

## 論文の内容の要旨 Thesis Summary

Title of Dissertation: A study on *in-situ* observation of oxidation reaction at a low temperature by Field Ion Microscopy and Atom Probe

論文題目: (低温における酸化反応の電界イオン顕微鏡とアトムプローブによるその場観察に関する研究)

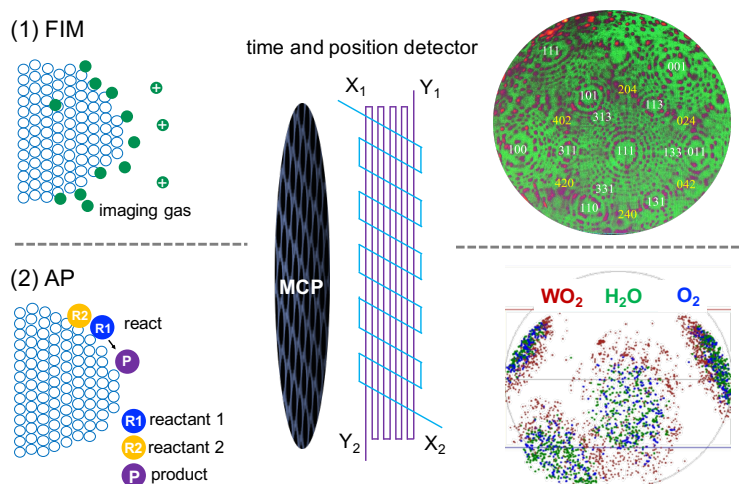
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### 1. Introduction

APM is the only material analysis technique providing 2D and 3D mapping of chemical composition and structure at the atomic scale, which offers a compelling and unique insights into the way material behavior. In despite of the prosperity of the application of APM in material analysis, the studies of surface chemistry, especially an on-going reaction process by APT has seldomly been reported. And the AP sample can be considered as a well-defined model of a single catalyst nanoparticle, which allows to bridge the “material gap”. Besides, to understand the process of heterogeneous catalysis in a microscopic or atomic way is of great interest in surface science, which can elucidate the reaction mechanism and lead to efficient and cheaper catalysts. The emphasis of this research focuses on *in-situ* observation of oxidation reaction at an atomic level by APM, which can be regarded as a new function and application of APM.

Experiments were carried out by means of FIM and AP, which were originally designed and developed by our lab and have been described in detail elsewhere. As shown in the Fig.1, the specific surface structure of sample surface can be gained by an FIM image. As the reaction taking place on the sample surface, the 2D distribution information of the reactants and products on the sample surface can be obtained by AP.

To achieve this goal, a proper and simple reaction, hydrogen oxidation reaction catalyzed by Pt, was chosen as a tentative model on the first try in AP analysis. Due to the operation conditions during AP analysis, the reaction surface is subjected to a high electric field and the pressure of reactant gas should be kept in vacuum condition, which is different from the real reaction conditions. Therefore, the influence of the EF variation



**Fig.1** FIM images of clean specimens were taken under helium gas atmosphere ( $10^{-5}$  Pa) at 60 K. In AP analysis, the chemical composition distribution on sample surface can be obtained.

over specimen surface on active site identification should be explored. Besides, during AP experiment, the effects of the laser/voltage pulse, the surface corrosion caused by the reaction et al. also need to be investigated.

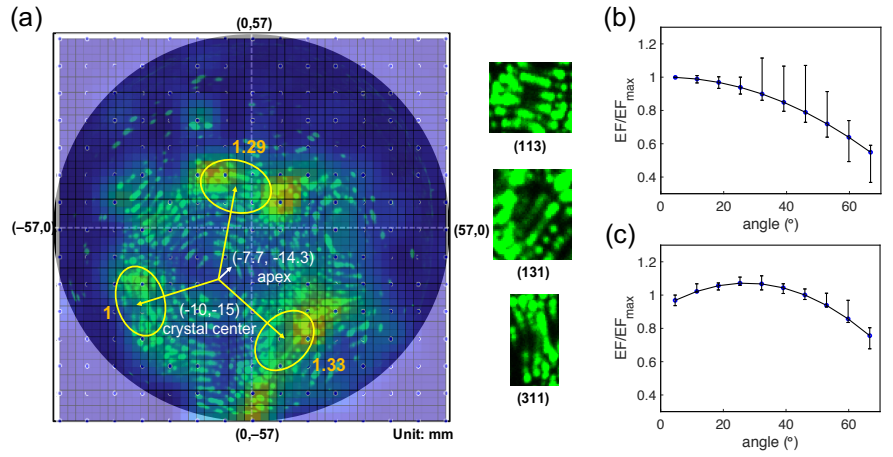
### 3. EF distribution on sample surface

