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Energy-Resolved Field Ion Spectroscopy of Surface Reactions: H₂/O₂ and H₂/H₂O on Platinum

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Abstract. Applications of field ion mass and appearance energy spectroscopy on catalytic surface reactions are reviewed. The investigations have been stimulated by in-situ FIM observations in the group of the late J.H. Block suggesting that single, active sites can be visualized. We have especially examined the energetics and kinetics of H₂/O₂ and H₂/H₂O reactions on [001] oriented Pt-tips. For single surface sites field ion yields have been measured as a function of H₂ partial pressure showing (different) hysteresis behavior for both reaction systems. For H₂/O₂/Pt the results agree qualitatively with features earlier observed at field-free conditions. This finding and the different kinetics of the two reaction systems suggest a less pronounced influence of the applied electric field on the surface catalyzed H₂O formation for H₂/O₂/Pt. At distinct control parameter (pressures, temperature) dynamic phenomena, such as kinetic instabilities and oscillating reaction diffusion fronts, were characterized by probe hole FIM combined with FIMS and FIAPS. For H₂/O₂/Pt comparative measurements have recently revealed a different behavior in FIM and FEM modes possibly caused by the different facets contributing to FI and FE emission currents.

1. INTRODUCTION

Basic research in the area of heterogeneous catalysis has a long-standing tradition in physical chemistry. There are a lot of technological applications, like in the purification of exhaust gases of cars and power plants. Much efforts have been and are still being devoted to the characterization of the molecular processes underlying surface catalyzed reactions, such as the ammonia-synthesis and carbon monoxide oxidation. Recently, pioneering in-situ observations on surface catalyzed reactions, using FEM in Leiden in the group of Nieuwenhuys [1] and using FIM in Berlin in the group of Block [2], have opened a novel application of field emission techniques. These efforts aimed at the identification of single reactive sites at catalytic active surfaces and at the characterization of nonlinear surface phenomena, such as kinetic instabilities reported by Voss and Kruse [3] and oscillating chemical waves described by Block et al. [4] in a recent review. These fascinating new observations prompted field ion spectroscopic investigations, especially in the Berlin group which are reviewed in this contribution. For the (oscillating) NO reduction (by H₂) mass spectrometric results will be reported elsewhere [5]. From their FEM and FIM observations Gorodetskii et al. [6-8] concluded that in the case of the H₂ oxidation (by O₂ over Pt) the ion image is largely produced by the product molecules H₂O, leaving the catalyst surface as presumably H₂O⁺. Preliminary, low resolution mass analyses reported by Drachsel, Gorodetskii and Block [9] in fact suggested that conclusion. However, the mass resolution did not allow to distinguish mass number 18 (H₂O⁺) from mass number 19 (H₃O⁺), which - as we know today [10,11] - is an important prerequisite for the field ion spectroscopic characterization of surface reactions producing H₂O, such as the Pt catalyzed H₂-O₂ reaction.

Like other high-resolution imaging methods, such as STM and electron microscopy, the act of imaging in FIM does effect the object under study to a certain extent. The processes which are relevant here concern effects of the high electrostatic field and field gradients on the adsorption-desorption kinetics and field-induced surface reaction pathways. Aiming to contribute to an experimental characterization of these effects, we have employed a variant of a probe hole FIM-FEM combined with field ion mass spectrometry (FIMS) and field ion appearance potential (energy) spectroscopy (FIAPS) on selected surface reaction systems. In this paper we would like to present FIMS and FIAPS results obtained for the oxidation of H₂ and the (field driven) H₂-H₂O reaction over Pt. The data allow to characterize surface reaction field
desorption pathways and the energetics of ion formation processes (Section 3.1). Such data are also valuable for an understanding of the kinetics of surface reactions and of dynamic surface phenomena which we have also examined by time resolved measurements (Section 3.2).

