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Effect of adsorbed impurities on catalytic CO oxidation

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The effect of inactive adsorbed impurities on kinetics of catalytic synthesis of carbon dioxide is investigated in the framework of the lattice-gas model. Namely, two cases of equilibrium impurities with fast, compared with the reaction's rate, and slow self dynamics are analyzed. It is revealed that the adsorbed impurities shift the phase diagram to the region of lower temperatures and higher pressures p_{CO}. In the case of slow impurities the bistable region is narrowed far more than in the case when their dynamics is fast and their distribution on the surface can be assumed to be equilibrium. The critical concentration of impurities at which the bistable region disappears, is found. From analysis of the kinetic equations the condition of the existence of the bifurcation region is analytically obtained.

Key words: *lattice-gas model, catalysis, oxidation, carbon monoxide, oxygen*

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1. Introduction

Poisoning phenomenon has played a great role in the development of the theory of catalysis. Considering heterogeneous catalytic reactions one often speaks about poisons which reduce the activity of catalysts. These impurities can exist in raw materials which are used for preparation of catalysts or can be entered together with the reactants. It is usually assumed that they are chemosorbed at active sites of the surface, block up interactions between reagent and the surface and are inhibitors for the reaction. Mexted [1] mentioned that metals are the most sensitive to poisoning. Oxides and sulfides used as catalysts are more persistent. Metallic catalysts can be poisoned by: 1) molecules which consist of elements of groups VB and VIB if their active atoms are not completely saturated; 2) compounds or ions of some metals; 3) molecules or ions with multiple bonds. Typical catalytic poisons are sulphur compounds ($\mathrm{H_2S}$, $\mathrm{CS_2}$, mercaptan), hydrocyanic acid (HCN), carbon monoxide (CO), free halides ($\mathrm{J_2}$, $\mathrm{Cl_2}$, $\mathrm{Br_2}$), mercury and mercury salts ($\mathrm{HgCl_2}$, $\mathrm{Hg(CN)_2}$), compounds of phosphorus, arsenic, lead. Since sorption of impurities can be reversible and irreversible, one can distinguish reversible and irreversible poisoning. For example, Pt catalyst is poisoned in the presence of CO and $\mathrm{CS_2}$ but its activity can be quickly restored in pure initial mixture of gases. At $\mathrm{H_2S}$ and $\mathrm{PH_3}$ poisoning Pt deactivates irreversibly and completely.

To prevent catalysts from poisoning, special demands are set to the equipment and to the cleaning of initial reactants. However, it is practically impossible to remove all the impurities in a real crystal sample. Considering catalytic reactions theoretically we take into account the presence of impurity atoms or molecules which do not take part in the reaction course but decrease the number of active sites on the catalyst's surface and lower its activity [2–4]. It is experimentally known [5–7] that active reaction-diffusion media can be constructed containing poisons and that the scale and nature of these poisons can drastically affect spontaneous pattern formation on the modified substrate. Increments of the density of impurities lead to a smaller regions of existence of oscillations [2]. Eventually a critical concentration of inert sites is reached at which the region vanishes and oscillations are no longer possible, due to inability of the lattice to reach the minimum local concentration of adsorbate required to trigger the surface reconstruction mechanism.

An attempt to investigate the effect of impurity atoms on one of the catalytic reactions, namely the reaction of catalytic CO oxidation on Pt surface [8–14], is made in the paper. Specifically, our purpose is to take into account the effect of equilibrium impurities with fast and slow self-dynamics on the reaction within the lattice-gas model with interactions on a surface.

2. Lattice-gas model of CO oxidation reaction with equilibrium impurities

2.1. A case of equilibrium impurities with fast self dynamics

Let us consider a model of the reaction of catalytic CO oxidation by incorporating the effect of passive impurities on a surface. In the case when impurities can be considered as equilibrium ones the Hamiltonian of the system is

$$\begin{aligned} H \;=\; & -\mu_1 \sum_i n_i^1 - \mu_2 \sum_i n_i^2 - \mu_3 \sum_i n_i^3 + w_1 \sum_{\langle ij\rangle} n_i^1 n_j^1 + w_2 \sum_{\langle ij\rangle} n_i^2 n_j^2 + \varepsilon_{12} \sum_{\langle ij\rangle} n_i^1 n_j^2 \\ & + \varepsilon_{13} \sum_{\langle ij\rangle} n_i^1 n_j^3 + \varepsilon_{23} \sum_{\langle ij\rangle} n_i^2 n_j^3 \,, \end{aligned} \quad (1)$$