To evaluate the EF effects on active sites identification, the author developed an approach to experimentally calculate the EF distribution on a nano-sized sample surface by comparing the normalized  $H^+$  ion intensity in AP analysis. To determine the EF distribution on a real sample surface, first we located the sample apex of the sample surface by comparing the ion intensity of the FIM image, as shown in Fig.2a. Next, the contour maps with various  $EF_{max}$  showing the intensity of the  $H^+$  was obtained. Finally, a plot of relative EF with respect to the emitting angle can be extracted from the contour maps (Fig.2b). This fast and non-destructive method could be employed to determine the appropriate EF for accurate AP analysis.

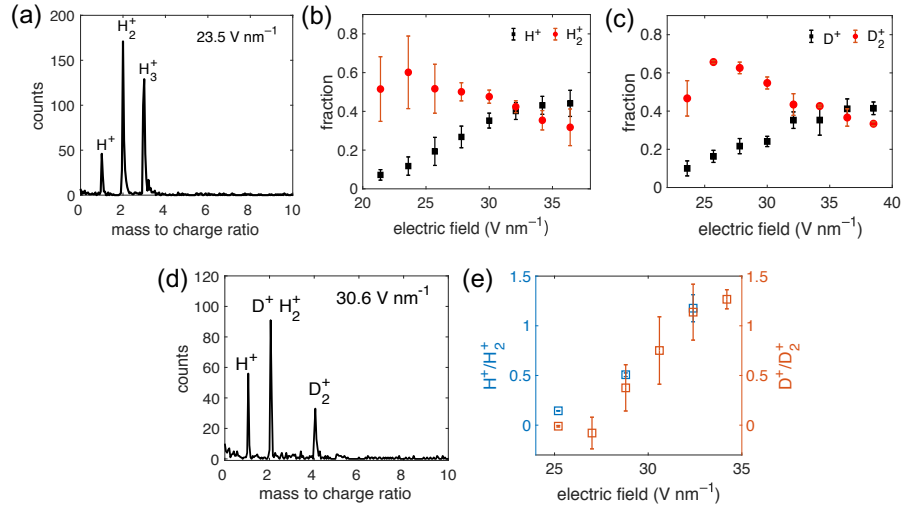
In addition, the specimen emitter evolves to be an EF-constant surface except the outer boundary, after sufficient field evaporation when the emitter develops into an equilibrium end shape (Fig.2c). As a result, the ion intensity of the 2D mapping of such surface can exactly reflect the real distribution of the chemical composition on the emitter.

### 4. Quantitative analysis of residual hydrogen (H) in AP analysis

This part explores the behaviour of residual hydrogen on AP sample surface in ultra-high vacuum. The residual hydrogen in AP was studied under high-vacuum condition ( $2.0 \times 10^{-8}$  Pa). Totally,  $H^+$ ,  $H_2^+$  and  $H_3^+$  ions were detected (Fig.3a). Upon increasing EF, the relative intensity of  $H^+$  dramatically increased, while the relative ratio of  $H_2^+$  ions decreased (Fig.3b). Isotope-labelling experiment by introducing  $D_2$  (Pa) showed the  $D^+$  and  $D_2^+$  signals. Increasing EF led to a higher intensity of  $D^+$  and a lower  $D_2^+$  as shown in Fig.3c, in accordance with the  $H^+$  and  $H_2^+$  fraction alterations measured under base pressure ( $2.0 \times 10^{-8}$  Pa). Three signals of 1 Da, 2 Da, and 4 Da with comparable intensity were observed by reducing the  $D_2$  pressure to  $6.0 \times 10^{-8}$  Pa, in which the 2 Da signal is composed of both  $H_2^+$  and  $D^+$  ions (Fig. 3d). The proportions of  $H^+/H_2^+$  and  $D^+/D_2^+$  against EF were plotted, respectively, by separating the 2 Da signal into  $H_2^+$  and  $D^+$  (Fig.3e), showing an almost superimposable variation trends. These results indicated



