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INFRARED REFLECTANCE SPECTRA OF CHEMISORBED FORMATES ON EVAPORATED COPPER AND ALUMINUM SURFACES

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Infrared spectra of $HCOO^-$ and $DCOO^-$ chemisorbed on evaporated copper and aluminum surfaces have been observed by high sensitivity reflection techniques. The absence of the antisymmetric OCO stretching band for species on the copper film suggests that the chemisorbed formate molecules are orientated almost vertically on smooth surfaces.

Recent investigations on chemisorption on the bulk metal have indicated the feasibility of using infra-red reflection method$^{1)}$. At high incident angles, the electric field is predominantly perpendicular to the mirror surface$^{2)}$, therefore, it can interact with vibrational modes for which the effective component of dipole moment change is perpendicular to the surface. The formate ion has strong infrared absorption bands at 1360, 1590 cm^{-1}, and these bands were assigned to be the symmetric OCO stretching vibration, in which the dipole moment change is parallel to the C_2 axis of the ion, and the antisymmetric vibration, in which the change is perpendicular, respectively. So, it can be expected that the symmetric mode of vibration appears strong in the reflection spectra but the antisymmetrical mode abnormally weak, provided the adsorbed ions are orientated perpendicularly to a smooth metal surface.

The copper and aluminum mirrors were prepared by evaporation in a stainless-steel bell-jar maintained at a background pressure of 2.0×10^{-6} Torr. An infrared beam was incident upon the first mirror at an angle of 85°, and after a reflection the beam was incident, for another reflection, at 70° upon the second of the same metal as the first. Further experimental details will be found in other papers$^{3)}$. The chemisorbed formates spectra are given in Fig. 1. Repetitive scanning capability of the computer-assisted spectrometer aided by signal enhancement procedures (x10) effectively reduced the noise level$^{3)}$.

The spectra of chemisorbed species on aluminum show two absorption bands with maxima near 1600 and 1360 cm^{-1}. On deuteration, the band maxima shifted to lower frequencies(1590,1355 cm^{-1}), although deuteration resulted in a slight change in band shape. These bands remained undiminished upon evacuation below 10^{-5} Torr at room temperature. On the other hand, the only 1355 cm^{-1}(1350 cm^{-1} for deuterated species) band appeared in the spectra of formates on copper, and no other absorption band could be observed, whereas in the transmission spectrum (dashed line) of the same species on deposited copper appeared only the 1600 cm^{-1} band of antisymmetric

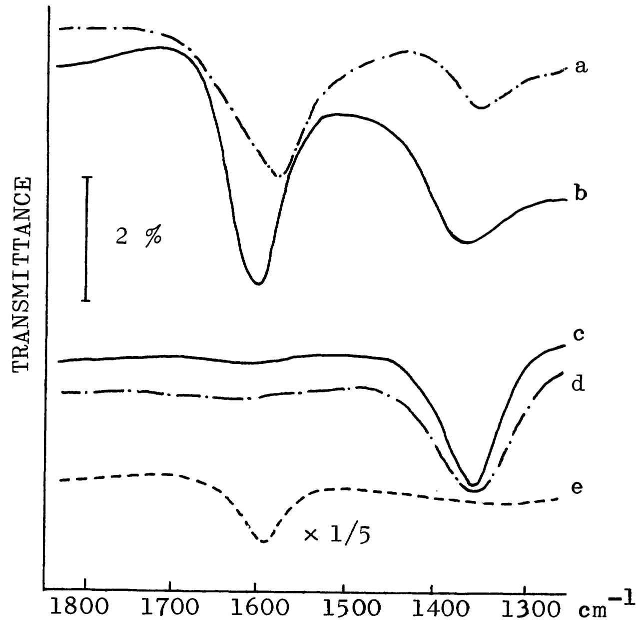

Fig. 1. Reflection-absorption spectra of adsorbed $HCOO^-$(b,c) and $DCOO^-$(a,d).

The upper two curves a,b on aluminum and others c,d,e on copper. The dashed curve e shows the transmission spectrum of adsorbed species on copper evaporated KBr.

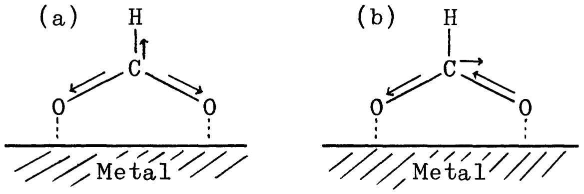

Fig. 2. Adsorptive form of formates on metal.

(a) symmetric stretching vibrational mode.

(b) antisymmetric stretching vibrational mode.

vibration.

Copper films deposited at room temperature are sintered and the total surface area is approximately equal to its geometric area in contrast to the aluminum surface which is porous. Scanning electron microscope photographs evidently represented these features of the surfaces. We observed the rapid increase in reflectance after evaporation of copper corresponding to the sintering.

HCOOH (DCOOD) is dissociatively chemisorbed to form the surface layer which Kishi et al.$^{4)}$ had deduced by their transmission measurement. The observed frequencies are in good accord with the corresponding metal formates by transmission techniques except the band near 1600 cm^{-1} which disappeared in the reflection spectra of species on copper surface, showing the dissociative chemisorption occured in the present work (Fig. 2).

The absence of the 1600 cm^{-1} band should show the orientation of formate ion nearly vertical to the smooth copper surface, and the appearance of this band in the spectrum of species on aluminum could be elucidated with the relatively random orientation of the ions to the macroscopic metal surface due to the surface roughness.

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