Imaging the oscillating CO-oxidation on Pt-surfaces with field ion microscopy

V. Gorodetskii [a], W. Drachsel and J.H. Block

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-1000 Berlin 33, Germany
[a] *Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia*

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The oxidation of carbon monoxide on platinum surfaces is investigated by field ion microscopy (FIM) and compared to earlier work by field electron microscopy (FEM). The reaction gas is used as the field ion imaging gas at pressures of $< 10^{-4}$ mbar and at temperatures of the catalytic reaction. In FIM the surface is imaged by O_2^+-ions which are preferentially ionized at oxygen-covered surface areas. During temperature variations regions of bistability could be detected by FEM and FIM. Finally self-sustained isothermal oscillations of the catalytic CO-oxidation could be measured from the periodic fluctuations of the O_2^+-field ion current. Atomic resolution shows that the Pt-(331) planes are the pace makers of the oscillation.

Keywords: Oscillatory behaviour; rate oscillation; field ion microscopy; CO-oxidation; Pt

1. Introduction

The oscillatory behaviour of catalytic reactions has attracted a great deal of attention during the last years [1,2]. In order to elucidate details of the reaction mechanism which are involved in oscillations, various new microscopic techniques have recently been introduced. Photoemission-electron microscopy (PEEM) [3–7] was particularly successful in detecting dissipative adsorption structures and the spatio-temporal formation of islands, target patterns, wave fronts, spirals etc. The lateral resolution of PEEM, ~ 0.1 µm, was improved upon when field electron emission microscopy (FEM) was adapted to investigate oscillating surface reactions with a resolution of ~ 20 Å [7–10]. The field electron emission current of a platinum surface could be measured at temperatures of the catalytic CO-oxidation ($T = 350$–400 K). Since the work functions of oxygen-covered Pt-surfaces are greater than those of CO covered planes, the nature of the surface layers can be determined from the intensity of field emission currents and allow the oscillating cycles to be recorded [8,9]. In a similar way Van Tol et al. investigated the oscillation of the reduction of NO by H_2 [10]. In the present communication we show that the oscillating CO-oxidation can be imaged in situ in the field ion microscope (FIM) during the catalytic reaction on an atomic scale.

2. Experimental

The equipment for FIM consisted of a stainless steel vacuum chamber with a base pressure of 10^{10} mbar. The Pt-field emitter – etched in molten NaCl + $NaNO_3$ – was mounted on a tungsten loop which was connected to a glass-cooling finger. Clean Pt-surfaces were prepared by field evaporation. Reaction gases of highest purity (O_2 and CO spectral purity) were introduced with a controlled flow rate. The ion microscope was operated with low ion currents ($< 10^{13}$ A). The FIM images were amplified by a highly sensitive channel-plate and recorded in real-time using a video camera.

3. Field ion images of adsorption layers

In fig. 1 the clean Pt-surface imaged at 78 K with He/Ne as imaging gas (fig. 1a) is compared with the CO-covered (fig. 1b) and oxygen-covered (fig. 1c) Pt-surface when the reaction gas mixture is used for imaging the surface at 300 K. The "titration reaction" was started with a CO-covered surface (fig. 1b, $p_{O_2} = 5 \times 10^{-4}$ mbar, $p_{CO} = 5 \times 10^{-5}$ mbar). Then, the p_{CO} was reduced to $p_{CO} < 10^{-7}$ mbar and the oxygen adlayer appeared (fig. 1c). The dark image of the CO adsorption layer indicates a low ionization probability of the imaging gas and the bright oxygen adsorption layer (fig. 1c) a high one. The field strength, F_0, in front of the Pt-emitter (as determined by the Fowler–Nordheim equation) has a value of $F_0 \approx 12$ to 15 V/nm (at a tip potential of 7.8 kV). Under these conditions only molecular oxygen with an ionization potential of $I_p = 12.06$ eV is ionized. In order to ionize CO ($I_p = 14.01$ eV) as imaging gas, higher voltages ≈ 10 kV are required.

