Infrared reflection-absorption spectroscopy (IRAS) has been used to study the adsorption of carbon monoxide on a Cu(100) surface. Adsorption isotherms were determined at CO pressures from $10^{-6}$ to 10 Torr, and at temperatures from 115 to 340 K, and the isosteric heats of adsorption ($\Delta E_{\text{ads}}$) evaluated as a function of CO coverage. For increasing CO coverages between 0-0.15 monolayers (ML), $\Delta E_{\text{ads}}$ decreases sharply from 16.7 to 12.7 kcal/mol. From 0.15 to 0.35 ML, $\Delta E_{\text{ads}}$ remains approximately 12.7 kcal/mol and exhibits little coverage dependence. These results are in excellent agreement with previously reported data for the CO/Cu(100) system acquired at much lower pressures ($< 10^{-4}$ Torr) and temperatures ($< 275$ K). At substrate temperatures above 240 K and at pressures $> 10^{-4}$, significant bathochromic shifts of the CO stretch frequency to lower wavenumbers are observed.

1. Introduction

The ultrahigh vacuum (UHV) approach to the study of catalysis has many advantages over traditional methods in that a variety of optical and particle spectroscopies are available to establish in great detail the structure and composition of the surface, and to identify stable surface species. However, a common criticism of the UHV approach is that it is too far removed from reality, since catalytic reactions typically are carried out under quite different conditions, namely, at atmospheric (or higher) pressures and with much less well-defined surfaces. Also, in the “real world” of commercial applications of catalysis, reactions are typically carried out at temperatures well above 300 K whereas adsorption studies in UHV frequently employ temperatures between 90–300 K.

This so-called “pressure and material gap”, which has separated ultrahigh vacuum (UHV) and technical chemical or catalytic investigations has been bridged, to some extent, in recent years by combining in a single apparatus the ability to measure kinetics at elevated pressures on single crystals with the capability to carry out surface analytical measurements [1]. This approach has established the validity of using single crystal surfaces, at least for certain reactions, to model more complex technical catalysts. However, the UHV approach in many respects is rather limited in that most of the commonly available surface characterization techniques cannot be used at elevated pressures, and are typically used ex situ, studying the surface before and after reaction. Thus the specific nature of the surface under the conditions of the reaction generally must be extrapolated indirectly from these ex situ measurements. Ideally, to more completely establish the continuity between the ideal world of UHV surface science and the operational conditions of the “real world” technical catalyst, the equivalence of surface measurements on model surfaces from UHV pressures to elevated pressures (approaching those employed in technical catalytic processing) needs to be demonstrated.

1 Present address: Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, NY 11973, USA.
* To whom correspondence should be addressed.
An optical technique such as infrared reflection-absorption spectroscopy (IRAS) provides an ideal tool to characterize the surface under "working" conditions. To date, however, there are only a limited number of examples in the literature where the IRAS technique has been utilized at elevated pressures $> 10^{-3}$ Torr [2-7].

Here we report the results of a study of CO adsorption on Cu(100) at elevated pressures ($\leq 10$ Torr) and temperatures ($\leq 340$ K) using the IRAS technique. Adsorption isotherms have been determined over a CO pressure range from $10^{-6}$ to 10 Torr and at temperatures ranging from 115 to 340 K. The agreement between the isosteric heats of adsorption determined in the present investigation and those found in a previous UHV study clearly establish for the CO/Cu(100) system the equivalence of the adsorption energetics determined at low temperature/low pressure conditions and the corresponding energetics measured in a high temperature/high pressure environment. That is, the UHV results extrapolate remarkably well into the elevated pressure regime.

2. Experimental

The experiments were performed in an ultrahigh vacuum chamber equipped with an Auger spectrometer and a direct interface to a high-pressure infrared cell. This apparatus has been described in detail elsewhere [8,9]. The adjoining infrared cell is outfitted with flange-mounted CaF$_2$ windows and a sliding-seal interface which serves to separate the infrared cell from the ultrahigh vacuum surface analytical chamber during operation at high pressures. This setup allows experiments in the infrared cell to be carried out at pressures as high as several atmospheres. For the CO pressure range of $5 \times 10^{-3}$ to 10 Torr, the pressure was measured using: 10 Torr, four-decade Baratron capacitance manometer mounted directly to the infrared cell. To monitor lower CO pressures, a Bayard–Alpert ionization gauge was used.

