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Field ion microscopic studies of the CO oxidation on platinum: Bistability and oscillations

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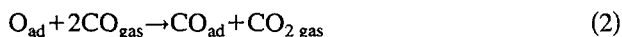
The oscillating CO oxidation is investigated on a Pt-field emitter tip by using the field ion mode of surface imaging of O_{ad} sites with O_2 as imaging gas. Based on data of the titration reactions [V. Gorodetskii, W. Drachsel, and J. H. Block, *J. Chem. Phys.* **100**, 6907 (1994)], external control parameters for the regions of bistability and of self-sustained isothermal oscillations could be found. On a field emitter tip, oscillations can be generated in a rather large parameter space. The anticlockwise hysteresis of O_2^+ ion currents in temperature cycles occurs in agreement with results on single crystal planes. Unexpected regular oscillation sequences could occasionally be obtained on the small surface areas of a field emitter tip and measured as function of the CO partial pressure and of the temperature. Different stages within oscillating cycles were documented by field ion images. Oscillations of total ion currents are correlated with variations in the spatial brightness of field ion images. In the manifold of single crystal planes of a field emitter {331} planes around the {011} regions are starting points for oscillations which mainly proceed along [100] vicinals. This excludes the {111} regions from autonomous oscillations. With slightly increased CO partial pressures fast local oscillations at a few hundred surface sites of the Pt(001) plane display short-living CO islands of 40 to 50 Å diameter. Temporal oscillations of the total O_2^+ ion current are mainly caused by surface plane specific spatial oscillations. The synchronization is achieved by diffusion reaction fronts rather than by gas phase synchronization.

I. INTRODUCTION

Recent investigations have shown that the field ion microscope (FIM) can be used “*in situ*” to identify surface species of a heterogeneous catalytic reaction on an atomic scale.^{1,2} While the catalytic reaction—the CO oxidation—proceeds, one of the reacting molecules O_2 serves simultaneously as imaging gas for producing field ion images of the Pt surface with a 10^6 -times magnification. The preferential field ionization of these O_2 molecules on those surface sites, which are occupied by O_{ad} , was used to identify the surface areas with oxygen coverage and to measure the composition of adsorption layers at different Pt-crystal planes. Thus, the overall titration reactions



and



could be determined, where stoichiometric reactions steps of a Langmuir–Hinshelwood mechanism are measured at a turnover frequency of one.¹ Pronounced surface specificities have been observed for this reaction at different Pt-single crystal planes of the field emitter tip.

In the present work the continuous catalytic CO oxidation with high turnover frequencies will be investigated under conditions where adsorption layers are excitable, where they display bistability and show eventually oscillatory behavior. There are three particular problems which can be approached by work on a field emitter tip and which are

inaccessible with macroscopic studies on extended single crystal planes³ or with work on a mesoscopic scale with photoemission electron microscopy (PEEM).^{4,5}

(a) The surface specificity of the CO oxidation and its dynamical behavior can be investigated simultaneously on a manifold of crystal planes which are exposed on the surface of a field emitter tip. Such kind of work on surface specificity was already performed on a macroscopic single crystal rod exposing some low index single crystal planes to the reaction.⁶ A field emitter, in comparison, has much more numerous planes of different symmetry and size for comparing these dynamic reaction properties. Since all existing low- and high-index planes are exposed to the reaction, the most active plane for the oxidation and the most important for feedback reactions in oscillations should be determined in this experiment.

(b) The collective behavior of adsorption structures, of island formation etc. which has been observed in macroscopic and mesoscopic measurements resulted in the theoretical requirement of a minimum size of nuclei and islands for establishing diffusion reaction fronts.⁷ In FIM work, many well-defined small size single crystal planes are exposed to the reaction and conclusions may be expected for this theoretical statement of a minimum size of a collective phenomenon in adsorption structures.

(c) In several observations on oscillatory schemes on Pt single crystal planes “surface defects” have been registered as starting points of oscillations. In repeated experiments diffusion/reaction fronts or traveling waves started always at the same spots of the extended surface, namely at these so-called “surface defects.” An analysis of the oscillatory behavior on an atomic scale may elucidate the nature of these defects.

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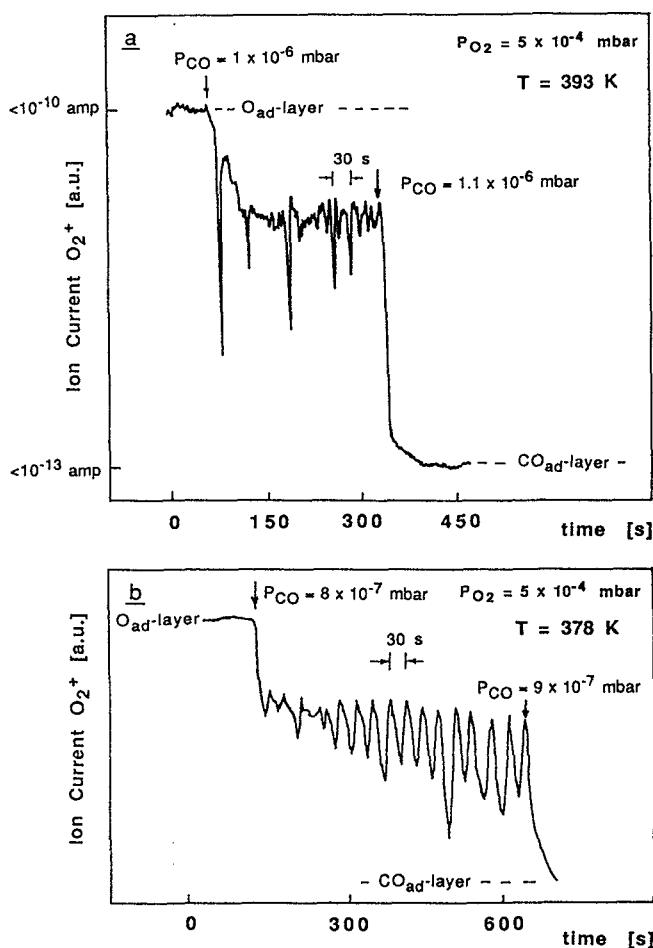


