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Field Desorption Pathways of Water during the H₂- Oxidation on a Pt Field Emitter

W. Drachsel, C. Wesseling and V. Gorodetskii*

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

** Boreskov Institute of Catalysis, 630090 Novosibirsk, Russia*

Abstract: Using the field ion microscope as a flow reactor the catalytic oxidation of hydrogen by O₂ on Pt has been studied by the ToF coincidence technique. The "imaging ions" consist mainly of H₃O⁺, less H₂O⁺ and to some extent field and coverage sensitive O₂⁺ species. The product ion spectrum qualitatively coincides with that of pure water field desorbed at 300 K. On the oxygen side of the H₂/O₂/Pt system, H₃O⁺ is formed by the field induced disproportionation of two water molecules leaving behind an OH_{ad}.

For the system H₂O/Pt, the observed emission of O₂⁺ during field ionisation is striking in so far as O_{ad} recombination at 300 K is improbable. To clarify the nature of the precursor of this reaction channel a coincidence experiment was performed and a simultaneous emission of O₂⁺ and H₃O⁺ ions from the same site was detected. We propose the following disproportionation for this step: a hydroxyl forms a transition complex with a peroxy-surface species, which then desintegrates into molecular oxygen and hydronium, which emit as O₂⁺ and H₃O⁺ in the field.

During the ongoing hydrogen oxidation this coincidence is also observed on the oxygen side of the reaction; on the hydrogen side of the reaction no coincidence is observed, as in this case the pathway H_{ad} + H₂O⁺_{ad} → H₃O⁺ is predominant.

1. INTRODUCTION

Two aspects prompted us to investigate heterogeneous catalytic reactions in situ by field related methods:

- (i) the field emitter tip appears to be a suitable model of a catalyst grain with respect to size and shape and
- (ii) the direct observation of "reactive sites" on an atomic scale by field ion microscopy (FIM) is feasible as demonstrated recently [1].

Concerning the hydrogen oxidation by O₂ the latter point becomes even more advantageous as the reaction product water will field-desorb as H₃O⁺. Thus, the field ion image during the ongoing reaction directly displays a map of the local reaction rate, while additional information about the surface coverage of the educts can be extracted from the corresponding field electron micrographs [2].

The reaction kinetics of the hydrogen oxidation on Pt under field conditions at applied field strenghts of 1.5 V/Å in the FIM can involve isothermal oscillations at distinct control parameters [2, 3]. The product water is field-desorbed mainly as H₃O⁺ [4]. This desorption channel under field conditions releases oxygen from stoichiometric reasons on the oxygen side of the reaction. This becomes even more obvious if the field desorption (FD) spectrum of pure water is analyzed [5, 6]. One concern of this contribution is to uncover the field induced pathways for oxygen formation. Basic information on the energetics for the FD-channels are given by the work of Ernst et al., investigating the systems H₂/H₂O and H₂/O₂ on Pt by measuring the appearance energy of the product ions [4, 7].

In present experimental work we looked alternatively for the correlated formation of product field ions for H₂/O₂ and H₂O on Pt to deduce field induced reaction pathways and evidence for intermediates of the reaction.

2. PREVIOUS WORK

Since 1822, when Döbereiner discovered the cold combustion of H_2 by dispersed Pt, the kinetics of the hydrogen-oxygen reaction has been studied by many groups. A review is given by Norton [8]. There is a general agreement that the reaction follows a Langmuir-Hinshelwood mechanism according to the steps (1) to (3) (* means an empty site).

The reaction starts even above 120 K [9] on Pt, which is well below the desorption temperature of H_2O^+ at 180 K. At higher temperatures the water, after formation, will desorb from an equilibrated state, as indicated by the cosine-angular distribution of the desorbing molecules [10].

The water synthesis on Pt has been studied in the limit of low coverages [11] and also in the limit of high coverages [12], where the interaction of adjacent adspecies shifts the activation energies to lower values.

Collective phenomena are also observed in the FIM: during isothermal oscillations of the reaction rate the propagation of reaction diffusion fronts across adjacent crystal planes becomes visible [2]. These fronts are distinguished by high rates of water synthesis, expressed by a high H_3O^+ emission in the presence of a field. At the so called oxygen side of the reaction ($\Theta(O_{ad}) > \Theta(H_{ad})$) [19] the hydronium ions are formed by the reaction scheme:

The hydroxyls will then further react according to step (2) or (3), forming oxygen species.