As recently shown by Suchorski et al. [11], the local field strength, F_{loc}, in close vicinity to the emitter metal surface is greatly effected by adsorbed atoms or molecules. The relation F_{loc}/F_0 may have values of $\geqslant 1.2$ even for noble gases. Although there are still no experimental results available, we postulate that the local field F_{loc} in front of the oxygen layer is greater than the field in front of the CO-covered adsorption layer at the same applied external field. Thus, the ionization probability of gaseous O_2 is increased in front of the CO_{ad}-layer. This hypothesis is in agreement with the fact, that oxygen adsorption on platinum increases the work function, Φ, to a larger extent than CO-adsorption. Consequently the minimum distance for ionization $x_c \approx (I_p - \Phi)/F$ is decreased and the ionization probability increased by an oxygen adsorption layer.

The field ion image is produced by molecular oxygen ions, O_2^+, which are field

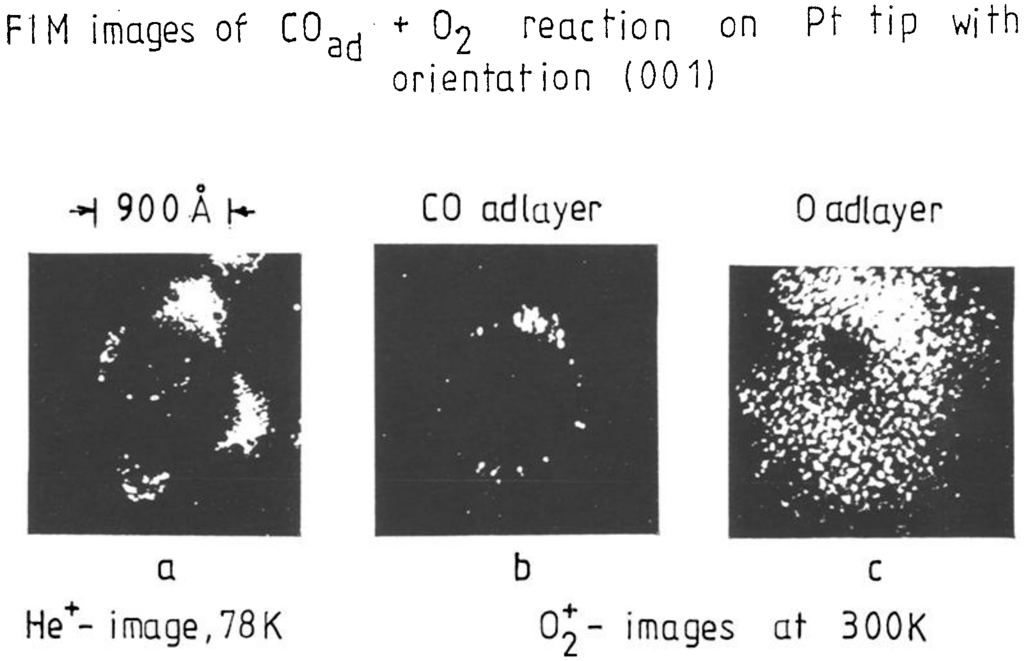

Fig. 1. FIM-images of the $CO + O_2$ reaction oscillations on a (111)-oriented Pt field emitter. (a) Clean surface, FIM He/Ne at 16 kV, $p_{He} = 3 \times 10^{-4}$ mbar, $p_{Ne} = 8 \times 10^{-6}$ mbar, $T = 78$ K, tip radius 850 Å. (b) O_2^+-image, CO_{ad}-surface at 7.8 kV. $p_{O_2} = 5 \times 10^{-4}$ mbar, $p_{CO} = 5 \times 10^{-5}$ mbar, $T = 300$ K. (c) O_2^+-image, O_{ad}-surface after "titration reaction". Time of reaction 700 s at 300 K at 7.8 kV, $p_{O_2} = 5 \times 10^{-4}$ mbar, $p_{CO} \approx 10^{-7}$ mbar.

ionized only at the oxygen-covered surface. Due to this preference in field ionization, oxygen- and CO-adsorption layers can be distinguished in situ.

