

Paper

The Interaction of O₂ and Residual H on Pt Surface Studied by Field Ion Microscopy and *in-situ* Surface Atom Probe

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The reaction of O₂ and residual H over platinum in high vacuum, at temperatures from 60 K to room temperature, was studied by using field-evaporation techniques, including field ion microscopy (FIM) and atom probe (AP), which enabled *in-situ* analysis of surface structure and chemical composition analysis at atomic scale. This study aimed to obtain detailed information about the reaction of O₂ and residual H on a Pt surface. Hydrogen is a near-ubiquitous element and field-evaporation technique can be used to study the residual H in high vacuum conditions. Three H species on a Pt surface were observed H⁺, H₂⁺, and H₃⁺ in high vacuum (10⁻⁸ Pa). Upon the exposure of the nanoscale Pt surface to O₂ atmosphere (10⁻⁵ Pa), H₂O was produced for the temperatures above 135 K. According to the peak intensity ratio between H_{2.3}O⁺ and O₂ during the warming up process, H₂ surface diffusion along the shank and the bulk H diffusion were faster at higher temperatures. In addition, we found that the planes surrounding the {111} plane, such as the {240} plane, were more active owing to their particularly rough atomic corrugation.

1. Introduction

Field ion microscopy (FIM) and Atom Probe (AP) are typical instruments in field-evaporation technology, which can provide real-time atomic-level information about the surface structure and local chemical composition of the analyzed sample. In the FIM analysis, by applying a high electric field on a sample tip (diameter < 100 nm), the imaging gas is ionized at the steps and kinks of the surface, which is accelerated, and finally travels to a position sensitive detector (PSD). The AP analysis, composed of a laser/voltage pulser, a time-of-flight mass spectrometer and a traditional FIM, is capable of reconstructing elemental composition mapping of a sample [1].

In the FIM and AP analyses, the tip surface can be considered as a well-defined model of a single catalyst nanoparticle, owing to the coexistence of a considerable number of small planes and facets separated by steps [2,3], which allowss the possibility to bridge the “material gap” between the analyzed sample and real

catalyst, where different crystal planes are exposed to the reactant gas. Field-evaporation technology, therefore, has attracted significant attention as a tool for navigating the surface structure and reaction dynamics. To develop more efficient catalysts, it is indispensable to be able to monitor atomic events on the surfaces of catalyst materials under reaction conditions, for developing a deep understanding of the reaction mechanisms, kinetics, and active sites of the catalysts at atomic level. For more than a decade, various heterogeneous catalysis reactions have been extensively studied. Gorodetskii revealed the bistability and oscillation phenomenon of CO oxidation, the H₂ oxidation reactions on a Pt surface at relatively high temperatures (above 300 K) [3-5]. Bocarme *et al.* studied water formation and NO and NO₂ hydrogenation on noble metals and alloys, for temperatures ranging from 300 K to 500 K, using FEM, FIM, and pulse field desorption mass spectrometry (PFDMS) [6-8]. Nieuwenhuys' group explored O₂, CO, NO, and H₂ behaviors for group VIII metals [9,10]. These studies

significantly contributed to establishing the intrinsic interrelation between the reaction mechanism and surface structure.

Chemical composition analysis, however, was addressed in these studies using probe holes, suggesting that only a small and limited surface area of the sample can be analyzed at one specific time point. However, our AP can identify the chemical species on a whole-view surface area at one specific time point [11]. As shown in Figure 1, our own developed FIM-AP can obtain the information about the surface structure, chemical composition distribution, and three-dimensional (3D) structure of the sample tip. Moreover, the previous research paid less attention to reactions that occur in cryogenic conditions. In addition, H₂ is the dominant gas present in a high-vacuum chamber (10⁻⁸ Pa), and can be chemisorbed and easily dissociated and stored in the metal bulk [12]. The H_{ad} reservoir on the metal surface is not only in the apex region but also in the shank [7]. The residual H in the analysis chamber may participate in or influence the oxidation reaction on the metal tip. Accordingly, the behavior of the residual H on the metal tip during the oxidation process merits some studies.

