KINETICS OF THE PROCESSES OF CATALYTIC CO OXIDATION

I.M. MRYGLOD, I.S. BZOVSKA

UDC 530.1; 535.37 ©2008 Institute for Condensed Matter Physics, Nat. Acad. Sci. of Ukraine (1, Sventsitskyi Str., Lviv 79011, Ukraine; e-mail: iryna@icmp.lviv.ua)

We have investigated the kinetics of the processes of catalytic CO oxidation. The stationary points of the model are found, and the analysis of their stability in the time evolution of the equations of chemical kinetics is carried out. It is revealed that, at intermediate CO pressures, the system has two stable points, so it is in the bistable state. The condition of the existence of a bifurcation region for the model is analytically found. We have deduced the equation for the critical value of pressure $p_{\rm CO}^c$, at which the first-order phase transition from a reactive state with medium O coverage to an inactive state, where the surface is predominantly covered by CO, is occured. The results obtained are compared with those of the lattice-gas reaction model in the mean-field approximation.

1. Introduction

Catalytic reactions on solid surfaces are of great complexity, and they are thus inherently very difficult to be dealt with. However, the understanding of the kinetics of catalytic reactions is important, because heterogeneous catalysis is the mainstay of the chemical industry. The scientific interest in the study of these processes is due to the emergence of a rich complex variety of physicochemical phenomena including the chaotic behavior, bistability, critical phenomena, phase transitions, oscillatory behavior of some reactions, etc. In recent years, a number of computer models has been proposed to study catalytic surface reactions [1–7]. Many of chemical reactions, which have been studied on catalytic surfaces, occur via the Langmuir-Hinshelwood mechanism, in which both reactants are initially adsorbed on the surface [8].

A number of mathematical models have been constructed to explain experimental data [9–12]. A variety of mechanisms has been proposed to explain

ISSN 0503-1265. Ukr. J. Phys. 2008. V. 53, N 6

the oscillatory phenomena in CO oxidation: adsorbateinduced surface reconstruction and microfaceting during the reaction [13–15], alternate oxidation and CO reduction of a catalyst [16, 17], changes in the surface temperature [18], etc. In [19], an attempt to take into consideration the surface close interactions through the surface close concentrations of CO and O₂ is made. Using the curve displaying the dependence between adsorbed CO and the O coverage as a qualitative index, the best initial conditions are found.

Dynamical phenomena that lead to the formation of the temporal or spatio-temporal oscillations have been reported for the O-mediated CO oxidation on Pt(100), Pt(110), Pt(210), and Pd(110) surfaces. Among all these reaction systems with their quite complex dynamical behavior, the CO+O/Pt(111) system is somewhat exceptional, because it does not show any spatio-temporal oscillations. On the macroscopic scale, as determined by mass spectrometry [20], the system only exhibits two stable steady states, namely, a state of low reactivity with a predominantly CO covered surface, and a state of high reactivity with a largely oxygencovered surface. Transitions between these two states are, of course, possible and manifest themselves in a hysteresis, if an external control parameter, e.g., the CO partial pressure, is varied back and forth.

In this paper, we investigate the catalytic CO oxidation dynamics on the Pt(111) surface by using the kinetic equations for coverages of the adsorbed species. The characteristic feature of the reaction is that the diffusion rates of CO and O differ very much from each other, because CO molecules are very mobile on the surface in comparison with adsorbed oxygen atoms which are practically immovable. Therefore, in

our earlier paper [21], two different cases of high and low reaction rates were studied separately within simple lattice models. In particular, it was shown that the phase diagrams in the plane $(p_{\rm CO}, 1/T)$ contain, within the model under consideration, a bistable range terminating at a cusp point with increase in T. However, one of the open problems is to understand more clearly the meaning of high and low reaction rates in practice. In addition, the average coverages of the adsorbed species were calculated in the bistable region. It still remains a question about the exact calculation of the first-order transition pressure from a reactive state with intermediate O coverage to an inactive state in the bifurcation diagram. The aim of this work is to study the problems mentioned above in more details.