FIG. 1. (a) Initial fluctuations of the total O_2^+ -field ion current of an O_{ad} precovered Pt-field emitter surface during the "precursor state" of kinetic oscillations within the limits of parameter space which produce oscillations. (b) Field-ion currents, O_2^+ , after "conditioning" the surface. Self-sustained oscillations of the O_2^+ current appear still rather irregularly.

II. EXPERIMENTAL METHODS

The FIM and its operation have been described before.^{1,2} The UHV system was equipped with a field emitter tip assembly, a controlled temperature and field strength device, a channel plate and an image recording CCD-video camera, for documenting surface processes with a 40 ms time resolution. With a photo cathode local ion currents of ≈ 400 surface sites could be measured by evaluating the local brightness of the video television screen. Total ion currents were measured as electron currents of the channel plate.

The Pt field emitter tips were prepared in the conventional way by electrochemical etching and were field evaporated before used for the catalytic CO oxidation. Different tips have been used with (111) or (100) orientation. The field strength at the Pt-emitter surface was determined either by Fowler-Nordheim plots or by the onset voltage of rare gas field ionization. A thermocouple at the loop of the field emitter was used for precise temperature control. The gas inlet

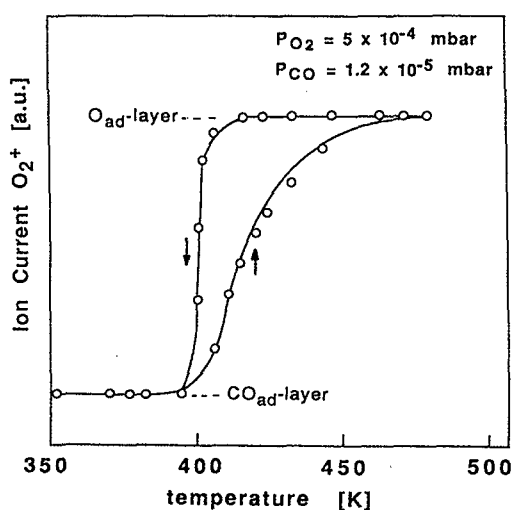


FIG. 2. The hysteresis in O_2^+ -ion currents during temperature variations. The measured points of total O_2^+ -ion currents were obtained by stepwise increasing the temperature from $T=350$ to 475 K in ≈ 5 min intervals, isothermal measurements of total ion currents with intensities between $>10^{-13}$ Amp and $\approx <10^{-10}$ Amp are recorded. The direction of temperature alteration is indicated by arrows.

system took care for the supply of specially purified reaction gases.

III. EXPERIMENTAL RESULTS

The reaction conditions for the titration reaction indicated the temperature region, where a bistability behavior could be expected.¹ In Fig. 1(a), the intensity of O_2^+ -ion currents is shown, when the oxygen covered surface is reacting with gaseous CO (introducing a $p_{CO}=1 \times 10^{-6}$ mbar at 393 K). The high ion current of O_2^+ , characteristic for the O_{ad} layer at Pt planes diminishes suddenly and then performs rather irregular fluctuations until after about 300 s (and $p_{CO} \rightarrow 1.1 \times 10^{-6}$ mbar) it drops to a low current which is characterizing the CO_{ad} layer. This irregularity in ion current is typical for the beginning of an oscillating regime which will be much more regular after "conditioning" the surface, i.e., after a repeated application of $P_{CO} + P_{O_2}$ adsorption and reaction cycles for an extended time of many minutes. This is demonstrated in Fig. 1(b) where O_2^+ -ion currents are measured after such an extended treatment of the surface with reacting gas. Oscillation amplitudes are still rather irregular, but repetition periods with a time of 30 s are reproducible in a time scale of many minutes. This "conditioning" time which is required before self-organized oscillations can start is a well known phenomenon on single crystal planes. It was reported for Pt(210) planes,⁸ as well as for Pt(110) surfaces.^{9,10} It is still undisclosed whether this "conditioning" is connected with reconstruction processes or with the formation of subsurface oxygen species.^{8,10} Field ion microscopic methods offer new techniques to explore such problems as to be discussed later on.