In the case of the FD of water the same reaction steps are relevant. The formation of an O_{ad} -layer on Pt is expected according to the FD of H_3O^+ following reaction (4) and successive step (3). After having applied a field $> 1.2 \text{ V/\AA}$ at 300 K during the exposure of the tip to H_2O_{gas} this was verified by titration with H_2 in the field electron and field ion microscope [13].

The emission of O_2^+ during field desorption of pure water from Pt at 300 K [6], however, cannot be explained by recombination of thermally equilibrated O_{ad} -species. If now equation (4) is formulated in a stoichiometric way (5), a correlated emission of H_3O^+ and O_2^+ might be expected (5a).

The alternative formation of H_3O^+ by protonation as observed for the hydrogen side of the reaction ($\Theta(O_{ad}) < \Theta(H_{ad})$) will be discussed in detail by Sieben et al. in this volume [19].

3. EXPERIMENTAL

The details of the experimental setup are given in [14]. In short: The FI microscope with probe hole mass and correlation analysis was used. The purified gases were introduced at a constant flow. The pressure control system kept the partial pressures of H_2 and O_2 or H_2O within 1%, the temperature of the (001) oriented Pt field emitter was controlled within 0.1 K. The Pt emitter tip was cleaned by field evaporation and characterized by neon imaging (Fig. 1a). During the reaction (Fig. 1b), the field ion image was recorded by a CCD video camera, the chemical identification of field-desorbed ions passing the probe hole can be achieved by mass separation (Wien filter, $m/\Delta m \approx 10$) [15]. Surface species were also field desorbed by pulsed laser irradiation (pulse width 10 ns) and mass analyzed by time of flight measurements [14]. The time correlation of emitted ions was measured with a fast clock. This clock was started by the arrival of a light ion and stopped by the arrival of the next heavy one [16]. To achieve a better signal to noise ratio the ions were mass separated by the Wien filter and separately detected. In this mode the laser is not active.

Figure 1: FI image of the (100) Pt emitter, white dot in black center: probe hole
 (a) neon, 78 K (b) during H_2/O_2 -reaction, $T = 400\text{ K}$, $F = 1.2\text{ V/\AA}$

4. RESULTS AND DISCUSSIONS

According to the reaction (4) followed by step (3) we have searched for a correlated emission of ion pairs like: H_3O^+ , O^+ or H_2O^+ , O^+ or the two water species H_3O^+ , H_2O^+ , for both reaction systems: $\text{H}_2\text{O}/\text{Pt}$ and $\text{H}_2/\text{O}_2/\text{Pt}$. It turned out that all these emission events were statistically independent of each other at a time scale of ns.

The H_3O^+ and O_2^+ emission, however, was correlated for $\text{H}_2\text{O}/\text{Pt}$ (Fig. 2a). The sharp peak at 667.2 ns on top of randomized pair events exactly corresponds with the difference of flight times (Δt_f) of these ions. The absolute flight times t_f are known from pulsed laser field desorption experiments.

Doing the same measurement during ongoing H_2 oxidation, the same correlation (Fig. 2b) is observed at the oxygen side of the reaction. The tailing of the correlation peak is less developed, and a small additional peak can be identified as the simultaneous emission of H_3O^+ and HO_2^+ . Within the experimental error the coincidence of emission of H_3O^+ and O_2^+ occurs from the selected site within less than 100 ps. Therefore, we conclude that these H_3O^+ and O_2^+ species are originating from the same transition complex. To get an indication of its nature, we analysed the pulsed laser field desorption spectrum, as obtained during H_2/O_2 reaction (Fig. 3).

The minority species are identified as OH^+ , HO_2^+ and H_2O_2^+ , which were also detected in the water FD spectrum by Schmidt [6]. The peroxy complex H_2O_2 as an intermediate in H_2 oxidation has been already proposed by Verheij et al. [17] who investigated the reaction on Pt(111) by modulated molecular beam transient spectroscopy.