The IRAS spectra were acquired using a Mattson Cygnus 100 spectrometer, with the single beam optics adjusted for 85° incident angle. All spectra were averages of 250 scans, at 4 cm$^{-1}$ resolution. At CO pressures above $10^{-3}$ Torr, the IRAS spectra were a convolution of adsorbed and gas-phase CO. In order to eliminate the contribution of gas-phase CO to the adsorption spectra, a series of reference spectra were acquired at CO pressures ranging from $10^{-2}$ to 10 Torr, while maintaining the sample temperature at 750 K. At this temperature, the amount of CO adsorbed on Cu is negligible, hence the observed spectra contain only those features characteristic of gas-phase CO (i.e., the sample merely serves as a reflecting mirror). The absorption spectrum of CO/Cu(100), then was found by subtracting the appropriate gas-phase reference spectrum from the total absorption spectrum.

Carbon monoxide (99.995% from Matheson Gas Products) was stored in a glass bulb at liquid nitrogen temperature throughout the study to preclude metal carbonyl contamination of the CO admitted into the infrared cell. The Cu(100) sample was prepared by Ar$^+$-sputtering at room temperature and then annealing to 850 K [10]. Cleanliness was verified by Auger electron spectroscopy.

3. Results

In fig. 1, a series of IRAS spectra of CO on Cu(100) are shown that were taken at a sample temperature of 265 K, and at various CO pressures. Adsorption onto atop sites corresponds to the prominent feature which is always below 2090 cm$^{-1}$. The shoulders at higher frequency (2110–2095 cm$^{-1}$) likely are due to CO adsorbed onto stepped copper surfaces [11], rather than a consequence of adsorption at high pressures and temperatures. Auger analysis immediately following evacuation of the IR cell showed the Cu(100) to be clean, thus eliminating surface contamination (e.g. oxides, metal carbonyl, etc.) as a possible cause of these high-frequency features. The actual quantity of CO on these stepped Cu surfaces is probably much smaller than suggested by the intensities of the high frequency shoulder peaks in that intensity transfer caused by dipole coupling can result in rather large intensities. Similar
bands with anomalously strong intensities have been observed previously for CO on Cu(110) [12]. These bands also appeared at slightly higher frequencies than those of normal CO on atop sites of Cu(110). However, measurements using $^{12}$CO/$^{13}$CO isotopic mixtures have shown that these high frequency bands gain almost all of their intensities through transfer from the low frequency species [12]. Therefore the total integrated intensity of both peaks can be taken as representative of the coverage of the CO adlayer.

The intensity of the infrared bands displayed in fig. 1 increases as the CO pressure in equilibrium with the surface is raised. This behavior is characteristic of an unsaturated substrate. Under UHV conditions ($P_{CO} < 1 \times 10^{-5}$ Torr), adsorption of CO was observed only at temperatures below 190 K. The relatively weak Cu–CO bond leads to a short residence time for the molecule on the surface at high temperatures. For example, at 265 K, pressures above $1 \times 10^{-6}$ Torr are necessary to produce an appreciable amount of adsorbed CO.