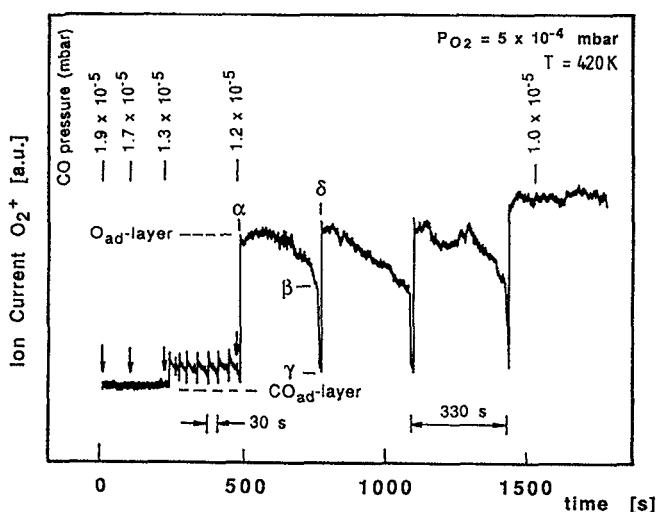


FIG. 3. The O_2^+ -field ion current during the oscillating CO oxidation at different decreasing CO-partial pressures. The points α , β , γ , δ are described in the text.

Figure 2 characterizes the bistability regions and represents the hysteresis behavior for the total O_2^+ -ion current at

increasing and decreasing temperatures between 350 and 480 K. The hysteresis proceeds anticlockwise. With increasing temperature the transfer from the CO_{ad} layer into the O_{ad} layer is delayed, with decreasing temperature it is the reverse reaction. The catalytic activity, i.e., the rate of CO_2 production follows the same cycle as known from literature.¹¹ The temperature range where bistability exists and where oscillations may be expected shifts with p_{O_2} and p_{CO} . With constant control parameters this hysteresis behavior can be reproduced repeatedly. On single crystal planes of Pt the same anticlockwise hysteresis is found.¹² This direction for the hysteresis is an agreement with predictions of the Langmuir-Hinshelwood mechanism.¹³

In order to understand details of the mechanism of this oscillation it is necessary to investigate the oscillatory behavior under different external control parameters. Figure 3 represents the dependence of oscillation amplitudes and frequencies on the p_{CO} at $p_{O_2} = \text{const}$ and $T=420$ K, an elevated temperature for oscillations. A platinum emitter with a CO_{ad} layer at $p_{CO} > 2 \times 10^{-5}$ mbar starts to display small current fluctuations. With decreasing p_{CO} at $p_{CO} \approx 1.3 \times 10^{-5}$ mbar, after about 250 s a complex oscillatory structure appears. A fast switch-over in direction to an O_{ad} layer reaches only 20% of the maximum O_2^+ -ion current.

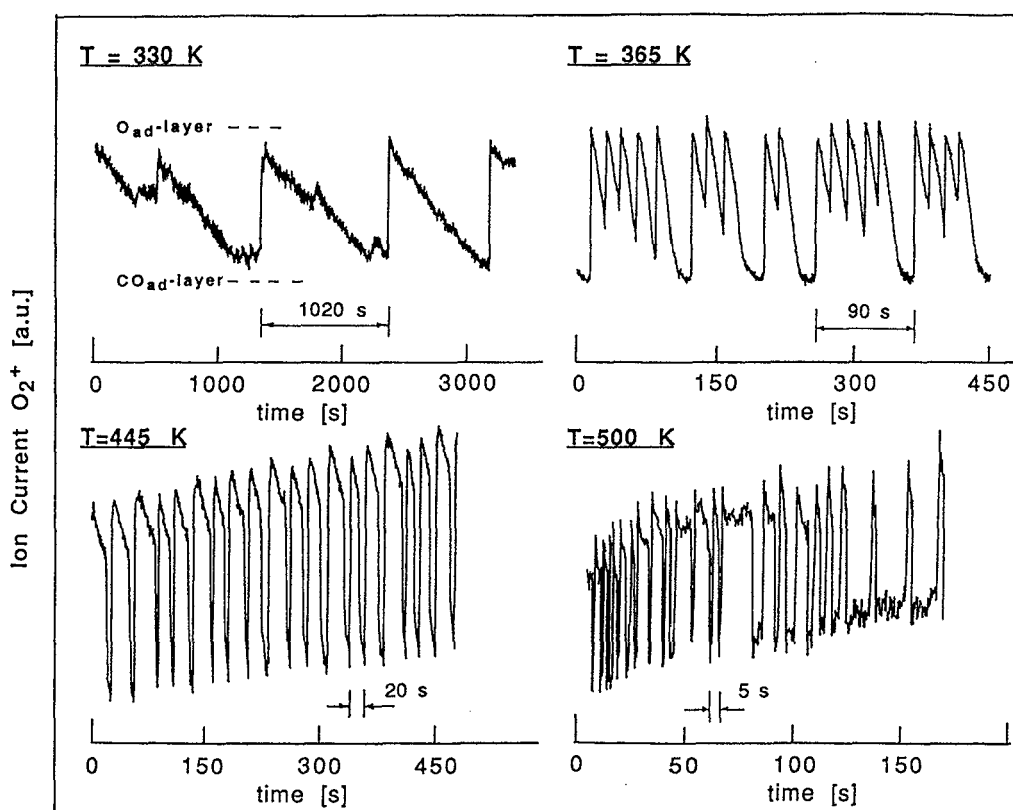


FIG. 4. The oscillating behavior at different temperatures $T=330, 365, 445,$ and 500 K; $p_{O_2} = 5 \times 10^{-4}$ mbar. In order to achieve oscillations in the control parameter space p_{CO} values had to be adapted. $p_{CO}=3 \times 10^{-6}$ (330 K); 5×10^{-6} (365 K); 3×10^{-5} (445 K); 1.2×10^{-4} (500 K).

