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ON Ni

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ABSTRACT

At low temperatures (1.5K-40K), CO has been found to chemisorb into terminal, bridge, and three-fold sites on evaporated Ni films. The chemisorption takes place directly, rather than through a precursor state. At least two distinct terminal sites are occupied at high coverages. After the sample is warmed from 1.5K to 40K the infrared spectra change dramatically, showing substantial surface diffusion even at these low temperatures.

INTRODUCTION

We have used far infrared absorption spectroscopy to study the adsorption of CO on nickel at low temperatures (1.5K - 40K). The high resolution of this technique, $2 - 4 \text{ cm}^{-1}$ in the data presented, allows the measurement of vibrational peak widths and positions, even for peaks separated by as little as 50 cm^{-1} (6.2 meV). Measurements made at substrate temperatures of 1.5K - 40K, when compared with data recorded at higher temperatures, permit an evaluation of the temperature dependence of the measured quantities and of adsorbate kinetics.

Our samples consist of nickel evaporated onto a thin sapphire substrate, and then exposed to calibrated quantities of CO. The use of evaporated thin film substrates results in adsorption sites which are not uniform and well defined, and all of the data must be interpreted accordingly. The study of evaporated films does, however, permit the study of adsorption when there is a multiplicity of possible adsorption sites.

Since a detailed description of our experimental apparatus may be found elsewhere (ref.1) only an outline will be given here. The data were recorded by directly measuring the absorption of infrared radiation incident from a rapid-scan Fourier transform spectrometer. Detection was accomplished by attaching a small, appropriately doped, germanium crystal to a low heat capacity sample and

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cooling the assembly to 1.5K. At low temperatures, the germanium resistance is extremely sensitive to changes in temperature (ref.2). With the sample weakly heat-sunk, the absorbed infrared radiation resulted in easily measured changes in the sample temperature.

A reference spectrum was first measured using a nickel film freshly evaporated in UHV ($p < 2 \times 10^{-10}$ torr). The film was then exposed to calibrated quantities of CO and subsequent spectra were measured. The reference spectrum was used to correct for variations in the system responsivity as a function of infrared frequency.

CHEMISORPTION AT 1.5K

Typical data are shown in Fig. 1, showing the infrared absorption of the C-O stretch mode as a function of exposure. All of these data were measured for room temperature CO adsorbed onto a substrate which was held at 1.5K. During adsorption the sample temperature rose measurably, but never by more than a few millikelvin.

Two broad infrared absorption bands are seen in Fig. 1, one in the range $1840\text{--}1950\text{ cm}^{-1}$, and another in the range $2010\text{--}2095\text{ cm}^{-1}$. These bands have been attributed to chemisorption on bridge and terminal sites, respectively (ref.3). Since the thermal energy available at 1.5K seems inadequate for activation of a precursor state, the chemisorption must take place directly. At the highest exposures ($> 0.7\text{L}$) a narrow peak at 2143 cm^{-1} is seen due to physisorbed CO.

The bands, due to chemisorbed molecules, shift in position and change in width and shape with increasing coverage. The bridge site band is broad

Fig. 1. Infrared spectra of CO adsorbed on a Ni film at 1.5K at various exposures in Langmuirs (L).

(40-75 cm^{-1} FWHM) and asymmetrical at all coverages, while the terminal site band (2010-2095 cm^{-1}) is narrower ($\sim 22 \text{ cm}^{-1}$ at 0.05L exposure) at the lowest coverages, and broadens at intermediate coverages. At the highest coverages the terminal site band is seen to consist of at least two overlapping peaks. Since the "fundamental" line shape is unknown, the peaks cannot be unambiguously separated. We define the peak position as the frequency of the maximum of the band in a given spectrum, and the area as the integrated area of the whole band. The appearance of two terminal adsorption sites may result from the inhomogeneous nature of the substrate. Only one of the sites (2020 cm^{-1}) is occupied at low coverages. As the CO exposure increases, a second peak appears at 2090 cm^{-1} and increases in intensity, becoming dominant at 0.7L. At the highest exposures, there is a shift of oscillator strength from the lower to the higher frequency peak, though the total area of the band does not change appreciably. A similar multiplicity of terminal sites has been seen for CO adsorption on Ni(110) (ref.4).

