

Formic Acid Decomposition on Evaporated Nickel and Copper Surfaces by Infrared Reflectance Spectroscopy

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Infrared reflection studies of DCOOD decomposition on deposited Ni film at 230 and 300 K showed that the reaction products remaining on the surface include CO, formate ion, and formic acid anhydride. Bands appeared at 2120, 2065, 1910, and 1880 cm^{-1} and are identical to the bands of CO chemisorbed on deposited Ni. Formate antisymmetric and symmetric OCO stretching bands were observed on deposited Ni in addition to the CO and COC stretching bands due to the reaction intermediate formic acid anhydride. On deposited Cu the formate and the formic acid anhydride bands were also found and discussed.

1. INTRODUCTION

Infrared spectroscopy can afford direct evidence concerning the structure of chemisorbed molecules and the nature of chemical bonding between chemisorbed molecules and the catalyst surface. The great majority of infrared work so far reported has been made by transmission methods with fine metal particles supported on infrared transparent materials such as silica or alumina under poor vacuum conditions. Recently, high sensitivity reflection spectroscopy (1) using a multiple reflection or a single reflection technique has been successfully applied to the submonolayer adsorption study of carbon monoxide on polycrystalline Ni (2), Pd (3), W (4), and noble metal surfaces (5), and on particular crystal surfaces of Cu (6) and Pt (7) under ultra-high vacuum conditions. One great advantage of this method is its application to bulk metal surfaces, and another is its ability to determine orientations (8) of adsorbed

species in relation to the plane of the metal surface. However, the great majority of work using these methods has so far dealt with CO chemisorption, probably because CO has an exceptionally intense absorption and the infrared bands of its adsorbed species lie outside the atmospheric water vapor region.

Formic acid decomposition on metal surfaces has been used as a test catalytic reaction and has been widely investigated by using many different techniques. Early transmission infrared investigations (9, 10) of HCOOH decomposition, conducted on supported materials or films under relatively poor vacuum conditions, revealed intense absorption bands of formate ions with peaks usually located around 1580 and 1350 cm^{-1} . Falconer and Madix (11) investigated formic acid decomposition on a clean Ni (110) surface by the thermal desorption method. They observed the selective evolution of water and then stoichiometric quantities of H_2 , CO, and

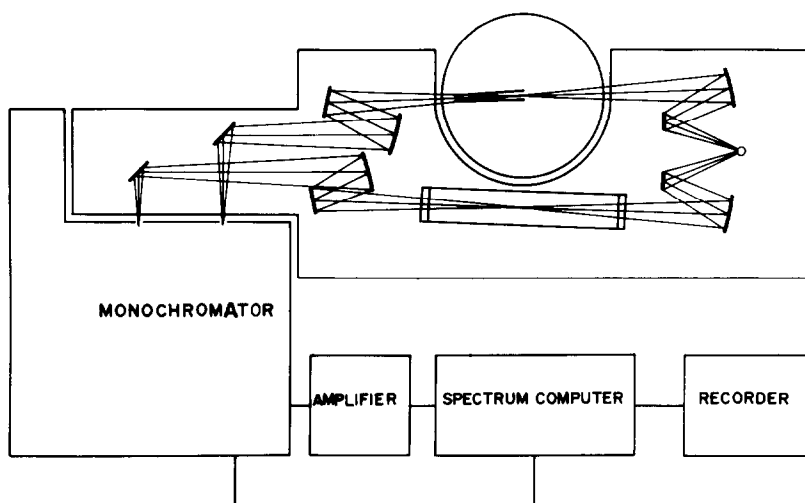


Fig. 1. Schematic view of the ir instrument.

CO₂ were produced in the decomposition on the surface; this suggested that formic acid anhydride was formed as a stable reaction intermediate.

Our previous reflection study (8) on Cu and Al deposited films revealed that chemisorbed formates are adsorbed perpendicularly on the metal surfaces. The surface used, however, was contaminated by residual gas or the diffusion pump oil and had possibly become oxidized. Consequently, the formic acid decomposition on copper and nickel films prepared under UHV conditions has been reexamined in order to obtain further information as to the existence of the above mentioned reaction intermediate, decomposition products, and their orientations on the metal surfaces. We report here ir reflection results for the decomposition of deuterated formic acid (DCOOD) on evaporated nickel and copper surfaces.