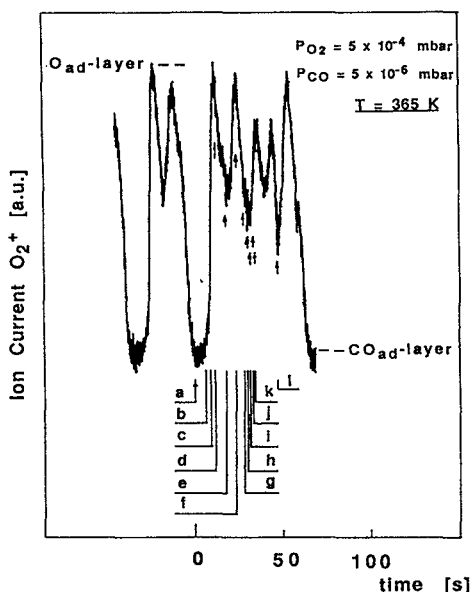


FIG. 5. A detailed analysis of the total ion current during different stages during the oscillating CO oxidation. The different arrows [(a)–(l)] in the time sequence correspond to the frames in Fig. 6(a)–(l).

A slow and irregular surface process reacts towards the CO_{ad} layer until, after ≈ 30 s, a new cycle begins. The small decrease of p_{CO} from 1.3×10^{-5} to 1.2×10^{-5} mbar causes a great change in amplitude and frequency of oscillations. Now the system is mainly operating on the O_{ad} -layer surface. A slow process of partial CO_{ad} formation starting at α leads to a critical CO coverage at β where the O_{ad} layer is removed completely for few seconds (γ). A subsequent fast reaction, the feedback reaction, reestablishes the O_{ad} layer (δ), and the whole process is repeated in a time scale of 330 s. A further small decrease of $p_{\text{CO}} \rightarrow 1.0 \times 10^{-5}$ mbar leads to a steady O_{ad} layer where only small local instabilities create certain fluctuation in the total ion current. There is further information available on the spatial contribution to the total O_2^+ -ion current from FIM images. At the completed O_{ad} layer, at α , a bright emission of O_2^+ ions is observed from all surface planes except $\{111\}$. A slow process diminishes the emitting area gradually, such that, at β , only the (001) plane still emits. A fast process then darkens also the (001) plane at γ . The further quick feedback reaction starts in $\{011\}$ regions (at the $\{331\}$ planes) and renovates the O_{ad} layer immediately, at δ [for the indication of Miller indices see Fig. 6(a)].

A kinetic surface regime which has established oscillations, as in Fig. 3, may display an unexpected reproducibility in sequential amplitudes and frequencies of oscillating cycles and a most sensitive dependence on control parameters. Only a few percent change of the CO pressure (from 1.3 to 1.2×10^{-5} mbar) switches the oscillation basis from the CO_{ad} side to the O_{ad} side. The oscillation then follows a relaxation-type process. A long-lasting reaction in the O_{ad} layer connected with the gradual decrease of the O_2^+ -ion current until a critical surface composition is reached at β . From FIM

images it can be concluded that this process leading to point β is a diffusion reaction front of CO_{ad} starting from the $\{111\}$ planes and moving into the oxygen-covered $[001]$ vicinals. At the point β where a critical surface composition is obtained, the (001) plane suddenly transfers to the CO_{ad} side, a process which differs qualitatively from the previous slow reaction. The surface plane specific behavior will be documented later on in FIM images (Figs. 6–8).

Of further interest is to study these isothermal oscillations at different temperatures. In Fig. 4, data between $T=330$ and 500 K are displayed. It is obvious that at low temperatures ($T=330$ K) a slow reaction of the O_{ad} layer with CO_{gas} leads in an oscillating cycle on a time scale of 1020 s to a surface of CO_{ad} layer, which in a quick “switch-on” reaction—the feedback—is then transferred to O_{ad} . With increased temperature ($T=365$ K) an intermediate state is reached where the total transfer of the O_{ad} layer toward the CO_{ad} layer is not always established. In most cases the reaction switches back to the O_{ad} layer after 16 to 20 s without reaching the current minimum. This will be shown later, in a detailed FIM map in Figs. 5 and 6. In a certain temperature region ($T \approx 445$ K) very regular oscillations with a time scale of 20 s can be found. Here the fast transfer of the O_{ad} layer toward the CO_{ad} layer starts at rather higher oxygen coverages. After the current minimum is reached, again a fast feedback reaction to the O_{ad} layer is noticed. At 500 K, the highest investigated temperature, an oscillation repetition time of 5 s is dominant at the beginning, but irregularities and a “switch-over” of the oscillations now starting from the CO_{ad} side (after 130 s), are probably imitating the beginning transfer to an irregular behavior at still higher temperatures.