where μ_1, μ_2 and μ_3 denote the chemical potentials of CO, O and impurity respectively, and w_1, w_2, ε_{12}, ε_{13} and ε_{23} are the interaction energies between the nearest-neighbor CO–CO, O–O, CO–O, CO-impurity and O-impurity respectively. The following notations for three types of adsorbate occupancies of ith surface site are: n_i^1 for an adsorbed CO molecule, n_i^2 for adsorbed oxygen and n_i^3 for adsorbed impurity, $n_i^l = [0,1]$ and l=1,2,3. The condition $n_i^1 + n_i^2 + n_i^3 \leqslant 1$ precludes the adsorbed particles from occupation of the same adsorption site. $\sum_{\langle ij\rangle}$ means the sum over the nearest-neighbor pairs.

The Hamiltonian of the system in the mean-field approximation looks like

$$H = -\widetilde{\mu}_1 \sum_i n_i^1 - \widetilde{\mu}_2 \sum_i n_i^2 - \widetilde{\mu}_3 \sum_i n_i^3 + AN, \quad (2)$$

where the following notations are introduced:

$$A \;=\; -w_1 \langle n^1\rangle^2 - w_2 \langle n^2\rangle^2 - \varepsilon_{12}\langle n^1\rangle\langle n^2\rangle - \varepsilon_{13}\langle n^1\rangle\langle n^3\rangle - \varepsilon_{23}\langle n^2\rangle\langle n^3\rangle, \quad (3)$$

$$\widetilde{\mu}_1 \;=\; \mu_1 - 2w_1\langle n^1\rangle - \varepsilon_{12}\langle n^2\rangle - \varepsilon_{13}\langle n^3\rangle, \quad (4)$$

$$\widetilde{\mu}_2 \;=\; \mu_2 - 2w_2\langle n^2\rangle - \varepsilon_{12}\langle n^1\rangle - \varepsilon_{23}\langle n^3\rangle, \quad (5)$$

$$\widetilde{\mu}_3 \;=\; \mu_3 - \varepsilon_{13}\langle n^1\rangle - \varepsilon_{23}\langle n^2\rangle. \quad (6)$$

The grand partition function of the whole system is equal to

$$\Xi = \exp\left(-\frac{AN}{kT}\right)\left[1 + \exp\left(\frac{\widetilde{\mu}_1}{kT}\right) + \exp\left(\frac{\widetilde{\mu}_2}{kT}\right) + \exp\left(\frac{\widetilde{\mu}_3}{kT}\right)\right]^N, \quad (7)$$

whence we obtain the following expression for the grand thermodynamic potential:

$$\begin{aligned} \Omega \;=\; & -kT\ln\Xi = -Nw_1\theta_1^2 - Nw_2\theta_2^2 - \varepsilon_{12}\theta_1\theta_2 N - \varepsilon_{13}\theta_1\theta_3 N - \varepsilon_{23}\theta_2\theta_3 N \\ & - kTN\ln\left[1 + \exp\left(\frac{\widetilde{\mu}_1}{kT}\right) + \exp\left(\frac{\widetilde{\mu}_2}{kT}\right) + \exp\left(\frac{\widetilde{\mu}_3}{kT}\right)\right]. \end{aligned} \quad (8)$$

Making use of this formula, we can calculate all the thermodynamic functions of the system in the mean-field approximation.

Using the thermodynamic formula

$$\theta_i = -\frac{1}{N}\left(\frac{\partial\Omega}{\partial\mu_i}\right)_T, \quad (9)$$

we obtain the following system of equations for the coverages θ_i:

$$\theta_i = \frac{\exp\left(\dfrac{\widetilde{\mu}_i}{kT}\right)}{1+\sum\limits_{i=1}^{3}\exp\left(\dfrac{\widetilde{\mu}_i}{kT}\right)}, \qquad i=1,2,3. \tag{10}$$