2. EXPERIMENTAL

The experimental method has been described elsewhere [12-14] and will only shortly be sketched. A differentially pumped UHV chamber houses a probe hole FIM which has been combined with a sixty degree, single-focusing magnetic sector field mass spectrometer followed by an electrostatic, five-electrode retarding potential analyzer (Fig. 1).

![Diagram](image-url)

**Figure 1:** Experimental set-up [12-14]. A glass container houses a probe hole FIM-FEM in a differentially pumped UHV chamber allowing automated measurements of total field ion (FI, upper right panel) and total field electron (FE) currents on the phosphor screen after (channel plate) amplification. For selected surface sites of a field emitter tip such as Pt, local ion yields are mass analyzed (right FIMS panel) and energy analyzed (lower right FIAPS panel). Measurements of total currents and local ion yields (lower left panel) as a function of (H₂ or O₂) partial pressure allow detailed studies of the kinetic behavior of a surface-catalyzed reaction such as H₂/O₂/Pt.
The apex of the field emitter (mostly [001] oriented Pt spot-welded on a W wire) acts as a catalyst grain in a flow reactor, e.g. fed with H₂ and O₂. The temperature of the specimens could be controlled between 80 K and 1000 K using a conventional glass coldfinger set-up. To avoid effects of hot filaments pressures of reactive gases were measured with a spinning ball (frictional) manometer. The cleanliness of the gases was controlled in-situ by FIMS which has also been used to characterize the chemical identity of product ion species for single surface sites. Information on the energetics of ion formation was derived from retarding-potential (energy) spectroscopy (FIAPS). Thus, one discriminates between different surface reaction field desorption pathways for a selected ion beam, for example of (slow and fast) H₃O⁺ as in the lower right panel of Fig. 1. The dynamics of surface reaction phenomena was imaged by probe hole FIM and FEM. During FIM, ion yields were simultaneously mass and energy analyzed.

During FEM (Fig. 2), electron emission currents (directions of work function changes, ΔΦ) have also been registered supplementing the kinetic studies, especially for the H₂/O₂/Pt reaction. Using a newly in-
stalled computer-assisted data acquisition system, the field ion yields and the field electron emission currents have been measured as a function of automatically varied partial pressures [14]. Fig. 2a) shows H₂ partial pressure dependencies of FEM and FIM video frames and total field electron (e⁻, ΔΦ) and field ion currents (M⁺, reaction yields averaged over the tip as a whole) measured on the phosphor screen after amplification by a factor of 10³. The observed hysteresis behavior differs for FEM and FIM modes which could not be explained by the (differently) field enhanced supply rates for H₂ and O₂ [15]. This difference might have been caused by the different facets contributing to the total FE and total FI currents, respectively. Also, the opening of additional surface reaction field desorption pathways in the FIM mode could have an effect on the kinetics (see Fig. 4b) further below).

Fig. 2b) shows local ion (reaction) yields successively analyzed as a function of H₂ partial pressure. For different species such as O₂⁺, H₂O⁺ and H₃O⁺ there is, albeit different, hysteresis behavior. From such data it was concluded that the maximum of the total FI current (total reaction yield) is dominated by the emission of H₃O⁺. Transitions from the O- to the H-side (and vice versa) shift to higher H₂ pressure with increasing temperature for results shown in a) and b).

3. RESULTS AND DISCUSSION

3.1 Energetics and pathways: H₂/O₂/Pt

The two field ion pattern in Fig. 3 show a [001]-oriented platinum tip acting as a catalyst grain during the oxidation of hydrogen. The control parameter (T(Pt), P(H₂), P(O₂)) have been chosen to achieve a view at the surface at (i) low reactivity (H-side) visualized in the upper video frame and at (ii) high reactivity

