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Chemical oscillations in catalytic CO oxidation reaction

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Temporal dynamics of a heterogeneous catalytic system, namely of the catalytic CO oxidation on Pt(110) surface at low pressures, is investigated with taking into account the adsorbate-driven structural transformations of the catalyst surface. Uniform temporal periodic chemical oscillations of the CO and oxygen coverages, and the fraction of the surface of the 1×1 structure are obtained in a narrow region of phase diagram between two uniform stable states of high and low catalytic activities, respectively.

Key words: *chemical oscillations, bifurcation, catalytic oxidation, carbon monoxide, oxygen*

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Since Langmuir's pioneering studies, the oxidation of CO over Pt is a classical example of a heterogeneous catalytic reaction. It is considered to be generic due to its apparently simple mechanism, richness of spatio-temporal behavior, and practical relevance [1]. In particular, the temporal behavior of the reaction, for given constant control parameters, may either be constant (including bistability) or may become oscillatory or even chaotic [2, 3]. First kinetic oscillations in this reaction were found by Hugo in 1970 on a supported catalyst. Later on, this phenomenon was also observed for other types of catalysts (polycrystalline wires and single crystals) both at ultrahigh vacuum (UHV) and subatmospheric conditions.

Based on the knowledge about individual steps forming the reaction mechanism, temporal dynamics (with the exception of chaotic kinetics) could be successfully modelled by the solution of sets of ordinary differential equations (ODE's) for the variables describing the surface concentrations of the species involved [4–6]. For a close-packed Pt(111) surface, these are the coverages for adsorbed CO and O, respectively [7]. We will study the more open Pt(110) plane where the oscillatory behavior in the catalytic CO oxidation can be experimentally observed [8, 9].

So, the oxidation of CO on platinum is known to proceed via the classical Langmuir-Hinshelwood (LH) mechanism (see [10–12]),

$$\begin{gathered}
\mathrm{O}_2 + 2* \to 2\mathrm{O}_{\mathrm{ads}}\,, \\
\mathrm{CO} + * \rightleftharpoons \mathrm{CO}_{\mathrm{ads}}\,, \\
\mathrm{CO}_{\mathrm{ads}} + \mathrm{O}_{\mathrm{ads}} \to \mathrm{CO}_2 + 2*\,.
\end{gathered} \tag{1}$$

Here * denotes an empty site, adsorbed species are written with the subscript ads. CO_2 desorbs immediately at the temperatures under consideration and therefore constitutes an inert product. The other gases exhibit only small variations of their partial pressure under the applied conditions so that they can be assumed constant.

Mathematical modelling of the experiments is conducted using a realistic model of catalytic CO oxidation on Pt(110) first studied by Krischer et al. [13]. The model takes into account adsorption of CO and oxygen molecules, reaction and desorption of CO molecules. For simplicity, surface diffusion of adsorbed CO molecules, surface roughening, faceting, formation of subsurface oxygen, and the effects of internal gas-phase coupling are not taken into account. The system of differential equations describing the dynamics behavior of the model is

$$\frac{\mathrm{d}u}{\mathrm{d}t} = F_1(u,v) = p_{\mathrm{CO}} k_{\mathrm{CO}} s_{\mathrm{CO}} (1-u^q) - k_d u - k_r uv, \tag{2}$$

$$\frac{\mathrm{d}v}{\mathrm{d}t} = F_2(u,v) = p_{\mathrm{O}_2} k_O s_O (1-u-v)^2 - k_r uv. \tag{3}$$

The variables u and v represent the surface coverage of CO and oxygen, respectively. The variables can vary in the interval from 0 to 1. The difference between model (2)–(3) and the model considered in our earlier paper [7] is that the precursor-type kinetics of CO adsorption is accounted for by the exponent $q = 3$ in the right hand part of equation (2). It makes the model more realistic since the inhibition of adsorption of CO and O_2 is asymmetric and preadsorbed CO blocks oxygen adsorption but not vice versa. The parameters, corresponding to Pt(110) surface, were chosen such that the reaction was oscillatory. For explanation and values of the parameters see table 1 taken from [14].

Table 1. Parameters of the model.

T	540 K	Temperature
p_{CO}	4.81×10^{-5} mbar	CO partial pressure
p_{O_2}	13×10^{-5} mbar	O_2 partial pressure
k_{CO}	3.14×10^5 s^{-1}mbar^{-1}	Impingement rate of CO
k_O	5.86×10^5 s^{-1}mbar^{-1}	Impingement rate of O_2
k_d	10.21 s^{-1}	CO desorption rate
k_r	283.8 s^{-1}	Reaction rate
s_{CO}	1	CO sticking coefficient
$s_{O,1\times1}$	0.6	Oxygen sticking coefficient on the 1×1 phase
$s_{O,1\times2}$	0.4	Oxygen sticking coefficient on the 1×2 phase
u_0, δu	0.35, 0.05	Parameters for the structural phase transition
k_5	1.61 s^{-1}	Phase transition rate

