in interval  $[0, 1]$  and describes the probability of transition of the catalyst surface from one structure to another.

Taking into account this structural transition, the sticking and desorption rate coefficients of carbon monoxide and oxygen molecules in equations (6) and (7) are written as a linear combination of the values for structures of “type 1” and “type 2” (by analogy with Pt [2, 16]):

$$s_\gamma = s_{\gamma,1}z + s_{\gamma,2}(1-z), \quad d_\gamma = d_{\gamma,1}z + d_{\gamma,2}(1-z). \quad (18)$$

Here  $s_{\gamma,1}$ ,  $d_{\gamma,1}$  ( $\gamma = u, v$ ) are the sticking and desorption rate coefficients for the structure of “type 1”;  $s_{\gamma,2}$ ,  $d_{\gamma,2}$  are the respective coefficients for the structure of “type 2”.

Equations (6)–(7), (17) are transformed into dimensionless form, using the substitution (8) and dimensionless parameters (11):

$$\frac{du}{d\tilde{t}} = [s_{u,1}z + s_{u,2}(1-z)](1-u) - [\tilde{d}_{u,1}z + \tilde{d}_{u,2}(1-z)]u - 2\tilde{r}u^2v \equiv F(u, v, z), \quad (19)$$

$$\frac{dv}{d\tilde{t}} = \tilde{P}_v [s_{v,1}z + s_{v,2}(1-z)](1-v) - [\tilde{d}_{v,1}z + \tilde{d}_{v,2}(1-z)]v - \tilde{r}u^2v \equiv G(u, v, z), \quad (20)$$

$$\frac{dz}{d\tilde{t}} = \tilde{k}_z [f(u) - z] \equiv H(u, z), \quad (21)$$

where

$$\tilde{k}_z = t_c k_z, \quad \tilde{d}_{\gamma,i} = t_c d_{\gamma,i}, \quad i = 1, 2. \quad (22)$$

System (19)–(21) is a system of three nonlinear differential equations and can have steady-state solutions ( $u^s, v^s, z^s$ ), which satisfy the system of algebraic equations:

$$F(u^s, v^s, z^s) = 0, \quad G(u^s, v^s, z^s) = 0, \quad H(u^s, z^s) = 0.$$

Solutions ( $u^s, v^s, z^s$ ) can be found analytically:

$$z^s = f(u^s), \quad v^s = \frac{a - (a+b)u^s}{2\tilde{r}(u^s)^2}, \quad (23)$$

where  $u^s$  is the solution of equation

$$2\tilde{r}\tilde{P}_v c(u^s)^2 = \left[ \tilde{P}_v c + d + \tilde{r}(u^s)^2 \right] [a - (a+b)u^s], \quad (24)$$

with

$$a = f(u^s)(s_{u,1} - s_{u,2}) + s_{u,2}, \quad b = f(u^s)(\tilde{d}_{u,1} - \tilde{d}_{u,2}) + \tilde{d}_{u,2}, \quad (25)$$

$$c = f(u^s)(s_{v,1} - s_{v,2}) + s_{v,2}, \quad d = f(u^s)(\tilde{d}_{v,1} - \tilde{d}_{v,2}) + \tilde{d}_{v,2}. \quad (26)$$

Further, we consider only the case when steady-state solutions (23) exist and satisfy conditions (12) and constrain on the value of fraction of the catalyst surface in the structure of “type 1”:

$$0 \leq z^s \leq 1. \quad (27)$$

The problem of stability analysis of steady-state solutions (23) is reduced to finding the eigenvalues of Jacobian matrix  $\mathbf{J}_1$  for the system of functions (19)–(21):

$$\mathbf{J}_1 = \begin{vmatrix} F'_u & F'_v & F'_z \\ G'_u & G'_v & G'_z \\ H'_u & 0 & H'_z \end{vmatrix} \quad (28)$$

or solving the cubic equation:

$$\lambda^3 - \lambda^2 \operatorname{tr} \mathbf{J}_1 + \lambda \sum_{1 \leq i < j \leq 3} \det_{(i,j),(i,j)} \mathbf{J}_1 - \det \mathbf{J}_1 = 0, \quad (29)$$

where  $\det_{(i_1 \dots i_k), (j_1 \dots j_k)} \mathbf{J}_1$  is the minor of order  $k$  of matrix  $\mathbf{J}_1$ , formed by elements located at the intersection of rows  $i_1 \dots i_k$  and columns  $j_1 \dots j_k$ .