![Figure 3: FIAPS (left) and FIM (right) during the H₂ oxidation reaction over Pt [18]. The lower H₃O⁺ retardation curve (appearance energy, A(slow)) was measured at P(O₂) = 5.0 × 10⁻⁴ mbar and at P(H₂) = 1.08 × 10⁻⁴ mbar (T(Pt) = 360 K, F = +1.8 V/Å); the FIM pattern shows a highly reactive surface (O-side) characterized by a cross-like structure. The stepped curve in the middle (A(fast) and A(slow)) was measured at slightly higher H₂ pressure (H-side, FIM: cross-like structure has almost disappeared). The retardation curve on top, measured at highest H₂ pressure reveals no discernible step structure (A(fast)). The energy scale was calibrated using an experimentally determined value of the retarder work function, Φ_R.](image-url)
(O-side) visualized in the lower video frame. At conditions specified for the O-side, H$_3$O$^+$ was the most abundant product species in the field ion mass spectrum [10,11]. Using FIMS as shown in Fig. 1, we have detected an O$_2^+$ signal produced by field ionization of O$_2$ and field-induced surface reactions of water [16,17]. To contribute to an elucidation of surface reaction field desorption pathways for H$_2$O$^+$ formation, FIAPS was employed in detailed studies [11,18]. Fig. 3 shows semi-logarithmic plots of H$_3$O$^+$ retardation curves measured at constant O$_2$ and at three different H$_2$ pressures. The scale on top has been calibrated using an in-situ measured value for the work function of the retarder electrode for determination of the field ion appearance energy (A) obtained from the onset of a retardation curve [19].

Below a critical H$_2$ partial pressure we measured A(slow) = 10.4 eV (O-side, H$_3$O$^+$ retardation curve on the bottom in Fig. 3). A shift to lower H$_3$O$^+$ appearance energy, i.e. higher kinetic energy of approximately 0.8 eV was observed as the H-side was reached, A(fast) = 9.6 eV (H$_3$O$^+$ retardation curve in the middle). Just above the critical H$_2$ pressure, a step structure was detected characterizing two peaks in the H$_3$O$^+$ energy distribution. As the H$_2$ pressure was further increased the low kinetic energy peak with A(slow) = 10.4 eV disappeared (H$_3$O$^+$ retardation curve on top). We note that the phenomena observed by FIM and FIAPS were completely reversible as the H$_2$ pressure was lowered again, involving hysteresis behavior [18]. The appearance and disappearance of fast H$_3$O$^+$ was used to characterize different kinetic regimes as will be discussed later. Thereby, the appearance energy data have provided valuable information on the energetics of surface reaction field desorption pathways [11].

The energy diagram in Fig. 4a) illustrates our current interpretation of the H$_3$O$^+$ appearance energy, A(fast) = 9.6 eV measured for the H-side of the H$_2$ oxidation reaction. Detailed mass and energy resolved measurements including isotope exchange experiments have proven a surface reaction field desorption pathway for H$_3$O$^+$ formation which involves chemisorbed H from dissociative adsorption of H$_2$ and field-adsorbed, presumably more strongly bound H$_2$O. Our data suggest a distinct shift to lower total energy
for adsorbed water. This shift includes the long-range polarization and the short-range, field-modified binding energy. Thermal field desorption of $H_2O^+$ from an intermediate field adsorbed $H_2O$ species appears conceivable. Following the energetic model consideration as in Fig. 4a), the initial state relevant for appearance energy analysis is given by a field adsorbed $H_2O$ at the instant of field desorption over a Schottky hump \cite{[11,13]}. For the O-side of the kinetic regime slow $H_2O^+$ species were exclusively measured ($A(\text{slow}) = 10.4 \text{ eV}$) suggesting a reaction pathway proposed earlier by Heinen, Röllgen and Beckey \cite{[20]}. This pathway mainly involves the field induced proton transfer between two water molecules but additional pathways contributing with smaller rates are still under discussion \cite{[17]}. On the O-side the $H_2O^+$ appearance energy is greater, thus the formation of $H_2O^+$ would be less favored in this kinetic regime. However, the actual yield of $H_2O^+$, which is in fact at its maximum on the O-side, is governed by kinetic effects which largely depend on the partial surface coverage of adsorbed species like $H$, $O$, and OH.