2. EXPERIMENTAL

2-1. Optical System

Figure 1 shows an overall schematic diagram of the whole system. The spectrometer was operated in a double beam mode as shown in the figure. The external optical system was attached to introduce

the reflected radiation into the monochromator. The measurements were carried out in the ranges of 2200–2035, 1990–1740, and 1650–1050 cm⁻¹. Careful balance between sample and reference paths was necessary and the compensation cell was used in the reference beam path in order to eliminate the considerable features due to water vapor in the atmosphere. Further residual features due to path difference could be subtracted by the spectrum computer.

Greenler (12) calculated the optimum number of reflections which depends on the angle of incidence and the optical constants of the metal. The optimum number of reflections on nickel is two to three for incident angles from 80–85°. Our sample system satisfies such optimum conditions. The single reflection measurements were also made at an angle of incidence of 84°, with an incident beam angular spread of about 6°. This yields a reflection sensitivity which is 70% as large as the optimum. A Jasco IR-G grating spectrometer (Japan Spectroscopic Co. Ltd.) was used, to which a spectrum computer JEC-5 (Japan Electronic Co. Ltd.) equipped with signal amplifiers was attached.

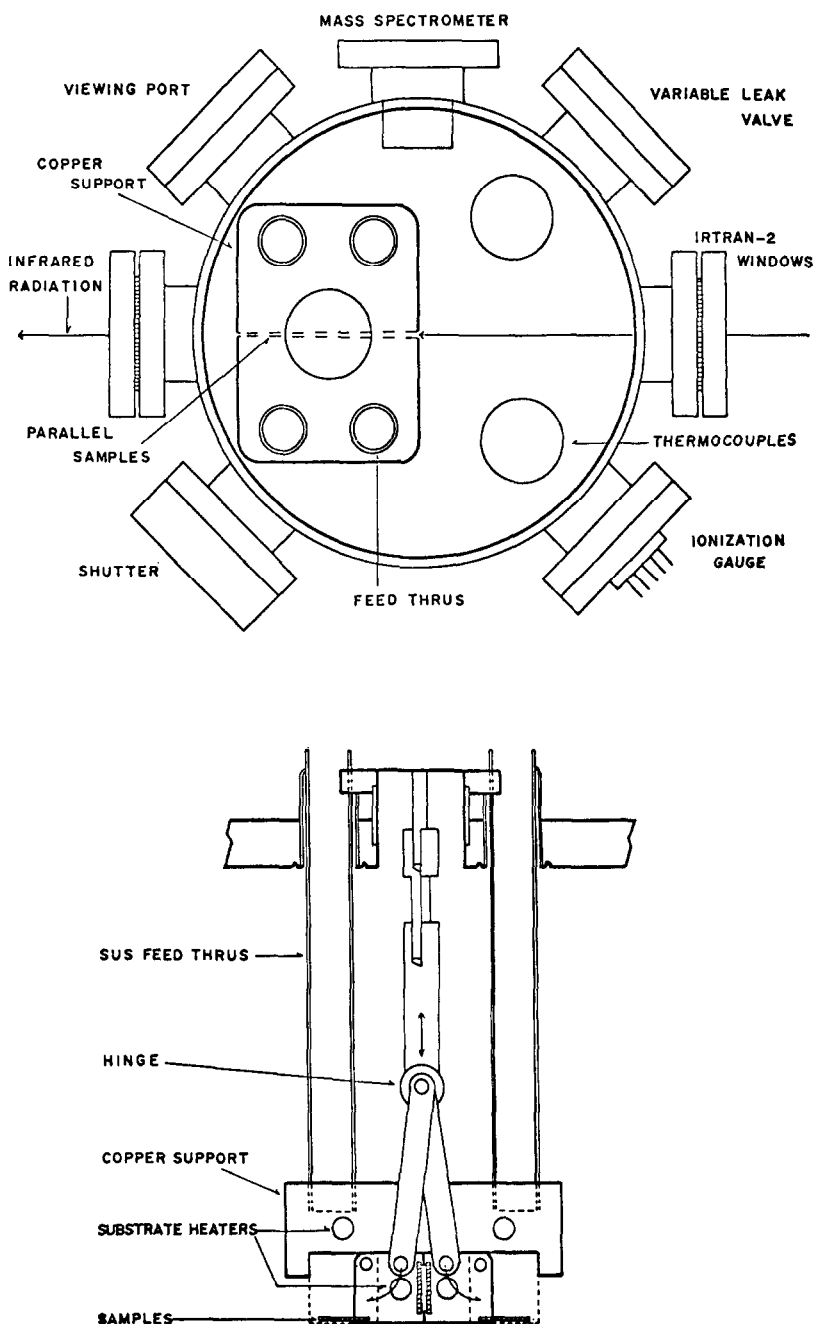


FIG. 2. Arrangement of UHV ir chamber.

2-2. Infrared Cell

A stainless-steel ultra-high vacuum chamber was used for infrared reflection measurement. It was pumped by a 2000

liter/sec titanium sublimation getter pump, a 500 liter/sec vac-ion pump, and sorption roughing pumps. A nude ionization gauge monitored the working pressure inside the chamber. A quadrupole mass spectrometer

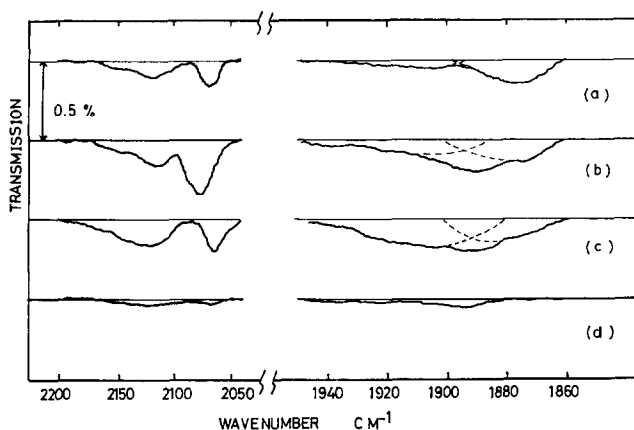


FIG. 3. Infrared reflection spectra of chemisorbed CO on evaporated nickel film at 230 K. (a) 10 L exposure of CO, (b) 1×10^{-8} Torr equilibrium pressure of CO, (c) evacuation to 1×10^{-8} Torr, and (d) warming and evacuation, raising the temperature up to 450 K.