Note that all partial derivatives in  $\mathbf{J}_1$  are calculated at a steady-state point  $(u^s, v^s, z^s)$  and look as follows:

$$\begin{aligned} F'_u &= -(s_{u,1} + \tilde{d}_{u,1})z - (s_{u,2} + \tilde{d}_{u,2})(1-z) - 4\tilde{r}uv, \\ F'_v &= -2\tilde{r}u^2, \quad F'_z = (s_{u,1} - s_{u,2})(1-u) - (\tilde{d}_{u,1} - \tilde{d}_{u,2})u, \\ G'_u &= -2\tilde{r}uv, \quad G'_v = -(\tilde{P}_v s_{v,1} + \tilde{d}_{v,1})z - (\tilde{P}_v s_{v,2} + \tilde{d}_{v,2})(1-z) - \tilde{r}u^2, \\ G'_z &= \tilde{P}_v(s_{v,1} - s_{v,2})(1-v) - (\tilde{d}_{v,1} - \tilde{d}_{v,2})v, \\ H'_u &= \tilde{k}_z f'(u), \quad H'_z = -\tilde{k}_z. \end{aligned}$$

Solutions  $(u^s, v^s, z^s)$  are stable when  $\operatorname{Re}(\lambda_i) < 0$ ,  $i = 1, 2, 3$ . According to the Routh–Hurwitz criterion [17], for this it is necessary and sufficient that

$$\det \mathbf{J}_1 < 0, \quad \operatorname{tr} \mathbf{J}_1 \sum_{1 \leq i < j \leq 3} \det_{(i,j),(i,j)} \mathbf{J}_1 < \det \mathbf{J}_1. \quad (30)$$

In order to investigate the conditions for appearance of rate oscillations in system (19)–(21) we consider the possibility of Hopf instability [7] to exist in the model. It is a local dynamic instability which causes the steady-state point to lose stability, and a limit cycle (the auto-oscillations) arises in the system. In this case all eigenvalues of the Jacobian matrix  $\mathbf{J}_1$  of the linearized system have negative real parts except for a pair of imaginary conjugate nonzero eigenvalues.

In our case the conditions for Hopf instability to occur are as follows:

$$\det \mathbf{J}_1 < 0, \quad \operatorname{tr} \mathbf{J}_1 \sum_{1 \leq i < j \leq 3} \det_{(i,j),(i,j)} \mathbf{J}_1 = \det \mathbf{J}_1. \quad (31)$$

Therefore, unlike model (6)–(7), which does not take into account the possibility of structural changes of the catalyst surface and remains stable for any physical parameters of the model, system (19)–(21) is stable only when conditions (30) are satisfied. Moreover, for some model parameters (see conditions (31)), an auto-oscillatory mode occurs in the system as a result of Hopf instability. Under these conditions the phase trajectory should spiral into the closed curve — the limit cycle, while the average adsorbate coverages  $u$ ,  $v$  and the fraction of catalyst surface  $z$  should undergo periodic oscillations. The amplitude and period of auto-oscillations are determined only by the properties of the system itself.