**Fig.2 (a)** An FIM image of the Pt sample laid on a coordinate system. The relative EF as a function of emitting angle on (b) a fresh sample and (c) a fully evaporated sample.



**Fig. 3. (a)** Mass spectrum of residual hydrogen (Pt, 60 K,  $10^{-8}$  Pa). A plot of (b) residual hydrogen signal fractions and (c) deuterium (Pt, 60 K,  $D_2$  pressure:  $2.0 \times 10^{-6}$  Pa) signal fractions with respect to electric field from  $21.4 \text{ V nm}^{-1}$  to  $40 \text{ V nm}^{-1}$ . (d) Mass spectrum of residual hydrogen and deuterium with  $D_2$  gas pressure of  $6.0 \times 10^{-8}$  Pa. (e) A plot of the variation of the intensity ratios of  $H^+/H_2^+$  and  $D^+/D_2^+$  against electric field (Pt, 60 K,  $D_2$  pressure:  $6.0 \times 10^{-8}$  Pa).

that the residual H detected in AP measurement originates from the H<sub>2</sub> gas adsorbed on Pt surface rather than the hydrogen in the Pt tip.

The adsorption and accumulation of H<sub>2</sub> gas on the AP sample surface is interpreted by dipole-dipole interaction when the sample is subjected to a high electric field and the binding energy of H<sub>2</sub> gas molecule on Pt metal surface is proportionally related to electric field, suggesting that H<sub>2</sub> molecules diffuse along the shank to sample apex due to EF gradient, which considerably enhances the H<sub>2</sub> molecule concentration on the top of sample surface even in extremely high vacuum.

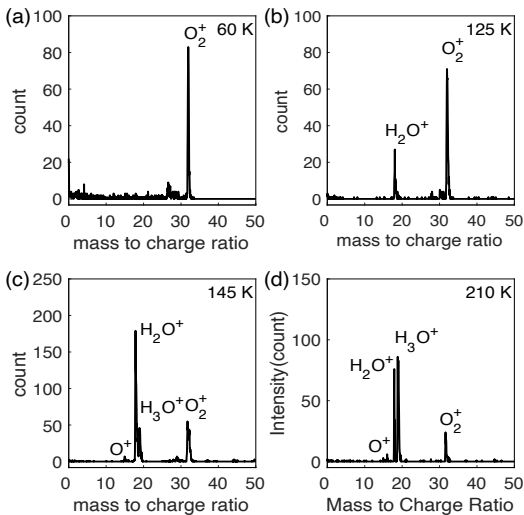
As the mechanism of the formation and desorption of H<sup>+</sup>, H<sub>2</sub><sup>+</sup> and H<sub>3</sub><sup>+</sup> on the Pt surface, the formation of H<sub>2</sub><sup>+</sup> (D<sub>2</sub><sup>+</sup>) ions is attributed to H<sub>2</sub> (D<sub>2</sub>) gas desorption triggered by a thermally activated process. Although H<sub>3</sub> (D<sub>3</sub>) molecules are unstable in free space, they could be stabilized in the presence of a high electric field. The formation of triatomic cation thereby can be expressed by  $H_2 + H \rightarrow H_3 \rightarrow H_3^+$ , implying the coexistence of molecules H<sub>2</sub>(D<sub>2</sub>) and atoms H(D) on sample surface. The author infers the formation of H<sup>+</sup> (D<sup>+</sup>) ions is caused by the desorption of the strongly adsorbed H(D) atoms, generated from the dissociation of H<sub>2</sub> (D<sub>2</sub>) on the Pt surface.