was used for analyzing the residual gas and measuring partial pressure of thermally desorbed gases. After 10 hr baking at 200°C a typical working pressure less than 2×10^{-9} Torr ($1 \text{ Torr} = 133.3 \text{ N m}^{-2}$) was obtained routinely. During the evaporation the pressure inside the chamber rose to 6×10^{-9} Torr.

Figure 2 shows the inner arrangement of chamber. The shutter plate between the evaporation source and the sample mirrors was used to prevent contamination of the sample surface by impure metal of the evaporation source during initial deposition, and another cylindrical shield enabled the metal to be evaporated onto the sample plate itself but not onto the infrared windows and the cell walls.

The infrared windows (Irtran-2, Eastman Kodak Co.) circular plates, 38 mm in diameter and 2 mm thick, were sealed into a standard Varian rotatable flange with Vaseal (Space Environment Lab. Inc.) using the same method described by Kottke and Greenler (13). The top flange (200 mm) was fitted with a cooling tube which carried the copper block support for the sample mirror plates as shown in the figure. The sample mirror plates were tightly clipped to the copper support.

Temperatures as low as 200 K could be reached on the front surfaces using liquid nitrogen as coolant. The copper support could also be heated by a tungsten heater inside the hole of the support up to 600 K. The sample plate size was $20 \times 80 \times 1$ mm. Temperatures of the plates were measured with an alumel-chromel thermocouple situated very near the plates. Sample temperatures between 200 and 600 K could be achieved by liquid nitrogen cooling or tungsten filament heating. Thermocouple wires and sample heater tungsten wires were also introduced by way of electrical feedthroughs in the top flange. To the under part of the cell, optical windows, gauge ports, viewing ports, some electrical feedthroughs, and the gas inlet variable leak valve were attached.