To conclude this section, we would like to discuss adsorption, desorption and reaction steps which are in line with the ion spectroscopic results \cite{[4]}. The first three reaction pathways in Fig. 4b) describe a Langmuir-Hinshelwood (LH) reaction mechanism for the Pt catalyzed $H_2O$ formation from $H_2$ and $O_2$. This mechanism has been suggested from experiments on field-free single crystal facets \cite{[21]}. Reactions (4) to (5) of Fig. 4b) describe (presumably very fast) surface reaction field desorption pathways giving $H_2O^+$ used to "probe" the formation rate of field adsorbed $H_2O$ \cite{[4]}. As indicated in the reaction sequence (4) of Fig. 4b) it is conceivable that hot $O_{ads}$ are produced in a disproportionation reaction. These hot $O_{ads}$ are thermally field desorbed as $O_2^+$, possibly mediated via a field induced molecular precursor state \cite{[22]}. A new reaction pathway for $H_2O^+$ formation invoked by Drachsel and Wesseling \cite{[17]} considers the reaction between adsorbed, intermediate $H_2O_2^+$ and OH species. Their $H_2O^+-O_2^+$ ion coincidence data suggest that such a pathway contributes less than 10% to the total $H_2O^+$ yield. A clarification of the details involved in the surface reaction field desorption processes (producing slow $H_2O^+$) deserves further experimental and theoretical investigations, if realistic kinetic models are to be developed. In spite of this we have attempted to characterize the kinetic and dynamic behavior for two selected reaction systems discussed in the next section.

### 3.2 Kinetics and dynamics: $H_2/O_2/Pt$ and $H_2/H_2O/Pt$

To characterize the kinetics of the $H_2/O_2/Pt$ reaction system we have especially examined the $H_2$ partial pressure dependence of the $H_2O^+$ yield for a single surface site \cite{[18]}. Fig. 5 shows two FIM pattern obtained during local $H_2O^+$ yield measurements (upper data in the double-logarithmic plot on the right of Fig. 5). This particular result was obtained from a fit through single measurement points taken as a function of $H_2$ pressure. Starting on the O-side ($A(\text{slow}) = 10.4 \text{ eV}$, pathway (4) of Fig. 4b)), the local, slow $H_2O^+$ yield increased until the $H_2/O_2$ pressure ratio reached a value of approximately 0.25 where the yield showed a sudden jump to lower values of slow and fast $H_2O^+$ (H-side, $A(\text{fast}) = 9.6 \text{ eV}$, pathway (5) of Fig. 4b)). When the $H_2$ pressure was further increased we measured even smaller, exclusively fast $H_2O^+$ yields in a regime where hydrogen "poisoned" the catalytic activity. Lowering the $H_2$ pressure again, revealed hysteresis behavior; at an $H_2/O_2$ pressure ratio of 0.20 the reaction system was still on the H-side characterized by the emission of fast $H_2O^+$. Hysteresis behavior was also observed in the FIM pattern in Fig. 5. Actually, the two images were observed at the same $H_2/O_2$ pressure ratio (the upper for increasing, the lower for decreasing $H_2$ partial pressure).

The hysteresis behavior measured for a Pt-tip was compared with results earlier reported for the $H_2$ oxidation over a macroscopic Pt-foil \cite{[18]}. Such an experiment was carried out in Moscow by Slin’ko \cite{[23]} almost 20 years ago and is also shown in Fig. 5. Here, the reaction rate of $H_2O$ formation has been plotted as a function of $H_2/O_2$ pressure ratio in the same double logarithmic plot as the $H_2O^+$ results. Although the (field-free) Pt-foil experiment was performed at higher total pressure and temperature, the qualitatively similar features, such as the slope of the reaction yield on the O-side and the occurrence of a hysteresis suggest a relatively small field influence for the field ion emission data. However, there are significant differences, especially in the values of critical pressures and in the hysteresis behavior on the H-side. For selected parameter values, such as partial pressures and temperature, kinetic instabilities involving spatio-temporal fluctuations have been observed. This will be illustrated by an example at the end of this section.