The oscillatory behavior of total ion currents in Fig. 4 is characterized by corresponding *in situ* FIM images in Fig. 7. The images [7(a)] and [7(b)] are taken at $T=330$ K for the O_{ad} - and CO -layer states of Fig. 4 and illustrate that the O_{ad} layer [7(a)] is only partially removed to the CO_{ad} -layer side, keeping the (001) plane and parts of the $\{110\}$ planes still covered with oxygen [7(b)]. At 365 K [Fig. 7(c)] the dark $\{111\}$ areas are further extended into the O_{ad} -layer side and oscillations proceed mainly at the $[100]$ vicinals between the (001) and the $\{011\}$ planes. The (001) plane may resist the CO adsorption in several cycles, in others a complete CO_{ad} layer involves also this plane [Fig. 7(d)]. At 445 K a faster oscillation of the image brightness is observed. The O_{ad} -layer side displays a characteristic black cross from (001) to $\{011\}$ planes and bright emission in the $\{012\}$ areas [Fig. 7(e)], which vanishes when the CO_{ad} layer is completed [Fig. 7(f)]. At $T \geq 445$ K structural changes seem to occur. The O_{ad} side [Fig. 7(g)] displays many irregular reflexes and a certain coarsening appears when the CO_{ad} layer is imaged [Fig. 7(h)]. From these experiments two conclusions arise: (i) The temporal variation of the total O_2^+ -ion current is caused by a spatial variation in the local image brightness. A pronounced surface plane specificity is involved in these processes. At increased temperatures ($T \geq 445$ K) morphological changes of the Pt surface during the oscillating reaction may lead to irreversible processes in the surface dynamics. For reestablishing the initial shape of the surface, several surface layers of the field emitter had to be evaporated.

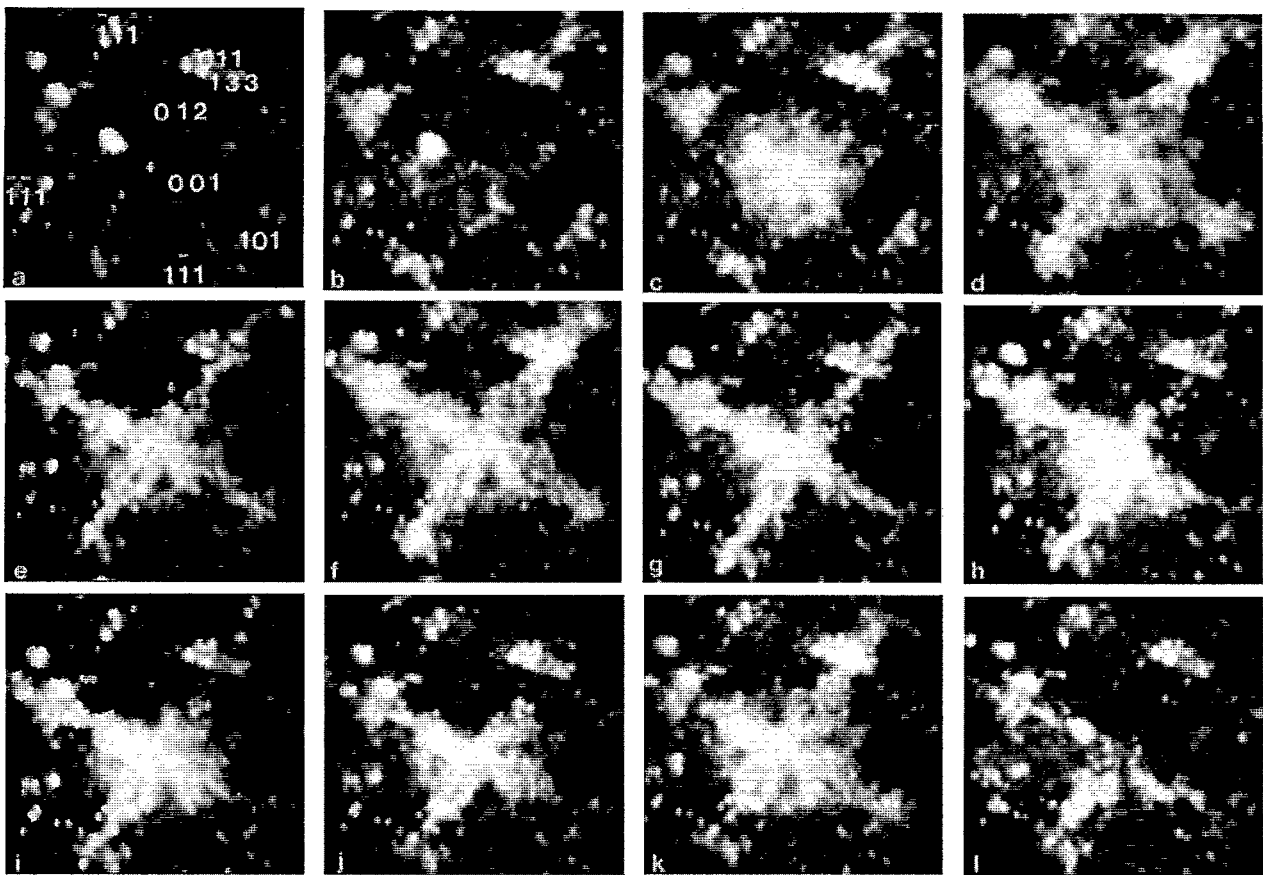


FIG. 6. Field ion images during different stages of an oscillating cycle. The FIM images [(a) to (l)] correspond to total O_2^+ -ion currents marked by (a) to (l) in Fig. 5.