A filament of 1 mm ϕ nickel wire was evaporated by heating resistively. Copper was evaporated from small chips held in a basket of 0.5 mm ϕ tungsten wire. The stainless-steel hinge was connected to the manipulator mounted to the top flange. In the open position (broken line in the figure) nickel or copper could be deposited on the sample plates from the evaporation source situated 120 mm below. The sample

plates were then rotated by the hinge to the parallel position (full line) to provide a multiple reflected light with high incident angles.

The above mentioned multiple reflection attachment can easily be changed to the single reflection attachment by exchanging the top flange, when the simultaneous measurement of flash desorption is required. The procedure of the sample mounting, sample cooling, and heating is the same as the multiple reflection apparatus, but the simple sample holder enabled us to obtain infrared reflection results simultaneously with the thermal desorption spectrum.

CO gas used in this study was spectroscopically pure gas (99.9%, Nishio Co. Ltd.). Vapors of formic acid and dideuteroformic acid gas were purified by vacuum distillation from reagent grade liquid. Pure metals of nickel (99.998%) and copper (99.999%) were used in vacuum deposition.

2-3. Procedure

The nickel filament was outgassed just below its evaporation temperature for 30 min. After rigorous system baking and outgassing two sample plates were opened to a horizontal position using the manipulator and deposited. The sample plates were then faced at the parallel position and background spectra were measured. HCOOH (DCOOD) was then admitted, usually at pressures between 1×10^{-7} and 1×10^{-5} Torr, for a measured exposure and then pumped out. A spectrum was again recorded, and both spectra of successive scans were stored in the separate memories of the JEC-5 spectrum computer. At the end of each series of scans, the background data were subtracted from the sample data, and computed spectra could be plotted out on the recorder. The spectrum was usually scanned at $1 \text{ cm}^{-1} \text{ sec}^{-1}$ with a spectral resolution of 2 cm^{-1}

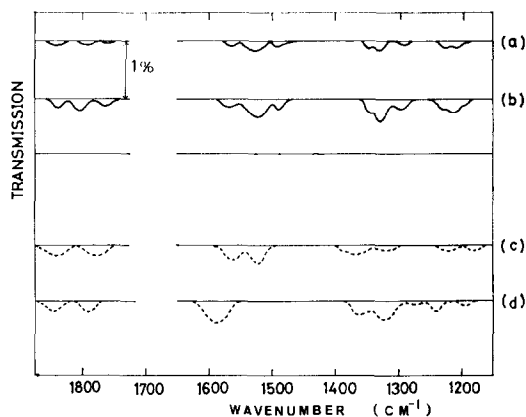


FIG. 4. Infrared reflection spectra of decomposition products of adsorbed DCOOD on evaporated nickel and copper surfaces at room temperature. (a) 1×10^{-6} Torr equilibrium pressure of DCOOD (on copper), (b) 1×10^{-3} Torr equilibrium pressure for 10 min and evacuation (on copper), (c) 10 L exposure of DCOOD (on nickel), and (d) 1×10^{-3} Torr equilibrium pressure (on nickel).

and usually 16 times repeat scans were carried out. It took about 15 min to obtain the whole spectrum. A scale expansion of 10-fold or 20-fold was adopted. The computed difference spectra thus obtained are shown in Figs. 3 and 4.

3. RESULTS

3-1. Carbon Monoxide Region ($2200-1850 \text{ cm}^{-1}$)

When formic acid was introduced into the cell at 230 and 300 K, dissociation and decomposition of the formic acid proceeded simultaneously. Among the many adsorbed species due to the formic acid decomposition, CO showed the most detectable absorptions in the whole range. Accordingly, it was felt that the CO adsorption study on metal surfaces was also of major importance in order to ascertain the assignment of infrared bands appearing the the adsorption of formic acid.