Herein, we reported the *in-situ* analysis of the chemical composition and surface structure of the reaction between O₂ and the residual H on a Pt surface using FIM and AP, for different temperature conditions (60 K to 300 K). The products of the reaction and the factors affecting the reaction were investigated in detail.

2. Experiment

Experiments were performed by means of FIM and AP,

which were developed by our lab and have been described in detail elsewhere [11]. The machine was equipped with a femtosecond pulse laser (532 nm, 300 fs, 2.5 nJ/pulse) and a direct current (DC) high-voltage pulse (width < 100 ns, repetition= 1kHz). The pulse fraction was ~10% ~30% during the analysis. The entire experiment was performed in the pulse voltage mode except residual H₂, which can be detected only using a pulse laser on a Pt surface at 10⁻⁸ Pa. The same results have been published elsewhere [13], and the phenomenon occurred probably owing to a strong field-induced dipole-dipole binding energy between hydrogen and the Pt surface [14]. The surface structure of the sample tip was observed by FIM. The Chemical composition of the entire surface can be analyzed at the same time by *in-situ* AP for an ongoing surface reaction. With this surface AP, the detected ions could serve as imaging species and information about the atoms and molecules participating in the reaction could be collected.

Platinum tips were prepared as follows. A thin Pt wire (Nilaco, φ = 0.1 mm, 99.99%) was electro-polished in a saturated CaCl₂ solution to obtain a 2-micrometer-diameter Pt tip. Then, the etched Pt tip was annular milled by focused ion beam scanning electron microscope (FIB-SEM, SII Nanotechnology Inc, SMI-3050 SE) with a gallium liquid metal ion source (LMIS). The diameter of the sample tip should be below 100 nm, and this was confirmed by TEM (JEOL, JEM1010). The tip surface was usually cleaned up by cycles of field evaporation, until observing a clean FIM image. Oxygen (O₂) and helium (He) (Takachiho, purity

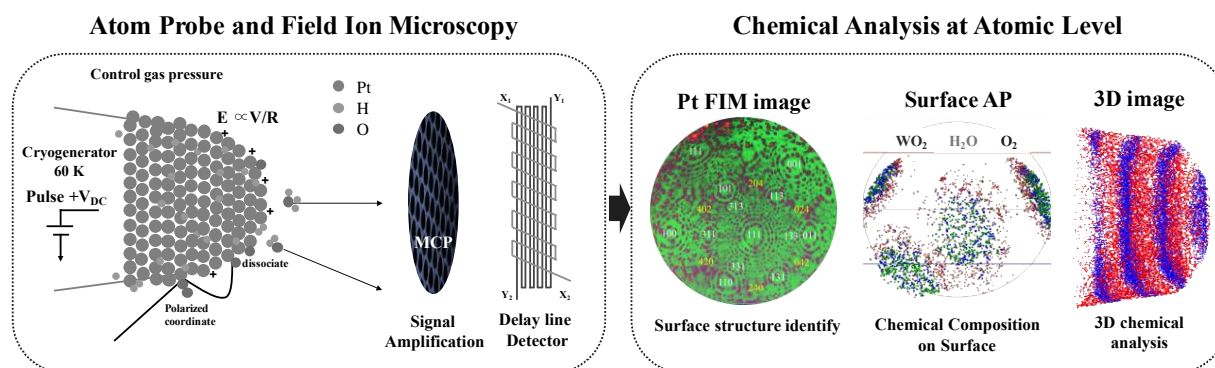


Fig. 1. Left: schematic diagram of FIM and AP. Right: FIM image obtained by image gas field ionization; chemical distribution obtained by surface components field desorption; 3D structure obtained by sample tip field evaporation. (color online)

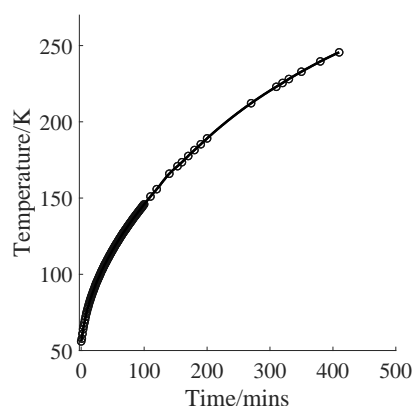


Fig. 2. Sample holder temperature as a function of the time since turning off the cryogenerator.