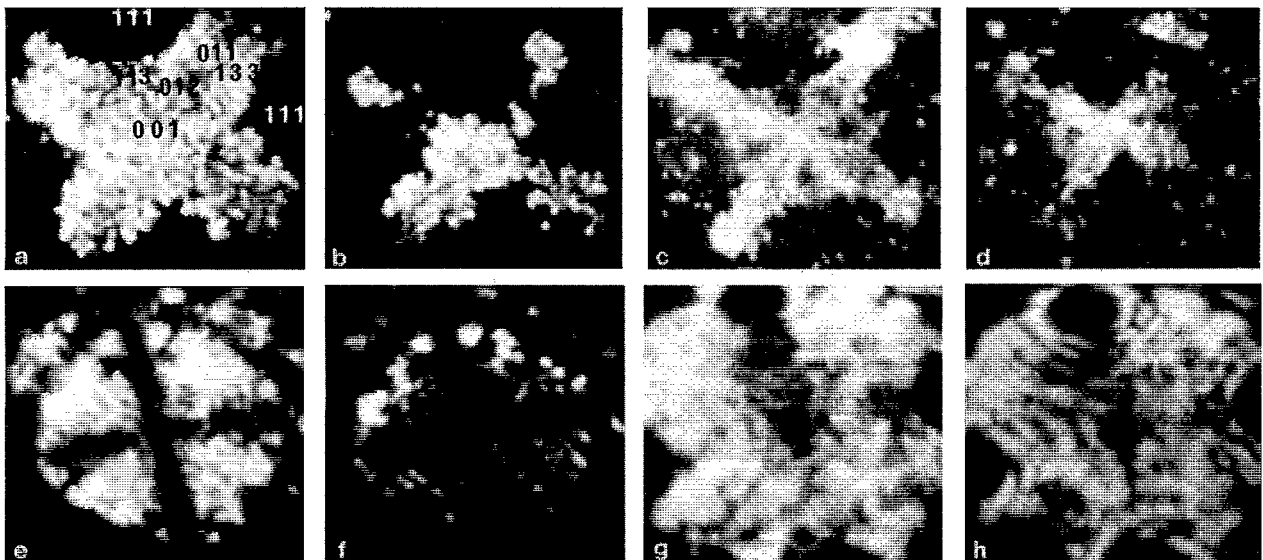


FIG. 7. Field ion images of the (001)-oriented Pt-field emitter surface during the kinetic oscillations at different temperatures, imaging the ion currents of Fig. 4 with spatial resolution. The image frames characterizing the initial saturated O_{ad} layer and the final O_{ad} layer after a complete oscillating cycle are imaged. $T=300$ K: (a), (b); $=365$ K: (c), (d); $=445$ K: (e), (f); $=500$ K: (g), (h).

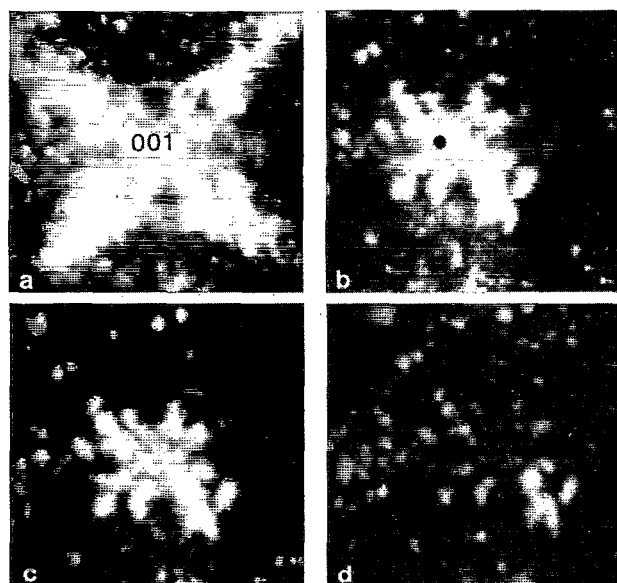


FIG. 8. Local oscillations of the oxidation reaction on the Pt(001) plane in a small region of CO partial pressures. $p_{\text{O}_2} = 5 \times 10^{-4}$ mbar, $T = 391$ K. At $p_{\text{CO}} = 5 \times 10^{-6}$ mbar, the [100] vicinals oscillate (a), at $p_{\text{CO}} = 1.7 \times 10^{-5}$ mbar a long-lasting oscillation is locally restricted to the (001) plane [(b) and (c)]. A small further increase to $p_{\text{CO}} = 2 \times 10^{-5}$ mbar terminates the oscillation (d).

In order to characterize the surface specificity of the oscillating regime in a more detailed map, different intermediate stages of the oscillating O_2^+ -ion current are correlated with corresponding FIM images (Figs. 5 and 6). The different arrows in Fig. 5 (a–l) are correlated with the FIM images in Fig. 6 denoted (a)–(l). The CO_{ad} -covered surface with the minimum O_2^+ -ion current [Fig. 5(a)] is represented by a dim field ion image [Fig. 6(a)] where only few structural irregularities are imaged: three characteristic spots at 11:00, as well as other defects which are immanent for this tip and can be used for land marking. At the increasing O_2 -ion current [Fig. 5(b)] the surface coverage starts at the {011} regions, precisely the {133} terraces [Fig. 6(b)], continues over to the (011) plane [Fig. 5(c)] and reaches finally the maximum ion current [Fig. 5(d)] and brightest image [Fig. 6(d)], where all the planes on the [001] vicinals starting from {011} and leading to the central (001) are emitting. The {111} and their surroundings remain black, being covered with CO_{ad} all the time. The intermediate minimum in Fig. 5(e) develops while CO diffuses from the {111} regions into directions of {011}, {012}, {013}, etc. planes. The emitting cross pattern which consists of the central (001) and the [001] vicinals toward the {110} planes narrow accordingly [Fig. 6(e)]. An intermediate increase in O_2^+ -ion current [Fig. 5(f)] is correlated with a local oscillation around the (001) plane where a bright emission [Fig. 6(f)] is followed by a less intense one [Fig. 6(g)] with an intermediate minimum of ion [Fig. 5(g)]. The following local current maxima [Figs. 5(i) and 5(k)] and minima [Figs. 5(h), 5(f), and 5(l)] are mainly caused by local oscillations around the (001) plane and only at longer time