As an initial step, therefore, we examined the CO adsorption on deposited nickel films prepared at 230 and 300 K. The experimental procedures were the same as

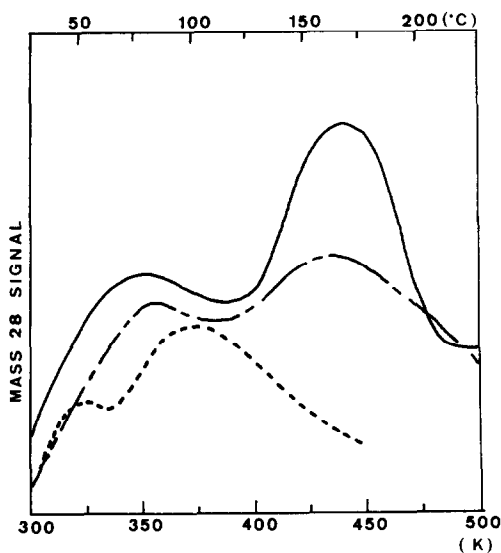


FIG. 5. Thermal desorption spectra obtained after exposure 1×10^{-4} Torr equilibrium pressure and evacuation. (a) —, CO adsorption on nickel; (b) --- HCOOH adsorption on nickel; (c) - - - HCOOH adsorption on copper.

that of formic acid adsorption. Figure 3 shows the reflection spectra for CO adsorption on a nickel film deposited at 230 K and observed frequencies are given in Table 1. We refer to the range 2200–2000 cm^{-1} and the range 2000–1850 cm^{-1} hereafter simply as the L and B regions, respectively. Two split bands appeared with comparable intensities in both regions. This band splitting was also observed in the other lower frequency regions as described below. After 10 L exposure of CO to the nickel surface (Fig. 3a) all of these bands began to occur at 2120 and 2065 cm^{-1} in the L region and 1910 and 1880 cm^{-1} in the B region. After dosing 1×10^{-6} Torr equilibrium CO pressure (Fig. 3b) the above peaks fully developed in intensity. The peak frequency of 2065 cm^{-1} band shifted continuously to 2085 cm^{-1} as the coverage was increased. The 2120 cm^{-1} band shifted only slightly to 2125 cm^{-1} at high coverages. The 1880 cm^{-1} band moved to 1895 cm^{-1} but the shoulder at 1910 cm^{-1} shifted slightly to 1915 cm^{-1}

at high coverages. For the lower temperature adsorption (230 K) the lower frequency band at 2085 cm^{-1} was more intense than the higher frequency 2125 cm^{-1} band and the 1895 cm^{-1} band showed larger intensity than the 1915 cm^{-1} band, but the reverse was true for room temperature adsorption (300 K). Prolonged exposure resulted in a slight decrease in intensity and increase in band width of all the absorption bands. The change of absorption was reversible and the spectrum at low exposure was obtained by evacuation to 1×10^{-8} Torr. The bands of the L region are rather sharp having a half-width of 20 cm^{-1} , whereas the half-width of the B region bands was 30 cm^{-1} . Continued pumping caused no change in intensity until heating up to 400 K. Through all the experiments the positions of those absorption maxima varied by as much as $\pm 5 \text{ cm}^{-1}$. Adsorption caused a change in reflectivity over the whole frequency range, amounting to a decrease of 2% at CO saturation.

The reflection spectra and their behavior on formic acid adsorption on a nickel film deposited at 230 and 300 K were completely identical in this region with the CO chemisorption results, so the corresponding spectra are omitted.

3-2. Formate and Formic Acid Anhydride Region (1850–1150 cm^{-1})

A careful search was made for infrared bands in the range 1850 to 1150 cm^{-1} since it is well known that adsorbed formate ions or formic acid anhydrides play important roles in formic acid decomposition. Figure 4 represents the reflection spectra of adsorbed DCOOD on copper (solid lines, a and b) and nickel (dashed lines, c and d) surfaces deposited at room temperature, respectively. There is a discontinuity in the wavenumber scale since the measurements of higher and lower wavenumber regions have been separately made because of scaling out of the back-

ground level. Table 2 shows the observed frequencies of this region.

We found many absorption bands of adsorbed species on both nickel and copper surfaces in this range: There were bands between 1600 and 1300 cm^{-1} (which we shall refer to as the formate region) and bands around 1800 and 1200 cm^{-1} (which we shall refer to as formic acid anhydride regions). All of these bands are split into subpeaks with comparable intensities, as found in the CO region. The reflection spectra in the formate region on nickel (Fig. 4c and d) deposited at 300 K show the appearance of 1570 and 1520 cm^{-1} bands and also 1370 and 1320 cm^{-1} bands. On the copper surface, 1565, 1525, and 1490 cm^{-1} bands and also 1345, 1328, and 1295 cm^{-1} bands appeared. The middle bands of these groups, 1525 and 1328 cm^{-1} , have the largest intensity in the group. This intensity relation was found also for all the other bands observed on copper. When copper films which had been well annealed at 350°C were used, the former three bands disappeared completely. All of these peaks appeared after 10 L exposure and did not change their intensities and frequencies on further addition of DCOOD until 1×10^{-5} Torr equilibrium pressure. The bands mentioned above can be assigned to the formate ion as discussed below.