In the case when the reaction rate is higher than the rates of adsorbate adsorption and desorption, the evolutions of the CO and O coverages in time are determined by the kinetic equations

$$\frac{\mathrm{d}\theta_1}{\mathrm{d}t} = p_{\mathrm{CO}}k_{\mathrm{CO}}s_{\mathrm{CO}}(1-\theta_1-\theta_2-\theta_3) - d\theta_1 - k\theta_1\theta_2\,, \tag{11}$$

$$\frac{\mathrm{d}\theta_2}{\mathrm{d}t} = 2p_{\mathrm{O}_2}k_{\mathrm{O}}s_{\mathrm{O}}(1-\theta_1-\theta_2-\theta_3)^2 - k\theta_1\theta_2\,, \tag{12}$$

where p_{CO} and p_{O_2} are the partial pressures of CO and oxygen respectively, k_{CO} and k_{O} are the CO and oxygen impingement rates, s_{CO} and s_{O} are the corresponding sticking coefficients. The coefficient k denotes the reaction rate constant and is given by: $k = k_{\mathrm{CO}_2}\exp(-\beta E_0)$ where E_0 is the activation energy of the reaction. The coefficient $d = d_0\exp(-\beta E_{\mathrm{d}})$ is the rate of CO desorption. The first equation, equation (11), describes variations in the amount of adsorbed CO, chemical reaction with adsorbed oxygen, and desorption of CO with desorption constant d. The first term in equation (12) describes the dissociative adsorption of oxygen, and the second one refers to the reaction between adsorbed oxygen and CO. Then, in order to analyse the stable states, it is necessary to solve the equations $\mathrm{d}\theta_1/\mathrm{dt}=0$ and $\mathrm{d}\theta_2/\mathrm{dt}=0$ together with equations (10) with respect to the average coverages for CO and oxygen.

2.2. A case of equilibrium impurities with slow self dynamics

Let us now consider a case of equilibrium impurities with slow self-dynamics on a catalyst surface. In this case, the distribution of impurities on the surface can not be assumed to be equilibrium as in the previous case. So, the kinetic equation for such impurities can be written as

$$\frac{\mathrm{d}\theta_3}{\mathrm{d}t} = k_a(1-\theta_1-\theta_2-\theta_3) - k_{\mathrm{d}}\theta_3\,, \tag{13}$$

where the coefficients k_a and k_{d} are the rates of adsorption and desorption of the impurities. Again, to analyse the stable states of the system, it is necessary to solve the equation $\mathrm{d}\theta_3/\mathrm{dt}=0$ together with equations (10)–(12) with respect to the average coverages for CO and oxygen.

3. Results and discussion

3.1. Phase diagrams of the model

In figure 1 phase diagrams $(p_{\mathrm{CO}}, 1/T)$ for various values of s_{CO} and s_{O} in the cases of clean Pt surface (case a) and the surface containing equilibrium impurities with fast self-dynamics (cases $b-d$) are shown. According to the known experimental results, we can make allowance for the variation of the sticking factors for CO and oxygen, which is caused by the presence of impurity atoms. Notice that in the case of modified sticking coefficients (case b in the figure) the bistable region is shifted towards higher CO pressures. On the other hand, taking into account the impurities via the average coverage θ_{d} in the kinetic equations with unaltered sticking coefficients (case c) causes a shift of the bistable region towards lower pressures and lower temperatures. Finally, taking into account the impurities on the surface via both the coverage θ_{d} and the modification of the coefficients s_{CO} and s_{O} (case d) shifts the phase diagram to the region of lower temperatures and higher pressures p_{CO} in comparison with the case of pure surface (case a). We also note that the phase diagram of equilibrium lattice model (1)–(9) does not contain the region of bistability.

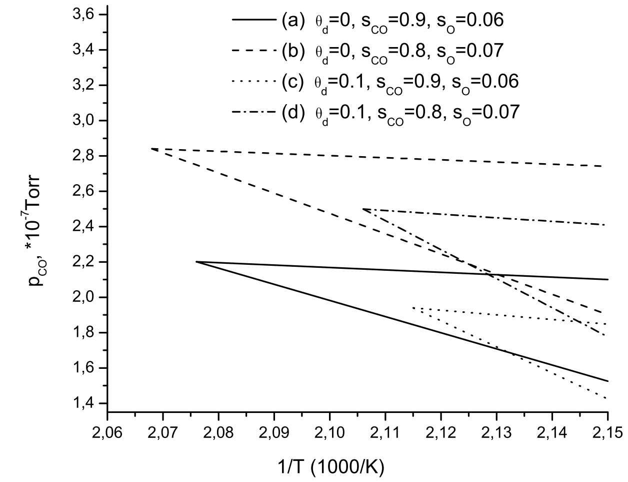

Figure 1. Phase diagrams $(p_{\mathrm{CO}}, 1/T)$ for various values of θ_{d}, s_{CO} and s_{O}.

In figure 2 the dependences of the CO and oxygen coverages on the pressure p_{CO} are exhibited for two cases. In the first case the catalyst's surface is pure and in the second case it is poisoned by fast impurities. It is clearly seen from the figure, that impurities give rise to a significant shift of the region of bistability. The shift of the region is also accompanied by a reduction of the average CO coverage and by an increase of the oxygen one, which is in agreement with experimental results.