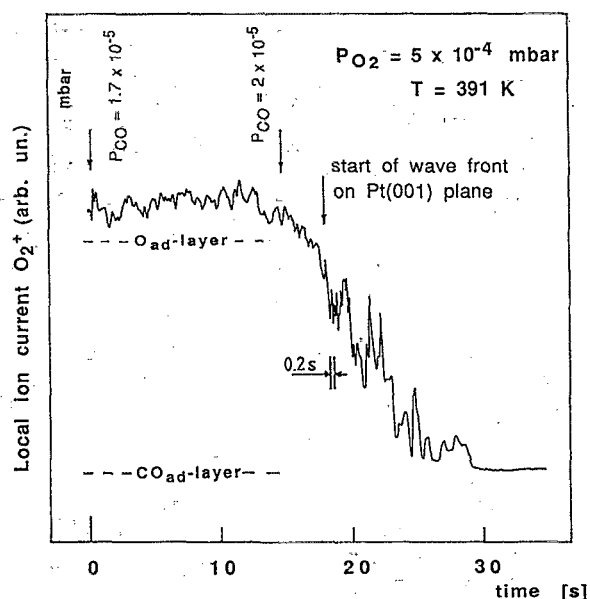


FIG. 9. Oscillations of Fig. 8 measured as local field ion currents, characterizing about 400 surface sites at the left-hand border of the (001) plane [marked as circle in Fig. 8(b)].

(≈ 70 s) a complete CO_{ad} layer is formed resembling Fig. 6(a). With this correlation between total ion currents and the local values of image brightness the spatial distribution of oscillations can be precisely determined. The conclusion is that the observed variations in the total ion current of oscillatory cycles are mainly due to the local variations in the size of emitting areas and not to the brightness of constantly existing areas.

In an even further detailed map, Fig. 8, locally changing oscillatory regions are observed only at the (001) plane after small changes in the pressure of CO, ($p_{\text{O}_2} = 5 \times 10^{-4}$ mbar and $T = 391$ K are constant). At the beginning [Fig. 8(a)] in a partial pressure of $p_{\text{CO}} = 5 \times 10^{-6}$ mbar, most of the emitter area, the [001] vicinals toward {011} planes are oscillating, except the bright center of the central (001) plane and the black {111} regions. A small increase of the CO pressure to $p_{\text{CO}} = 1.7 \times 10^{-5}$ mbar initiates conditions of an extremely local oscillation. In the manner of a “flip–flop” interplay a bright (001) plane [Fig. 8(b)] quickly transfers into a dim one [Fig. 8(c)] and then as quickly it turns back. In the dim (001) plane black CO_{ad} islands of a diameter of 40 to 50 Å can be localized. The local oscillations started near the borders of the (001) plane, and then, produced fast wave fronts which passed along the plane. Oscillations were quenched after a small further increase of p_{CO} [Fig. 8(d)]. These dynamic processes have been measured as local O_2^+ -ion currents (Fig. 9) by using a method which integrates the ion yield of only ≈ 400 surface sites. The measured area, as indicated in Fig. 8(b), is located at the left side of the (001) plane. Oscillations in the small (001) region are rather unsteady as demonstrated in Fig. 9. A fast switching between bright and dim areas near the (001) plane occurs (for about 18 s in Fig. 9), until the

oscillations move into the central (001) plane, where wave fronts with short sequences (0.2 s) pass repeatedly through the (001) plane creating and removing these dark CO islands of 40 to 50 Å diameter. A small further increase in the CO partial pressure terminates the oscillations. This interesting behavior of the Pt(001) surface will be discussed in detail elsewhere.¹⁴ It is based on the reconstruction of the Pt(001) plane where the driving mechanism is caused by the Pt(001)·hex \leftrightarrow Pt(001) 1 \times 1 transition.

IV. DISCUSSIONS

In the presented experimental work kinetic oscillations in the surface dynamics of the CO oxidation on platinum could be directly imaged by FIM. The field ion technique presents a new tool to investigate surface processes which are inherent in the mechanism of oscillations with a lateral resolution which was so far beyond any discussion. Individual surface sites of a platinum surface can be imaged *in situ* with a lateral atomic resolution and in real time while this surface acts as catalyst and even performs kinetic oscillations.

From earlier work on single crystals it was concluded that kinetic oscillations represent a collective phenomenon. There was a minimum size (of >1000 Å diameter) postulated which is requested to form stable adsorption islands. These adsorption islands which are formed on account of intermolecular attractive forces of adsorbed molecules are considered as one of the important reasons for the nonlinearity of the surface reaction kinetics. The reaction zone in such systems could for instance be only the one-dimensional borderline between these CO_{ad}- and O_{ad}-adsorption islands.

