The Analysis of Metal Catalyst Nanoparticle by Atom Probe Tomography*

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Nano alloys based on platinum form the basis for automobile exhaust catalyst, one of the most successful and important families of heterogeneous catalysts used in industry today. In this study, the structure of Pt–Pd catalyst is analyzed by atom probe tomography (APT). APT which has high spatial resolution and high detection sensitivity with single atomic level is widely used in the world in order to evaluate atomic structure of metals and semiconductor materials as typified by field effect transistor. The transformation of catalyst surface composition was observed by several thermal and environmental conditions in order to discuss the deterioration of catalyst. To observe the existence of catalytic reaction under APT condition, the field evaporated ions which originated from C, H thin film on Pt–Pd or W needle were compared. In the result of this study, the transformation of composition at surface micro region occurs by thermal treatment of Pt–Pd alloy.

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I. INTRODUCTION

The atom probe tomography (APT) is one of the most unique three dimensional imaging techniques and it is now known as powerful tools in materials science. Recently, by introducing very short pulsed laser into the atom probe instrument, the semiconductor materials such as electric device can be analyzed [1]. The two major advantages of APT, as compared to other microanalysis technique, are its high spatial resolution and high detection sensitivity. In general, the atom probe instrument is combined with delay line detector and time-of-flight mass spectrometry in field ion microscope [2]. The principle of this technique is based on field evaporation of surface atoms from very sharp needle shape sample of which radius of curvature is less than 100 nm [3]. The high positive voltage is applied to the sample in order to create strong electric field at the sample apex more than 10 V/nm. The field evaporated ions are accelerated and fly toward to the delay line detector. Then, the elemental identities of evaporated ions are determined by time-of-flight mass spectrometry. The x–y position of each atom is calculated from detected position and z position is calculated from sequence of detection [4]. The 3D image of micro region is created by this information with atomic scale.

On the other hand, nano alloys based on platinum form the basis for automobile exhaust catalyst, one of the most successful and important families of heterogeneous catalysts used in industry today. Especially, platinum, palladium and rhodium are three important metals in heterogeneous catalyst, extensively utilized together, for example in automobile exhaust emission control and ammonia oxidation [5]. These elements, along with other platinum group metals are highly successful catalysts in a wide range of applications owing to their superior activity and stability in harsh operating environments. These environments can often be strongly oxidizing, and the catalytic performance can be heavily influenced by the oxidation state of the platinum group metals surface. Additionally, the atomic scale structure and surface composition of the catalyst may be altered during the various stages of a reaction. Investigating how the environment affects catalyst surfaces is critically important, for a fuller understanding of these important materials, to enable catalyst manufactures to performance improvements. Recently, for saving the rare metal, the nano alloy catalysts which are composed of 3d-transition metals, for example copper and iron, are often studied [6]. The catalyst is deteriorated and deactivated by repeated use. Especially, the automobile exhaust catalytic reaction occurs in high temperature of 573–873 K or more, and its deterioration by thermal effect is very serious problem. To observe the structure and composition of catalyst with nano-scale is very important in order to create new or upgrade catalyst. The APT is one of the most appropriate methods to observe the structure and composition of alloy. As early work using APT, the segregation of alloy surface was investigated by Ahmad and Tsong [7]. In this study, the transformation of catalyst surface composition was observed by several ther-

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nal and environment conditions in order to discuss the deterioration of catalyst by APT. Moreover, we tried to observe the catalytic reaction using APT. In general, the peripheral \( d \)-orbital electron of platinum group metal is bound to the reaction species temporarily and dissociates it. It is expected that the field-evaporated ions affected catalytic reaction become low molecular mass caused by \( d \)-orbital electron. To observe the existence of catalytic reaction under APT conditions of electric field, gas pressure and sample shape, the field evaporated ions which originated from \( \text{C}_x\text{H}_y \) thin film on Pt–Pd or W needle were compared.

II. EXPERIMENTAL

A. The transformation of surface composition by thermal treatment

A Pt–Pd (Pd 20 at.\%) alloy in the form of wire (0.1 mm diameter) was obtained from Nilaco. Atom probe samples were prepared by electropolishing using a solution of 50\% \( \text{CaCl}_2 \) by volume in water for the first step, starting at about 35 Vac with a graphite counter electrode [8]. Then, the samples were fabricated to have the curvature radius of less than 100 nm by focused ion beam (FIB, SM3050, SIINT). Finally, the samples were cleaned by field evaporation of the first few atomic layers before being exposed to any thermal treatment. For all samples, the (100) direction was parallel to the sample axis. Samples were heated by the electrical heating at 573 K, 723 K, or 873 K for 5 h in atmospheric air or vacuum. When the thickness of organic or oxide layer product by thermal treatment was excessively thick, the organic or oxide layer was removed so as to be its thickness of 10-30 nm by FIB. Finally, all samples were analyzed focusing on the interface of organic/oxide/metal by APT.

B. The change of mass spectrum from \( \text{C}_x\text{H}_y \) deposition thin film

The Pt–Pd alloy sample was prepared by the method described above, and W sample was prepared by electropolishing using a solution of 1M-\( \text{NaOH} \). Each sample was cleaned by field evaporation. The \( \text{C}_x\text{H}_y \) thin layer (< 10 nm) was deposited on each sample surface by electron beam deposition of phenanthrene (\( \text{C}_{14}\text{H}_{10} \)). Each sample was heated by laser irradiation for 2 h without cooling. The sample temperature is perhaps more than 573 K. In general, normal APT condition, the rise in temperature of sample by pulsed laser irradiation is approximately 300 K [9]. Then, the atom probe analysis was carried out under the condition described below.