Although formic acid anhydride is not known to form even in solution, it may be stabilized by chelation on a metal surface as Falconer and Madix (11) maintained. We could find other appreciable absorption bands which are shown in Fig. 4 and which cannot be assigned to formate ion. The room temperature adsorption on nickel deposited at 300 K gave rise to absorption bands split usually at 1230 and 1180 cm^{-1} . These absorption bands already occurred after only 2–3 L dosing on metal surfaces. The room temperature adsorption on copper surface deposited at 300 K also produced the bands at 1227, 1212, and 1197 cm^{-1} .

TABLE 1

Observed Frequencies of Carbon Monoxide Adsorbed on Nickel Films. The Metal Deposition Temperature and Also the Temperature of Adsorption were 230 K^a

Peak frequency low coverage (cm^{-1})	Peak frequency high coverage ^b (cm^{-1})	Frequency shift (cm^{-1})	Half-width ^b (cm^{-1})	Band height ^b (%T)
2120	2125	5	35	0.18
2065	2085	20	30	0.37
1910	1915	5	60	0.11
1880	1895	15	50	0.15

^a The results for 300 K were the same except for the band intensity.

^b Parameters corresponding to spectrum (b) of Fig. 3.

Anhydrides are expected to have another strong band in the carbonyl region. Noncyclic saturated anhydrides adsorb intensely near 1820 cm^{-1} (14). We found bands splitting around 1820, 1790, and 1775 cm^{-1} on copper deposited at room temperature. On nickel, the first two of these bands were observed. These bands in the formate and formic acid anhydride regions reduced in intensity or disappeared upon pumping at the elevated temperature of 400 K.

4. DISCUSSION

4-1. CO Adsorption

An ir multiple reflection study of CO on nickel deposited at room temperature has already been made by McCoy and Smart (2). They observed two very broad bands around 2060 and 1920 cm^{-1} at equilibrium pressures above 10^{-6} Torr, and suggested initial dissociative adsorption to form C and O adatoms at pressures less than 10^{-6} Torr. In their paper, these two broad bands were attributed to adsorbed CO in two different modes dependent on different faces at the surface. The most striking feature of our spectra is the splitting of each band. Therefore, their 2060 cm^{-1} band may correspond to our split bands of 2065 and 2120 cm^{-1} , and their 1920 cm^{-1} band possibly corre-

TABLE 2

Observed Frequencies of Chemisorbed Formates and Formic Acid Anhydrides (Decomposition Products from DCOOD) on Nickel and Copper Films. The Metal Deposition Temperature and Also the Temperature of Adsorption were 300 K

	Formate		Formic acid anhydride	
	Asymm. OCO stretching (cm ⁻¹)	Symm. OCO stretching (cm ⁻¹)	C-O-C stretching (cm ⁻¹)	C=O stretching (cm ⁻¹)
DCOOD/Ni	1570	1370	1230	1820
	1520	1320	1180	1790
DCOOD/Cu	(1565) ^a	1345	1227	1820
	(1525)	1328	1212	1790
	(1490)	1295	1197	1775
Previous work (8)	(1590)	1355		

^a Parentheses mean that those bands were not observed on well-annealed films.

sponds to our 1880 and 1910 cm⁻¹ bands. These split bands occurred already after 10 L exposure and the presence of 1×10^{-6} Torr equilibrium pressure of CO was enough to develop them to maximum intensity. The spectra of adsorbed species could therefore be obtained at a much earlier stage of adsorption in the present work than in the investigation of Smart and McCoy. Our repetitive scanning of the spectrum and computer averaging and careful background subtraction might give a better S/N ratio than the previous study of McCoy and Smart.