Impinging oxygen molecules can experience different reaction pathways,

$$O_{2gas} \rightarrow 2O_{ad} , \tag{1}$$

$$O_{ad} + CO_{ad} \rightarrow CO_{2gas} , \tag{2}$$

$$O_{2gas} \xrightarrow{\text{field}} O_{2gas}^{+} + e^{-}_{(\text{emitter})} . \tag{3}$$

For the dissociative chemisorption of oxygen (reaction (1)) two adjacent empty surface sites are required. Furthermore, the sticking coefficient of oxygen has been shown to differ by orders of magnitude on different crystallographic (reconstructed) structures [12]. Chemisorbed atomic oxygen can either contribute to the island growth of O_{ad} or react with CO_{ad} (reaction (2)) if the adsorption site is close enough to the reaction borderline. At catalytic reaction temperatures CO molecules are mobile; in a Langmuir–Hinshelwood mechanism they react with O_{ad} to give CO_2-molecules which immediately desorb. Reactions (1) and (2) compete with the field ionization process (reaction (3)) and therefore the brightness of the field ion image is reduced at catalytically active areas of the surface (see below).

4. Hysteresis in field ion currents

From work on Pt-single crystal planes it is well known that the hysteresis in the formation of CO- or O-adsorption layers leads to regions of bistability where oscillating reaction rates may exist [13].

Fig. 2 compares field electron and field ion currents which have been measured during the catalytic CO-oxidation in the region of bistability. The FEM-studies (above) start at $\sim$ 300 K with a CO-covered surface. With a heating rate of 4.7 K s^{-1} a strong increase of the electron current is registered at $T > 370$ K until a transition point is reached at $T = 393$ K, where the current suddenly decreases. The intensity remains low upon further temperature increases up to $T = 450$ K. With decreasing temperature the low current intensity increases slowly and reaches the initial value only at $T \approx 300$ K. This behaviour can be explained by the temperature dependence of the surface reaction. The CO-adsorption layer with an initial work function of $\Delta\Phi = 700$ meV (compared to clean Pt) reacts with oxygen in a clean-off reaction between 370 and 393 K. During this "titration reaction" a gradual decrease of the CO-coverage leads to an increase of the total emission current, until after $\sim$ 5 s the transition point is reached at $T = 393$ K. At this point a sufficient number of empty pair sites is formed at a certain surface region and a fast reaction wave front of <100 ms duration moves along the emitter surface and the oxygen-covered surface is quickly formed. This surface, with $\Delta\Phi = 1200$ meV, represents the catalytically active one. While the temperature is gradually reduced, the CO_{ad}-layer is only formed slowly and reestablished at $T = 300$ K.

A similar hysteresis is shown for the O_2^+-ion current in the FIM (below). Starting with a catalytically active oxygen covered surface at 300 K, the decrease in the ion current demonstrates the slow formation of a CO_{ad} layer. At the transition point, $T = 393$ K, the sudden increase of the O_2^+-ion current indicates the reoccurrence of oxygen adsorption. A temperature decrease again leads to a CO_{ad}-layer at $T = 300$ K. The following cycle starts from this point (2 →) with a low ion current (not shown) until the transition point at $T = 393$ K again is reached. With these results the region of bistability in the CO-oxidation is clearly established by FEM and FIM.

5. Oscillations of the CO-oxidation

Self-sustained oscillations in the O_2^+-field ion current could be detected in the region of bistability. Fig. 3 shows a reaction system that starts with an oxygen-cov-

