Spontaneously Adsorbed Mo Layers on Pt(111) and Pt(100) Single Crystal Electrode Surfaces

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The voltammetric behavior of spontaneously adsorbing Mo layers on Pt(111) and Pt(100) electrodes has been studied to estimate the number of electrons involved in the electrochemical processes of spontaneously adsorbed Mo and the number of the blocked Pt sites for hydrogen adsorption. On Pt(111) and Pt(100) surfaces, the spontaneously adsorbed Mo layers showed redox peaks at 0.10 V and 0.15 V, respectively, and continuous current-potential waves in the conventional hydrogen region. Since the potential range of the Mo redox processes on both surfaces overlapped partially with the potential range of hydrogen adsorption, the variation in the ratio of the total charge of Mo and H ($Q_H + Q_{Mo}$) to the hydrogen charge of clean Pt electrode (Q_H^o) was analyzed. From the analysis, six electrons were estimated to be involved in the electrochemical processes of the spontaneously adsorbed Mo, and four Pt sites for hydrogen adsorption were calculated to be blocked by one adsorbed Mo atom. Based on these figures and the pH dependence of the Mo redox processes, we have proposed an electrochemical equation for the spontaneously adsorbed Mo. This electrochemical equation led us to conclude that the saturation coverage of the spontaneously adsorbed Mo is 0.25. The coverage of Mo less than 0.25, however, could not be determined voltammetrically due to the convolution of the charges of Mo and H.

Keywords : Mo, Adsorption, Pt(111), Pt(100), Voltammetry.

Introduction

In the research of fuel cells using Pt catalysts toward small organic molecules, the modification of electrode surfaces with foreign metal layers has been emphasized.[1,2] The surface modification is carried out mainly by underpotential deposition[3] and immersion method.[4-8]

The two surface modification methods differ from each other in stripping behavior. In the underpotential deposition, a metal ion is deposited and stripped in a reversible manner ($M(ad) - ne^- \rightleftarrows M^{n+}(aq)$). In the immersion method, a metal ionic oxygenated layer is produced spontaneously by simply immersing an electrode into a solution containing the metal ion ($M^{n-}(aq) \rightarrow M^{m-}(ad)$). The resulting ionic layer typically shows a reversible redox behavior at a certain potential ($M^{m+}(ad) + ne^- \rightleftarrows M(ad)$), but strips irreversibly at a higher potential than the redox potential ($M^{m-}(ad) \rightarrow M^{n'+}(aq) + (n' - n)e^-$, where $n' > n$). Because of the irreversibility in stripping, the spontaneous adsorption is called irreversible adsorption.

The spontaneously adsorbed metallic layers of various elements[9-22] were investigated extensively in conjunction with the oxidation of small organic molecules.[23-44] Specifically, it has been found that Ru and Bi modifiers enhanced dramatically the catalytic activity of Pt in methanol[30,40,41] and formic acid[23,24,28,29,31,33,43,44] oxidation, respectively. Although three mechanisms (electronic effect, third body effect and bifunctional effect) have been proposed,[8] the actual enhancing mechanism concerning Ru and Bi were not clearly understood.

On the other hand, the characteristic electrochemical properties of a spontaneously adsorbed metal ionic layer itself cannot be negligible. For example, the spontaneously adsorbed layer of Sb became electrochemically inactive upon reduction,[21] which was possibly caused by the lateral movement of the reduced Sb atoms. We have observed such a lateral movement of Te on Pt(111) with in-situ STM.[45] In addition, we have found that the spontaneous adsorption and underpotential deposition take place sequentially or simultaneously in achieving a full monolayer of an irreversibly adsorbing metal ion.[21,46] These observations clearly indicate that the electrochemical deposition of spontaneously adsorbed metal ion may be different from the conventional underpotential deposition.

In the present study, we present the electrochemical behavior of spontaneously adsorbed Mo on Pt(111) and Pt(100) single crystal electrodes. The main focus of this work is the estimation of the number of electrons involved in the electrochemical processes of spontaneously adsorbed Mo and the number of the blocked Pt sites for hydrogen adsorption.

Experimental Section

The platinum single crystal electrodes employed in the present work were prepared by the bead method.[47] Pt single crystal beads were produced by melting Pt wire (diameter = 0.5 mm, Aldrich, 99.99%) in a hydrogen-oxygen flame and aligned to the desired direction using a home-built 3 dimensional goniometer and a He-Ne laser. The aligned single crystal beads were cut to reasonable surface areas and

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the crystal surfaces were polished down to 1/4 μm to be mirror-like. A clean and ordered surface of Pt(111) was routinely obtained after flame annealing treatment. However, a well-defined surface of Pt(100) was obtained with the application of 50 Hz sawtooth wave between −0.3 V and 0.7 V after flame annealing treatment.[48]

The solutions used in this work were made of ultrapure water (> 18 MΩ · cm^{-1}, Barnsted). H_2SO_4 (Merck, Suprapur) and MoO_3 (Aldrich, 99.99%). Particularly, the solution of Mo was obtained by saturating ultrapure water with MoO_3 and the concentration of Mo was measured to be approximately 6 mM of MoO_3.

