A Study of Adsorption of CO on Hydrogen Covered Pt(111) Surface Using Electron-Stimulated Desorption Spectroscopy

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In cooling process of Pt(111) in an ultra high vacuum (UHV), hydrogen segregates and saturates on the surface. A time-of-flight type electron-Stimulated desorption (TOF-ESD) spectroscopy measures hydrogen ions desorbed from Pt(111) surface. The H⁺ signal intensity decreases with increasing of CO exposures on the H-saturated Pt(111) surface. After saturation of CO adsorption, TOF-ESD measures various intensities of the H⁺ and O⁺ (from CO) depending on specimen temperature. From the TOF-ESD results in the CO saturated surface, hydrogen is hidden under the subsurface due to CO adsorption. Desorption of hydrogen under layer of CO necessitates 80 K higher temperatures compared with CO free layer on Pt(111). [doi:10.2320/matertrans.MRA2008093]

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1. Introduction

A study of adsorption and desorption of carbon-monoxide (CO) on Pt(111) has been an important issue in the field of catalysis.1–5) Recently, in development of fuel cell, platinum-black as electrode has been intensively studied to prevent a catalytic poison of CO. In particular the initial adsorption process of CO is important to understand the mechanism of CO poisoning on the Pt surface.

Electron-stimulated desorption (ESD) spectroscopy has advantages for adsorption studies; first, it is non-destructive, and second the focused electron beam used to probe the surface is highly localized. The ESD has a weak point for quantitative analysis due to a large reneutralization probability of desorbed ions in spite of its high sensitivity. In this sense it is necessary to investigate further to establish a quantitative method.

In this report, since a cross section of ESD H⁺ is strongly affected by CO adsorption, we will discuss the H⁺ yield in ESD depending on CO existence accompanied with thermal desorption spectroscopy (TDS) and Fourier transform infrared reflection spectroscopy (FTIR) on CO covered H/Pt(111) system.

2. Experimental

Since the experimental apparatus has been described previously,6) we describe it only briefly here. As shown in Fig. 1, a time-of-flight type electron-stimulated desorption (TOF-ESD) spectrometer is mounted in an ultra-high vacuum (UHV) chamber, which evacuated by a turbo molecular pump, sputter-ion pump and a sublimation pump with a liquid nitrogen shroud. The final base pressure is less than 1.3 × 10⁻⁸ Pa. A low energy electron gun for LEED and TOF-ESD is controlled by a home made gun-controller connected to a computer. Pulsed electron beam irradiates a specimen surface to desorb positive ions (H⁺, O⁺, CO⁺ etc.) from the surface. Desorbed ions fly from the specimen surface to a detector which consists of hemispherical grid meshes and chevron type micro-channel plates (MCP’s) and a phosphorous screen. The pulse width of the electron beam is 150 ns and the duty cycle of the pulse is ca. 40 kHz, so desorbed ions are accumulated over 10⁴ repetitions to make a histogram which is the TOF spectrum in computer memory. Normally positive specimen bias (normally 10 V) is applied to the specimen that accelerates positive ions to make sharper peaks in the TOF spectrum.

3. Experimental Result and Discussion

3.1 On cooling the Pt(111) surface

The Pt(111) surface was cleaned according to conventional treatments, namely, annealing at 800 K after heat treatment at 1000 K in 10⁻⁴ Pa of oxygen circumstance and flashing at 1300 K for 5 min in UHV. Clean surface was confirmed by a clean LEED pattern and Auger electron spectroscopy (AES) before the ESD experiment. Below 700 K the TOF-ESD measures surface hydrogen signal intensities depending on surface temperature. In cooling process of the specimen from 440 K hydrogen starts to appear on the top surface and abruptly takes a peak maximum near 340 K as shown in Fig. 2. When the specimen is heated again, the ESD H⁺ intensity decreases as indicated

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by the down arrow with a small hysteresis. Where the ESD yields are plot as integrated intensities of the H\(^+\) and O\(^+\) in the TOF spectra. An inset figure shows TOF-ESD spectra during heating period, in the inset P stands for photon signal generated by primary electron irradiation as soft X-ray and this notation will also appear later on. This behavior of hydrogen has been observed previously in the case of Ni(110) surface by Takano and Ueda.\(^7\) The ESD spectroscopy is highly sensitive to the surface hydrogen due to a large isotope effect in the desorption probability of desorbed ions.\(^8\) This amount of the H\(^+\) yield in ESD corresponds exposing the specimen in to a hydrogen pressure of \(10^{-4}\) Pa for 2000 s below 460 K. Therefore, in this case in UHV, it is appropriate to conclude that the hydrogen segregates from subsurface due to cooling of the specimen. Therefore, it is considered that segregated hydrogen, which diffused into the surface layers at higher temperatures in the vacuum circumstance. The speed and amounts of hydrogen segregation depend strongly on the specimen temperature and heating period, heating temperature and partial pressures of hydrogen and water vapor.