## 2.2. Step-by-step transformation of reagents

Now we consider a mathematical model of catalytic CO oxidation when adsorption of reagents occurs according to equations (1)–(2) and reaction between the adsorbed substances — according to scheme (4)–(5). The corresponding system of kinetic equations for describing the temporal change of surface coverages of adsorbed CO ( $u$ ), O<sub>2</sub> ( $v$ ) and O ( $w$ ) is proposed in [15]:

$$\frac{du}{dt} = P_u I_u s_u (1 - u) - d_u u - r_1 uv - r_2 uw, \quad (32)$$

$$\frac{dv}{dt} = P_v I_v s_v (1 - v - w) - d_v v - r_1 uv, \quad (33)$$

$$\frac{dw}{dt} = r_1 uv - r_2 uw. \quad (34)$$

Here  $r_1$ ,  $r_2$  are the rate coefficients of reactions (4) and (5), respectively.

We nondimensionalize system (32)–(34), using the substitution (8) and dimensionless parameters (11):

$$\frac{du}{dt} = s_u (1 - u) - \tilde{d}_u u - \tilde{r}_1 uv - \tilde{r}_2 uw \equiv C(u, v, w), \quad (35)$$

$$\frac{dv}{dt} = \tilde{P}_v s_v (1 - v - w) - \tilde{d}_v v - \tilde{r}_1 uv \equiv D(u, v, w), \quad (36)$$

$$\frac{dw}{dt} = \tilde{r}_1 uv - \tilde{r}_2 uw \equiv E(u, v, w), \quad (37)$$

with

$$\tilde{r}_{1,2} = t_c r_{1,2} \quad (38)$$

System (35)–(37) can have steady-state solutions  $(u^s, v^s, w^s)$ , which satisfy the system of algebraic equations:

$$C(u^s, v^s, w^s) = 0, \quad D(u^s, v^s, w^s) = 0, \quad E(u^s, v^s, w^s) = 0,$$

and can be found analytically (see [15]). We consider the case when steady-state solutions  $(u^s, v^s, w^s)$  exist and satisfy conditions (12) and constrain on the value of adsorbed O surface coverage:

$$0 \leq w^s \leq 1. \quad (39)$$

Again we analyze the stability of steady-state solutions  $(u^s, v^s, w^s)$  and search for the eigenvalues of Jacobian matrix  $\mathbf{J}_2$  for the system of functions (35)–(37):

$$\mathbf{J}_2 = \begin{vmatrix} C'_u & D'_v & E'_w \\ C'_u & D'_v & D'_w \\ C'_u & D'_v & E'_w \end{vmatrix}, \quad (40)$$

where all partial derivatives are calculated at a steady-state point  $(u^s, v^s, w^s)$ :

$$\begin{aligned}
 C_u &= -s_u - \tilde{d}_u - \tilde{r}_1 v - \tilde{r}_2 w, & C'_v &= -\tilde{r}_1 u, & C'_w &= -\tilde{r}_2 u, \\
 D'_u &= -\tilde{r}_1 v, & D'_v &= -\tilde{P}_v s_v - \tilde{d}_v - \tilde{r}_1 u, & D'_w &= -\tilde{P}_v s_v, \\
 E'_u &= \tilde{r}_1 v - \tilde{r}_2 w, & E'_v &= \tilde{r}_1 u, & E'_w &= -\tilde{r}_2 u.
 \end{aligned}$$

Since the eigenvalue equation for matrix  $\mathbf{J}_2$  has the form of equation (29), the steady-state solutions  $(u^s, v^s, w^s)$  are stable if and only if conditions similar to (30) are satisfied. It can be seen that these conditions are true for any physical values of model parameters  $(P_{u,v}, I_{u,v}, s_{u,v}, d_{u,v}, r_{1,2})$ , so system (35)–(37) is always stable.