### 5. In-situ observation of hydrogen oxidation reaction on Pt surface

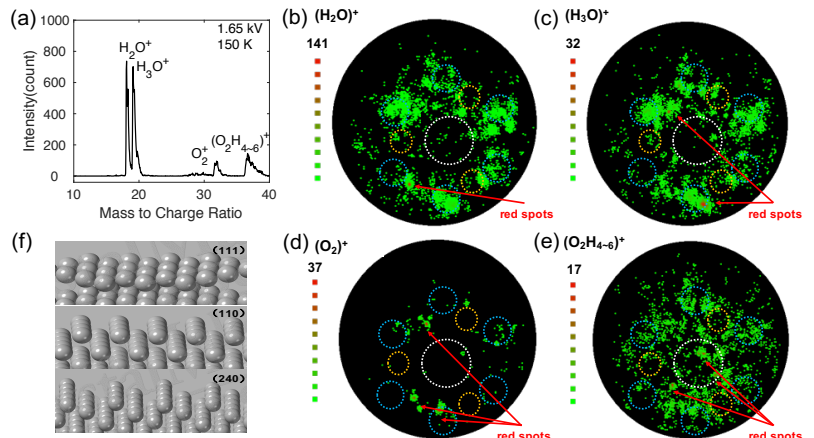
In light of the conclusion drawn above, the author studies the reaction of O<sub>2</sub> with residual H<sub>2</sub> on the Pt surface by only introducing O<sub>2</sub> gas (10<sup>-5</sup> Pa) to the chamber. The AP was employed to *in-situ* observe the on-going oxidation reaction at temperatures from 60 K to 300 K.

At 60 K, the signal of O<sub>2</sub><sup>+</sup> was solely detected on the Pt surface without the formation of H<sub>2</sub>O as exhibited in Fig.4a. When the temperature increased to 125 K, the H<sub>2</sub>O<sup>+</sup> peak appeared (Fig.4b). Upon further increasing the temperature, the signal of H<sub>3</sub>O<sup>+</sup> and O<sup>+</sup> signals emerged, suggesting the protonation of H<sub>2</sub>O species and the dissociation of O<sub>2</sub>, respectively (Fig.4c). Apparently, H<sub>2</sub>O<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> were the products of the reaction between oxygen and residual H on the Pt surface. The intensity of the products, H<sub>2</sub>O<sup>+</sup> and H<sub>3</sub>O<sup>+</sup> increased significantly from 145 K to 210 K, compared with the reactant O<sub>2</sub><sup>+</sup> (Figs.4c and 4d), resulting from reaction accelerating as the temperature increased. The 2D mappings of the chemical species distribution on the Pt surface at 150 K were also studied. Four signals of H<sub>2</sub>O<sup>+</sup>, H<sub>3</sub>O<sup>+</sup>, O<sub>2</sub><sup>+</sup> and O<sub>2</sub>H<sub>4-6</sub><sup>+</sup> were obtained as shown in Fig.5. It is found that O<sub>2</sub> species (O<sub>2</sub><sup>+</sup> and O<sub>2</sub>H<sub>4-6</sub><sup>+</sup>) were adsorbed evenly on the surface and there was almost no formation of H<sub>2</sub>O in the {111} planes. The active sites for the H<sub>2</sub>O generation were on the {240} and {113} planes, where the red spots were spread. In addition, H<sub>3</sub>O<sup>+</sup> was sparsely distributed in the {111} planes, but clustered in the {240} and {113} planes. The author attributed the particular reactivity of the planes surrounding the {111} plane to their large specific surface area. Fig.5f shows the atomic structures of the {240} and {111} planes, based on which the author speculated that the adsorption of molecular O<sub>2</sub> and the dissociation of O<sub>2</sub> to atomic O are stronger for the more corrugated planes.