C. Instrumentation

Transmission electron microscopy (TEM, JEM-1010, JEOL, operated at 100 kV) was used to observe selected samples pre- and post-reaction. Samples were characterized by APT using a three-dimensional atom probe instrument developed in our laboratory [10]. The analyses were carried out using pulsed laser with a sample temperature of 70 K, pulse energy of 2.0 nJ, pulse repetition frequency of 5 kHz, wave length of 532 nm, a laser spot size of approximately 20 \( \mu \)m and evaporation rate of 5-10 ions per 100 pulses. The standing voltage was changed in order to maintain a constant evaporation rate.

III. RESULTS AND DISCUSSION

A. The change of surface composition by thermal treatment

The TEM images of post-reaction samples at each temperature are shown in Fig. 1. It was indicated that the oxide and organic layer grew at the surface depending on both time and temperature. In the case of the condition at lower temperature or short time, some colonies which were composed of organic or oxide were formed, and it grew to layer covering sample surface depending on thermal condition. It is a serious problem that the catalyst activity is decreased by this colony or layer. The APT images and depth profiles of the thermally treated at 873 K for 5 h in atmospheric air or untreated sample are shown in Fig. 2. Figure 2 (a)-(e) indicate the sample with thermal treatment, and (f) and (g) indicate the untreated sample. Figure 2 (a) and (f) are total ions maps, and (b)-(e) and (g) are specific ion maps. In the case of untreated sample, the atomic concentration is uniform anywhere. On the other hand, the segregation of Pd at surface can be observed in the thermally treated sample. Since Pd tends to be oxidized compared to Pt, several Pd atoms which moved to the surface from the inside by thermal agitation were trapped with oxygen, and they were segregated on the surface as an oxide. The TEM images of post-reaction samples at each temperature showed the original composition. Therefore, this phenomenon is not the reason for mix crystal by thermal effect but special reaction at catalyst surface. There are
FIG. 2: The APT images (a)-(g) and depth profiles (h) and (i) of the thermally treated at 873 K for 5 h in atmospheric air or untreated sample. The (a)-(e) indicate the sample with thermal treatment, and (f), (g) indicate the untreated sample. (a) and (f) are total ion maps, and (b)-(e) and (g) are specific ion maps.

FIG. 3: (a) and (b) are mass spectra at surface of CₓHᵧ on Pt–Pd and W, respectively. (c) and (d) are mass spectra at interface of CₓHᵧ/metal of Pt–Pd and W, respectively. The drastic difference of mass spectrum between (b) and (d) is not observed. On the other hand, the detected chemical species between (a) and (c) are changed. In the case of Pt–Pd sample, the catalytic reaction may occur at the interface of Pt–Pd/CₓHᵧ. In general, there are two reaction mechanisms of Eley-Rideal and Langmuir-Hinshelwood model when explaining catalytic reaction. In both of models, the peripheral d-orbital electron of platinum group metal is bound to the reaction species temporarily and dissociates it. Therefore, in the case of this study, since there was no oxygen supply material, C⁺ and C₂⁺ were increased at interface of

\[ \text{mass spectra at interface of } C_xH_y / \text{metal of } \text{Pt–Pd and } \text{W, respectively.} \]

some differences of condition between this study and real catalytic reaction, for example the ratio of each chemical species in catalytic environment. Therefore, when analyzing of the real catalyst, this phenomenon may have the difference in degree of segregation.

B. The change of mass spectrum from CₓHᵧ deposition thin film

The mass spectra of each sample are shown in Fig. 3. Figure 3 (a) and (b) are mass spectra at surface of CₓHᵧ on Pt–Pd and W, respectively. Figure 3 (c) and (d) are mass spectra at interface of CₓHᵧ/metal of Pt–Pd and W, respectively. The drastic difference of mass spectrum between (b) and (d) is not observed. On the other hand, the detected chemical species between (a) and (c) are changed. In the case of Pt–Pd sample, the catalytic reaction may occur at the interface of Pt–Pd/CₓHᵧ. In general, there are two reaction mechanisms of Eley-Rideal and Langmuir-Hinshelwood model when explaining catalytic reaction. In both of models, the peripheral d-orbital electron of platinum group metal is bound to the reaction species temporarily and dissociates it. Therefore, in the case of this study, since there was no oxygen supply material, C⁺ and C₂⁺ were increased at interface of...
Pt–Pd/C$_2$H$_4$. The C$^+$ and C$^{2+}$ are identified to field-evaporated ion species affected catalytic reaction. We must note that this reaction proceeds inside the atom probe instrument. The reason is that the catalytic reaction may be reproducible under APT conditions of pressure, electric field and sample shape. Therefore, it has possibility to be able to observe the correlation between catalyst surface composition and catalytic reaction with nearly atomic scale by using APT.

IV. CONCLUSIONS

The transformation of composition at surface small region occurs by thermal treatment of platinum based nano alloy. Especially, at 873 K, the sample surface is rich with palladium. Therefore, in the case of using the real platinum based nano alloy, it is possible that the transformation of the surface composition and structure occurs. Furthermore, in atom probe analysis condition, it was indicated that the catalyst reaction maybe occurred at atom probe tip surface. Therefore, it has possibility to be able to observe the correlation between catalyst surface composition and catalyst reaction with nearly atomic scale by using APT.

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