Analysis of the system (2)–(3) reveals that there is a bistability in one, and a cusp in two control parameters. It is known that in a system, the relaxation oscillations can emerge in bistable state if the system depends on a parameter slowly varying in time. It would be a model parameter connected with the variations of average coverages and the structural changes of the surface as a function of time, since at the experimental conditions, depending on the CO coverage, the reconstructed 1×2 Pt(110) surface may revert to the 1×1 structure. In this case the kinetic equation for the surface transformation should be taken into consideration. The structural phase transition $1 \times 2 - 1 \times 1$ of the Pt(110) surface is considered through a simple relaxation law [14]:

$$\frac{\mathrm{d}w}{\mathrm{d}t} = F_3(u,w) = k_5\left(p[u] - w\right). \tag{4}$$

The variable w denotes the local fraction of the surface area found in the nonreconstructed 1×1 structure.

$$p[u] = \frac{1}{1 + \exp\left(\dfrac{u_0 - u}{\delta u}\right)} \tag{5}$$

is a nondecreasing and smooth function of the interval [0,1] that appears in the equation for $\mathrm{d}w/\mathrm{d}t$. It is shown in figure 1.

The oxygen sticking coefficient s_O in equation (3) was modified and taken as a linear combination of the values for the $1 \times 2 - 1 \times 1$ structure:

$$s_O = s_{1\times1} w + s_{1\times2}(1-w). \tag{6}$$

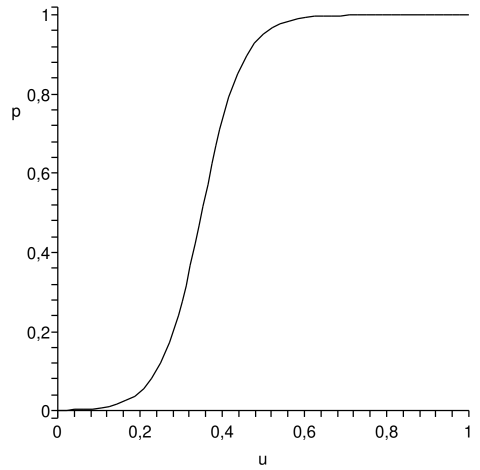

Figure 1. Function $p[u]$ that appears in the equation for $\mathrm{d}w/\mathrm{d}t$.

The steady states of the system are defined as the time independent solutions of the kinetic equations (2)–(4):

$$F_i(u_{ss}, v_{ss}, w_{ss}) = 0, \quad i = 1, 2, 3. \tag{7}$$

Linear stability analysis requires the solution of the secular equation for any given steady state:

$$\det \left\| \lambda - \left(\frac{\partial(F_1, F_2, F_3)}{\partial(u, v, w)} \right)_{ss} \right\| = 0. \tag{8}$$

We solve the secular equation (8) and obtain two types of stationary points, namely these are stable nodal points, when all the roots are real and negative, and stable nodal-spirals, when one root is real negative, and the other two are complex with negative real part. As the control parameters are varied, we have transitions from one stability regime to another. We compute several regimes in the phase space of partial pressures. A phase diagram in (p_{CO}, p_{O_2}) parameters is reproduced in figure 2. As we see, the stable regime corresponds to the region where the partial CO pressure is

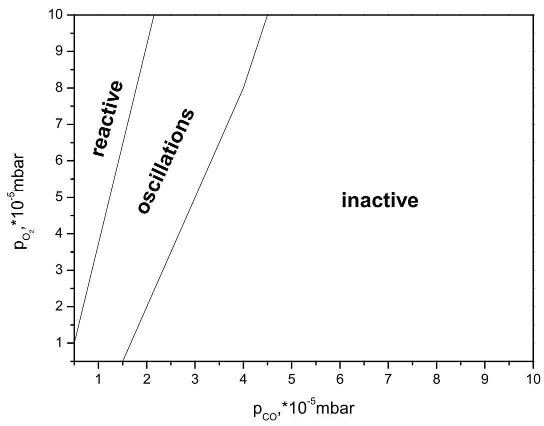

Figure 2. Phase diagram of the model of surface oscillations in the $(\mathrm{p_{CO}}, \mathrm{p_{O_2}})$ parameter plane.

small compared with the O_2 partial pressure. Beyond that phase space region, unstable oscillatory regime appears. Furthermore, we obtain the surface poisoning by CO in qualitative agreement with experimental data found previously on Pt(100) surface in the field electron microscope (FEM) experiments [15]. In the experimental kinetic phase diagram, the region in which the O_{ads} layer is found at a high p_{O_2} to p_{CO} ratio, is separated by a region of the occurrence of kinetic oscillations from the region of the CO_{ads} layer at a lower partial pressure ratio.