2. Model and its General Properties

The equations of reactions that can proceed in the course of carbon monoxide oxidation on the catalyst surface look like

$$O_2 + 2* \to 2O^{ads},\tag{1}$$

$$CO + * \rightleftharpoons CO^{ads},$$
 (2)

$$\mathrm{CO}^{\mathrm{ads}} + \mathrm{O}^{\mathrm{ads}} \to \mathrm{CO}_2 + 2*,$$
 (3)

where the asterisk denotes a free active site on the catalyst surface. Oxygen desorption is not considered because it is usually almost impossible at the temperature conditions of most experiments [22].

Let us consider a model that represents an ideal adsorbate layer where the interactions between adsorbed molecules are neglected. In addition, the high surface mobility of CO molecules is assumed. In work [19], the exchange by particles with the subsurface layer is taken into account. In our work, we are mainly interested in the temporal behavior of the adsorbed species on the catalytic surface, that is why we consider only one plane – a layer of adsorbed particles. The subsurface layer is not taken into consideration.

So the evolution of the CO and oxygen coverages in time on the catalyst surface is determined by the system of simple kinetic equations

$$\frac{\mathrm{d}\theta_{\mathrm{CO}}}{\mathrm{dt}} = p_{\mathrm{CO}}k_{\mathrm{CO}}s_{\mathrm{CO}}(1-\theta_{\mathrm{CO}}-\theta_{\mathrm{O}}) - d\theta_{\mathrm{CO}} - k\theta_{\mathrm{CO}}\theta_{\mathrm{O}}, \ (4)$$

$$\frac{\mathrm{d}\theta_{\mathrm{O}}}{\mathrm{d}\mathrm{t}} = 2p_{\mathrm{O}_2}k_{\mathrm{O}}s_{\mathrm{O}}(1-\theta_{\mathrm{CO}}-\theta_{\mathrm{O}})^2 - k\theta_{\mathrm{CO}}\theta_{\mathrm{O}},\tag{5}$$

where $d = d_0 \exp(-\beta E_d)$ denotes the rate of CO desorption, $p_{\rm CO}$ and $p_{\rm O_2}$ are the partial pressures of CO and oxygen, respectively, $k_{\rm CO}$ and $k_{\rm O}$ are the CO and oxygen impingement rates, $s_{\rm CO}$ and $s_{\rm O}$ are the corresponding sticking coefficients. The coefficient kdenotes the reaction rate constant and looks as $k = k_{\rm CO_2} \exp(-\beta E_0)$, where E_0 is the activation energy of the reaction. The first equation, Eq. (4), describes variations in the amount of adsorbed CO, the chemical reaction with adsorbed oxygen, and the desorption of CO with desorption constant d. The first term in Eq. (5) describes the dissociative adsorption of oxygen, and the second one refers to the reaction between adsorbed oxygen and CO.

In general, the model as described by Eqs. (4), (5) can exhibit four stationary points. One is given by

$$\theta_{\rm CO}^s = 0, \quad \theta_{\rm O}^s = 1,\tag{6}$$

which corresponds to the oxygen poisoning of the substrate. It should be noted that this solution is never observed experimentally. The others are given by the roots of the cubic equation for $\theta_{\rm CO}$,

$$A(\theta_{\rm CO}^s)^3 + B(\theta_{\rm CO}^s)^2 + C\theta_{\rm CO}^s + D = 0, \tag{7}$$

and the corresponding oxygen concentration is given by

$$\theta_{\rm O}^s = \frac{p_{\rm CO}k_{\rm CO}s_{\rm CO}(1-\theta_{\rm CO}^s)}{p_{\rm CO}k_{\rm CO}s_{\rm CO}+k\theta_{\rm CO}^s} - \frac{d\theta_{\rm CO}^s}{p_{\rm CO}k_{\rm CO}s_{\rm CO}+k\theta_{\rm CO}^s}.$$
 (8)

The coefficients of the cubic equation are

$$A = 2p_{O_2}k_{O}s_{O}k^{2},$$

$$B = -4p_{O_2}k_{O}s_{O}k(k+d) + k^{2}(p_{CO}k_{CO}s_{CO}+d),$$

$$C = 2p_{O_2}k_{O}s_{O}k(k+2d) + 2p_{O_2}k_{O}s_{O}d^{2} + kp_{CO}k_{CO}s_{CO}(p_{CO}k_{CO}s_{CO}+d-k),$$

$$D = -p_{CO}^{2}k_{CO}^{2}s_{CO}^{2}k.$$
(9)