99.99%) were used without further purification.

The experiments were performed as follows. FIM images of clean tip specimens were taken in the helium gas at 60 K. Surface reactions were studied using an *in-situ* AP at the oxygen pressure of 10^{-5} Pa and at temperatures ranging from 60 K to 300 K. For all the experiments, no H₂ gas was introduced into the chamber. A reaction at the temperature of interest was monitored by implementing the experiment at the specific time after turning off the cryogenerator. The temperature of the sample holder as a function of time is shown in Figure 2.

3. Results and discussion

3.1 FIM results

An FIM image of a Pt tip prepared as described in the experimental section is shown in Figure 3. The tip was imaged in helium at 60 K with a static voltage 8.6 kV (the field strength around of 44 V nm^{-1}), after cleaning

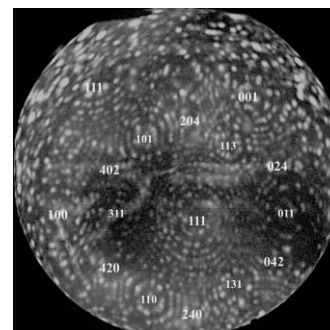


Fig. 3. Field ion micrograph of the Pt surface, imaged under helium gas (10^{-5} Pa) at 60 K. The radius of curvature was ~ 40 nm.

the tip by cycles of evaporation. The radius of curvature was estimated to be ~ 40 nm by counting the number of rings between the (111) and (131) planes [15].

3.2 Hydrogen species on the specimen tip

The detection of H species on the Pt surface under a high vacuum condition (10^{-8} Pa) and low temperature (60 K) condition was achieved using a pulse laser. Figure 4 shows the mass spectra of H species for different electric field. The signals of H₂⁺ and H₃⁺ appeared (Fig. 4a) at a relatively low electric field of 20 V nm^{-1} . As electric field increased, H⁺ species was detected (Figs. 4b and 4c). Note also that, H₂⁺ was observed as dominant species. These results were in consistent with the observation by E. W. Muller that H⁺ was formed on a tip surface, in a strong electric field [16]. We infer that there are two major hydrogen sources for the detected H species: residual H₂ gas in the chamber under a high-vacuum

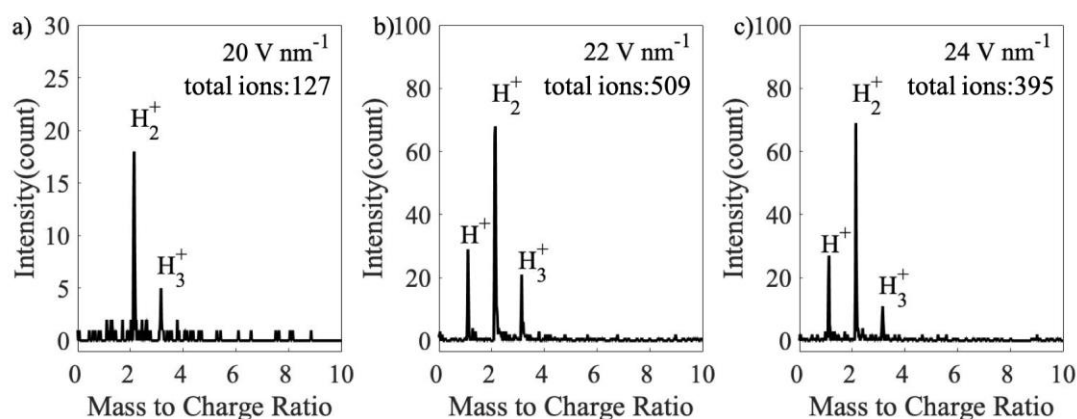


Fig. 4. Mass Spectrum of residual H acquired from the 60 K Pt surface in high vacuum (10^{-8} Pa) by pulse laser (pulse energy was constant at 2.5 nJ/pulse). Evaluated experimental conditions: (a) static field $\sim 20 \text{ V nm}^{-1}$; (b) static field $\sim 22 \text{ V nm}^{-1}$; (c) static field $\sim 24 \text{ V nm}^{-1}$.

condition and the hydrogen atoms/molecules stored in the metal tip. The formation of H⁺ can be ascribed to the dissociation of the primarily formed H₂⁺ on the Pt surface into H⁺ and a H atom, or the ionization of H atoms evaporated from the tip [17]. The formation of H₃⁺ presumably arose from the reaction between H₂ and chemisorbed H⁺ species on the Pt surface.