When carbon-monoxide (CO) was introduced stepwise into the vacuum on the hydrogen segregated surface, the H\(^+\) peak decreased abruptly in TOF spectrum and an X\(^+\) peak associated with CO was gradually increased as shown in Fig. 3, where the abscissa is shown in Langmuir (\(L, 1L = 1.3 \times 10^{-6}\) Pa-s). Plots between the H\(^+\) and the X\(^+\) (associated with CO) are expressed for different scales due to different sensitivity of ESD. The reasons of decrease of the H\(^+\) depended on CO exposure are considered as follows,

1. substitution between H and CO,
2. diffusion of H into the bulk,
3. H is hidden under the subsurface,
4. surface potential change due to CO adsorption resulting in a lower desorption probability of H\(^+\),
5. formation of a composite molecule from CO and H.

According to in-situ Fourier transform type infrared reflection (FTIR) measurements revealed a stretch vibration mode of CO at 2081 cm\(^{-1}\) up to 1L-CO exposure, and 2085 cm\(^{-1}\) from 2L-CO exposure as shown in Fig. 4. Similar results have been observed on Pt surfaces at 300 K by Shigeishi-King (2063 shifts to 2100 cm\(^{-1}\))\(^9\) and by Crossley and King (2064 shifts to 2101 cm\(^{-1}\)).\(^10\) This peak has broadened after 6 to 20L-CO exposure. Since this means hydrogen affects the vibration mode of CO, this is evidence that the hydrogen still exists in surface layers. This is highly notable that the ESD detects mostly desorbed ions from a top surface. Therefore, from among reasons described above (3) and (4) are plausible.

### 3.2 Comparison of TDS of H\(_2\) from H/Pt(111) with CO/ H/Pt(111)

Thermal desorption spectroscopy (TDS) is also useful to understand if the hydrogen still exists on the surface or is already desorbed due to displacement by CO adsorption. Figure 5(a) indicates hydrogen desorption intensities from
hydrogen segregated Pt(111) surface where the hydrogen peak in TDS is rather sharp against temperature. In contrast, Fig. 5(b) reveals completely broad peak of H$_2$ in the range from 380 to 720 K after 2000 L CO exposure. The CO peaks show doublet in spectra. Figure 5(b) is also an evidence that hydrogen still exists on the surface even after CO adsorption in spite of disappearance of ESD intensity.

Fortunately the ESD spectra can be observed during elevating temperature of the specimen below 700 K. The ESD yields as a function of temperature from CO/H/Pt(111) reveals curious behavior as shown in Fig. 6. A variation of the H$^+$ yield shows a strong dependence to OX$^+$ associated with CO adsorption. An initial increase of H$^+$ is considered to be a decrease of CO coverage. A reason why an abrupt decrease of the H$^+$ above 450 K is considered is that the ESD ions are easily re-neutralized by thermally excited electrons resulting in no signal of ions, or diffusion of surface hydrogen into the subsurface again as shown in Fig. 2. In this sense, inconsistent results between Fig. 5(b) and Fig. 6 are possible. If the electronic structure on the surface is thermally varied, the ESD yield is decreased. Nevertheless, the decrease of the H$^+$ yield in Fig. 6 is prolonged approximately 80 K beyond that of Fig. 2 due to the existence of CO. Therefore, from the experimental results, in the coadsorption system of CO and H, CO postpones the desorption of atomic hydrogen as molecules as a result of encountering H and H in order to desorb as H$_2$ during elevating temperature. In Fig. 6, though slightly increased O$^{2+}$ (no identified specie) indicated in enlarged scale at higher temperatures, it is supposed that residual oxide particles were activated thermally after desorption both of CO and H. After peak maximum of H$^+$ at 450 K, the signal intensity is disappeared abruptly at 480 K in coincidence with OX$^+$ disappearance. According to Fig. 6 and Fig. 2, the temperature required to remove hydrogen from a CO-adsorbed Pt(111) surface is 80 K higher than the temperature needed to remove hydrogen from a CO-free surface.

In the experimental results between Fig. 2 and Fig. 6, the H$^+$ signal intensity decreases at lower temperatures compared with CO-H coadsorbed surface. This is because that CO prevents diffusion of H near the surface. However, in TDS experiments of CO-H coadsorption on the surface H$_2$ signal intensity of Q-MAS decreases gradually even at 700 K in spite of no signal intensity of CO.

Those different results of Fig. 5(b) (TDS) and Fig. 6 (ESD) are understood as follows; adsorbed hydrogen desorbs thermally as H$_2$ from the Pt surface as a result of encountering H and H atoms near the surface. In contrast, because the ESD ions can desorb only from the top surface, hydrogen in underlayer can not desorb as ions due to strong reneutralization effect by metal electron.

4. Summary

When carbon monoxide (CO) molecules cover the segregated hydrogen on Pt(111) surface, hydrogen atoms are shadowed from the electron beam resulting in weak signal intensity of electron-stimulated desorption (ESD) spectroscopy. In spite of its high sensitivity to surface H, it is notable that ESD detects desorbed ions only from the top surface. Hydrogen desorption from Pt(111) surface is influenced by coadsorbed CO because associative desorption needs more 80-K-higher temperature in order to combine with atomic hydrogen under the coverage of CO. In other words, hydrogen from CO free Pt(111) surface is easily desorbed thermally 80 K below than the CO-adsorbed surface. That means CO prevents hydrogen desorption due to catalytic poisoning on the Pt surface.

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