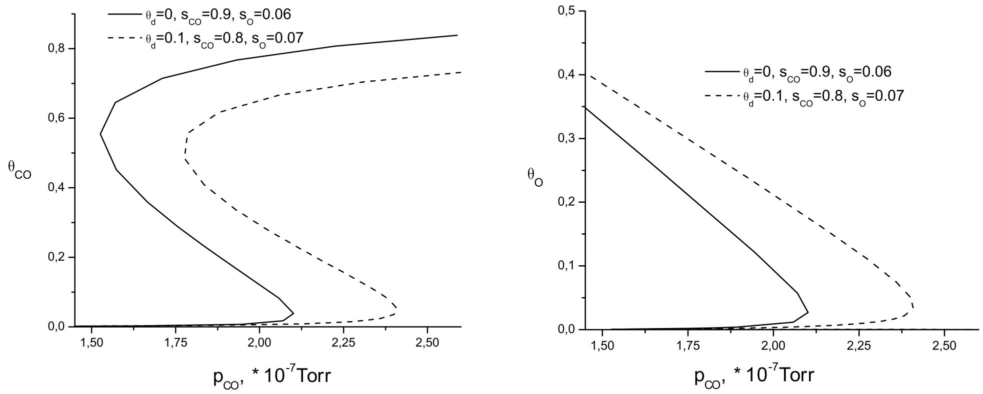

Figure 2. Average CO and oxygen coverages as the functions of p_{CO} at T=466 K and for various values of θ_{d}, s_{CO} and s_{O}.

At some rather high concentration of impurities, the bistable region disappears and we have only a monotonous dependence $\theta_{\mathrm{CO,O}} = f(p_{\mathrm{CO}})$. This phenomenon is accompanied by an increase of the CO coverage and a decrease of the oxygen one. It is interesting to find, in the same approximation, the highest possible concentration of impurities, at which the region of bistability still exists. Figure 3 demonstrates that $\theta_{\mathrm{d}} = 0.7$ is the critical value, at which the bifurcation of the solution is still observed. At higher values of θ_{d}, the bistable region disappears. Taking into account the interactions between impurities we should expect a decrement of concentration θ_{d}.

In figure 4 the dependencies of the average CO and oxygen coverages as the functions of p_{CO} are shown for three different cases – for a pure surface without any impurities, for the surface with fast

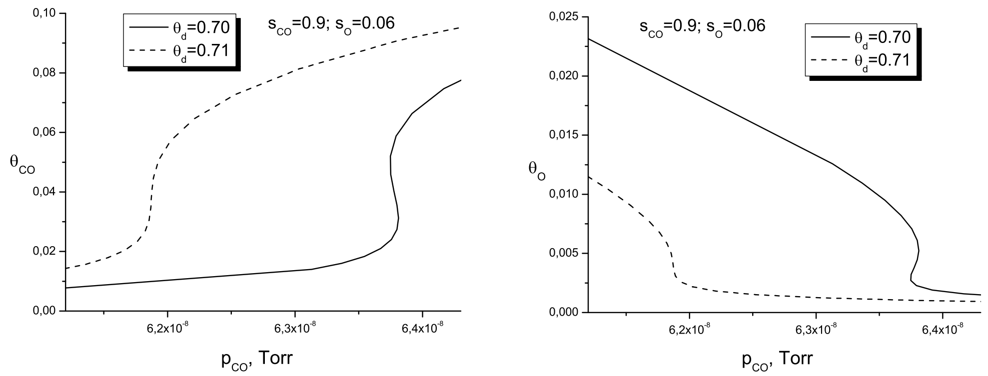

Figure 3. Average CO and oxygen coverages as the functions of p_{CO} at T=466 K and for various values of concentrations θ_{d}.