In general, for the numerical values of the adsorption constants, there is only one positive real root of this equation, the two others being imaginary. All the roots can be real if the condition

$$\left(\frac{C}{3A} - \left(\frac{B}{3A}\right)^2\right)^3 + \left(\left(\frac{B}{3A}\right)^3 - \frac{BC}{6A^2} + \frac{D}{2A}\right)^2 < 0$$
(10)

is satisfied. From the physical point of view, when all the roots of the cubic equation are real, we have the

ISSN 0503-1265. Ukr. J. Phys. 2008. V. 53, N 6

530

bistable region in the phase diagrams. So inequality (10) gives, in fact, the condition of existence of the bifurcation region that follows from the kinetic level of description. This condition can be compared with our previous result [21] derived within the mean-field theory for the lattice model of adsorbed particles.

We now characterize the stationary points by their eigenvalues in the time evolution equations (4) and (5). This analysis reveals the stability of the stationary points. For this, we introduce small perturbations around the stationary solutions and write $\theta_{\rm CO}$ and $\theta_{\rm O}$ as

$$\theta_{\rm CO} = \theta_{\rm CO}^s + \delta \theta_{\rm CO}(t), \quad \theta_{\rm O} = \theta_{\rm O}^s + \delta \theta_{\rm O}(t), \tag{11}$$

where $\theta_{\rm CO}^s$ and $\theta_{\rm O}^s$ are the coordinates of the stationary point *i*, and $\delta\theta_{\rm CO}$ and $\delta\theta_{\rm O}$ are small time-dependent perturbations. Then the linearized equations are

$$\frac{\mathrm{d}}{\mathrm{d}t} \begin{pmatrix} \delta\theta_{\mathrm{O}} \\ \delta\theta_{\mathrm{CO}} \end{pmatrix} = \begin{pmatrix} -4h_{\mathrm{O}}v^{s} - k\theta_{\mathrm{CO}}^{s} & -4h_{\mathrm{O}}v^{s} - k\theta_{\mathrm{O}}^{s} \end{pmatrix} \begin{pmatrix} \delta\theta_{\mathrm{O}} \end{pmatrix}$$

$$-\left(-h_{\rm CO}-k\theta_{\rm CO}^{s}-h_{\rm CO}-d-k\theta_{\rm O}^{s}\right)\left(\delta\theta_{\rm CO}\right),$$
(12)

with $v^s = 1 - \theta_{\rm O}^s - \theta_{\rm CO}^s$ as the stationary density of empty adsorption sites. The notations $h_{\rm O} = p_{\rm O_2}k_{\rm O}s_{\rm O}$, $h_{\rm CO} = p_{\rm CO}k_{\rm CO}s_{\rm CO}$ are introduced for the convenience. The determination of the eigenvalues of the matrix in Eq. (12) allows us to analyze the type of stability of the stationary solutions found above.

For the first solution, Eq. (6) ($\theta_{\rm CO} = 0, \theta_{\rm O} = 1$), the corresponding eigenvalues are

$$\lambda_{1,2} = \frac{-b \pm \sqrt{b^2 + 4c}}{2},\tag{13}$$

where $b = (p_{CO}k_{CO}s_{CO} + k + d)$ and $c = p_{CO}k_{CO}s_{CO}k$. One of the eigenvalues is always negative, while the other is always positive. Therefore this point represents a saddle point. The eigenvalues for the other stationary points depend of the solutions of the cubic equation, Eq. (7).

