Mechanism for CO Oxidation and Oscillatory Reactions on Pd Tip and Pd(110) Surfaces: FEM, TPR, XPS Studies

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Abstract

Detailed studies of the coadsorption of oxygen and carbon monoxide, hysteresis phenomena and oscillatory reaction of CO oxidation on Pd(110) and Pd tip surfaces have been carried out with the molecular beam (MB), field electron microscope (FEM), temperature programmed reaction (TPR) and X-ray photoelectron spectroscopy (XPS). It has been found that the occurrence of kinetic oscillations over Pd surfaces is associated with periodic formation and depletion of subsurface oxygen (O_{sub}). Transient kinetic experiments show that CO does not react chemically with subsurface oxygen to form CO₂ below 300 K. It has been found that CO does react with an atomic O_{ads}/O_{sub} state beginning at temperature ~150 K. Analysis of Pd tip surface with a local resolution of ~20 Å shows the availability of a sharp boundary between the mobile CO_ads and O_ads fronts.

INTRODUCTION

Unslackened interest in self-oscillatory phenomena in catalytic reaction over metal surfaces [1] is for a large part caused by the possibility to perform the catalytic processes more effectively using the unsteady-state operation. The extensive study of model reactions (CO + O₂, CO + NO, NO_reduction, etc.) has been stimulated by the relevance of these reactions to an air pollution control [2]. The automotive catalyst is based on the precious metals, usually Pt, Rh or Pd. The CO oxidation and NO_x reduction on noble metal surfaces are highly non-linear systems. Usually these reactions are operated under conditions far from the thermodynamic equilibrium, where temporal and spatial organization becomes possible. In the oscillating regime of the reactions, the reaction mixture periodically affects the metals properties. These processes can be accompanied by (i) surface phase transition; (ii) faceting of the surface; (iii) formation of oxide layers. Two different mesoscopic and microscopic analytical tools have been introduced and successfully applied to learn details about the reaction dynamics at catalyst surfaces [3]. During catalytic reactions the formation of the target pattern and the propagation of reaction-diffusion fronts were observed [3–8]. Inspired by these experimental results Field Electron Microscopy (FEM) with higher lateral resolution of ~20 Å and Field Ion Microscopy with atomic resolution of ~3–6 Å have been developed to investigate a dynamic surface phenomena at CO oxidation over Pt tip surfaces. Sharp tips of Pt and Rh in size up to several hundreds of Angströmns have been used to perform in situ investigations of real dynamic surface processes in which different crystallographic nanoplanes of the emitter-tip are simultaneously exposed to the reacting gas [4–7]. These tips were used for the first time as an excellent model for metal supported catalyst to study oscillations in CO + O₂, NO + H₂, H₂ + O₂ reactions in situ. The principal result of these studies was that non-linear reaction kinetics is not restricted to macroscopic planes since: (i) the planes ~200 Å in diameter show the same non-linear kinetics; (ii) regular waves appear under the reaction rate oscillations; (iii) the propagation of reaction-diffusion waves includes
the participation of the different crystal nanoplanes and indicates an effective coupling of adjacent planes.

It is well known that the Langmuir – Hinshelwood mechanism is used to describe the CO oxidation on platinum group metals. In order to explain the occurrence of kinetic oscillations an additional feedback reaction is required. Mechanisms of these oscillations on the platinum surfaces are connected with the surface reconstruction \((\text{Pt}(100)-(\text{hex}) \leftrightarrow (1 \times 1))\) [8]. The palladium surfaces are known not to reconstruct and isothermal oscillations are associated with subsurface oxygen formation \((\text{Pd}(110): O_{\text{ads}} \leftrightarrow O_{\text{sub}})\) [9].

The reaction kinetics on the Pd tip (model catalyst, grain diameter \(\sim 10^3 \text{ Å}\)) might be quite various as compared to that on the single crystal surfaces as a result of an interplay between different nanoplanes present on emitter surfaces [4]. On the supported metal catalyst with a crystallite size of \(\sim 500 \text{ Å}\), these surfaces are formed by the most dense \((111), (100), (110)\) nanoplanes which differ dramatically in adsorption and oscillation behaviour.