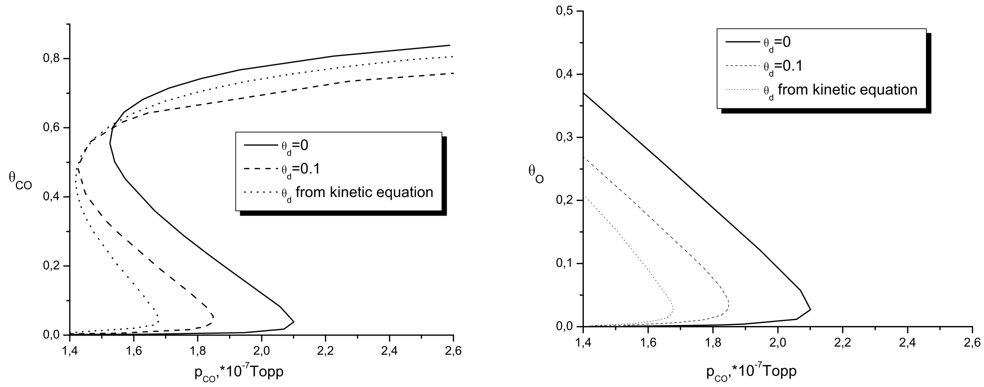

Figure 4. Average CO and oxygen coverages as the functions of p_{CO} at T=466 K and for various values of concentrations θ_{d}.

impurities when their concentration θ_{d} on the surface is constant, $\theta_{\mathrm{d}} = 0.1$, and for the surface with slow impurities, the concentration of which is determined by kinetic equation (13). The sticking coefficients s_{CO}, s_{O} are constants for all three cases and have the following values: $s_{\mathrm{CO}} = 0.9$ and $s_{\mathrm{O}} = 0.06$. We can see from the figure that the presence of the impurities narrows the bistable region and shifts it to the region of lower pressures p_{CO}, but in the case of impurities with slow self-dynamics the bistable region is narrowed far more than in the case when their dynamics is fast.

Thus, the presence of impurities on the surface significantly affects the kinetics of the catalytic CO oxidation reaction. Impurities shift the bistable region and change the average coverages on the surface. The variations of s_{CO} and s_{O}, caused by the presence of impurity atoms, play an important role.

3.2. Analysis of the kinetic equations

To analyse the system of kinetic equations (11)–(13) it is convenient to rewrite it in dimensionless form:

$$\frac{\mathrm{d}\theta_{\mathrm{CO}}}{\mathrm{d}\tau} = \frac{p_{\mathrm{CO}} k_{\mathrm{CO}} s_{\mathrm{CO}}}{d}(1 - \theta_{\mathrm{CO}} - \theta_{\mathrm{O}} - \theta_{\mathrm{d}}) - \theta_{\mathrm{CO}} - \frac{k}{d}\theta_{\mathrm{CO}}\theta_{\mathrm{O}}\,, \tag{14}$$

$$\begin{aligned}\frac{\mathrm{d}\theta_{\mathrm{O}}}{\mathrm{d}\tau} &= \frac{2p_{O_2}k_{\mathrm{O}}s_{\mathrm{O}}}{d}(1-\theta_{\mathrm{CO}}-\theta_{\mathrm{O}}-\theta_{\mathrm{d}})^2 - \frac{k}{d}\theta_{\mathrm{CO}}\theta_{\mathrm{O}}\,, &(15)\\ \frac{\mathrm{d}\theta_{\mathrm{d}}}{\mathrm{d}(k_{\mathrm{d}}t)} &= \frac{k_a}{k_{\mathrm{d}}}(1-\theta_{\mathrm{CO}}-\theta_{\mathrm{O}}-\theta_{\mathrm{d}}) - \theta_{\mathrm{d}}\,, &(16)\end{aligned}$$

where $\tau = d\cdot t$ is a new scale of time for θ_{CO} and θ_{O}.

Let us find stationary points of the model described by equations (14)–(16). One is given by

$$\theta^s_{\mathrm{CO}} = 0, \qquad \theta^s_{\mathrm{O}} = 1, \qquad \theta^s_{\mathrm{d}} = 0, \tag{17}$$

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

$$A\theta^3_{\mathrm{CO}} + B\theta^2_{\mathrm{CO}} + C\theta_{\mathrm{CO}} + D = 0, \tag{18}$$

and the corresponding oxygen and impurities concentrations are given by

$$\theta_{\mathrm{O}} = \frac{\frac{h_{\mathrm{CO}}}{k_i d}(1-\theta_{\mathrm{CO}}) - \theta_{\mathrm{CO}}}{\frac{h_{\mathrm{CO}}}{k_i d} + \frac{k}{d}\theta_{\mathrm{CO}}}\,, \qquad \theta_{\mathrm{d}} = \frac{k_i - 1}{k_i}(1-\theta_{\mathrm{CO}}-\theta_{\mathrm{O}})\,, \tag{19}$$

where the following notations $h_{\mathrm{O}} = 2p_{O_2}k_{\mathrm{O}}s_{\mathrm{O}}$, $h_{\mathrm{CO}} = p_{\mathrm{CO}}k_{\mathrm{CO}}s_{\mathrm{CO}}$, $k_i = k_a/k_{\mathrm{d}} + 1$ are introduced for convenience. The coefficients of the cubic equation are