The linewidths of the two bands are similar to results obtained on single crystal substrates (ref.4-6). The difference in the widths for bridge- and terminal-bonded CO merits more careful investigation since, if the linewidths represent vibrational lifetimes, it would imply a significant site-dependence of the coupling of the molecular vibrations to the substrate. Such measurements would have to be made at extremely low coverages, or at saturation in order to eliminate peak broadening due to intermolecular interactions.

SURFACE DIFFUSION AT 40K

Spectra were also recorded from samples which were heated to 40K for one minute after exposure to CO. Essentially identical results were obtained if the sample was heated during the gas exposure, or if the period at 40K was extended to several minutes. Figure 2 shows spectra of a sample exposed to 0.2L CO, before and after heating to 40K. Substantial changes clearly occur when the sample is heated. Since the sample is in all cases returned to 1.5K for data-taking, the changes are certainly not reversible. The differences in the two spectra in Fig.2 were not found to result from changes in the substrate upon warming.

Before discussing the changes in detail, it is worth noting that the mere existence of noticeable changes is remarkable. The thermal energy corresponding to 40K is only $k_B T = 3.3 \text{ meV}$, far less than typical chemisorption and surface diffusion energies (ref.7), yet it is evidently enough to activate considerable surface rearrangement of the CO. The observation of thermally activated processes at temperatures well below thermal desorption temperatures also affects the interpretation of previous data on evaporated films obtained by successive heating of the substrate (ref.1).

Fig.2. Spectra of 0.2L CO adsorbed on a Ni film, after initial exposure at 1.5K (upper) and after heating to 40K for one minute (lower). The sample from which these data were obtained was different from those used for recording the data in the other figures.

In addition to the bridge and terminal site bands, the spectra of Fig.2 show a band in the range $1750\text{--}1830\text{ cm}^{-1}$, assigned to sites of three-fold coordination. When the sample is heated from 1.5K to 40K, there is a substantial loss of intensity from the terminal site band, but with little or no shift in the peak frequency. The lowest frequency band gains in intensity on heating. The intensity and peak frequency of the bridge site band change only slightly on heating. Figures 3 and 4, showing peak position and intensity for the three bands as a function of exposure, indicate that these qualitative observations are borne out at all exposures.

Usually a decrease in band intensity is accompanied by a shift of the peak frequency due to changes in the vibrational coupling to neighboring molecules. The lack of such a shift corresponding to the intensity change of the terminal site band could indicate the presence of islands in which the site populations do not change on warming. For our sample, the islands could correspond to structures in the evaporated film, such as microcrystallites.

The shift of molecules from the terminally bonded sites to sites of higher coordination number implies that the latter are more strongly bound. Figure 3 shows that the intensity of the three-fold site band reaches its maximum at an exposure of 0.3L, while the bridge site seems to saturate near 0.4L, and the terminal site near 0.8L. The sequence suggests an "order of preference" among the sites, the three-fold site being most preferred, and the on-top site the least. The activation energy for movement among the sites, however, is evidently only a few meV, at least in some parts of the surface.

The same order of preference among adsorption sites can also be seen in Fig. 4. The peak frequency of the three-fold site band appears to level off near 0.5L, that of the bridge site band near 0.6L, and that of the terminal site band near 0.9L.

Fig. 3. Integrated absorption as a function of CO exposure for (a) terminal site, (b) bridge site, (c) three-fold site. Data shown for adsorption at 1.5K (x's) and 40K (o's).

Fig. 4. Peak frequency as a function of coverage for (a) terminal site, (b) bridge site, (c) three-fold site. Data shown for adsorption at 1.5K (x's) and 40K (o's).

The shift of the peak frequency of a band with coverage provides a measure of the adsorbate-adsorbate interaction for molecules adsorbed on the corresponding site. The data of Fig. 4 show large differences in the frequency shift for the various sites, indicating that the coupling between molecules has considerable site-dependence. The bridge site peak varies rapidly at low coverages, leveling off above 0.6L at a frequency 100 cm⁻¹ above its zero-coverage value. By contrast, the three-fold site peak frequency changes by only 20-30 cm⁻¹ from zero coverage to saturation. The total dispersion of the terminal site peak is comparable to that of the bridge site peak, but the shift is due in part to the transfer of oscillator strength from a lower-lying peak into a higher frequency peak. The shift of the lower frequency peak alone appears to be only 30-40 cm⁻¹, while the higher frequency peak seems to shift by less than 10 cm⁻¹.

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