ISSN 0503-1265. Ukr. J. Phys. 2008. V. 53, N 6



Fig. 1. Phase portrait and typical trajectories of the model in the $(\theta_{\rm CO}, \theta_{\rm O})$ parameter space at $p_{\rm CO}=10^{-7}$ Torr

3. Results and Discussion

From the condition of existence of the bifurcation region (10) for the model parameters $p_{O_2} = 1.5 \times 10^{-5}$ Torr, $k_O = 7.8 \times 10^5 \text{s}^{-1} \text{Torr}^{-1}$, $k_{CO} = 7 \times 10^6 \text{s}^{-1} \text{Torr}^{-1}$, $k = 598 \text{s}^{-1}$, $d = 0.27 \text{s}^{-1}$, $s_{CO} = 0.9$, $s_O = 0.06$, which corresponded to Pt(111) surface [23], the bistable region exists at the following values of pressure p_{CO} :

$$p_{\rm CO}^{\rm (min)} < p_{\rm CO} < p_{\rm CO}^{\rm (max)} \tag{14}$$

with $p_{\rm CO}^{(\rm min)} = 1.53 \times 10^{-7}$ Torr and $p_{\rm CO}^{(\rm max)} = 2.05 \times 10^{-7}$ Torr. Let us consider separately these three cases of low ($p_{\rm CO} < p_{\rm CO}^{(\rm min)}$), intermediate ($p_{\rm CO}^{(\rm min)} < p_{\rm CO} < p_{\rm CO}^{(\rm max)}$), and high ($p_{\rm CO} > p_{\rm CO}^{(\rm max)}$) values of partial pressures $p_{\rm CO}$.

3.1. Low partial pressures $p_{\rm CO}$ ($p_{\rm CO} < p_{\rm CO}^{(\rm min)}$)

Let us consider first the case of low partial pressures $p_{\rm CO}$, namely the calculations are performed for $p_{\rm CO} = 10^{-7}$ Torr. The stationary points for this case, their eigenvalues and eigenvectors are shown in Table 1 and the corresponding types of stability are determined. The phase portrait and typical trajectories of the model in the $(\theta_{\rm CO}, \theta_{\rm O})$ parameter space for this pressure are shown in Fig. 1.

As is seen from Fig. 1, in the case of low pressure $p_{\rm CO}$, the system has only one steady point ($\theta_{\rm CO}=0.0009$,

531



Fig. 2. Phase portrait and typical trajectories of the model in the $(\theta_{\rm CO}, \theta_{\rm O})$ parameter space at $p_{\rm CO} = 1.68 \times 10^{-7}$ Torr

 $\theta_{\rm O}$ =0.55), which corresponds to the oxygen adsorption on the catalyst surface. This is a reactive region in the bifurcation diagram. This result can be easily understood from the physical point of view and in complete agreement with our study of the phase behaviour of lattice models [24] performed in the low-temperature limit. Note also a huge difference in the eigenvalues found in both cases of saddle point and stable node (by two orders in the magnitude). This, in particular, explains already the existence of two different time relaxation scales for the model under consideration.

3.2. Intermediate partial pressures $p_{\rm CO}$ $(p_{\rm CO}^{(\rm min)} < p_{\rm CO} < p_{\rm CO}^{(\rm max)})$

In the case of intermediate partial pressures $p_{\rm CO}$ ($p_{\rm CO} = 1.68 \times 10^{-7}$ Torr), the stationary points, their eigenvalues, and eigenvectors as well as the corresponding types of stability are shown in Table 2. Figure 2 depicts the phase portrait and typical trajectories for this case in the ($\theta_{\rm CO}, \theta_{\rm O}$) parameter space.

T a b l e 1. Analysis of the stability of the stationary points at $p_{\rm CO} = 10^{-7}$ Torr

Stationary points	Eigenvalues	Eigenvectors	Stability
$(\theta_{\rm CO} = 0, \ \theta_{\rm O} = 1)$	0.63	1.001	saddle
		-0.001	
	-599.5	0.488	
		0.512	
$(\theta_{\rm CO} = 0.0009, \ \theta_{\rm O} = 0.55)$	-0.63	1.004	stable
		-0.004	node
	-331	-0.506	
		0.494	



Fig. 3. Phase portrait and typical trajectories of the model in the $(\theta_{\rm CO}, \theta_{\rm O})$ parameter space at $p_{\rm CO} = 2.2 \times 10^{-7}$ Torr

It is evident from Fig. 2 that, at the pressure $p_{\rm CO} = 1.68 \times 10^{-7}$ Torr, the system has two stable nodes $(\theta_{\rm CO}=0.005, \theta_{\rm O}=0.24)$ and $(\theta_{\rm CO}=0.7, \theta_{\rm O}=0.0003)$. So the system can exhibit the properties of a bistable state with jumps from one stable branch onto the other. Once again, Table 2 shows the huge difference in the eigenvalues corresponding to each stationary point.