3.3 Effects on H₂O formation

O₂ gas (10⁻⁵ Pa) was introduced to the chamber to study the reaction of O₂ with H species on the Pt surface. At 60 K, the signal of O₂⁺ was solely detected on the Pt surface without the formation of H₂O (Fig. 5a). When the temperature increased to 135 K, the H₂O⁺ peak appeared as shown in Figure 5b. Upon further increasing the temperature, the signal of H₃O⁺ and O⁺ signals emerged, suggesting the protonation of H₂O species and the dissociation of O₂, respectively. Apparently, H₂O⁺ and H₃O⁺ were the products of the reaction between oxygen and residual H on the Pt surface. These results suggest that an appropriate high temperature (135 K for the Pt

tip) is essential for the formation of H₂O.

The intensity of the products, H₂O⁺ and H₃O⁺ increased significantly from 145 K to 210 K, compared with the reactant O₂⁺ (Figs.5c and 5d), which can be explained as follows: (1) the reaction accelerated as the temperature increased with sufficient H and O supply; (2) the release of H atoms/molecules in the Pt tip was facilitated by increasing the temperature.

Next, surface AP was conducted to analyze the chemical species distribution on the metal surface. Three peaks, H₂O⁺, H₃O⁺, and O₂⁺, were clearly observed in the mass spectrum (Fig.6a) at 150 K. The distributions of H₂O⁺, H₃O⁺, and O₂⁺ on the Pt surface are shown in Figures 6b, 6c and 6d, respectively. No target ions were evaporated from the black area. Generally, the green color captures the distribution of those ions that were locally evaporated from the Pt surface during the detection duration. Several red spots imply that the intensity of the target ion is extremely high at those points. This could be explained as follows. The evaporation rate of the process obeys the Arrhenius law