In the present work the mechanism of surface waves generation in the oscillating \(\text{CO} + \text{O}_2\) reaction has been studied on a Pd tip \((\sim 2000 \text{ Å} \text{ in radius})\) by a FEM that is responsible for experimental tool for \textit{in situ} imaging of real dynamic surface processes in which different nanoplanes of emitter-tip are simultaneously exposed to the reacting gas. The \(\text{O}_2\) adsorption and the reaction of atomic \(O_{\text{ads}}\) state as well as a subsurface atomic \(O_{\text{sub}}\) state with \(\text{CO}\) on the Pd(110) single crystal surface have been studied by TDS, TPR and XPS techniques. The hysteresis phenomena and oscillations of \(\text{CO} + \text{O}_2\) reaction have been studied by means of molecular beam (MB) techniques. The effect of subsurface oxygen state on the subsequent \(\text{CO}_{\text{ads}} + \text{O}_{\text{ads}}\) reaction at an oxygen preadsorbed Pd(110) surface has been studied with TPR techniques.

**EXPERIMENTAL**

Experiments were performed in a UHV chamber (base pressure \(<10^{-10} \text{ mbar}\)) which was used simultaneously as the catalytic reactor and field electron microscope. The catalyst was a Pd-emitter tip of a small radius \((\sim 2000 \text{ Å})\), prepared from spectroscopically pure Pd-wire \((0.1 \text{ mm } \varnothing)\), spot-welded to a metal heating loop of 0.25 mm diameter. The method for producing clean stable Pd tips, along with the experimental set-up has also been described elsewhere [10]. The temperature at the tip could be controlled to within 1 K and it was measured by means of a chromel/alumel thermocouple spot-welded to the metal loop near the tip. The reaction gases \(\text{CO}\) and \(\text{O}_2\) of highest purity were introduced with a flow rate of \(2.5 \text{ L s}^{-1}\) and controlled by a quadrupole mass spectrometer. The total field electron current and FEM image were continuously monitored during the catalytic surface reaction at an oxygen partial pressure of \(\sim 10^{-3} \text{ mbar}\) and carbon monoxide partial pressure of \(\sim 10^{-4} \text{ mbar}\). A double channel plate was used as an image amplifier of a small electron emission current \(<1 \text{ nA}\), and CCD camera recorded the behaviour of the catalytic CO oxidation \textit{in situ}. It was demonstrated that at a pressure of up to \(\sim 10^{-3} \text{ mbar}\), stable emission currents could be obtained and sputtering processes omitted. The surface analysis of the Pd emitter is based on the fact that due to adsorption of \(\text{CO}\) and \(\text{O}_2\), local work function changes \((\Delta \Phi)\) can be correlated with the total field electron current, as described before [10]. Electrostatic field effects at a field of \(\sim 0.4 \text{ V/Å}\) during these investigations have not been obvious in according with [11].

The TDS and TPR experimental device on the single crystal Pd(110) surface is described in detail in [12]. The UHV chamber is equipped with a VG QXK 400 quadrupole mass spectrometer, a sputtering ion gun and molecular beam doser. A detailed description of doser setup is given in [13]. The TD spectra were obtained with a heating rate of \(6 \text{ K s}^{-1}\). Steady-state rates and oscillations for the catalytic \(\text{CO} + \text{O}_2\) reaction on Pd(110) surfaces have been measured by using a molecular beam setup with mass spectrometry detection. The crystal is exposed to \(\text{CO} + \text{O}_2\) molecular beam through a capillary array doser with the gas flow controlled by mass spectrometer. XPS part of the present work was performed over Pd foil on
the basis of an X-ray photoelectron spectrometer VG ESCA-3.