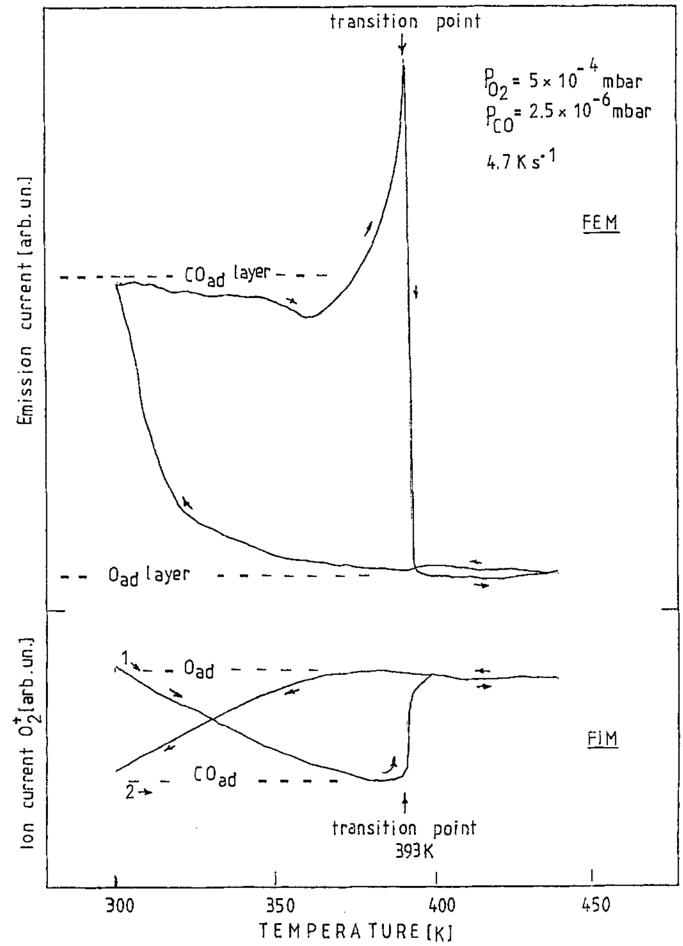

Fig. 2. The field emission total current in the region of bistability of CO-oxidation (above), starting at $T = 300$ K with an CO_{ad}-layer, passing the transition point at $T = 393$ K with the rapid formation of the O_{ad}-layer and, at decreasing temperature, slow reaction towards the initial CO_{ad}-layer. The FIM mode (below) describes the repeated temperature cycle at the same emitter tip for the total O_2-field ion current. Applied tip voltages FEM = −1 kV, FIM = +2.2 kV.

ered surface (region a). At a certain time, which is marked by the arrow ↓, a partial pressure of $p_{CO} = 8 \times 10^{-7}$ mbar is introduced. After a certain delay time (b) with irregular current fluctuations, the regular oscillations (c) with a period of ~ 30 s develop until at ~ 700 s after increasing p_{CO} to 9×10^{-7} mbar the CO_{ad}-layer poisons the catalytic reaction. In the FEM mode the same oscillations could be measured at this field emitter tip with inversed field, giving field-electron currents.

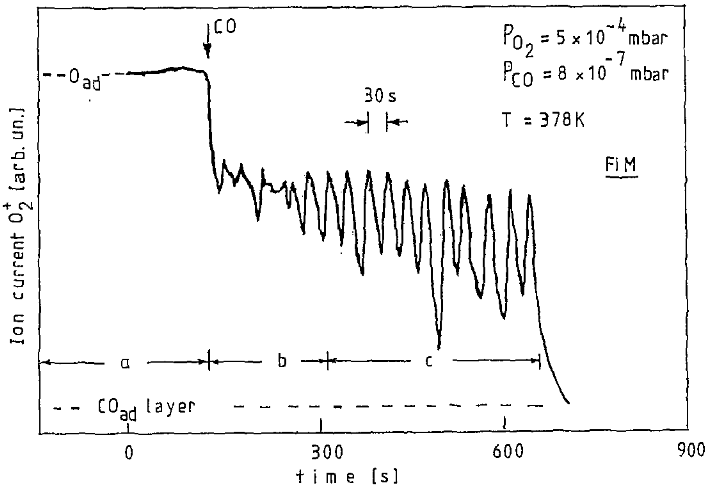

Fig. 3. Oscillations of the CO-oxidation at 378 K; FIM at 3.9 kV after introduction of $p_{CO} = 8 \times 10^{-7}$ mbar at a delay time of few minutes (b) is needed before regular oscillations (c) occur, until after ~ 650 s the CO pressure is further increased.