$$\begin{aligned} A &= \frac{h_{\mathrm{O}}k^2}{k_i^2}\frac{1}{d^3}\,,\\ B &= -\frac{2h_{\mathrm{O}}k^2}{k_i^2}\frac{1}{d^3} + \frac{h_{\mathrm{CO}}k^2}{k_i}\frac{1}{d^3} - \frac{2h_{\mathrm{O}}k}{k_i^2}\frac{1}{d^2} + k^2\frac{1}{d^2}\,,\\ C &= \frac{h_{\mathrm{O}}k^2}{k_i^2}\frac{1}{d^3} + \frac{h^2_{\mathrm{CO}}k}{k_i^2}\frac{1}{d^3} - \frac{h_{\mathrm{CO}}k^2}{k_i}\frac{1}{d^3} + \frac{2h_{\mathrm{O}}k}{k_i^2}\frac{1}{d^2} + \frac{h_{\mathrm{CO}}k}{k_i}\frac{1}{d^2} + \frac{h_{\mathrm{O}}}{k_i^2}\frac{1}{d}\,,\\ D &= -\frac{h^2_{\mathrm{CO}}k}{k_i^2}\frac{1}{d^3}\,. \end{aligned} \tag{20}$$

All the roots of cubic equation (18) can be real when the following condition

$$\left(\frac{C}{3A} - \left(\frac{B}{3A}\right)^2\right)^3 + \left(\left(\frac{B}{3A}\right)^3 - \frac{BC}{6A^2} + \frac{D}{2A}\right)^2 < 0 \tag{21}$$

is satisfied. From the physical point of view, in this case we have a bistable region in the phase diagram. So, inequality (21) is the condition of the existence of the bifurcation region obtained from the kinetic level of description. In linear approximation for small desorption constants this condition can be rewritten as follows:

$$d < -\frac{c_1 + c_2}{c_3 + c_4}\,, \tag{22}$$

where

$$c_1 = \left(\frac{1}{3} + \frac{h^2_{\mathrm{CO}}}{3h_{\mathrm{O}}k} - \frac{h_{\mathrm{CO}}k_i}{3h_{\mathrm{O}}} - \left(-\frac{2}{3} + \frac{h_{\mathrm{CO}}k_i}{3h_{\mathrm{O}}}\right)^2\right)^3, \tag{23}$$

$$c_2 = \left(\left(-\frac{2}{3} + \frac{h_{\mathrm{CO}}k_i}{3h_{\mathrm{O}}}\right)^3 + \frac{1}{3} - \frac{h^2_{\mathrm{CO}}}{3h_{\mathrm{O}}k} - \frac{h_{\mathrm{CO}}k_i}{2h_{\mathrm{O}}} - \frac{h^3_{\mathrm{CO}}k_i}{6h^2_{\mathrm{O}}k} + \frac{h^2_{\mathrm{CO}}k_i^2}{6h^2_{\mathrm{O}}}\right)^2, \tag{24}$$

$$c_3 = 3\left(\frac{1}{3} + \frac{h^2_{\mathrm{CO}}}{3h_{\mathrm{O}}k} - \frac{h_{\mathrm{CO}}k_i}{3h_{\mathrm{O}}} - \left(-\frac{2}{3} + \frac{h_{\mathrm{CO}}k_i}{3h_{\mathrm{O}}}\right)^2\right)^2\left(\frac{2}{3k} + \frac{h_{\mathrm{CO}}k_i}{3h_{\mathrm{O}}k} - \frac{2}{9}\left(-2 + \frac{h_{\mathrm{CO}}k_i}{h_{\mathrm{O}}}\right)\right.$$

$$\times \left(\frac{k_i^2}{h_{\rm O}} - \frac{2}{k}\right)\right), \tag{25}$$

$$c_4 = 2\left(\left(-\frac{2}{3} + \frac{h_{\rm CO}k_i}{3h_{\rm O}}\right)^3 + \frac{1}{3} - \frac{h_{\rm CO}^2}{3h_{\rm O}k} - \frac{h_{\rm CO}k_i}{2h_{\rm O}} - \frac{h_{\rm CO}^3k_i}{6h_{\rm O}^2k} + \frac{h_{\rm CO}^2k_i^2}{6h_{\rm O}^2}\right)\left(\left(-\frac{2}{3} + \frac{h_{\rm CO}k_i}{3h_{\rm O}}\right)^2 \times \left(\frac{k_i^2}{h_{\rm O}} - \frac{2}{k}\right) + \frac{1}{k} - \frac{h_{\rm CO}^2k_i^2}{3h_{\rm O}^2k} + \frac{h_{\rm CO}^2}{3h_{\rm O}k^2} - \frac{h_{\rm CO}k_i}{3h_{\rm O}k} - \frac{k_i^2}{6h_{\rm O}} + \frac{h_{\rm CO}k_i^3}{6h_{\rm O}^2}\right). \tag{26}$$