Now we supplement system (35)–(37) with equation (17), which describes the possibility of catalyst surface structure reconstruction, and represent  $s_{u,v}$  and  $d_{u,v}$  as (18). After nondimensionalization using substitution (8) and dimensionless parameters (11), (22) and (38), this new system can be rewritten as follows:

$$\frac{du}{d\tilde{t}} = [s_{u,1}z + s_{u,2}(1 - z)](1 - u) - [\tilde{d}_{u,1}z + \tilde{d}_{u,2}(1 - z)]u - \tilde{r}_1 uv - \tilde{r}_2 uw \equiv K(u, v, w, z), \tag{41}$$

$$\frac{dv}{d\tilde{t}} = \tilde{P}_v [s_{v,1}z + s_{v,2}(1 - z)](1 - v - w) - [\tilde{d}_{v,1}z + \tilde{d}_{v,2}(1 - z)]v - \tilde{r}_1 uv \equiv L(u, v, w, z), \tag{42}$$

$$\frac{dw}{d\tilde{t}} = \tilde{r}_1 uv - \tilde{r}_2 uw \equiv M(u, v, w), \tag{43}$$

$$\frac{dz}{d\tilde{t}} = \tilde{k}_z [f(u) - z] \equiv H(u, z). \tag{44}$$

System (41)–(44) can have steady-state solutions  $(u^s, v^s, w^s, z^s)$ , which satisfy the system of algebraic equations:

$$K(u^s, v^s, w^s, z^s) = 0, \quad L(u^s, v^s, w^s, z^s) = 0, \quad M(u^s, v^s, w^s) = 0, \quad H(u^s, z^s) = 0,$$

namely:

$$z^s = f(u^s), \quad w^s = \frac{\tilde{r}_1}{\tilde{r}_2} v^s, \quad v^s = \frac{a - (a + b)u^s}{2\tilde{r}_1 u^s}, \tag{45}$$

where  $u^s$  is the solution of equation

$$2\tilde{r}_1 \tilde{P}_v c u^s = \left[ \tilde{P}_v c \left( 1 + \frac{\tilde{r}_1}{\tilde{r}_2} \right) + d + \tilde{r}_1 u^s \right] [a - (a + b)u^s], \tag{46}$$

with values  $a, b, c, d$  determined by (25)–(26). Again we consider only the case when steady-state solutions (45) exist and satisfy constrains (12), (27) and (39).

The problem of stability analysis of steady-state solutions (45) is reduced to finding the eigenvalues of Jacobian matrix  $\mathbf{J}_3$  for the system of functions (41)–(44):

$$\mathbf{J}_3 = \begin{vmatrix} K'_u & K'_v & K'_w & F'_z \\ L'_u & L'_v & L'_w & G'_z \\ M'_u & M'_v & M'_w & 0 \\ H'_u & 0 & 0 & H'_z \end{vmatrix}, \tag{47}$$

or solving the following 4th degree equation:

$$\lambda^4 - \lambda^3 \text{tr } \mathbf{J}_3 + \lambda^2 \sum_{1 \leq i < j \leq 4} \det_{(i,j),(i,j)} \mathbf{J}_3 - \lambda \sum_{1 \leq i < j < k \leq 4} \det_{(i,j,k),(i,j,k)} \mathbf{J}_3 + \det \mathbf{J}_3 = 0.$$

Elements of the Jacobian matrix  $\mathbf{J}_3$  are calculated at a point  $(u^s, v^s, w^s, z^s)$  and have the form:

$$\begin{aligned}
 K'_u &= -(s_{u,1} + \tilde{d}_{u,1})z - (s_{u,2} + \tilde{d}_{u,2})(1 - z) - \tilde{r}_1 v - \tilde{r}_2 w, \\
 K'_v &= -\tilde{r}_1 u, \quad K'_w = -\tilde{r}_2 u, \quad K'_z = (s_{u,1} - s_{u,2})(1 - u) - (\tilde{d}_{u,1} - \tilde{d}_{u,2})u,
 \end{aligned}$$

$$\begin{aligned}
L'_u &= -\tilde{r}_1 v, & L'_w &= -\tilde{P}_v [s_{v,1} z + s_{v,2} (1 - z)], \\
L'_v &= -(\tilde{P}_v s_{v,1} + \tilde{d}_{v,1}) z - (\tilde{P}_v s_{v,2} + \tilde{d}_{v,2}) (1 - z) - \tilde{r}_1 u, \\
L'_z &= \tilde{P}_v (s_{v,1} - s_{v,2}) (1 - v - w) - (\tilde{d}_{v,1} - \tilde{d}_{v,2}) v, \\
M'_u &= \tilde{r}_1 v - \tilde{r}_2 w, & M'_v &= \tilde{r}_1 u, & M'_w &= -\tilde{r}_2 u, \\
H'_u &= \tilde{k}_z f'(u), & H'_z &= -\tilde{k}_z.
\end{aligned}$$