3.3. High partial pressures $p_{\rm CO}$ ($p_{\rm CO} > p_{\rm CO}^{(\rm max)}$)

Finally, we turn now to the case of a high partial pressure $p_{\rm CO}$, in particular we consider $p_{\rm CO} = 2.2 \times 10^{-7}$ Torr. Similar to the previous cases, we represent the stationary points, their eigenvalues, eigenvectors, and types of stability in Table 3. The corresponding phase portrait

T a b l e $\,$ 2. Analysis of the stability of the stationary points at $p_{\rm CO}=1.68\times 10^{-7}$ Torr

Stationary points	Eigenvalues	Eigenvectors	Stability
$(\theta_{\rm CO}=0, \ \theta_{\rm O}=1)$	1.05	1.002	saddle
		-0.002	
	-600.38	0.499	
		0.501	
$(\theta_{\rm CO} = 0.005, \ \theta_{\rm O} = 0.24)$	-1.00	1.031	stable
		-0.031	node
	-150.48	0.491	
		0.509	
$(\theta_{\rm CO} = 0.35, \ \theta_{\rm O} = 0.003)$	0.48	-0.017	saddle
		1.017	
	-211.68	0.508	
		0.492	
$(\theta_{\rm CO} = 0.7, \theta_{\rm O} = 0.0003)$	-0.50	-0.002	stable
		1.002	node
	-422.98	0.5	
		0.5	

ISSN 0503-1265. Ukr. J. Phys. 2008. V. 53, N 6

and typical trajectories for this value of pressure $p_{\rm CO}$ are shown in Fig. 3.

As is shown in Fig. 3, at $p_{\rm CO} = 2.2 \times 10^{-7}$ Torr, the system has only one steady point similarly to the case of a low pressure $p_{\rm CO}$, but the situation is changed, because the stable state is now characterized by both a high CO coverage on the surface and an insignificant amount of oxygen ($\theta_{\rm CO}=0.8$, $\theta_{\rm O}=0.0001$). This corresponds to an inactive region in the bifurcation diagram. As in all previous cases, we found a large difference in eigenvalues for both stationary solutions.

The same information can be alternatively shown through the time evolution of the stationary states. This is pictured in Fig. 4, where the CO pressure $p_{\rm CO}$ is varied, while the other parameters are constant. We have considered three different values for $p_{\rm CO}$. At low $p_{\rm CO}$ (Fig. 4,*a*), the surface of the catalyst is predominantly covered by adsorbed oxygen. Increasing the pressure $p_{\rm CO}$ causes the oxygen coverage to decrease (Fig. 4,*b*). At a certain value of $p_{\rm CO}^c = 1.683 \times 10^{-7}$ Torr, it tends sharply to zero, whereas the carbon monoxide coverage is suddenly increased. The first-order phase transition at $p_{\rm CO} = p_{\rm CO}^c$ from a reactive state with medium O coverage to an inactive state, where the surface is predominantly covered by CO (Fig. 4,*c*), is occured.

One should pay attention to the great difference in eigenvalues which actually determine the relaxation times in chemical kinetics. Thus, we can say now that the cases of low and high reaction rates considered in our previous paper [21] are realized at low (the first case) and intermediate values of $p_{\rm CO}$ (the second). The third possible case, that was not considered in [21], corresponds to the situation where only the kinetic equation for CO should be taken into account in the lattice-gas model.

The phase diagram in the $(p_{\rm CO}, 1/T)$ parameter space depicted in Fig. 5 reveals a bistability region. The lower and upper branches of the bifurcation are calculated from Eq. (10).