Relation (22) works well for the parameter range considered at $h_{\rm CO}/h_{\rm O} \leqslant 0.7$.

We take the following values of our model parameters which correspond to Pt(111) surface: $p_{\rm O_2} = 1.5\cdot10^{-5}$Torr, $k_{\rm O} = 7.8\cdot10^5{\rm c}^{-1}{\rm Torr}^{-1}$, $k_{\rm CO} = 7\cdot10^6{\rm c}^{-1}{\rm Torr}^{-1}$, $k = 598{\rm c}^{-1}$, $d = 0.27{\rm c}^{-1}$, $s_{\rm CO} = 0.9$, $s_{\rm O} = 0.06$. Coefficients $k_a = 0.05{\rm c}^{-1}$, $k_{\rm d} = 0.2{\rm c}^{-1}$ are chosen under the condition that keeps the impurities concentration on a surface sufficiently small. This allows us to study the effect of impurities on the bistable range. Since this model is formulated at the phenomenological level, these coefficients can be adjusted to different kinds of impurities if experimental data are available. Then, the bistable region exists at the following values of pressure $p_{\rm CO}$:

$$1.42\cdot10^{-7}\quad {\rm Torr} < p_{\rm CO} < 1.67\cdot10^{-7}\quad {\rm Torr}. \tag{27}$$

The characteristic equation for eigenvalues is as follows:

$$\det\left\|\lambda - \left(\frac{\partial(F_{\theta_{\rm CO}}, F_{\theta_{\rm O}}, F_{\theta_{\rm d}})}{\partial(\theta_{\rm CO}, \theta_{\rm O}, \theta_{\rm d})}\right)_{ss}\right\| = 0 \tag{28}$$

or for the system considered

$$\det\begin{Vmatrix} -\frac{h_{\rm CO}}{d} - 1 - \frac{k}{d}\theta_{\rm O}^s - \lambda & -\frac{h_{\rm CO}}{d} - \frac{k}{d}\theta_{\rm CO}^s & -\frac{h_{\rm CO}}{d} \\ -\frac{2h_{\rm O}}{d}v_s - \frac{k}{d}\theta_{\rm O}^s & -\frac{2h_{\rm O}}{d}v_s - \frac{k}{d}\theta_{\rm CO}^s - \lambda & -\frac{2h_{\rm O}}{d}v_s \\ -k_i + 1 & -k_i + 1 & -k_i - \lambda \end{Vmatrix} = 0 \tag{29}$$

with $v_s = 1 - \theta_{\rm d}^s - \theta_{\rm O}^s - \theta_{\rm CO}^s$ the stationary density of empty adsorption sites.

Determination of eigenvalues of stationary points of the model allows us to analyse the type of their stability. Let us consider three cases. One case is when the partial pressure $p_{\rm CO}$ has such a value that we are in the bistable region at the phase diagram. The other two cases are presented when we consider the regions situated lower or higher than the region of bistability. The stationary points, their eigenvalues and the corresponding types of their stability are shown in table 1. As expected, at the intermediate values of pressure $p_{\rm CO}$ the system has four stationary points, but only two of them are stable. In other cases, there is only one stable point in the system, i. e., a stable node.

There should be noted a great difference in the eigenvalues for the stationary solutions by two or even by three orders of magnitude. It actually determines the relaxation times of the model. However, it is unlikely that this phenomenon has anything to do with the presence of impurities on the catalyst's surface. In paper [15] where the reaction kinetics on a pure metal surface is studied, a similar situation is observed. Speaking about the width of the bistability region we observe a tendency to its narrowing as a result of a presence of impurities. For comparison, we can give the results of calculations for the boundaries of the bistable region for the model of the reaction of catalytic CO oxidation without impurities: $p_{\rm CO}^{\rm min} = 1.53\times10^{-7}$ Torr and $p_{\rm CO}^{\rm max} = 2.05\times10^{-7}$ Torr. As we see, the impurities considerably narrow the bistable region.