Information on the effect of the applied field strength has also been deduced from a comparison of the $H_2$ partial pressure dependence of the $H_2O^+$ reaction yield for the two systems $H_2/O_2/Pt$ and $H_2/H_2O/Pt$ \cite{[18]}. The latter (field-driven) reaction showed a completely different behavior which was explained by a kinetic model involving the supply of diffusing $H$ from the shank to the apex of the tip \cite{[10]}. For $H_2/H_2O/Pt$, we measured a 0-th order dependence of the yield of slow $H_2O^+$ on $H_2$ pressure on the "water-side" (until a critical $H_2$ pressure had been reached). This kinetic regime was dominated by reaction pathway (4) of Fig. 4b); water was directly supplied from gas phase (from an external source) and...
produced H$_3$O$^+$ during field induced protonation reactions between H$_2$O molecules at the Pt-tip. The situation differed for the H$_2$/O$_2$/Pt system whereby H$_2$O was formed during LH surface reactions at the apex of the Pt-tip. For the O-side, a reaction order of approximately 1.2 was deduced from H$_3$O$^+$-pressure dependencies as in Fig. 5 in good agreement with measured [23] and calculated [21] field free data for H$_2$O reaction yields. The different kinetic behavior observed for the two reaction systems thus gave a further indication that an external electric field (of approximately 1.5 V/Å) did not influence the kinetics of the H$_2$/O$_2$/Pt reaction, at least to a large extent. As a consequence of this reasoning, we used the H$_3$O$^+$ yield as a local probe for the characterization of dynamic surface phenomena which could be observed for the two reaction systems at judiciously chosen control parameter.

**Figure 5**: Reaction yields for a Pt-tip: H$_3$O$^+$ [18], and a Pt-foil: H$_2$O [23]. The H$_2$ partial pressure dependence of the H$_3$O$^+$ yield was determined by fitting single data points in a double logarithmic plot. For increasing H$_2$ pressure a highly reactive state appears at $P$(H$_2$) / $P$(O$_2$) = 0.2 (O-side, FIM: bright cross-like structure). Lowering the pressure ratio to = 0.2 establishes hysteresis behavior (H-side, FIM: rather dim, $T$(Pt) = 363 K, $P$(O$_2$) = 5.1 × 10$^{-4}$ mbar, $F$ = 1.5 V/Å). Earlier results for H$_2$O formation on a Pt-foil show similar features ($T$(Pt) = 408 K, $P$(O$_2$) = 220 mbar).

It is well known from experimental and theoretical analyses that hysteresis behavior of reaction yields characterizes a nonlinear kinetics for surface-catalyzed reactions far from thermodynamic equilibrium [23-25]. Nonlinear differential equations (including suitable feedback mechanisms) have been employed for describing the functional dependence of surface coverages of reacting species as a function of space and time. Thus, spatio-temporal oscillations and chemical waves have not only been calculated but also imaged with surface analytical tools probing for example work function changes at the micron scale. It was only recently that EFM [1] and FIM [2-4] studies demonstrated the capability to image such phenomena at higher lateral resolution. We would like to give two examples for these phenomena we have recently analyzed using the energy-resolved ion spectroscopic technique shown in Fig. 1.
At first, we discuss the results of time-resolved probe hole FIM analyses for the $\text{H}_2/\text{O}_2/\text{Pt}$ reaction system (Fig. 6a)). FIM observations of Block, Gorodetskii and Drachsel [7] had already revealed time dependent changes of the brightness in the (001) region of a [001] oriented Pt-tip at selected control parameter. From our kinetic measurements we know that these phenomena can occur on the oxygen side close to the maximum of the $\text{H}_3\text{O}^+$ formation rate. Furthermore, appearance energy spectroscopic investigations had shown that at these particular conditions, the slow $\text{H}_3\text{O}^+$ were the main reaction product [10-11, 18]. These slow $\text{H}_3\text{O}^+$ were most probably formed according to reaction (4) of Fig. 4b), if we neglect other pathways which might have contributed with smaller rates [17]. It was clearly established, that the time dependence of the locally measured slow $\text{H}_3\text{O}^+$ yield (right panel of Fig. 6a)) was synchronized with almost periodic brightness changes of the Pt(001) region appearing as a square of approximately 20 nm side length (FIM in Fig. 6a)) [4,18].