RESULTS AND DISCUSSION

Carbon monoxide and oxygen adsorption

WF. At 300 K, the work function (ΔΦ) over Pd tip increases with an increase of oxygen exposure up to a value of 0.37 eV above that of the clean surface. This value compared to ΔΦ = 0.4 eV for the Pd(110) single crystal surface at T_{ads} = 304 K [14]. This value is already reached at O_2 exposure of ~2.3 × 10^{-6} mbar (Fig. 1), suggesting a sticking probability near unity. The change in work function (ΔΦ = 0.98 eV) with CO exposure on Pd tip at 300 K is shown in Fig. 1. Similar measurements at 300 K on Rh tips led to changes in work function, ΔΦ = 1.20 eV [15]. Measurements on different Pd single crystal surfaces give a maximum increase in work function in the range 0.75–1.27 eV for the various planes, with Pd(111) showing a maximum increase of 0.98 eV [16]. The work function variation with coverage was used for determination of the isosteric heat of CO adsorption on the clean Pd tip surface. This value was found to be ~154 kJ mol^{-1} in the limit of zero coverage, decreasing to ~133 kJ mol^{-1} at coverage of 0.5 ML (monolayer) [10].

TDS. Figure 2 illustrates a series of CO TD spectra as a function of exposure. During CO adsorption at 100 K on the Pd(110) surface several molecular CO_{ads} states with the desorption peak temperatures at 230 (α_1), 280 (α_2), 330 (α_3) and 410 (β_1), 470 K (β_2) appear (see Fig. 2) to be in agreement with [17].

Figure 2, b shows TD spectra of O_2 from Pd(110) surface after different oxygen exposures at 100 K. Above 0.3 L exposure (1 L = 1.33 × 10^{-6} mbar), there are three peaks in the TD spectrum located around 125 (α_1-O_2 molecular state) and 740 (β_1-O_{sub} subsurface atomic state) and 815 K (β_2-O_{ads} surface atomic state). The β_1-oxygen state was attributed to subsurface layer oxygen formation (O_{ads} + σ → [O_{sub}] as a result of appearance of efficient desorption channel for recombination of oxygen adatoms in the atomic states: [O_{sub}] + [O_{sub}] → O_2 + 2σ, where σ is a subsurface empty site. In the O/Pd(110) system, indirect evidence for the for-
and CO. In contrast to Fig. 3, a, low temperature CO₂ formation begins immediately above oxygen exposure 0.5 L. Five distinct CO₂ desorption peaks are observed at 160, 225, 320, 370, and 420 K from the (110) surface. The complexity of CO₂ formation may be the result of different reaction rates of adsorbed CO with two types of adsorbed atomic oxygen: 1) \( \text{CO}_{\text{ads}} + \text{O}_{\text{ads}} \rightarrow \text{CO}_2 \text{gas} + 2e^- \); 2) \( \text{CO}_{\text{ads}} + [\text{O}_{\text{sub}}] \rightarrow \text{CO}_2 \text{gas} + 2e^- + e^- \). In addition the reaction complexity might be expected since the coadsorption of CO and oxygen may result in the formation of either a segregated layer, where the COₐds molecules and Oₐds atoms form separate layer on the surface, or a mixed layer where the two adsorbates mix completely [19]. In a mixed layer new sites for the coadsorption layer are usually occupied. Adsorption of CO at low temperature on an oxygen atomic \( \beta_2\text{-O}_{\text{ads}} \) and \( \beta_1\text{-O}_{\text{sub}} \) states might produce a segregated layer and form islands of each species. Annealing of this adlayer up to \( \sim 160 \) K in TPR experiments leads to dispersing the islands and mixing the adsorbate layer at temperatures where reaction with CO is significant. The Pd–O bond is weakened in well-mixed \( \text{O}_{\text{ads}} + [\text{O}_{\text{sub}}] + \text{CO} \) adlayer, indicating that the \( \text{O}_{\text{ads}} + [\text{O}_{\text{sub}}] \) repulsive interaction proceeds throughout the metal surface rather than directly between the adsorbed atoms. On the other hand the effect of adsorbed oxygen \( \text{O}_{\text{ads}} + [\text{O}_{\text{sub}}] \)) on the CO adsorption rate is an important part of the low temperature CO oxidation reaction. Ladas et al. [20] have shown that the subsurface oxygen formation leads to the diminish of the CO residence time owing
to a decrease of the CO adsorption energy and reduction of the CO sticking probability.