One of the unexpected results of the present work proves that very local structures can be formed. In Fig. 8(b) and 8(c), for instance, CO_{ad} islands with a diameter of only 40 to 50 Å are produced which appear and disappear in quick oscillatory sequences correlated with particular properties of the Pt (001) plane.

Another astonishing observation concerns the perfect reproduction of oscillatory patterns which may be obtained with precisely constant control parameters, for instance in Figs. 3 and 4. Some of these oscillatory patterns are created by very limited surface areas. In Fig. 3 the small amplitudes with 30 s repetition rates in oscillation sequences, for instance, are correlated with some 10³ surface sites. These reproducibilities are further demonstrated after small changes in the CO partial pressure (Fig. 3) or in temperature (Fig. 4). In Fig. 3 the oscillation patterns with the 330 s repetition rate show only small deviations in their oscillation sequences. Now, however, many different field emitter planes—except the {111} planes—are involved in the oscillation cycles.

At the field emitter tip all possible crystallographic orientations are exposed simultaneously. The low index planes (001), (111), (011), (012)—which have been investigated for oscillations on single crystals—are usually formed with larger diameters (up to \approx 100 Å). In addition, dozens of smaller high index planes are observed. On a (001)-oriented Pt tip with its fourfold symmetry each of these planes appears four times at crystallographically well-defined remote positions.

This crystallographic constellation immediately answers questions which cannot be solved easily on extended single crystal planes. The synchronization of oscillations in remote areas of an extended plane may be ruled by gas phase synchronization or the surface diffusion/reaction waves. On extended single crystal planes this problem was studied on a specially prepared Pt rod, oriented in the [001] direction and exposing four (100), (110), and (210) planes simultaneously to the reaction.⁶

On a field emitter tip this question of synchronization is solved automatically. A simple gas phase synchronization implies—at Knudsen gas flow—a simultaneous “switch-on” process of the four planes with identical orientation, which should occur in the same frame of the video film if a time resolution of 40 ms is achieved. Contrary to this the sequence of video frame displays the reaction fronts or chemical waves which pass over the surface (for instance in Fig. 6) with a propagation of \approx 10⁻¹ to \approx 10³ Å s⁻¹. The comparison of an extended isolated plane of a macroscopic single crystal and smaller planes of the same orientation at a field emitter tip leads to the following consequences.

(1) Gas phase synchronization is connected with a nucleation problem. At the bistability point, a minimum pressure variation, for instance, a certain CO pressure drop is required to initiate the transition. In the flow reactor this minimum pressure drop is achieved when the adsorption process of CO on the single crystal plane competes remarkably with the flow rate of CO_{gas}, which is regulated by the pumping speed. Only if Δp_{CO} reaches a certain minimum value at the bistability point, gas phase synchronization of remote planes is possible. The planes at the field emitter surface with only some 10² to 10⁴ sites may be too small to create this required minimum drop in p_{CO} . The field emitter planes and macroscopic planes would—although their external control parameters are identical—act differently on account of their different size. Then one could also say that the size of the crystal plane is an additional control parameter for an oscillating reaction.

(2) The existence of regions of oscillations in the parameter space may be different for macroscopic single crystal planes and planes of a field emitter. Isolated extended single crystal planes of Pt like Pt(001), Pt(011), Pt(012) oscillate in quite different regions of the parameter space.^{8,15} On a field emitter tip, in contrary, all these planes may oscillate simultaneously, as for instance in Fig. 6. The open question is, however, which of these regions perform autonomous oscillations and which are just driven by diffusion processes. On account of the broader reaction parameter space it seems to be more easy to trace oscillating regimes on field emitters, than on single crystal planes.

(3) On macroscopic surfaces, where oscillations are monitored by work function, Fourier transform IR or mass spectrometry, an integral information only of large parts (\approx mm²) of the surface is obtained and with PEEM^{4,5} still some extended areas (μ^2) are imaged simultaneously. The atomic resolution on field emitter tips directly gives information on questions which still have been unsolved in previous experiments.

(a) The properties of reaction wave fronts can be illumi-

nated and their propagation rates determined. It also is remarkable how sharp boarderlines are even in atomic dimensions.

(b) This high lateral resolution also gives the possibility to locate the initiating areas of reaction diffusion fronts.

(c) While these areas are unknown defects on macroscopic surfaces, FIM work shows that {331} planes play a remarkable role in both cycles of the oscillating CO oxidation, in the initiation of CO_{ad} removal, as well as in the reaction of O_{ad}. The specialities of chemical bond formation on the (331) plane has been found earlier¹⁶ and will be discussed elsewhere.¹⁴

(d) Thus nucleation phenomena which are important in order to understand the role of pacemakers or leading edges on macroscopic crystals may receive new evidence from work with field emitters.

So far, only a qualitative picture is drawn from the experiments with FIM. More quantitative data will be available when anisotropies of reaction fronts are determined more precisely.

In this article experiments were restricted to pure imaging of the CO/O₂ reaction by FIM. Work with mass spectrometric devices is in preparation. It can be expected that laser pulse field desorption mass spectrometry gives further information on local chemical composition. These questions are of particular interest not only for confirming the derived models of adsorption layers during the oscillatory sequences, but also for shedding light on the obscure processes during the conditioning treatment.

There are other oscillating regimes where macroscopic measurements left open questions for understanding reaction mechanisms. FIM investigations will be useful also in other reaction types.

ACKNOWLEDGMENT

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