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The CO Adsorbed Species Characteriation by *In situ* FTIR I. Polycrystalline Pt Electrode in a Wide pH Range

Satoshi TAGUCHI, Akiko ARAMATA*, Hideo NAOHARA† and Hideaki KITA†

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The CO adsorption and oxidation on Pt electrode have been widely studied by voltammetry¹⁾ and infrared spectrometry^{2,3)}. However, most of infrared spectroscopic works have been carried out in aqueous acidic media²⁾, some of which are directed to methanol or formic acid electrooxidation in fundamental viewpoint of methanol fuel cell⁴⁾, in order to clarify the self-poisoning for design of a highly active electrocatalyst. Adsorbed CO in neutral solutions has also received attention because of possible intermediate / poison in CO₂ electroreduction²⁾; the adsorbed CO from CO₂, called as reduced CO₂, is formed on Pt, but Pt does not produce CO and the other species. Since the state of the adsorbed CO is dependent on pH of the solutions¹⁾, we are going to compare IR spectra and anodic stripping voltammograms (ASV) at a wide range of pH's.

Experimental procedure has been described elsewhere³⁾. We introduced N₂ gas into sample chamber of FTIR spectrometer, in order to avoid interference of CO₂ and H₂O to spectrum observation. After electrode potential was imposed to 0.05 V(vs. RHE), where CO gas was bubbled for 5 min and then purged by N₂ gas for 15 min, spectra of 100 scans were recorded at certain potentials stepwise by 50 mV from 0.05 V.

Figure 1 shows a negative shift of main peak of ASV due to oxidation of the adsorbed CO with the increase of pH, while the position of prepeak at 0.4 V is nearly indifferent to the pH change and a higher pre-peak current

is observed at pH 12. Figure 2 shows IR spectra at pH 3, 7, and 12, where bridged CO bands of 1846 ~ 1856 cm⁻¹ of 0.05 V disappear at 0.5, 0.35, and 0.3 V for pH 3, 7, and 12, respectively, whereas linear CO (on-top CO) bands of 2054 ~ 2025 cm⁻¹ disappear at 0.7, 0.65, and 0.5 V for pH 3, 7, and 12, respectively. With the intensity decrease of the bridged CO bands from 0.2 V, bands of CO oxidized species appeared in all pH's, indicating the occurrence of bridged CO oxidation. Shift of the spectrum position with potentials has been already discussed in the case of neutral solution³⁾. In the case of pH 12, as shown in Fig. 3, IR band at 1980 cm⁻¹ is to be noted with higher IR intensity of bridged CO at 1847cm⁻¹ than that at pH 3 or 7, where the former IR band is taken to be linear or asymmetrically bridged CO⁵⁾. Both bands disappear at 0.3 V in the case of pH 12, which are together taken to contribute to prepeak.

Fig.1 Anodic stripping voltammograms of adsorbed CO at $E_{\text{ads}} = 0.05\text{V}$ on Pt(poly) in phosphate buffer solutions of pH=3, 7, and 12.

* To whom correspondence should be addressed.
Catalysis Research Center, Hokkaido
University, Sapporo 060 Japan

† Graduate School of Global Environmental
Science, Hokkaido University, Sapporo 060
Japan

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Fig. 2 *In situ* FTIR spectra of adsorbed CO on Pt(poly) in phosphate buffer solution of pH = 3, 7, and 12. Each spectrum was subtracted from spectrum at 0.75V.

Fig. 3 *In situ* FTIR spectra of adsorbed CO on Pt(poly) in phosphate buffer solution of pH = 12.

Since the current of adsorbed hydrogen at $E < 0.2$ V of Fig. 1 is completely smeared out by the adsorbed CO, and no other IR active species in the region of $4000 \sim 400$ cm^{-1} were observed, we presume that the surface is completely covered by the adsorbed CO in the form of either linear CO, bridged CO, or

asymmetrically bridged CO. With the charge density of full coverage of the adsorbed hydrogen, $Q_H^0 = 210 \mu\text{C}/\text{cm}^2$ at pH 3, the Q_H^0 's at pH 7 and 12 were obtained, and from these Q_H^0 's the charge densities of the adsorbed CO formed at 50 mV and oxidized at ASV, Q_{ox} , electron per site for oxidation of the adsorbed CO, ϵ_{ps} , and the coverage of CO, θ_{CO} , are estimated as given in Table 1, where the double layer charging current is corrected⁶⁾ and its correction uncertainty, if any, is less than $10 \mu\text{C}/\text{cm}^2$. We find in Table 1 that Q_H^0 decreases with the increase of pH. This decrease can be discussed by the change of surface topography with pH.

The surface of polycrystalline Pt, denoted as Pt(poly), is usually considered to consist of a mixture of Pt(110), Pt(100), and Pt(111) planes. However, cyclic voltammogram (CV) characteristics of Pt(poly) in Ar atmosphere do not hold those of

Table1 Charge densities of hydrogen adsorption (Q_H^0) charge densities(Q_{ox}), coverage (θ_{CO}), and electron per site (eps) for CO adsorption and oxidation.

pH	3	7	12
$Q_H^0 / \mu\text{Coul cm}^{-2}$	210	185	165
$Q_{ox} / \mu\text{Coul cm}^{-2}$	354	330	356
θ_{CO}	0.8	0.9	1.0
eps	1.7	1.8	2.1

Fig.4 Cyclic voltammograms of Pt(110), Pt(100) and Pt(poly) in Ar saturated phosphate buffer solutions of pH =3 and 12.

Fig.5 Model of bridged CO and linear CO with eps =2 on Pt.

a relatively wide terrace of Pt(111) plane because of lack of CV characteristic of Pt(111) in Pt(poly) CV but give features of hydrogen adsorption on Pt(110) and weakly bonded hydrogen on Pt(100) as shown in Fig.4. According to Ref. (7), the surface of Pt(110) is of the form of Pt(110)-(1x2) and Pt(110)-(1x1) in acidic and alkaline solutions, respectively, because of the decrease of Q_H^0 from 220 $\mu\text{C}/\text{cm}^2$ to 140 ~ 145 $\mu\text{C}/\text{cm}^2$ by the increase of pH^{7,8)}. For Pt(poly) as shown in Fig. 4, the peak intensity due to adsorbed hydrogen on Pt(100) decreases relative to the intensity due to Pt(110), when pH becomes from 3 to 12. The surface topographical changes, namely, removal of missing row surface structure of Pt(110)-(1x2) of Pt(110) domain and the decrease of Pt(100) domain at Pt(poly), are suggested to occur with increasing pH, because of the decrease of Q_H^0 from 210 $\mu\text{C}/\text{cm}^2$ to 165 $\mu\text{C}/\text{cm}^2$ with increasing pH as shown in Table 1. The θ_{CO} and eps increase with the increase of pH. Since eps of pH 12 is 2, which suggests only the presence of linear CO on Pt(poly), the presence of bridged CO in Fig. 3 is contradictory to the estimated eps. This discrepancy is solved by the argument that each Pt atom provides two adsorption sites with its oppositely adjacent Pt atoms toward bridged CO, and holds one adsorbed CO as a consequence, as schematically shown in Fig.5.

These considerations led us to conclude that the Pt(poly) surface is reconstructed according to various pH solutions studied and the determination of adsorbed species only from eps value sometimes fails in giving a true surface species information.

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