**Hysteresis and oscillations**

**MB.** Figure 4 illustrates the results of temperature dependence of the steady-state rate of CO oxidation over Pd(110) surface. At 300 K the reaction is limited by the activation of the surface reaction between CO$_{ads}$ molecules and β$_2$-oxygen atoms as shown in Fig. 3, a. In the temperature interval 370–650 K the initial rate diminishes, presumably as a result of CO adsorption, which reduces the CO$_{ads}$ coverage during the reaction. Figure 4 shows the bistability regions and represents the anticlockwise hysteresis behavior for the CO$_2$ formation in the temperature interval between 300 and 450 K. With temperature increasing the transfer from the θ$_{CO}$ layer into the O$_{ads}$ layer is delayed, with temperature decreasing it is the reverse reaction. The local single oscillations of the CO$_2$ rate at 372 and 382 K have appeared.

Figure 5 provides example of typical series of oscillations in the production of CO$_2$ when the Pd(110) single crystal surface is exposed at 390 K to a gas mixture of $P(O_2) = 5 \times 10^{-2}$ mbar and $P(CO) = 5 \times 10^{-5}$ mbar. The oscillation amplitude ranges from the O$_{ads}$ layer (high reactive state) to the O$_{ads}$/O$_{sub}$ layer (low reactive state) with a periodicity of 5 s.

**FEM.** Figure 6 represents series of oscillations (FEM) when the Pd-tip with [110]-orientation is exposed at 425 K to a CO + O$_2$ reac-

**Fig. 5.** Oscillatory behaviour of CO$_2$ production for the Pd(110) single crystal surface at constant control parameters.

**Fig. 6.** The variation of the local emission current from the Pd (100)$_{step}$ plane as a function of time during the oscillatory behaviour of the CO + O$_2$ reaction on a Pd field emitter tip at constant control parameters under reaction conditions. $T = 425$ K, $P(O_2) = 2.6 \times 10^{-3}$ mbar, $P(CO) = 1.3 \times 10^{-4}$ mbar. Low current levels reflect CO$_{ads}$- covered Pd(100) plane. $F = 0.4$ V/Å.

**Fig. 7.** Magnified view of a sequence of FEM images over (110)-oriented Pd-tip obtained during the CO + O$_2$ oscillating cycle at $T = 425$ K, $P(O_2) = 2.6 \times 10^{-3}$ mbar, $P(CO) = 1.3 \times 10^{-4}$ mbar. At $t = 0$ s formation of a large CO$_{ads}$-island (dark area over Pd(100) plane) and the (210) plane temporarily covered by oxygen O$_{ads}$ layer appear bright. Moving reaction front during regular oscillation, starting from (100) towards (210) plane. At 3 s the CO$_{ads}$ layer forms a final island size. After 4.0 s a reverse reaction front starts from (210) towards (100) plane.
tion mixture. The oscillation amplitude from the CO$_{ads}$ layer (low current) to the O$_{ads}$ layer (high current) has a periodicity of 5 s. A difference of work functions between CO$_{ads}$ and O$_{ads}$ of ~0.6 eV is connected with a change in the electron current. The study of the Pd-tip surface has shown that the CO oxidation reaction is characterized by a sharp boundary between the two spatially separated adlayers (CO$_{ads}$ and O$_{ads}$) over the Pd(100)$_{step}$ surfaces forming under oscillating conditions: 370 K < T < 450 K, P(CO) + P(O$_2$) (1 : 20) = 2.6 $10^{-3}$ mbar. The sequence of images in Fig. 7 corresponds to the following steps: the CO$_{ads}$-covered areas are formed only on the (100) nanoplanes, whereas O$_{ads}$-covered areas are formed only on the (110), (310) and (210) nanoplanes. Chemical waves appear on an emitter surface and propagate in phase with self-sustained isothermal oscillations. The initiating role of a subsurface oxygen layer formation has been established for the generation of regular waves along the certain crystallographic directions on the Pd-tip surface: (i) O$_{ads}$ wave follows the path in the direction (110) → (210) → (100); (ii) CO$_{ads}$ wave moves in the opposite direction. The emission pattern brightness of local regions of the Pd(100)$_{step}$ surface was accompanied by fluctuations of electron current. A difference of work function ($\Delta \Phi$) between CO$_{ads}$ and O$_{ads}$ over Pd surfaces is connected with a change in the emission current, as described by the Fowler - Nordheim equation:

$I = A V^2 \exp(-B \Phi^{3/2} / V)$

where $I$ is the current measured at the fluorescent screen, $V$ is the applied voltage at the tip, $A$ and $B$ are constants and $\Phi$ is the work function. From this equation a sensitive dependence of $I$ on $\Delta \Phi$ is expected. This large change in $\Delta \Phi$ gives an excellent tool for observing the transition in the adsorbed layers: the CO adsorption layer with low emission current, current increases for oxygen adsorption. Using a conventional video technique to monitor the FEM brightness variation, local time oscillations of the emission current were extracted from digitized video images [21].

**XPS.** Figure 8 shows a set of Pd 3p$_{3/2}$ XPS spectra for the Pd foil surface before and after oxygen exposure at 525 K. The difference spectra clearly show O 1s binding energy of 529.5 eV at surface coverage for atomic oxygen state ($P(O_2) = 10^{-7} - 10^{-2}$ Torr), which shifts to 530.5 eV after oxygen exposures for 2, 4 and 10 min at 5 mbar, showing the oxide growth. According to the XPS data, the state of palladium surface under the reaction oscillating conditions ($370 < T < 450$ K, $P(CO) + P(O_2)$ (1 : 20) = 2.3 $10^{-3}$ mbar) is not sufficient for bulk oxide formation.

**Reaction mechanism.** The knowledge of the mechanism steps is necessary to gain a better insight into the oscillating phenomena. The oscillating catalytic CO oxidation proceeds via a Langmuir – Hinshelwood mechanism:
1. $\text{CO}_{\text{gas}} + * \leftrightarrow \text{CO}_{\text{ads}}$
2. $\text{O}_2_{\text{gas}} + 2* \rightarrow 2\text{O}_{\text{ads}}$
3. $\text{CO}_{\text{ads}} + \text{O}_{\text{ads}} \rightarrow \text{CO}_2\text{gas} + 2*$

where two adjacent empty sites ($*$) are required for the dissociative adsorption of $\text{O}_2\text{gas}$. It is well known that under reaction conditions $\text{CO}_{\text{ads}}$ islands are formed as well as $\text{O}_{\text{ads}}$, whereas $\text{CO}_2$ desorbs immediately.

The catalytic CO oxidation over palladium surfaces exhibits the temporal oscillations in certain range of reaction parameters: $T$, $P$. A feedback mechanism of these oscillations is associated with the changes in the sticking probability of oxygen ($S_{O_2}$) induced by depletion of subsurface oxygen (Pd(110): $\text{O}_{\text{ads}} \leftrightarrow \text{O}_{\text{sub}}$). The oxide model assumes that the $\text{O}_{\text{sub}}$ layer blocks the oxygen adsorption simultaneously with the growth of $\text{CO}_{\text{ads}}$ layer and the surface reaction is poisoned (low rate of $\text{CO}_2$ formation). The slow $\text{CO}_{\text{ads}}$ reaction with $\text{O}_{\text{sub}}$ removes the subsurface oxygen and $\text{O}_2$ adsorption is again possible (high rate of $\text{CO}_2$ formation). Then, the subsurface oxygen layer is formed and the cycle is restored. Probably, the subsurface oxygen could produce a significant change of CO adsorption energies, decreasing the heat of adsorption in accord with [20].

Based on our TDS, TPR, XPS, MB, FEM data regarding to CO oxidation over Pd surfaces, some elementary steps have been added to LH scheme (scheme 1).

By this reaction scheme the model evolution was simulated with the standard Monte Carlo algorithm, that has been explored in our previous modeling of oscillatory behaviour of catalytic reactions due to the influence of the “subsurface” oxygen [22].

**CONCLUSIONS**

The palladium surface is catalytically active in CO + $\text{O}_2$ reaction due to the ability to dissociate $\text{O}_2$ molecules. At present, the $\text{O}_{\text{ads}}$ diffusion process may be proposed for the formation of subsurface oxygen layer $\text{O}_{\text{sub}}$, which is an important intermediate species in CO + $\text{O}_2$ reaction over Pd surfaces. $\text{O}_{\text{ads}}$ is highly active as compared to $\text{O}_{\text{sub}}$ species due to the rapid attachment of the carbon monoxide molecules, $\text{CO}_{\text{ads}}$, producing $\text{CO}_2$. As a result of this oxidized surface the oscillations over the Pd(110) single crystal surface and the Pd(100) step nano-planes can be obtained with fast repetition periods.

