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An Infrared Study of Carbon Monoxide Adsorbed on Platinum Electrode Modified with Bismuth Submonolayer

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Infrared spectra of CO adsorbed on Pt electrodes modified with underpotentially deposited Bi adatoms have been measured *in situ* as a function of Bi coverage (θ_{Bi}). Shape and position of the C-O stretching band changed depending upon θ_{Bi}. The observed spectral changes are explained by dipole coupling between CO molecules. Structure of Bi adlayer is discussed from the spectra of CO.

Underpotential deposition (UPD) is a phenomenon that submonolayer or monolayer of a metal deposits on substrate electrode surfaces at potentials positive from the reversible Nernst potential.1) Modification of surfaces by foreign metals can lead to either improvement or degradation in the reactivity of the surfaces. Oxidation of formic acid and formaldehyde on platinum electrode, e.g., are accelerated extremely by UPD of bismuth.2-4) This catalytic activity arises from two-dimensional arrangement of Bi adatoms which facilitates direct oxidation of the molecules2,3) and/or inhibits poison formation.4) The mechanism, however, has not been understood completely. For a fundamental understanding of the catalytic reaction, we studied the Bi-modified Pt surfaces by *in situ* infrared (IR) spectroscopy by using carbon monoxide as a probe molecule.

A thin-layer electrochemical cell equipped with a CaF_2 window was used with a Pt counter and a Ag/AgCl reference electrodes.5) Firstly, cyclic voltammogram (CV) of the Pt working electrode was recorded in 1 M(=mol dm^{-3}) $HClO_4$ deaerated by nitrogen. The number of surface Pt atoms (N_{Pt}) was estimated from the hydrogen wave in the CV. Next, a stock 1 M $HClO_4$ solution in which Bi_2O_3 had been dissolved was added into the cell, and UPD of Bi was conducted by holding the electrode at 0.2 V(Ag/AgCl) for 10 min. Coverage of Bi (θ_{Bi}) was changed by changing the concentration of Bi^{3+} in the solution (10^{-6}-10^{-4} M). Carbon monoxide was adsorbed on the Bi-modified Pt electrode by bubbling CO gas through the solution during final 5 min of the UPD. Soon after the adsorption of CO, the electrode was pushed against the CaF_2 window and the dissolved CO was purged by nitrogen. Then, IR spectrum of the electrode surface was measured *in situ* by polarization-modulation reflection method.5) Finally, the electrode was pull back from the window and CV was recorded. The oxidation wave of CO to CO_2 and the stripping wave of Bi ($Bi \rightarrow Bi^{+3} + 3e^-$) were observed around +0.6 V and +0.7 V, respectively. The adsorbed amounts of CO and Bi were calculated by integrating these waves and their coverages were estimated. Coverage of CO (θ_{CO}) reported here is relative to saturation at bare Pt surface (θ_{CO}=1 at θ_{Bi}=0). Coverage of Bi was defined by the ratio of the number of Bi adatoms (N_{Bi}) and N_{Pt}, as $\theta_{Bi}=N_{Bi}/N_{Pt}$.

Coverages of CO are plotted in Fig. 1 as a function of θ_{Bi}. As shown in this figure, uptake of CO at Pt surface is attenuated linearly by UPD of Bi up to θ_{Bi}=0.36, indicating that each Bi adatom blocks about three sites for CO adsorption.

Figure 2 shows IR spectra of CO adsorbed on Pt electrodes modified with Bi for increasing θ_{Bi}. All the spectra were measured at a constant potential of 0.0 V. Spectra were also recorded at other potentials and similar results were obtained. Several features are evident from these spectra. The bare surface shows an absorption at 2078 cm^{-1} which has been assigned to the C-O stretching vibration of CO adsorbed at linear (on-top) Pt site.[6] The band center shifts to lower wavenumbers with increasing θ_{Bi}. A shoulder appears on the low-wavenumber side of this band at θ_{Bi}=0.12 and grows at the expense of the high-wavenumber band, resulting in the doublet feature around θ_{Bi}=0.19. We note here that the first band shows downward shift with increasing θ_{Bi} while the second band (or shoulder) remains constant in peak position up to θ_{Bi}=0.23. After the complete disappearance of the first band, the second band shifts to further low wavenumbers with increasing