We use the Routh–Hurwitz criterion to analyze the necessary and sufficient conditions for the eigenvalues  $\lambda_i$ ,  $i = 1, 2, 3, 4$  of matrix  $\mathbf{J}_3$  to have negative real parts. In our case, system (41)–(44) is stable if and only if the following conditions are satisfied:

$$\det \mathbf{J}_3 > 0, \quad \Delta_1 > 0, \quad \det \mathbf{J}_3 \operatorname{tr}^2 \mathbf{J}_3 < \Delta_1 \sum_{1 \leq i < j < k \leq 4} \det_{(i,j,k),(i,j,k)} \mathbf{J}_3, \quad (48)$$

where

$$\Delta_1 = \sum_{1 \leq i < j < k \leq 4} \det_{(i,j,k),(i,j,k)} \mathbf{J}_3 - \operatorname{tr} \mathbf{J}_3 \sum_{1 \leq i < j \leq 4} \det_{(i,j),(i,j)} \mathbf{J}_3.$$

The necessary and sufficient conditions for Hopf instability to occur in the system are as follows:

$$\det \mathbf{J}_3 > 0, \quad \Delta_1 > 0, \quad \det \mathbf{J}_3 \operatorname{tr}^2 \mathbf{J}_3 = \Delta_1 \sum_{1 \leq i < j < k \leq 4} \det_{(i,j,k),(i,j,k)} \mathbf{J}_3. \quad (49)$$

Thus, as in the previous case, taking into account the possibility of reconstruction of the catalyst surface influences the stability region of a system. Unlike the model (35)–(37), proposed in [15], which does not take into account the possibility of structural changes, system (41)–(44) becomes unstable when at least one of conditions (48) is violated. In addition, if conditions (49) are satisfied, periodic rate oscillations (temporal variations of the surface coverages of the species involved in the reaction) may occur in the system as a result of Hopf instability.

### 3. Conclusions

In present paper the stability conditions for mathematical models of carbon monoxide oxidation on the surface of gold nanoparticles are investigated. The cases of reaction mechanisms of one-step and step-by-step transformation of reagents are consecutively considered. Using the stability analysis by Lyapunov method, it is shown that models which take into account the possibility of structural changes of the catalyst surface can predict occurrence of oscillatory mode in a system (as a result of Hopf instability). Whereas the solutions of systems which don't take such changes into account are stable under any physical values of model parameters, so no bifurcations, i.e. qualitative changes in the dynamic behavior of the system, can be observed.

The obtained stability conditions (30) and (48) (or conditions (31) and (49) for Hopf instability to arise in the system) depend on the experimental values of a number of parameters ( $I_{u,v}$ ,  $s_{u,1,2}$ ,  $s_{v,1,2}$ ,  $d_{u,1,2}$ ,  $d_{v,1,2}$ ,  $r_{1,2}$ ), as well as on the form of a model function  $f(u)$ . Unfortunately, not all of these parameters are experimentally defined, so constructing a theoretical stability region of parameter space (as well as the region of an oscillatory mode of reaction) to compare with experimental data for specific nanoparticles is a difficult task that needs further investigation.

- 
- [1] Freund H.-J., Meijer G., Scheffler M., Schlogl R., Wolf M. CO oxidation as a prototypical reaction for heterogeneous processes. *Angewandte Chemie International Edition*. **50** (43), 10064–10094 (2011).
- [2] Krischer K., Eiswirth M., Ertl G. Oscillatory CO oxidation on Pt(110): Modeling of temporal self-organization. *Journal of Chemical Physics*. **96** (12), 9161–9172 (1992).