T a b l e 3. Analysis of the stability of the stationary points at $p_{\rm CO} = 2.2 \times 10^{-7}$ Torr

Stationary points	Eigenvalues	Eigenvectors	Stability
$(\theta_{\rm CO} = 0, \ \theta_{\rm O} = 1)$	1.38	1.002	saddle
		-0.002	
	-601	0.491	
		0.509	
$(\theta_{\rm CO} = 0.8, \ \theta_{\rm O} = 0.0001)$	-1.09	-0.001	stable
		1.001	node
	-479.58	0.5	
		0.5	

ISSN 0503-1265. Ukr. J. Phys. 2008. V. 53, N 6



Fig. 4. Time evolution of the CO and oxygen coverages for various values of $p_{\rm CO}$ and for fixed values of the other parameters: $a - p_{\rm CO} = 10^{-7}$ Torr; $b - p_{\rm CO} = 1.68 \times 10^{-7}$ Torr; $c - p_{\rm CO} = 2.2 \times 10^{-7}$ Torr



Fig. 5. Phase diagram $(p_{\rm CO},1/T)$ of the model at the oxygen partial pressure $p_{\rm O_2}=1.5\times10^{-5}$ Torr

In Fig. 6, the dependences of the CO and O coverages on the pressure $p_{\rm CO}$ are exhibited. Full curves are obtained from the kinetic equations (4), (5), and the results of our calculations obtained from the consistent equations of chemical kinetics and the mean-field equations of a lattice-gas reaction model describing features of the surface coverage and nearest-neighbor interactions between adsorbates [21] are shown by dotted curves. As we see, the results of calculations in the frame of chemical kinetics agree well qualitatively and quantitatively with the results of the lattice-gas model in the mean-field approximation. Namely, this agreement occurs in the dependences of the average CO and O coverages on $p_{\rm CO}$. A bistable region is observed in both approaches.

In the model based on chemical kinetics, the critical value of pressure $p_{\rm CO}^c$ is determined by the separatrix that sets off for a saddle and separates two regions:

$$p_{\rm CO}^c = \frac{\theta_{\rm CO}^s (k\theta_{\rm O}^s + d)}{k_{\rm CO} s_{\rm CO} (1 - \theta_{\rm CO}^s - \theta_{\rm O}^s)},\tag{15}$$

where $\theta_{\rm CO}^s$ and $\theta_{\rm O}^s$ are the coordinates of the saddle point. For this model for the saddle with the coordinates $\theta_{\rm CO}^s = 0.3450$, $\theta_{\rm O}^s = 0.0029$, we have $p_{\rm CO}^c = 1.683 \times 10^{-7}$ Torr. For the lattice model, the critical value $p_{\rm CO}^c$ should be found from the Maxwell equation.

4. Conclusions and Final Remarks

We have investigated a kinetic model for the catalytic CO oxidation on a surface of Pt(111). We have found



Fig. 6. Average CO and oxygen coverages as the functions of $p_{\rm CO}$ at $T=466~{\rm K}$

the stationary points of the system and analyzed them by their eigenvalues to reveal their stability. We have established when the cases of high and low reaction rates investigated for the lattice models in our previous paper [21] are realized. For this, three different cases of low, intermediate, and high pressures $p_{\rm CO}$ have been considered. We have established that, at intermediate pressures, two stable states exist, and the system exhibits jumps from one stable branch onto the other. This is the bistability phenomenon. The condition of existence of the bistable region for the model has been analytically found, and the bifurcation diagram has been constructed. For the model parameters which correspond to the Pt(111) surface, the bistable region exists at the CO pressures 1.53×10^{-7} Torr $< p_{\rm CO} < 2.05 \times 10^{-7}$ Torr. We have derived the equation and calculated the critical value of pressure $p_{\rm CO}^c$, at which the first-order phase

ISSN 0503-1265. Ukr. J. Phys. 2008. V. 53, N 6

transition from a reactive state with medium O coverage to an inactive state, where the surface is predominantly covered by CO, is occured. The results are compared with those of the lattice-gas reaction model investigated earlier. We have obtained a good agreement of the dependences of the average CO and O coverages on $p_{\rm CO}$ for these both models.

It is clearly seen from the phase diagrams that the relaxation oscillations in system can emerge in a bistable state if the system depends on a parameter slowly varying in time. It would be a model parameter related to the variations of average coverages and the structural changes of the surface in the course of time. In this case, the kinetic equation for the surface transformation should be taken into consideration. Effects of such a type are important for other Pt surfaces, where the oscillatory behavior in the catalytic CO oxidation can be observed [13–15]. Consequently, the analysis of the oscillatory behavior in heterogeneous catalytic systems will be a subject of our further investigations.