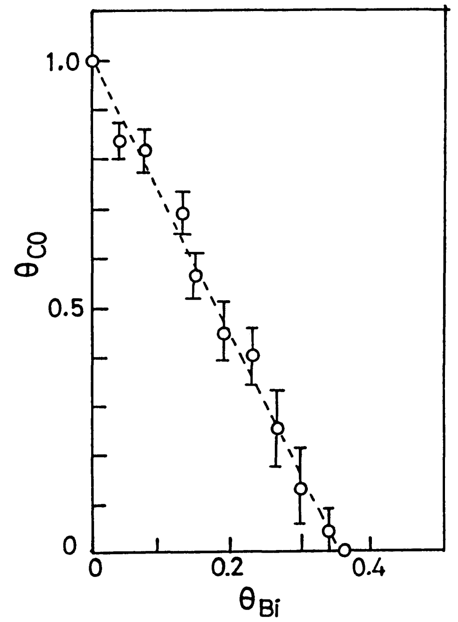

Fig.1. Uptake of CO at Bi-modified Pt electrodes as a function of Bi-coverage (θ_{Bi}).

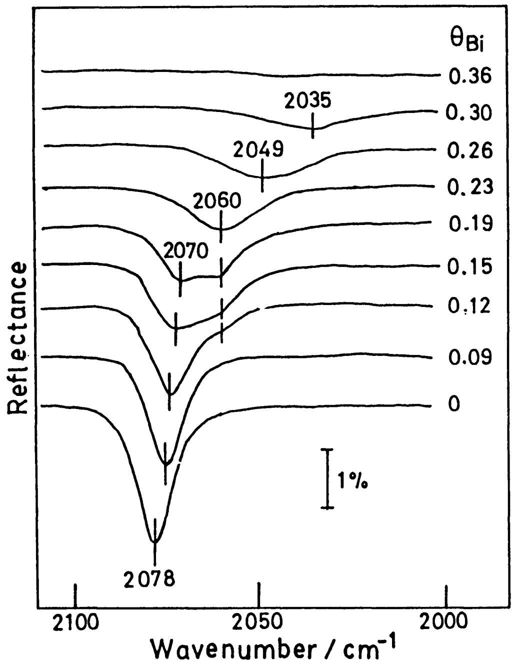

Fig.2. Infrared spectra of CO adsorbed on Bi-modified Pt electrode as a function of θ_{Bi}. E=0.0 V (Ag/AgCl).

θ_{Bi} and disappears around θ_{Bi}=0.35.

Another IR band of CO adsorbed at bridge (2-fold) Pt site was observed very weakly around 1850 cm^{-1} on bare Pt electrode as has been reported previously,$^{6)}$ but was missing on the Bi-modified electrodes.

The stretching vibration of CO adsorbed on bare Pt electrode shows a downward shift of ca. 40 cm^{-1} with decreasing θ_{CO}.$^{7)}$ Severson et al.$^{7)}$ demonstrated, by using isotopic mixtures of ^{12}CO and ^{13}CO, that the band shift is caused by dipole coupling (lateral interaction) between adsorbed CO molecules. Dipole coupling should be responsible also for the Bi-modified electrodes because average distance between CO molecules will be increased by coadsorption of Bi. Band shifts arising from other physical and chemical effects of Bi are also possible. Since Bi adatom on Pt surface is partially charged,$^{8)}$ adsorption of Bi will change the electric field in the double layer and/or backdonation of electron density from metal to $2\pi^*$ anti-bonding orbital of CO. It is well known that these changes result in IR band shift of adsorbates.$^{9,10)}$ However, these additional effects on the CO vibration are considered to be small in the CO/Bi/Pt system because the band shift from 2070 cm^{-1} to 2035 cm^{-1} observed in Fig. 2 is almost the same as the dipole coupling shift on bare Pt electrode.$^{7)}$