Bradshaw and Pritchard (15) examined the chemisorption of CO on evaporated nickel thin films at low and room temperatures by the transmission method. The reflection spectra obtained in the present paper are similar to their transmission spectrum except for the appearance of the abovementioned band splittings.

The intensity ratios of the 2120 to the 2065 cm⁻¹ band and of the 1910 to the 1880 cm⁻¹ band changed depending on the adsorption temperatures but not the coverage. Each band shifted to higher frequencies with increase in coverages by 5–20 cm⁻¹ and reverted to the original position on evacuation. The lower frequency bands

of the L and B regions, 2065 and 1880 cm⁻¹, showed the same tendency in intensity behavior and frequency shift. Thus there exist at least two kinds of adsorbed species and also two kinds of different sites or crystal planes responsible for the split bands in both regions.

From infrared reflection spectra of Pt (7) and Pd (3) metals a single CO stretching band is observed above 2000 cm⁻¹ in the former case and below 2000 cm⁻¹ in the latter, respectively, whereas on deposited Ni surface peaks appeared both below and above 2000 cm⁻¹. The observed intensities of these peaks are relatively weak compared with those on Pt or Pd surfaces. Many species should occur on nickel surface. A part of the CO decomposes to form C and O adatoms and partly oxidizes the nickel surface (20); therefore, the number of bare site for associative chemisorption of CO may be relatively small. Recent studies by electron energy loss spectroscopy (23, 24) showed C-O stretching vibrational loss peaks at 256 and 265 meV of chemisorbed CO on clean and oxygen pretreated Ni(100) surfaces, respectively. These frequencies are quite comparable with those of the split bands in the L region.

The decomposition of formic acid already occurred at low temperature (230 K). Complete identity was obtained between the CO chemisorption and the formic acid decomposition spectra in the 2200–1850 cm^{-1} region. The presence of the other decomposition products, therefore, did not affect the CO adsorption. The thermal desorption spectrum of adsorbed CO on nickel films was almost the same as that of HCOOH as described below. These results suggest that DCOOD decomposes to produce CO which chemisorbed in the same manner as CO itself.

Although we have not checked fully the presence of chemisorbed CO formed by DCOOD decomposition on copper film in this region, admission of large amount of DCOOD (1–10 Torr) on copper deposited under poor vacuum conditions gives rise to a sharp absorption band at 2100 cm^{-1} (21). The peak frequency and the band width agreed well with the previous report (5) of CO adsorption on evaporated copper film.

4-2. Orientation of Formate Ions

One of the primary objectives of the studies on decomposition of HCOOH has been to identify the catalytic intermediate. Eischens and Pliskin (9) studied the infrared transmission spectra of DCOOD chemisorbed on Ni at -61°C and obtained formate bands at 1546 and 1325 cm^{-1} and they assigned the bands to covalently chemisorbed species. Fukuda and co-workers (17) maintained that although a part of the overall decomposition proceeded via formate ions, most of the decomposition reaction occurred between formic acid molecules and the vacant sites on the surface. Inglis and Taylor (18) proposed that an intermediate species was formed most probably in a bimolecular process from a formate ion and formic acid molecules. A similar model assuming the existence of formic acid anhydride has recently been proposed by Falconer

and Madix (11) as described below. Although they rejected the possibility of the presence of formate ion, it was observed on our polycrystalline films. Formate ion, therefore, should be taken into account in the study of the reaction mechanism.

The formate ion usually has two strong absorption bands due to OCO stretching vibrations; these are a strong antisymmetric vibrational mode and a somewhat weaker symmetric mode. Sodium formate (16) in aqueous solution shows the corresponding values of 1585 and 1360 cm^{-1} , respectively. The former is about three or four times stronger than the latter.

The reflection spectra can also be used to obtain information about the orientation of adsorbed species in relation to the metal surface. When the adsorbed formate ions are oriented normal to the metal surface, the symmetric OCO stretching vibration has its oscillating dipole moment perpendicular to the metal surface and interacts with the standing wave field at the surface to produce a strong absorption band in the reflection spectra, while the antisymmetrical mode has its oscillating dipole moment parallel to the metal surface and cannot interact with the infrared radiation, with the result that the absorption band does not appear in the reflection spectra. Thus we would expect that the antisymmetric mode would be lower in intensity than the symmetric mode, because the orientation of adsorbed formate parallel to the surface is unlikely.