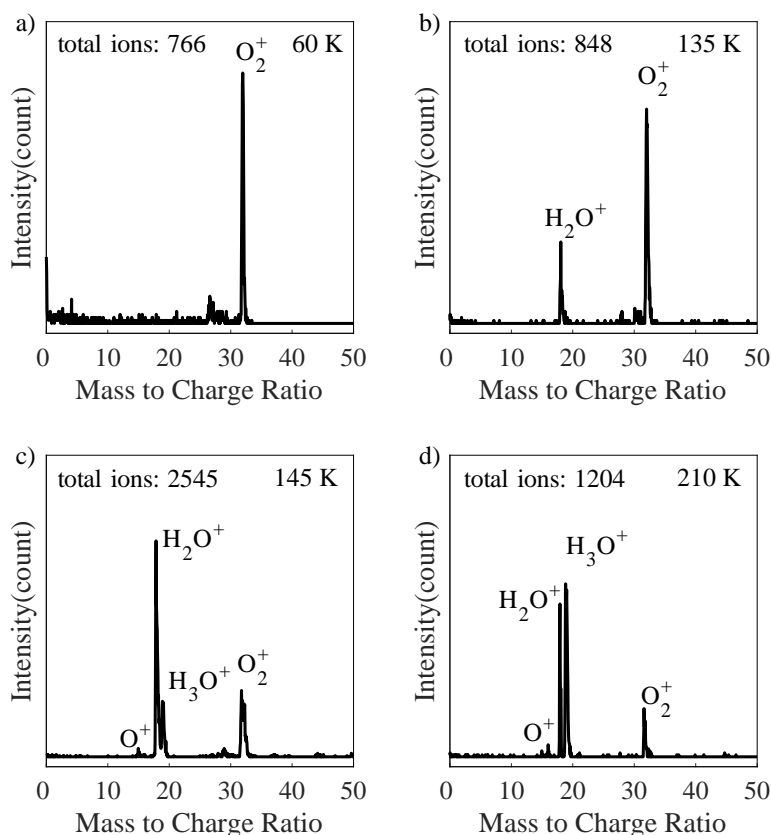


Fig. 5. Mass Spectrum of the interaction of O₂ (10⁻⁵ Pa) and H species on the Pt tip by pulse voltage, for different temperature: (a) 60 K; (b) 130 K; (c) 145 K; (d) 210 K. The static voltage was ~5.0 kV, and the pulse voltage was 1.0 kV.

[18]. The evaporation rate at time t , $\Phi(t)$, at temperature T and pulse duration t can be expressed as

$$\Phi(t) \approx Nv\tau_t \exp\left(-\frac{Q_n(F_o)}{k_B T}\right) \dots \dots \dots (1)$$

Where N is the number of the species present on the surface, v is the vibrational frequency of the surface atom, k_B is the Boltzmann's constant, and $Q_n(F_o)$ is the activation energy, which usually increases monotonically with electric field F_o . Therefore, the red spots may result from a large quantity of target ions produced or adsorbed around this point. Alternatively, the local electric field may be sufficiently high to induce evaporation of adsorbed molecules with sufficient supply. In short, there must be a mass of target ions adsorbed around red spots.

Comparison of these images with the FIM micrograph (Fig. 3) demonstrates that H₂O almost was not generated in the {111} planes. The active sites for the H₂O

generation, however, were in the {240} planes, where the red spots were spread. In addition, H₃O⁺ was sparsely distributed in the {111} planes, but was clustered in the {240} and {113} planes, as indicated by the red spots, suggesting that the planes surrounding the {111} planes have higher reactivity for H₂O⁺ and H₃O⁺ generation, such as the {240} and {113} planes. O₂⁺ was likely evaporated on the rim of the planes. We attributed the particular reactivity of the planes surrounding the {111} plane to their large specific surface area. Figure 7 shows the atomic structures of the {240} and {111} planes, based on which we speculated that the adsorption of molecular O₂ and the dissociation of O₂ to atomic O were stronger for the more corrugated planes. Accordingly, a possible reaction process was proposed. O₂ was adsorbed on the Pt surface and further dissociated to O atoms. The dissociated atomic O reacted with the