There exists a remarkable difference between the IR spectra of CO adsorbed on bare and Bi-modified Pt electrodes. The C-O stretching band splits into two in the CO/Bi/Pt system as described above. However, such clear band split is not observed for CO adsorbed on bare Pt electrode at any θ_{CO}.$^{7)}$ One might assign the low-wavenumber band observed at θ_{Bi}=0.12-0.23 in Fig. 2 to the C-O stretching of CO adsorbed on Pt atoms adjacent to Bi adatoms and, therefore, experiencing reduced dipole coupling compared with the rest of the adsorbed CO. If it were true, band split were expected also on Pt surfaces modified with other metal adatoms. However, a relatively sharp and symmetric band of the linear CO was observed on Pt surface modified with Pb.$^{11)}$

Carbon monoxide adsorbs uniformly on bare Pt surface due to repulsion between the molecules.$^{7)}$ In the present CO/Bi/Pt system, however, adsorption of CO will depend greatly on the structures of Bi-adlayer and, therefore, the adsorbed CO should experience dipole coupling conditions different from those on bare surfaces. We can explain the band split in Fig. 2 by assuming the change in structure of Bi-adlayer with θ_{Bi}, as follow.

At small θ_{Bi} up to 0.11, the C-O stretching band shifts slightly to low wavenumbers by UPD of Bi without changing band shape and band width (ca. 10 cm^{-1}). This indicates that the adstructure of CO is not disturbed greatly but average intermolecular distance of CO is increased slightly. Therefore, we can consider that Bi adatoms are distributed uniformly over the electrode surface so as to maximize their nearest-neighbor distances due to weak lateral repulsion between Bi adatoms.$^{8)}$ The appearance and growth of the low-wavenumber band at θ_{Bi}=0.12-0.23 indicates coexistence of two adsorption sites. Paffett et al.$^{8)}$ showed that the structure of Bi submonolayer evaporated on Pt(111) in ultra-high vacuum changes to more closely packed ones with increasing θ_{Bi}. Similar structural changes have been reported also in UPD of Pb on Ag(111).$^{12)}$ Considering the low-wavenumber band in Fig. 2 grows with increasing θ_{Bi}, we assign this band to CO adsorbed at domains of the Pt surface where Bi adatoms are packed more closely than the rest of the surface. Since the second band increases in intensity without changing its peak position, the more closely packed Bi islands grow as θ_{Bi} increases without changing the structure and, finally, covers all over the Pt surface around θ_{Bi}=0.23 where the high-wavenumber band disappears completely. Distributions of CO and Bi are considered to be uniform also in the second phase because the band shape at θ_{Bi}=0.23 is almost symmetric. The constant peak position and symmetric shape of the low-wavenumber band suggest probably some ordering of Bi adatoms within the second phase.

With further increase in θ_{Bi}, the C-O stretching band shows the downward shift again from 2060 cm^{-1} at θ_{Bi}=0.23 to 2035 cm^{-1} at θ_{Bi}=0.3. This low limiting peak position is in agreement with the vibrational frequency of an isolated or singleton CO on bare Pt electrode at the same potential,7) indicating that well separated vacant Pt sites are left on the electrode surface around θ_{Bi}=0.3. Therefore, the downward shift of the C-O stretching band at θ_{Bi} greater than 0.23 can be attributed to the structural change of the Bi adlayer to a close-packing monolayer.

In summary, the C-O stretching band of CO adsorbed on Pt electrode shifted to lower wavenumbers and splits into two by UPD of Bi. As θ_{Bi} increases, the low-wavenumber band grows at the expense of the high-wavenumber band. We note that the catalytic activity of Bi-modified Pt electrode for oxidation of HCOOH and HCHO increases with increasing θ_{Bi}.2) Therefore, we believe that the band split of adsorbed CO has some intimate relation to the improved catalytic activity of the modified electrode, details of which will be discussed in a following paper.11)

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