The intensity of the antisymmetric and symmetric bands obtained for copper and nickel surfaces are, in general, comparable. These results do not agree with our previous report (8). This may reflect the different surface conditions. However, when we used well-annealed copper, the antisymmetric stretching band completely disappeared. This fact is explained, as we have reported, by the orientation of formate ions normal to the smooth copper surface.

The origin of the band splitting may be the different sites or crystal faces, probably the same as in CO adsorption. The frequencies of the most intense peaks are 1530 and 1320 cm^{-1} for copper surface, in close accord with earlier transmission results (9).

Large exposure on copper surface produced an enormous growth of all the bands at higher wavenumbers. From their position, these peaks may be considered as due to copper formate. By contrast, large exposure on nickel surface does not produce large absorption. This fact may correspond to the faster decomposition rate of formic acid on Ni than on Cu.

4-3. Formic Acid Anhydride Intermediate

Falconer and Madix (11) have examined the decomposition of HCOOH on a clean Ni(110) single crystal surface using LEED, AES, and thermal desorption techniques. They observed that desorption of adsorbed HCOOH on Ni (110) yields four decomposition products (H_2 , CO_2 , CO, H_2O). At the coverage of one monolayer, the ratio CO_2 :CO was found to be 1:1. From these results they concluded that formic acid anhydride forms on the surface as an intermediate species. Previous infrared work indicated that the only chemisorbed species during the decomposition were formate ions and protons and no evidence was reported for the presence of CO and other intermediate species like formic acid anhydride.

Anhydrides are characterized by a very intense band in 1250–1100 cm^{-1} due to the C–O–C stretching vibration band and by strong bands near 1800 cm^{-1} due to the C=O stretching vibration (14). We observed bands in both the C–O–C and C=O stretching regions. The absorption bands at 1180 and 1230 cm^{-1} may be assigned as acid anhydride C–O–C stretching vibration bands although no reference data for formic acid anhydride are available. The

bands assigned to formic acid anhydrides appeared not only on nickel surface but also on copper surface. Thus, the formic acid decomposition mechanism on nickel assumed by Falconer and Madix may apply also on deposited copper surface.

4-4. Flash Desorption Results

The flash desorption was examined to confirm CO production in the decomposition of formic acid. A quadrupole mass spectrometer (NEVA-515) was used. The flash desorption spectra were obtained as a partial pressure rise in the chamber. After infrared reflection measurement the nickel or copper films on a quartz plate were heated by radiation from a tungsten filament in the copper support with a heating rate of 10°/min.

The desorption spectra obtained from nickel and copper surfaces are shown in Fig. 5. The observed broadening of the peaks may be due to the large copper support holding the sample mirror which has a large thermal inertia. The observed peaks can be attributed to the desorption from the sample surface and not from the sample holder or cell walls, because blank measurements without the sample mirror gave no substantial peak in these temperature ranges.

The desorption peaks from adsorbed HCOOH on nickel are identical to the peaks found in the desorption of adsorbed CO and are located at the same temperatures with nearly the same shape. This fact is in complete agreement with the infrared results which showed CO as the most important adsorbed species. The spectra clearly show two states of adsorption. The lower temperature peak appeared only with high CO or HCOOH coverages. Thus two peaks may be due to desorption from different crystal faces or different chemisorbed states (α_1 -CO or α_2 -CO) on the same crystal faces. This result accords with a recent thermal desorption study

(19). We could observe other decomposition products (CO_2 , H_2O , and H_2) but no peak due to formate or formic acid anhydride was detected in adsorption of HCOOH at 300 K.

The above mentioned infrared band of CO arising from DCOOD decomposition easily disappeared on evacuation at room temperature, which is in good agreement with a previous infrared reflection study of CO on deposited copper (22). Thus, the CO formed by decomposition of DCOOD should be desorbed from the surface before starting desorption measurements. However, flash desorption following HCOOH adsorption on deposited copper surface showed that the two peaks appeared around 325 and 375 K. Therefore, the observed CO desorption peaks are probably due to decomposition of the formate complexes which remain stable on the surface below room temperature.

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