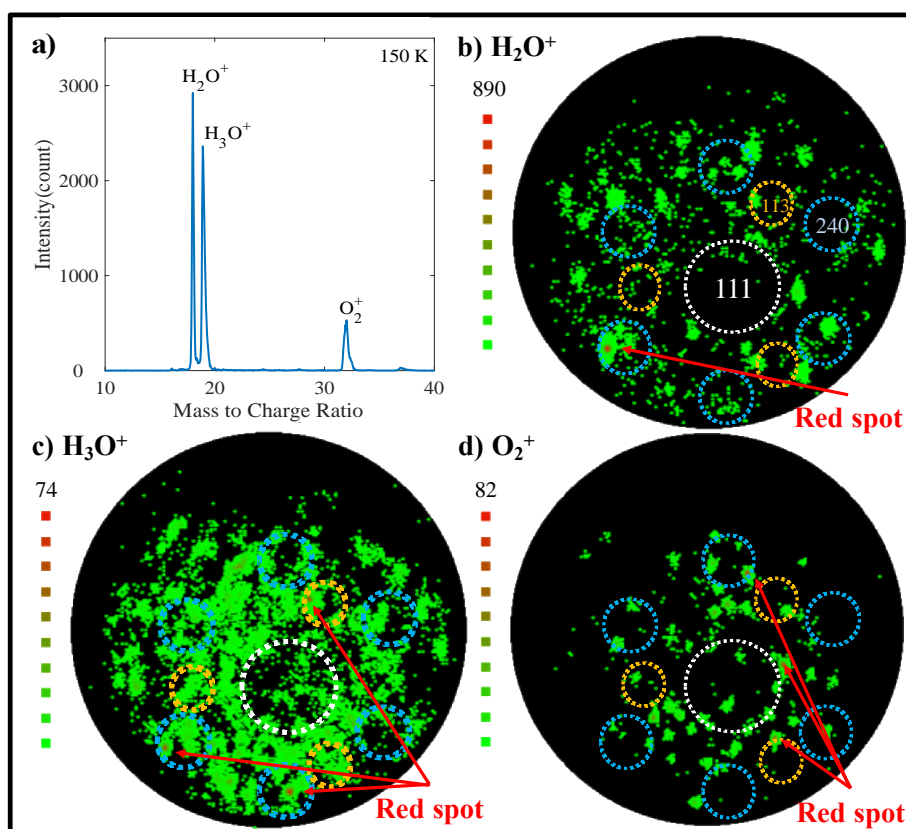


Fig. 6 a) Mass spectrum of the reaction between O₂ (10⁻⁵ Pa) and H species on the Pt tip by pulse voltage at 150 K, with the standing voltage of 2.5 kV and pulse voltage of 0.4 kV; b) H₂O⁺ distribution on the Pt surface; c) H₃O⁺ distribution on the Pt surface, d) O₂⁺ distribution on the Pt surface. In each picture, the pixel spans 200×200. The color of the pixels represents the intensity of the chemical components. Black corresponds to no signal counts. The color ranging green to red corresponds to the counts increasing linearly from 1 to a maximal number (shown on the top of the color scale). b), c) and d) are the chemical distributions of H₂O⁺, H₃O⁺, and O₂⁺, respectively, from the same Pt surface. The white dash ring, blue dash rings and orange dash rings in b) represent the {111}, {240}, and {113} planes, respectively. (color online)

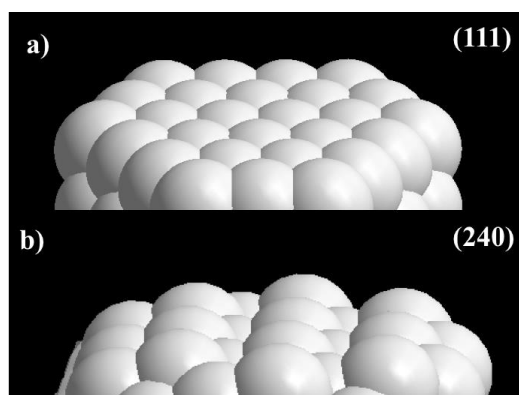


Fig. 7 a) Surface corrugation of the Pt (111) surface. b) Surface corrugation of the Pt (240) surface.

residual H, which can be derived from the H₂ diffused on the Pt surface or the H atoms/molecules stored in the Pt tip on the Pt surface at temperatures above 135 K, for the formation of H₂O.

4. Conclusion

In conclusion, we have investigated the O₂ and residual H reaction on the Pt surface by *in-situ* FIM coupled with atomic-resolution surface AP technique. Three types of H species, H⁺, H₂⁺, and H₃⁺ on the Pt surface were observed in high vacuum (10⁻⁸ Pa). Upon exposing the nanoscale Pt metal surface to the O₂ atmosphere (10⁻⁵ Pa), H₂O was produced only at temperatures above 135 K. Moreover, we found that the planes surrounding the {111} planes were more active owing to their particular rough atomic corrugation. This study shows that FIM and surface AP can be used as an *in-situ* reactor to monitor catalytic surface reactions. The atomic-level surface structure obtained by FIM and chemical composition-related information obtained by AP allow us to study ongoing catalytic reactions with a nanometer lateral resolution.

5. Acknowledgement

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6. Reference

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Discussion and Q&A with Reviewers

Reviewer #1 Kenji Nishida (Central Research Institute of Electric Power Industry)

[Q1_1]

In a situation where a lot of studies of the active site of a chemical reaction with the FIM / AP are being carried out, this paper focuses on the influence of residual hydrogen under UHV in oxidation reaction. Then, dissociation of residual hydrogen, oxidation reaction occurred only by residual hydrogen, and their temperature dependence are shown. Therefore, this paper is useful. On the other hand, it seems be still half way to identify reaction sites. I think that it is necessary to acquire systematic data with multiple chips and different orientations.