Voltammetric studies were performed using a conventional three-electrode system, and the potentials reported in the present work are against to an Ag/AgCl reference electrode whose chloride concentration was 1.0 M.

Results and Discussion

Figure 1 and 2 show the cyclic voltammograms of spontaneously adsorbed oxygenated Mo on Pt(111) and Pt(100) electrodes, respectively. After confirming well-ordered and clean surfaces of Pt single crystal electrodes, as shown in Figure 1(a) and Figure 2(a), the electrodes were immersed in the MoO_3-saturated solution for approximately 3 minutes without any applied potential to induce the spontaneous adsorption of Mo. Since a drop of the MoO_3containing solution was usually on the electrodes removed from the solution, the residual solution was completely rinsed with clean water. Then, the electrodes were brought into contact with 0.05 M H_2SO_4 solution with the open circuit potential close to 0.7 V.

Figure 1(b) and Figure 2(b) are the respective cyclic voltammograms of Pt(111) and Pt(100) saturated with spontaneously adsorbed oxygenated Mo in 0.05 M H_2SO_4 solution. The observed cyclic voltammograms of the spontaneously adsorbed oxygenated Mo on Pt(111) and Pt(100) show their own characteristic distinguishing them from those of other spontaneously adsorbing metal ions. The most contrasting voltammetric feature of Mo was a reversible redox peak observed at the positive end of the hydrogen region with a broad current-potential wave similar to the hydrogen adorption/desorption wave. On Pt(111), a redox peak was observed at 0.10 V, whose reduction charge was smaller than the corresponding oxidation charge. Since the reverse situation was observed in the conventional hydrogen region (from 0.05 V to −0.27 V), the missing charge in the reduction process at 0.10 V might be observed in the potential range. Indeed, the reduction charge from 0.20 V to −0.27 V was close to the oxidation charge in the same potential range. On Pt(100), the voltammetric behavior was similar to that observed on Pt(111). A single redox peak at 0.15 V was clearly observed, while several voltammetric features in the hydrogen region were convoluted. Here again, the reduction charge from 0.30 V to −0.27 V was identical to the oxidation charge.

Figure 1(c) and Figure 2(c) are the cyclic voltammograms of Pt(111) and Pt(100) covered with under-saturated Mo layers. Adjusting the immersion time and/or the concentration of MoO_3-contaning solution led us to various surface concentrations of the spontaneously adsorbed Mo. Clearly shown in the voltammograms is that the charges of the redox

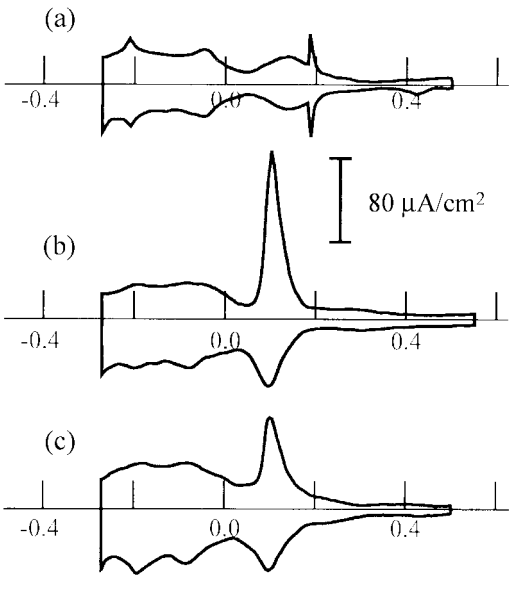

Figure 1. Cyclic voltammograms of Pt(111) in 0.05 M H_2SO_4 solution: (a) clean and ordered, (b) fully covered with spontaneously adsorbed Mo and (c) partially covered with spontaneously adsorbed Mo. Scan rate: 50 mV · sec^{-1}.