Accordingly, a possible reaction process was proposed that O<sub>2</sub> is adsorbed on the



**Fig. 4** Mass Spectrum of the interaction of O<sub>2</sub> (10<sup>-5</sup> Pa) and H species on the Pt tip by pulse voltage at different temperature.



**Fig. 5** (a) Mass spectrum of the reaction between O<sub>2</sub> (10<sup>-5</sup> Pa) and H species on the Pt tip by pulse voltage at 150 K. 2D distribution images of (b) H<sub>2</sub>O<sup>+</sup>, (c) H<sub>3</sub>O<sup>+</sup>, (d) O<sub>2</sub><sup>+</sup> and (e) O<sub>2</sub>H<sub>4-6</sub><sup>+</sup>. (f) Surface corrugation of the Pt (111) surface. (b) Surface corrugation of the Pt (111), (101) and (240) planes. The white dash ring, blue dash rings and orange dash rings in b) represent the {111}, {240} and {113} planes, respectively.

Pt surface and further dissociates to O atoms, which will react with the residual H as the temperature is higher than 125 K.

The absence of static voltage and the thermal power of laser pulse could decrease the local concentration of residual H<sub>2</sub> gas on Pt surface, which declined the speed of the hydrogen oxidation reaction.

The AP specimen surface was corrode by the hydrogen oxidation reaction. Pt was oxidized as the temperature increased. Various Pt-O complex ions could be detected, which in reverse promoted the hydrogen oxidation process.

## 6. *In-situ* observation of hydrogen oxidation reaction on W and PtPd alloy surfaces

The author investigated the O<sub>2</sub> and residual H reaction on the W metal and PtPd alloy surface. Upon exposing the nanoscale W metal and PtPd alloy surface to the O<sub>2</sub> atmosphere (10<sup>-5</sup> Pa), the lowest temperatures to trigger hydrogen oxidation reaction on PtPd and W surface were 106 K and 135 K, respectively. As shown in Fig.6, comparing to 125 K on Pt metal, the PtPd was proved to be more active for hydrogen oxidation reaction and W was less active. The oxidation of PtPd and W surface was also be observed, the oxidized metal can promote the hydrogen oxidation reaction.

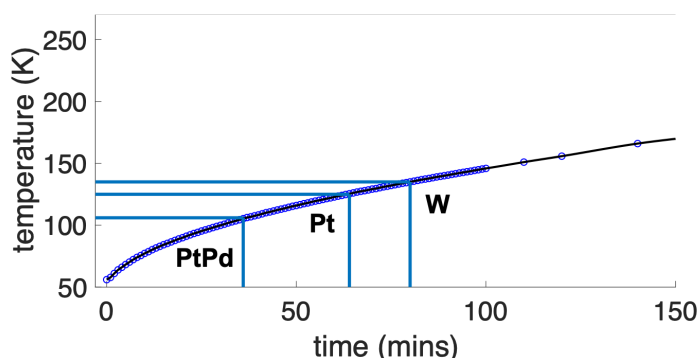


Fig. 6 The temperatures of hydrogen oxidation reaction taking place on PtPd (106 K), Pt (125 K) and W (135 K) surface.

## Conclusion

In conclusion, a new surface analysis method combined with FIM and AP has been successfully developed to *in-situ* observe catalytic surface reactions for the first time. The atomic-level surface structure obtained by FIM and chemical composition-related information obtained by AP allow us to study on-going catalytic reactions with atomic lateral resolution.

This surface analysis method may pave an avenue for exploring the heterogenous reaction with a nanometric lateral resolution. The experiment data leads to a new insight for surface reaction mechanism and theory, which partially narrow the gap between surface analysis approaches and catalysis/reaction.

In despite of this initial achievement, FIM and AP ought to challenge more complicated heterogeneous reaction for a vast application prospect. Besides, some inevitable problems cannot be ignored to study an on-going reaction by APM. The reaction can only be investigated in vacuum condition, which is a niche area for all surface analysis techniques. And high temperature will decrease the mass and spatial resolution. Other characterization methods, can be devoted for cross-references to investigate a reaction with comprehensive perspectives.