- [3] Haruta M., Kobayashi T., Sano H., Yamada N. Novel gold catalysts for the oxidation of carbon monoxide at a temperature far below 0°C. *Chemistry Letters*. **16** (2), 405–408 (1987).
- [4] Valden M., Lai X., Goodman D. W. Onset of catalytic activity of gold clusters on titania with the appearance of nonmetallic properties. *Science*. **281** (5383), 1647–1650 (1998).
- [5] Ryzha I., Matseliukh M. Carbon monoxide oxidation on the Pt-catalyst: modelling and stability. *Mathematical Modeling and Computing*. **4** (1), 96–106 (2017).
- [6] Kostrobij P., Ryzha I., Markovych B. Mathematical model of carbon monoxide oxidation: influence of the catalyst surface structure. *Mathematical Modeling and Computing*. **5** (2), 158–168 (2018).
- [7] Kuznetsov Y. A. *Elements of Applied Bifurcation Theory*. Springer, New York (1995).
- [8] Hoyle R. *Pattern Formation*. Cambridge University Press, New York (2006).
- [9] Imbihl R., Ertl G. Oscillatory kinetics in heterogeneous catalysis. *Chemical Reviews*. **95** (3), 697–733 (1995).
- [10] Gritsch T., Coulman D., Behm R. J., Ertl G. Mechanism of the CO-induced  $1 \times 2 \rightarrow 1 \times 1$  structural transformation of Pt(110). *Physical Review Letters*. **63** (10), 1086–1089 (1989).
- [11] Slinko M. M., Jaeger N. I. *Oscillating Heterogeneous Catalytic Systems (Studies in Surface Science and Catalysis)*. Vol. 86. Elsevier Science: Amsterdam (1994).
- [12] Qiao L., Li X., Kevrekidis I. G., Punckt C., Rotermund H. H. Enhancement of surface activity in CO oxidation on Pt(110) through spatiotemporal laser actuation. *Physical Review E*. **77** (3), 036214 (2008).
- [13] Uchiyama T., Yoshida H., Kuwauchi Y., Ichikawa S., Shimada S., Haruta M., Takeda S. Systematic morphology changes of gold nanoparticles supported on CeO<sub>2</sub> during CO oxidation. *Angewandte Chemie International Edition*. **50** (43), 10157–10160 (2011).
- [14] Elsgolts L. *Differential Equations and the Calculus of Variation*. Книга по Требованію, Moskva (2012), (in Russian).
- [15] Zhdanov V. P. Kinetic models of CO oxidation on gold nanoparticles. *Surface Science*. **630**, 286–293 (2014).
- [16] Reichert C., Starke J., Eiswirth M. Stochastic model of CO oxidation on platinum surfaces and deterministic limit. *Journal of Chemical Physics*. **115** (10), 4829–4838 (2001).
- [17] Korn G. A., Korn T. M. *Mathematical Handbook for Scientists and Engineers: Definitions, Theorems and Formulas for Reference and Review*. Dover Publications (2000).

## Стійкість процесу окиснення монооксиду вуглецю на наночастинках золота

Костробій П. П., Рижа І. А.

*Національний університет “Львівська політехніка”,  
вул. С. Бандери, 12, 79013, Львів, Україна*

Досліджено умови стійкості математичних моделей окиснення монооксиду вуглецю на поверхні наночастинок золота. Послідовно розглянуто випадки реакційних механізмів одноетапного та поетапного перетворення реагентів. За допомогою аналізу стійкості методом Ляпунова показано, що моделі, які враховують можливість структурних змін поверхні каталізатора, дозволяють змоделювати виникнення автоколивань у системі, які є результатом нестійкості Хопфа.

**Ключові слова:** *реакція каталітичного окиснення, моделювання окиснення CO, наночастинки золота.*