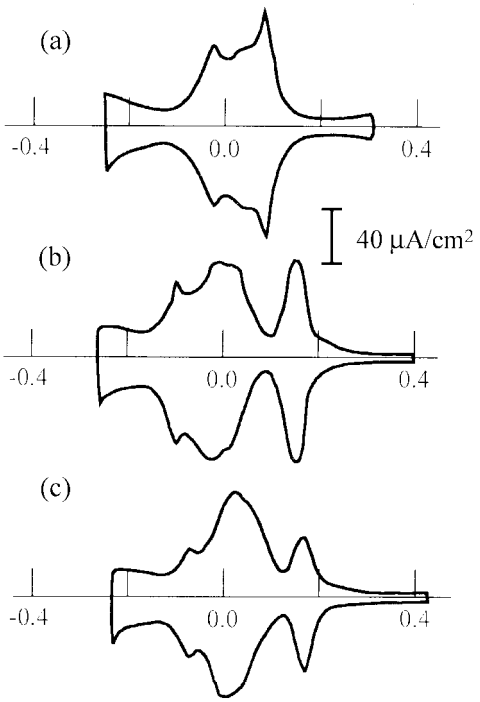

Figure 2. Cyclic voltammograms of Pt(100) in 0.05 M H_2SO_4 solution: (a) clean and ordered, (b) fully covered with spontaneously adsorbed Mo and (c) partially covered with spontaneously adsorbed Mo. Scan rate: 50 mV · sec^{-1}.

peaks at 0.10 V on Pt(111) and 0.15 V on Pt(100) decreased. These observations obviously indicate that the redox peaks are related to the spontaneously adsorbed Mo. On the other hand, the charges from the negative ends of the Mo redox peaks to the hydrogen evolution potential (−0.27 V) were measured to be constant within experimental error, regardless of the surface concentration of Mo. Specifically, the charges (235 ± 5 $\mu C/cm^2$ for Pt(111) and 208 ± 0.5 $\mu C/cm^2$ for Pt(100)) are close enough to the theoretical hydrogen charges, *i.e.* 241 $\mu C/cm^2$ for Pt(111) and 209 $\mu C/cm^2$ for Pt(100). Considering that the spontaneously adsorbed metal atoms generally block the Pt sites for hydrogen adsorption,[9-22] the constancy of the charge in this particular potential region on both Pt electrodes implies that the reduced charge, resulting from inhibition of hydrogen adsorption by adsorbed Mo atoms, was compensated by the redox charge of Mo. As a result, the charge in the conventional hydrogen region was constant. Therefore, it is logical to conclude that the electrochemical processes concerning hydrogen and Mo cannot be distinguished voltammetrically.

The number of electrons transferred in the electrochemical processes of the spontaneously adsorbed Mo and the number of the hydrogen adsorption sites blocked by an adsorbed Mo atom can be estimated using voltammetric results based on the following equation:

$$n_{Pt} = n_{Pt}^{\circ} - n_b \cdot n_{Mo}. \quad (1)$$

where n_{Pt}, n_{Pt}°, n_b and n_{Mo} are the number of Pt atoms not blocked by Mo atoms, the number of Pt atoms on a clean Pt electrode surface, the number of Pt sites blocked by one Mo atom and the number of spontaneously adsorbed Mo atoms, respectively. After inserting n_t (the number of electrons transferred in electrochemical processes of the spontaneously adsorbed Mo) into equation (1), multiplying both sides by one electron charge will result in the following equation:

$$Q_H = Q_H^{\circ} - (n_b/n_t) \cdot Q_{Mo}. \quad (2)$$

where Q_H, Q_{Mo} and Q_H° are the charges for hydrogen and Mo on a Mo-covered Pt electrode, and the hydrogen charge of a clean Pt electrode, respectively. If one obtains Q_H and Q_{Mo} separately, the experimental value of (n_b/n_t) can be easily estimated. In the present work, unfortunately, Q_H and Q_{Mo} cannot be measured separately as discussed before. When a Pt electrode is saturated with the spontaneously adsorbed Mo, *i.e.* $Q_H = 0$, however, it is possible to determine the ratio of (n_b/n_t). In this particular condition, equation (2) becomes as follows:

$$Q_{Mo}^{sat}/Q_H^{\circ} = n_t/n_b. \quad (3)$$

where Q_{Mo}^{sat} is the saturation charge of Mo on a Pt electrode.

Figure 3 shows the variation of $(Q_H + Q_{Mo})/Q_H^{\circ}$ as solution exposure changes. Since the surface concentration of the spontaneously adsorbed Mo was adjusted with immersion time and/or the concentration of Mo, solution exposure was defined as the product of concentration and immersion time (mM · sec), which is analogous to the unit of Langmuir (1 L = 10^{-6} Torr · sec) for gas exposure in UHV experiments.