The ODE system (2)–(4) exhibits uniform periodic chemical oscillations of the CO and oxygen coverages, as well as the oscillations of the fraction of the surface of the nonreconstructed 1×1 structure in a narrow region of the phase diagram between two uniform stable states of high and low catalytic activities. Examples of time series are shown in figure 3. As is seen from the figure, u and v oscillate in strictly opposite phases, variable w reaches its maximum after u. We see that the difference between the two cases (a) and (b) is that the oscillations have a larger period in the latter case of higher partial pressure p_{CO}. The similar tendency is observed in the experiment, where the period of oscillations increases (except in the region near the right bifurcation point) with p_{CO} pressure increasing [16]. A decrease in T is associated with an increase of the oscillation period as is observed in figure 3(c) at lower temperature $T = 535$ K.

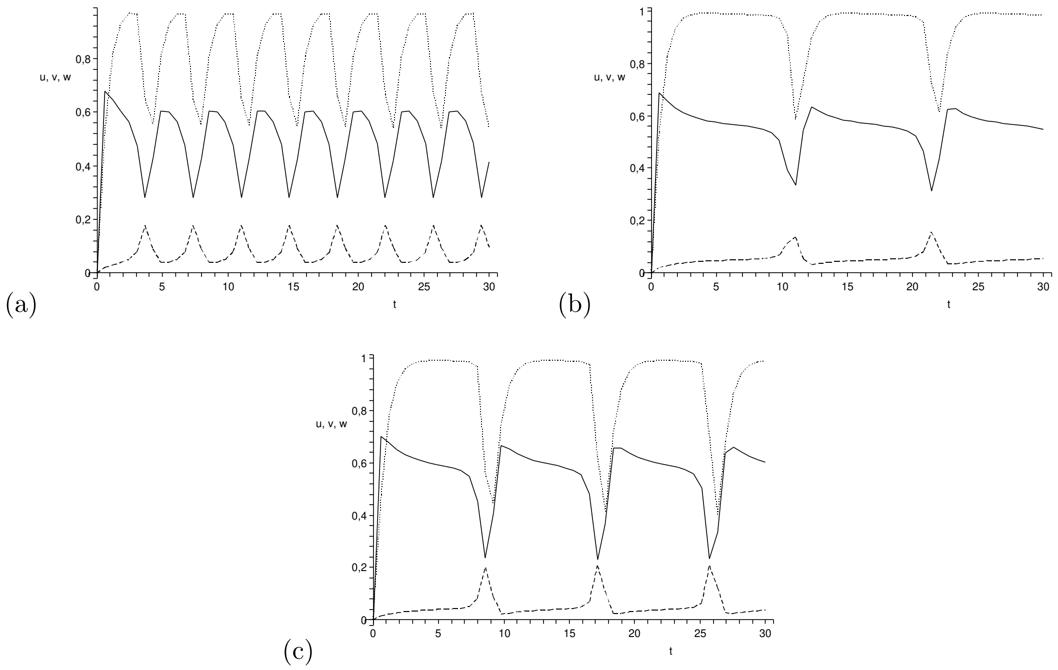

Figure 3. Examples of oscillations obtained by integration of equations (2)–(4) for the parameter $p_{O_2} = 13 \cdot 10^{-5}$ mbar. Panels (a) and (b) correspond to the values $p_{CO} = 4.81 \cdot 10^{-5}$ mbar and $p_{CO} = 4.86 \cdot 10^{-5}$ mbar, respectively, at T=540 K. Panel (c) corresponds to the value $p_{CO} = 4.81 \cdot 10^{-5}$ mbar at T=535 K. The symbols are as follows: full line for $u(t)$, long dashes for $v(t)$ and dotted line for $w(t)$.

In summary, we have investigated a kinetic model for the catalytic CO oxidation on a surface of Pt(110) at low pressures. From the analysis of stability of stationary points of the model, a phase diagram in the (p_{CO}, p_{O_2}) parameter plane has been constructed. We have found two types of stationary points which present two different stability regimes, namely the stable and the unstable oscillatory ones. Oscillatory regime arises due to the interplay between bistability and adsorbate-induced surface reconstruction $1\times2-1\times1$ exposing patches with different O_2 sticking probabilities.

The proposed model is obviously capable of qualitatively describing the experimentally observed features connected with kinetic oscillations in the catalytic CO oxidation on a Pt(110) surface at low pressures. However, it disregards many interesting phenomena of spatiotemporal behavior of the system such as mixed-mode oscillations, a period-doubling transition to chaos, and the formation of stationary as well as propagating spatial patterns. A successful description of the experimentally obtained behavior will most likely require to take spatial effects, namely diffusion of the reactants and faceting of the surface, into account.

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Хімічні коливання в реакції каталітичного окислення CO

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Досліджується часова динаміка гетерогенної каталітичної системи на прикладі реакції каталітичного окислення CO на поверхні Pt(110) при низьких тисках із врахуванням перетворення поверхні каталізатора під впливом процесів адсорбції-десорбції. Отримано однорідні часові періодичні хімічні коливання покриттів CO, кисню та частки поверхні структури 1×1 у вузькій області фазової діаграми між двома однорідними стійкими станами високої і низької каталітичної активності, відповідно.

Ключові слова: *хімічні коливання, біфуркація, каталітичне окислення, монооксид вуглецю, кисень*