![Figure 6: Dynamics (left: interpretation, middle: probe hole FIM, right: local, mass and energy resolved ion yields).](image)

The second example (Fig. 6b)) shows results obtained for the field driven $\text{H}_2/\text{H}_2\text{O}$ reaction system in the oscillating kinetic regime [10]. When a wave front reached the position of the probe hole, the rate of fast $\text{H}_3\text{O}^+$ increased and the rate of slow $\text{H}_3\text{O}^+$ decreased. The fast $\text{H}_3\text{O}^+$ were formed in accordance with pathway (5) of Fig. 4b), involving chemisorbed hydrogen and field adsorbed water. The observed spatio-temporal behavior can be viewed as a kind of periodic hydrogen titration reaction which is supported by kinetic lattice gas calculations of Kreuzer and Wang reported in reference [10]. In this model, a flux of atomic hydrogen, mostly from the shank of the tip, reacts with apex-adsorbed O, OH (from reaction
channels such as in the sequence (4) of Fig. 4b) thus producing field adsorbed H$_2$O at the apex of the tip. Adsorbed H and H$_2$O finally yield fast H$_3$O$^+$ illustrated in the left panel of Fig. 6b).

Comparisons of the spatio-temporal behavior of the two reaction systems suggested furthermore that the effect of the high electric field on the kinetics of the H$_2$O$_2$ reaction on Pt was relatively moderate. To our knowledge, periodic, spatio-temporal variations of the isothermal water production rate have not been reported on macroscopic Pt single crystals [23]. Gorodetskii et al. [8] concluded that a synergetic effect, produced by the coupling of kinetic properties of adjacent, differently oriented small facets, is a necessary condition for the occurrence of the dynamic phenomena (as in the case of the H$_2$ oxidation reaction on a Pt-tip). Based on their FIM work on the NO/H$_2$/Pt system Voss and Kruse [3] pointed out that reaction-induced morphological changes are a further necessary prerequisite for the occurrence of self-sustained kinetic oscillations. Their observations and conclusions are in line with the appearance of a striped FIM pattern such as in Fig. 6a) revealing reaction induced (reversible) surface-structural changes for the H$_2$/O$_2$/Pt system. To this end, our combined FIM and ion spectroscopic results support the view of Block, Gorodetskii and Drachsel [7] that such a FIM pattern provides an in-situ image of catalytic active sites at the surface.

Conclusions

For the H$_2$O$_2$/Pt and the (field driven) H$_2$/H$_2$O/Pt reaction systems the local yields of product ions, such as H$_3$O$^+$ showed markedly different H$_2$ partial pressure dependencies. These differences and comparisons with earlier experimental and theoretical results suggested that the influence of the applied field (= 1.5 V/Å) on the kinetics of the H$_2$O$_2$/Pt reaction was less pronounced. Most recently H$_2$ pressure dependencies (as presented in section 2) have been measured for H$_2$/O$_2$/Pt revealing different hysteresis behavior using FEM and FIM. This could have been caused by the different facets actually contributing to the measured FE and FI currents, respectively. Other effects of the applied field might also be important, such as the opening of additional surface reaction field desorption pathways during FIM and a field induced strengthening of the H$_2$O-Pt interaction. Further FIM and (probe hole) FEM analyses are certainly desirable. Such experimental efforts accompanied by kinetic calculations for H$_2$/O$_2$/Pt, along the lines already performed for H$_2$/H$_2$O/Pt, could give further insights inasmuch the electrostatic field and field gradients effect FIM observations. At the end we conclude that the field ion microscope can be used for the in-situ imaging of single catalytic active sites; but the effects of the field have to be quantified for every system under study.

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References