- R.M. Ziff, E. Gulari, and Y. Barshad, Phys. Rev. Lett. 56, 2553 (1986).
- 2. J.W. Evans and J. Chem. Phys. 98, 2463 (1993).
- 3. K.M. Khan and N. Ahmad, Physica A 280, 391 (2000).
- 4. K.M. Khan and K. Yaldram, Surf. Sci. 445, 186 (2000).
- 5. K.M. Khan, Surf. Sci. 470, 155 (2000).
- 6. N. Ahmad and K.M. Khan, Chem. Phys. **263**, 339 (2001).
- 7. K.M.Khan and E.V.Albano, Chem. Phys. 276, 129 (2002).
- 8. R.J. Baxter and P. Hu, J. Chem. Phys. **116**, 4379 (2002).
- N. Hartmann, K. Krischer, and R. Imbihl, J. Chem. Phys. 101, 6717 (1994).
- M.M. Slinko, E.S. Kurkina, M.A. Liauw, and N.J. Jaeger, J. Chem. Phys. **111**, 8105 (1999).
- N.V. Peskov, M.M. Slinko, and N.I. Jaeger, J. Chem. Phys. 116, 2098 (2002).
- 12. V.P. Zhdanov and B. Kasemo, Surf. Sci. 511, 23 (2002).
- G. Ertl, P.R. Norton, and J. Rustig, Phys. Rev. Lett. 49, 171 (1982).

- A. Hopkinson, J.M. Bradley, X.C. Guo, M. Gruyters, and D.A. King, Phys. Rev. Lett. 71, 1597 (1993).
- F. Chavez, L. Vicente, and A. Perera, J. Chem. Phys. 113, 10353 (2000).
- 16. M.R. Basset and R. Imbihl, J. Chem. Phys. 93, 811 (1990).
- I. Yuranov, L. Kiwi-Minsker, M.M. Slinko, E.S. Kurkina, E.D. Tolstunova, and A. Renken, Chem. Ing. Sci. 55, 2827 (2000).
- 18. M. Dumont and R. Dagonnier, Surf. Sci. 80, 394 (1979).
- P.P. Kostrobii, M.V. Tokarchuk, and V.I. Alekseyev, Phys. and Chem. Solid State 7, 25 (2006).
- M. Berdau, G.G. Yelenin, A. Karpowicz, M. Ehsasi, K. Christmann, and J.H. Block, J. Chem. Phys. 110, 11551 (1999).
- 21. I.M. Mryglod and I.S. Bzovska, Ukr. J. Phys. 52, 468 (2007).
- 22. R. Imbihl and G. Ertl, Chem. Rev. 95, 697 (1995).
- N. Pavlenko, P.P. Kostrobij, Yu. Suchorski, and R. Imbihl, Surf. Sci. 489, 29 (2001).
- I.M. Mryglod and I.S. Bzovska, Condens. Matter Phys. 10, 165 (2007).

Received 06.08.07

КІНЕТИКА ПРОЦЕСІВ КАТАЛІТИЧНОЇ РЕАКЦІЇ ОКИСЛЕННЯ СО

І.М. Мриглод, І.С. Бзовська

Резюме

Досліджується кінетика процесів каталітичної реакції окислення монооксиду вуглецю. Знайдено стаціонарні точки моделі та проаналізовано їх на стабільність за їхніми власними значеннями в часовій еволюції рівнянь хімічної кінетики. Виявлено, що при середніх значеннях тисків СО система має дві стійкі точки, тобто вона перебуває у бістабільному стані. Знайдено умову існування області біфуркацій даної кінетичної моделі. Знайдено аналітичний вираз для критичного значення тиску, при якому відбувається фазовий перехід І роду з реактивного стану з високим кисневим покриттям до неактивного стану, коли поверхня вкрита переважно СО. Отримані результати проаналізовано і порівняно з результатами моделі ґраткового газу в наближенні середнього поля.