Field adsorbed water agglomerates even at room temperature at the surface, as expressed by the emission of protonated water cluster ions as a minority route, and as well by the formation of H_3O^+ from two water molecules in step (4) and not by the energetically more favoured direct protonation, as is prevailing on the hydrogen side of the reaction or for the $\text{H}_2/\text{H}_2\text{O}$ system [4]. From these findings we conclude that the hydroxyls are formed in close vicinity, and that the peroxy complex emerges from two OH_{ad} . We explain the simultaneous emission of H_3O^+ and O_2^+ for the studied reaction systems by the following disproportionation:

This should not be misinterpreted as a triple collision (H_2O is also formed in successive steps from H_{ad} , H_{ad} and O_{ad}). By changing the probe hole position, we found out that only the reactive sites (bright in FIM

image) emitted H_3O^+ and O_2^+ simultaneously; the nature of these sites is still obscure. If the reaction switches to the hydrogen side (by applying higher hydrogen pressures), no correlation is detected any more, in agreement with the observed protonation of H_2O by H as discussed in Ref. [19].

Resuming the interpretation of the simultaneous ion emission events, a formation of O_2^+ from two hot O_{ad} may be conceived alternatively. Hot means that a fraction of the reaction enthalpy is released as kinetic energy of O_{ad} . For FD of water, O_{ad} can be exclusively produced by step (3). An H_2O may react immediately with a neighbouring one according to reaction (4) involving FD of H_3O^+ . The OH_{ad} may be attached to an O_{ad} to form the minority species HO_2^+ as observed in Fig. 2b. Raising the temperature to 400 K for the $\text{H}_2/\text{O}_2/\text{Pt}$ system the emission of ion pairs H_3O^+ , HO_2^+ is also detected at low intensities. If O_2^+ would emerge from fragmentation of HO_2^+ , one cannot explain the observability of HO_2^+ in the coincidence spectrum appearing only above 400 K.

A direct formation of O_2^+ from hot O_{ad} with a minimum of steps can be conceived. Two $\text{H}_2\text{O}_{\text{ad}}$ are produced adjacently according (3) from 4 hydroxyls, and then the O_{ad} recombine. At the same instant H_3O^+ could be formed by the disproportionation (4). If H_3O^+ and O_2^+ were formed in individual steps each, then the tailing of the coincidence would be symmetric in time. But only a delay for O_2^+ emission is observed. If this model is correct the H_2O diffusion to form the water dimer and the disproportionation in sequence would be very fast compared to the recombination of the two hot O_{ad} within the time scale of some hundred picoseconds.

It has to be stressed that the correlated O_2^+ formation is only a minority route, more than 90% of the O_2^+ current is uncorrelated as is derived from an analysis of the statistical background in Fig. 2a. For these ions a formation from thermally equilibrated O_{ad} is not possible at these temperatures, but as indicated before,

"hot O" species according to step (3) may be conceived. At least during H_2/O_2 reaction, the sum of the emitted H_2O^+ appear to carry up to 0.6 eV translational surplus energy with it, as the appearance energy data show [7].

Figure 3: Pulsed laser FD during reaction
 $P(\text{O}_2) = 2.2 \cdot 10^{-4}$ mbar
 $P(\text{H}_2) = 1.01 \cdot 10^{-4}$ mbar
 $T = 400$ K, $U_{\text{tip}} = 8.2$ kV

During the H_2/O_2 -reaction O_2^+ is also formed directly by field ionisation with a rate depending sensitively on the applied field. From the CO/O_2 -system [1] we know that oxygen is preferentially field ionised above oxygen-covered Pt, explained by a resonance effect [18].

The effect is even more predominant during the H_2 -oxidation due to consumption of the impinging O_2 . At a high reaction rate the surface offers more empty sites for dissociative adsorption whereas at low reactivity the field ionisation probability is increased for repelling oxygen. This "anticorrelation" of H_3O^+ product ion rate and O_2^+ current can be seen in Fig. 4.

Figure 4: Rate oscillations by temperature modulation
 $p(\text{O}_2) = 4.3 \cdot 10^{-4}$ mbar
 $p(\text{H}_2) = 1.3 \cdot 10^{-4}$ mbar
 $F_{\text{tip}} = 1.2$ V/Å

In the instable range of the reaction, the temperature was modulated sinusoidally by a small increment of 2 K around 400 K, which forced the reaction rate to oscillate in phase. At a low local production rate the corresponding local oxygen rate is higher (second trace) as during the time of high chemical activity.

In conclusion, the reaction pathway leading to an O_2^+ -abundance in the field ion spectrum of the H_2O -Pt and the O_2/H_2 -Pt system are a consequence of the preferential H_3O^+ emission under field conditions due to the proportionation reaction of two adjacent H_2O molecules. A peroxy intermediate or a recombination of non-equilibrated O species as precursors are proposed.

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