6. Identification of oscillatory behaviour by FIM

During the oscillating catalytic reaction the video camera monitored the surface with lateral atomic resolution. In fig. 4a the stereographic projection of the (111)-oriented Pt field emitter displays the position of the different single crystal planes. In fig. 4b the FIM-image of the clean Pt-surface (He/Ne) at 78 K shoes atomic resolution with a well-established central (111)-plane and surrounding {011}, {012}, {133}, {001} etc. planes. Individual atoms are clearly imaged at certain positions, for example, at steps of the crystal with various orientations and at borderlines of low index planes. In the inner regions of these flat planes atoms are no longer visible. The same surface is imaged at 78 K in the FEM-mode (see fig. 4c) with a lateral resolution of ~ 20 Å. The three low work function, bright {012}-planes are dominating in emission currents.

The field ion images of the catalytically reacting surface imaged by O_2^+-ions of the reacting gas mixture at 378 K showed an unexpected high lateral resolution which nearly resembles fig. 4b. Even individual surface sites and mobile surface molecules could be identified in certain surface areas.

Figs. 4d–4f represent single frames from the video tape showing the oscillating reaction. Fig. 4d shows the O_{ad}-layer of region a in fig. 3. The edge of the central (111)-plane is clearly visible as well as the {110}, the {012} and in the periphery the {001}-planes. In many cases single spots indicate atomic sites. Also the bright emitting area on the right-hand side displays a grainy spot structure which must originate from individual image gas ions.