The specificity of the kinetics of CO + $\text{O}_2$ reaction has been observed over Pd tip: (i) the maximum initial rate has been observed on the Pd(110); (ii) two spatially separated adlayers are formed on the tip surface. The oxygen layer forms only on the {110}, {320} and {210} planes, whereas $\text{CO}_{\text{ads}}$ layer or empty sites forms on the {100} and {100} step planes. Chemical waves are $\text{O}_{\text{ads}}$ and $\text{CO}_{\text{ads}}$ layers, interacting by a sequence of reaction steps with the reversible-oxygen sites transition of $\text{O}_{\text{ads}} \leftrightarrow \text{O}_{\text{sub}}$, which involves the feedback step $\text{O}_{\text{sub}} \rightarrow \text{O}_{\text{ads}}$ during oscillations.

**CO oxidation over Pd surface (model with subsurface oxygen)**

<table>
<thead>
<tr>
<th>Atomic oxygen route (LH)</th>
<th>Subsurface oxygen route (added)</th>
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<tbody>
<tr>
<td>$\text{O}<em>2\text{gas} + 2* \rightarrow 2\text{O}</em>{\text{ads}}$</td>
<td>$\text{O}<em>{\text{ads}} + * \rightarrow [\text{O}</em>{\text{sub}}]$</td>
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<tr>
<td>$\text{CO}<em>{\text{gas}} + * \leftrightarrow \text{CO}</em>{\text{ads}}$</td>
<td>$\text{CO}<em>{\text{ads}} + [\text{O}</em>{\text{sub}}] \rightarrow \text{CO}_2\text{gas} + 2* + *_v$</td>
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<tr>
<td>$\text{CO}<em>{\text{ads}} + \text{O}</em>{\text{ads}} \rightarrow \text{CO}_2\text{gas} + 2*$</td>
<td>$\text{CO}<em>{\text{gas}} + [\text{O}</em>{\text{sub}}] \leftrightarrow [\text{CO}<em>{\text{ads}} \text{ O}</em>{\text{sub}}]$</td>
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<tr>
<td>[\text{CO}<em>{\text{ads}} \text{ O}</em>{\text{sub}}] \rightarrow \text{CO}_2\text{gas} + * + *_v&lt;&lt;\text{cork-screw&gt;&gt;} reaction]</td>
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CO heat of adsorption: $q (\text{CO}_{\text{ads}} / [\text{O}_{\text{sub}}]) < q (\text{CO}_{\text{ads}} / *)$

CO diffusion: $\text{CO}_{\text{ads}} + * \rightarrow * + \text{CO}_{\text{ads}} < [\text{CO}_{\text{ads}} \text{ O}_{\text{sub}}] + [\text{O}_{\text{sub}}] \rightarrow [\text{O}_{\text{sub}}] + [\text{CO}_{\text{ads}} \text{ O}_{\text{sub}}]$

Scheme 1.
In summary it may be said that the character of the CO + O₂ oscillating reaction on Pd differs remarkably from that of Pt: (i) subsurface oxygen mechanism (Pd) and phase transition mechanism hex ↔ 1×1 on Pt; (ii) oxygen front travelling in the reverse direction: on Pd starts from (110) to (100); on Pt starts from (100) to (110).

The principal result of this work lies in the following: the appearance of regular waves under the reaction rate oscillations is an amazing example of a self-organization of catalytic reaction when the size of active catalyst is some hundreds Angströms at average. It becomes possible to study the catalysis on an atomic level which is necessary for understanding of the mechanism of the action of the high-dispersion supported metal catalysts having the metal microcrystallites 100−300 Å in size as an active part of the catalyst. This result opens new fields for the development of theoretical concepts of heterogeneous catalysis.

Acknowledgements

This work is supported in part by RFBR Grant No. 02–03–32568 and INTAS Grant No. 99–01882.

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