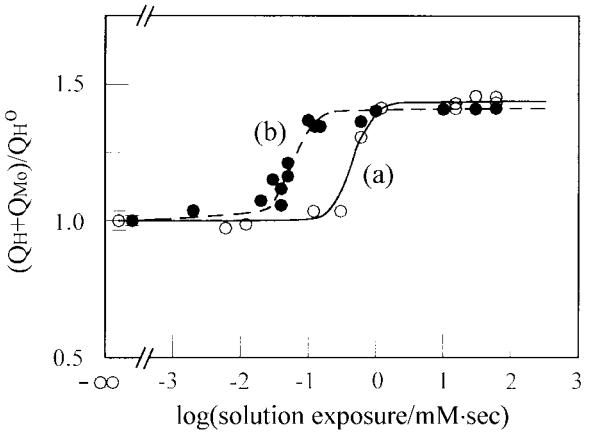

Figure 3. Variation in the ratio of the total charge of Mo and H ($Q_H + Q_{Mo}$) to the hydrogen charge (Q_H°) of clean Pt electrode: (a) Pt(111) (open circle) and (b) Pt(100) (filled circle). See the text for the details of solution exposure.

$(Q_H + Q_{Mo})$ is the charge from 0.20 V to −0.27 V for Pt(111) and 0.30 V to −0.27 V for Pt(100), respectively, after subtracting a capacitive charge. At low solution exposure, the value of $(Q_H + Q_{Mo})/Q_H$− remained close to 1, which indicates that no adsorption of Mo occurs ($Q_{Mo} \approx 0$). The spontaneous adsorption started taking place on Pt(111) and Pt(100) when the solution exposure was approximately 0.3 and 0.03 mM · sec, respectively. Then, the ratios observed on Pt(111) and Pt(100) at high solution exposure, *i.e.* Q_{Mo}^{sat}/Q_H°, converged to 1.48 ± 0.030 and 1.41 ± 0.004, respectively.

Table 1 shows possible combinations of n_t and n_b, and the ratios of n_t/n_b. The calculated ratio closest to the experimentally determined ratios (1.48 for Pt(111) and 1.41 for Pt(100)) is 1.50, which implies that six electrons are involved in the electrochemical processes of the spontaneously adsorbed Mo and that a single adsorbed Mo atom blocks four Pt sites for hydrogen adsorption. In addition to these, 60 mV/pH dependence of the spontaneously adsorbed Mo indicates that protons are involved in the redox processes of Mo and that the number of protons is equal to the number of electrons. Based on these results, we propose the following electrochemical equation:

$$\text{oxygenated Mo(VI, aq)} \rightarrow \\ MoO_3\text{(VI, ad)} + 6H^+ + 6e \rightleftarrows \text{Mo(0, ad)} + 3H_2O \quad (4)$$

From this equation, the saturation coverages of Mo (defined as the ratio of Mo atoms to Pt atoms) were calculated to be 0.25 and 0.24 for Pt(111) and Pt(100), respectively.

One may argue that the involvement of three electrons in the electrochemical processes of the spontaneously adsorbed

Table 1. Possible combinations of the number of electrons transferred in electrochemical processes of the spontaneously adsorbed Mo (n_t) and the number of Pt atoms blocked by one Mo atom (n_b)

n_t	4	5	5	6	6
n_b	3	3	4	4	5
n_t/n_b	1.33	1.67	1.25	1.50	1.20

Mo and the blockage of two Pt sites for hydrogen adsorption may be another possible combination accounting for the measured ratio of n_f/n_b. In such a case, the saturation coverage of Mo turns out to be 0.5, which is too large. Saturation coverages of spontaneously adsorbing oxygenated metal ions, when only spontaneous adsorption is carried out, span generally from 0.33 to 0.25.[9-22]

One more thing to be addressed is that the impossibility of measuring voltammetrically the coverage of Mo less than 0.25. The reason for this is that the redox peaks of Mo cannot be separated from the redox waves of hydrogen in the conventional hydrogen region. Therefore, other techniques, like electron spectroscopy and scanning probe microscopy, should be employed to measure the Mo coverage below 0.25.

Conclusions

The voltammetric behavior of spontaneously adsorbing Mo on Pt(111) and Pt(100) electrodes was studied to estimate the number of electrons involved in the electrochemical processes of spontaneously adsorbed Mo and the number of blocked Pt sites for hydrogen adsorption. The spontaneously adsorbed Mo layers on both surfaces showed respective redox peaks at the positive end of the conventional hydrogen region and continuous voltammetric waves down to the hydrogen evolution potential. Since it was impossible to measure the charge concerning Mo only, the variation in the ratio of the total charge of Mo and H to the hydrogen charge on a clean Pt electrode was analyzed as the solution exposure (defined in this work) changed. From the analysis, six electrons were estimated to be involved in the electrochemical processes of the spontaneously adsorbed Mo, and four Pt sites for hydrogen adsorption were calculated to be blocked by one adsorbed Mo atom. Based on these figures and the pH dependence of the Mo redox processes, we have proposed an electrochemical equation for the spontaneously adsorbed Mo. In turn, this electrochemical equation has led us to conclude that the saturation coverage of the spontaneously adsorbed Mo is 0.25. The coverage of Mo less than 0.25, however, was impossible to determine voltammetrically due to the convolution of the charges of Mo and H.

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