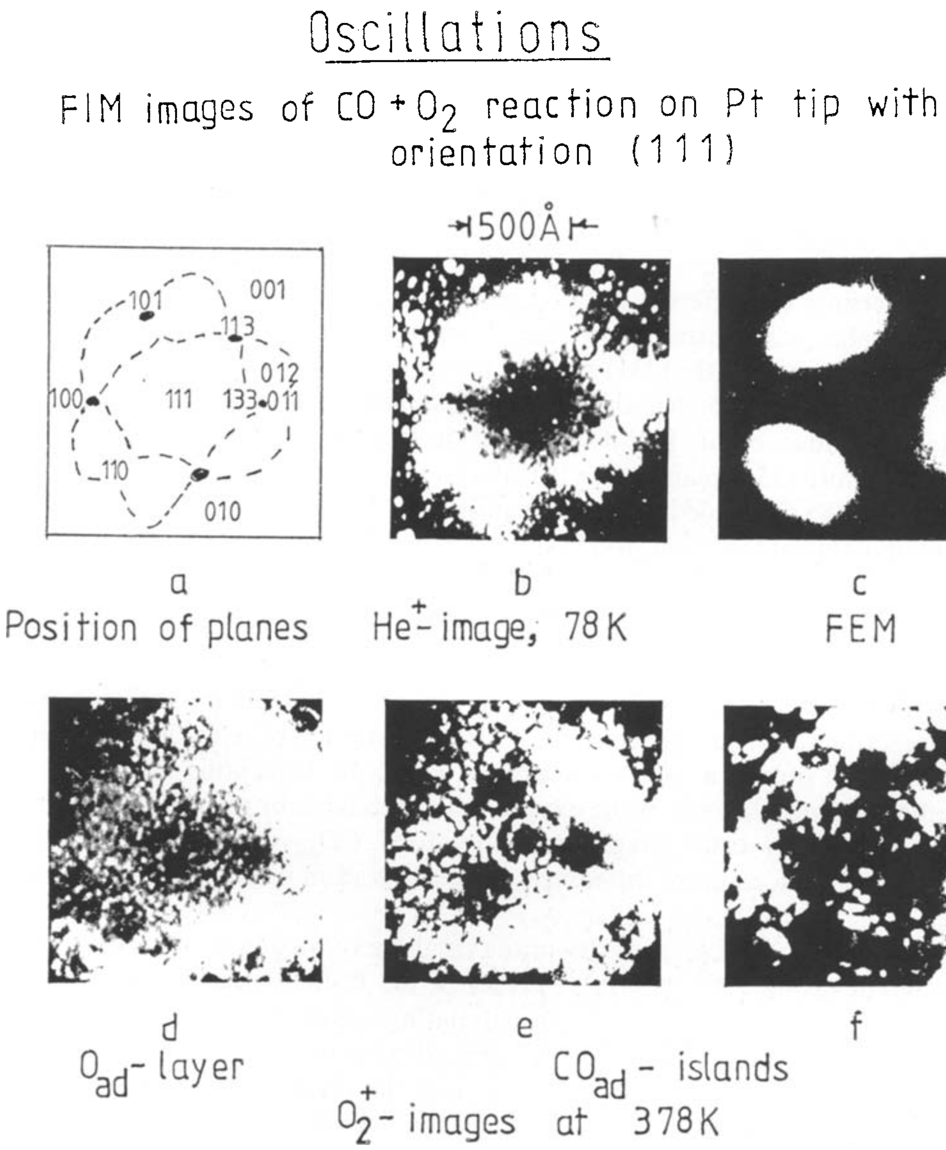

Fig. 4. FIM during catalytic CO-oxidation on Pt. (a) Stereographic orientations. (b) Field ion image of clean Pt at 78 K, 7.5 kV, He/Ne imaging gas, $p_{He} = 3 \times 10^{-4}$ mbar, $p_{Ne} = 8 \times 10^{-6}$ mbar. (c) Field electron image at 78 K, 0.8 kV, electron current ≈ 1 nA. (d) Field ion image, O_2^+-ions, of an oxygen-covered Pt-surface at 378 K, 3.9 kV, $F \approx 15$ V/nm, $p_{O_2} = 5 \times 10^{-4}$ mbar. (e) Field ion image, O_2^+-ions, of catalytically reacting surface at 378 K, 3.9 kV, $F = 15$ V/nm, $p_{O_2} = 5 \times 10^{-4}$ mbar, $p_{CO} = 8 \times 10^{-7}$ mbar, oxygen side of oscillating cycle in fig. 3. (f) Conditions lie in fig. 4e, CO-side of the oscillating cycle.

In fig. 4e the oxygen side of the oscillating cycle (in region c of fig. 3) is shown. The two concentric circles of steps in the central (111)-plane ~ 20 Å apart are much brighter than in 4d. The three (331)-planes are just starting to darken, as always observed at the beginning of the transformation towards the CO-side. The (331)-planes start the transformation towards the CO coverage, they also initiate the oxygen coverage of the (110)-region. Some of the outer (001)-planes are visible but most of the surface displays a dynamic behaviour with a multiplicity of light spots of a reacting system which images individual particles. Fig. 4f represents the CO-side of the same oscillating cycle. The main central areas such as the (111), the {011} and {331}-planes are covered with CO. The dark areas display sharp borderlines. At these borderlines the different reaction pathways of oxygen, as mentioned above may cause a sharp concentration profile in the oxygen adsorption layer.

The particular role of the (331)-plane in initiating the CO-oxidation by preferential oxygen chemisorption has already been observed during work with single crystal planes. Ladas et al. [14] found that in ceratin cases the Pt(110)-plane reconstructs into (331)-planes, which display a very high catalytic activity for this reaction, as also concluded from our results. The detailed mechanism connected with this dynamical behaviour will be discussed in a separate communication.

7. Conclusions

This work introduces field ion microscopy as a research tool for studying oscillating reactions in heterogeneous catalysis. The surface of a Pt-field emitter is imaged in situ during a catalytic reaction. Transient adsorption structures are imaged on the atomic scale, while oxygen of the catalytically reacting gas mixture acts simultaneously as the imaging gas in the FIM. CO_{ad}- and O_{ad}-structures are distinguished on account of differences in the ionization probability for the imaging O_2^+-ion.

A pronounced surface selectivity of the catalytic CO-oxidation is observed for the different exposed single crystal planes of the Pt-field emitter. The Pt(331)-planes, for instance, play a special role in initiating – as pace maker – the transition towards the CO_{ad}-layer. The question arises whether the electrostatic field which is applied for O_2-field ionization interferes with the catalytic reaction mechanism of the CO-oxidation. Although the electrostatic field in FIM with O_2 as imaging gas is approximately 2.2 times higher than in FEM, only one observation could be made so far. Due to field-compression the nominal pressure ranges for the oscillation regions are lower by a factor of three as compared for work on extended single crystal planes. More details of this oscillating reaction will be obtainable from the myriad of data in the real-time video movie.

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