4. Conclusions

We have investigated the effect of impurities on the kinetics of catalytic reaction of carbon dioxide synthesis. For the lattice-gas model in the mean-field approximation we have obtained kinetic phase diagrams $(p_{\rm CO}, 1/T)$ which contain bistable regions. Modification of the sticking

Table 1. Analysis of the stability of the stationary points at different values of pressure p_{CO} .

Pressure p_{CO}	Stationary points	Eigenvalues	Stability
$1.3 \cdot 10^{-7}$ Torr	$(\theta_{\mathrm{CO}} = 0,\ \theta_{\mathrm{O}} = 1,\ \theta_{\mathrm{d}} = 0)$	–2221.9 –1.06 2.84	saddle
	$(\theta_{\mathrm{CO}} = 0.003,\ \theta_{\mathrm{O}} = 0.269,\ \theta_{\mathrm{d}} = 0.146)$	–609.7 –3.3 –0.89	stable node
$1.5 \cdot 10^{-7}$ Torr	$(\theta_{\mathrm{CO}} = 0,\ \theta_{\mathrm{O}} = 1,\ \theta_{\mathrm{d}} = 0)$	–2222.8 –1.06 3.3	saddle
	$(\theta_{\mathrm{CO}} = 0.007,\ \theta_{\mathrm{O}} = 0.154,\ \theta_{\mathrm{d}} = 0.168)$	–364.9 –3.5 –0.91	stable node
	$(\theta_{\mathrm{CO}} = 0.264,\ \theta_{\mathrm{O}} = 0.003,\ \theta_{\mathrm{d}} = 0.147)$	–603.5 –1 1.26	saddle
	$(\theta_{\mathrm{CO}} = 0.589,\ \theta_{\mathrm{O}} = 0.0004,\ \theta_{\mathrm{d}} = 0.082)$	–1312.3 –1.33 –1	stable node
$1.8 \cdot 10^{-7}$ Torr	$(\theta_{\mathrm{CO}} = 0,\ \theta_{\mathrm{O}} = 1,\ \theta_{\mathrm{d}} = 0)$	–2224.2 –1.05 3.98	saddle
	$(\theta_{\mathrm{CO}} = 0.7,\ \theta_{\mathrm{O}} = 0.0002,\ \theta_{\mathrm{d}} = 0.06)$	–1555.8 –2.95 –1	stable node

coefficients s_{CO} and s_{O} induced by the presence of impurities plays an important role. There is observed a shift of the diagram to the region of higher pressures p_{CO}. It leads to a decrease of the CO and to an increase of the oxygen coverages which agrees well with the experimental results. Taking into account the impurities on the surface via both the coverage θ_{d} and the modification of the coefficients s_{CO} and s_{O} shifts the phase diagram to the region of lower temperatures and higher pressures p_{CO}. In the case of slow impurities, the bistable region is narrowed far more than in the case when their dynamics is fast and their distribution on the surface can be assumed to be equilibrium. The critical concentration of impurities at which the bistable region still exists, as follows from our estimations, is $\theta_{\mathrm{d}} = 0.7$. Taking into account the interactions between impurities we should expect a decrement of concentration θ_{d}. From the analysis of kinetic equations, the condition of the existence of bifurcation region has been analytically found.

In our work the interactions between the impurities and coadsorbates have been taken into account within the mean field approximation for the Hamiltonian (1). In general, it is also possible to include such interactions into the level of kinetic equations and to use more sophisticated approximations that allow one to consider more in detail the surface modifications (phase transitions, inhomogeneous patterns, etc) and diffusion effects. Some of these problems will be considered in our further studies.

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Вплив домішок на реакцію каталітичного окислення CO

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В рамках ґраткової моделі досліджується вплив неактивних домішок на кінетику реакції каталітичного синтезу вуглекислого газу, зокрема аналізуються випадки рівноважної домішки з швидкою (в порівнянні зі швидкістю реакції) та повільною власними динаміками. Показано, що домішки на поверхні зміщують фазову діаграму до області нижчих температур і вищих тисків p_{CO}. У випадку, коли концентрація домішки змінюється на поверхні досить повільно, область бістабільності звужується значно більше, ніж коли динаміка домішки є швидкою і її розподіл на поверхні можна вважати рівноважним. Знайдено критичну концентрацію домішок, при якій ще спостерігається область бістабільності. З кінетичних рівнянь аналітично знайдено умову існування області бістабільності.

Ключові слова: *модель ґраткового газу, каталіз, окислення, монооксид вуглецю, кисень*

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