[A1_1]

Thanks for the valuable suggestions and comments.

Reviewer #1 suggested me to analyze reactivity of every plane. It is a little difficult based on my data. First, according to FIM image, there are many steps between different planes. And relatively small areas of the {240} and {311} planes are exposed. Therefore, it is difficult to differentiate different planes very strictly. Secondly, according to my repeated experiment results, the intensity of the products (H₂O and H₃O) was very weak in the center of {111} plane, but strong on the {240} plane, {311} plane and the steps between these planes, which was surrounding {111} planes. Therefore, I carefully made the conclusion that the {111} plane is less active than its surrounding planes, such as {240}, {311} planes.

[Q1_2] (Revision notes)

FIM and AP are not 'field emission' but 'field evaporation'.

Laser pulse is used for the analysis of residual H₂, and voltage pulse is used for reaction with O₂, so it should be written like this. Furthermore, if there is a reason for selectively using each method, the reason should also be shown.

The reasons for using both electrochemical etching and FIB milling are not mentioned. If there is a difference in each result, you should describe the

difference, and it is better to describe that there is no difference if there is no difference.

[A1_2]

Thanks for reviewer #1's notes, and I had modified my manuscripts accordingly.

Reviewer #2 Masahiro Taniguchi (Kanazawa Institute of Technology)

[Q2_1]

Many studies have been done on the behavior of hydrogen and oxygen atoms on platinum surface. Prof. Block and co-workers reported the oxygen island (oxygen layer) formation on platinum and the desorption of H₃O⁺ reduced by hydrogen from gas phase. (V. Gorodetskii, N. Ernst, W. Drahsel, J. H. Block, Appl. Surf. Sci., 87/88 (1995) 151-158.) The Pt surface covered by oxygen was prepared by exposure to water gas of 10⁻⁴ Pa at 300 K and the surface reaction with hydrogen molecule supplying at p = 10⁻⁴ Pa was investigated in their work. Contrarily to Gorodetskii-Block's work, the experiment in this paper is performed at lower temperature and under lower pressure focusing on the survey of reactive site on the tip surface.

1) In the title, the one reactant is defined as "residual H". There are two origins for residual hydrogen atom as authors mention in the text (residual gas in the UHV chamber and hydrogen dissolved in bulk, subsurface of metal sample). Do you have any idea of using (dosing) D₂ for the discrimination of the origin?

2) Can you estimate the relative contribution of the two hydrogen sources (from gas phase, from bulk). For a rough estimation, the gas phase H₂ could be assumed as T = 300 K and p = 10⁻⁸ Pa. (sticking probability enhancement by cooling and polarizing under high electric field might be omitted here.) The collision number of H₂ molecule per unit area of the Pt tip from gas phase can be compared with the ion count of AP analysis in that time scale. As the area size of the emitting surface can be directly evaluated from FIM/AP in this case, the density (ions/area) might be obtained; (collision number of H₂ × area × time of AP analysis) comparison of order (ion counts of AP).

[A2_1]

Thanks for the valuable suggestions and comments. Reviewer #2 was interested in the residual H and H supply speed, which is exactly my next research topic.

1) Reviewer #2 suggested us to use (dosing) D₂ for the discrimination of the origin. I think it is a good idea to discriminate the residual H₂ gas and H atom in metal after systematical experiments. Residual H can be discriminated by comparing the mass spectrum before and after D₂ introduced into the main chamber. Maybe, the D₂ partial pressure and D₂ residence time are important parameters.

2) Reviewer #2 asked us to calculate the collision number of H₂. According to my research for now, I am sorry to say I don't see it that way. First, if the residual H is gas or H in metal, the supply of residual H₂ is not by collision, but diffusion. And there are some factors affecting the diffusion. Secondly, the residual H sticking probability enhancement by cooling and polarizing under high electric field cannot be omitted. Thirdly, the density [ions (H₂O and H₃O)/area/time] was varied with temperature and O₂ adsorption condition (O₂ desorbed partially at certain temperature). So, the density is not constant.