In fig. 1, the position of the peak at lower frequency increases from 2064 to 2086 cm$^{-1}$ as the coverage of CO on the Cu(100) surface increases. This frequency shift (22 cm$^{-1}$) is considerably larger than that observed after adsorption of CO at 100 K under UHV conditions (2077 → 2086 cm$^{-1}$ [12]) and is probably a consequence of the higher surface temperature. At temperatures higher than 240 K, the stretch frequencies were at appreciably lower wavenumbers than previously seen in spectra of comparable CO coverages taken at temperatures below 100 K. For example, at $5 \times 10^{-4}$ Torr and 265 K, the CO band is at 2078 cm$^{-1}$, whereas the same CO coverage, when measured at 77 K, indicates a feature at 2080 cm$^{-1}$ [13]. The lowest reported frequency of CO adsorbed on Cu(100) is 2076 cm$^{-1}$ by Ryberg [13], at 77 K and at CO coverages below 0.10 ML. In the present study, even lower frequencies than 2078 cm$^{-1}$ were recorded at 265 K as the pressure was reduced below $5 \times 10^{-4}$ Torr. For example, at $1 \times 10^{-4}$ Torr ($\sim 0.10$ ML), the peak position drops to 2071 cm$^{-1}$. The lowest CO frequency measured in our study was at 2065 cm$^{-1}$, at $1 \times 10^{-5}$ Torr and 265 K. Similar shifts with pressure were also observed in our measurements at 315 and 340 K. This shift to lower frequency is consistent with the observations of Taylor and Pritchard [3] for CO adsorption on Cu(100) at 300 K and 2.7 kPa and 44 Pa (i.e., at 20 and 0.33 Torr, respectively). The origin of the bathochromic shift in frequencies at higher temperatures relative to spectra taken below 100 K remains to be established. A similar temperature-dependent frequency shift has been reported for CO adsorbed on Ru(0001) and Pt(111), and interpreted as a consequence of anharmonic coupling of the CO stretching mode with a low-frequency frustrated translation mode [14]. Coupling of the CO stretching frequency with substrate phonon modes at these high temperatures also could lead to homogeneous broadening. The presence of the high-frequency feature precludes a detailed study of the spectral line-shape.
In fig. 2, the adsorption isotherms of CO on Cu(100) are shown for substrate temperatures of 115, 190, 215, 240, 265, 315 and 340 K. The isotherms are expressed as a plot of integrated absorption intensity versus the natural logarithm of the CO pressure. In our measurements, the maximum intensity (~ 0.10 integrated intensity unit) is observed for the isotherms at 190 and 215 K, at pressures in the Torr range. This intensity is assumed to correspond to a CO coverage of 0.50 ML. It is also assumed that at low CO coverages, the integrated absorption intensity is linearly related to the adsorbate coverage. These assumptions are supported by the work of Ryberg [13] that showed that IR intensities vary linearly with CO coverage up to 0.45 ML, at which point a c(2 x 2) LEED structure abruptly developed. The IR absorption and the intensity of the LEED spots reach a maximum at ~ 0.5 ML, then decrease ~ 15% at higher coverages. Concomitantly the CO overlayer evolves into the compressed structure corresponding to a p(7√2 x 7√2)R45° LEED pattern and a saturation coverage of 0.57 ML. Similar results have also been observed by Pritchard and Horn [15] who showed that the drop in IR intensity above 0.5 ML coincided with a change in the adsorbate dipole moment. The change in the IR absorption cross-section likely relates to the depolarization of the CO molecules at very high coverages. This behavior is also indicated in the 190 and 215 K isotherms of fig. 2. The attenuation of the IR cross-section at CO coverages > 0.5 ML explains the negative slopes of these isotherms at CO pressures near 10.0 Torr.

The reversibility of the CO chemisorption was clearly demonstrated by initiating measurements at temperatures in excess of the isotherm temperature then lowering the temperature to that of the isotherm. The results were reproducible and independent of the initial temperature. The isotherm data consist of IRAS measurements acquired initially at 10^-6 Torr and continued as the equilibrium CO pressure was increased, and alternatively beginning at 10.0 Torr and recording IR spectra as the equilibrium CO pressure was decreased. No hysteresis was evident in all the isotherms of fig. 2.

The isosteric heats ($\Delta E_{\text{ads}}$) were obtained from the slope of the plots of ln($P_{\text{CO}}$) versus $1/T$
(shown in fig. 3) at constant integrated intensity, according to the Clausius-Clapeyron equation:

$$\frac{d(\ln P)}{d(1/T)} \bigg|_\theta = \frac{E}{R}.$$

Since the integrated CO absorption intensity is essentially linear with coverage below 0.45 ML [12], $\Delta E_{\text{ads}}$ have been evaluated only for CO coverages below 0.4 ML.

4. Discussion

CO adsorption onto Cu(100) has been previously studied in great detail, by IRAS, LEED and HREELS [13,14,17]. The isosteric heats of adsorption of CO on Cu(100) as a function of coverage have been reported by Tracy [10]. This work, which relied on work function measurements, was restricted to CO pressures below $1 \times 10^{-4}$ Torr and temperatures below 275 K. The isosteric heats determined by Tracy are plotted in fig. 4 as a function of CO coverage. These are the only equilibrium adsorption data that have been reported in the literature for the CO/Cu(100) system. Fig. 4 also shows for comparison the isosteric heats of adsorption ($\pm 0.5$ kcal/mol) determined in the present study from the slopes of the plots of fig. 3, as a function of the CO coverage. There is excellent agreement between the IRAS-determined values and the values found by Tracy. It is noteworthy that the decrease of $\Delta E_{\text{ads}}$ in the IRAS-determined heats of adsorption for CO coverages between 0–0.2 is much less abrupt than in those from Tracy. Above 0.2 ML, the heats of adsorption evaluated from the IRAS isotherms are very similar to those reported by Tracy and are essentially constant with CO coverage. The slightly lower values reported here for the intermediate CO coverages may very well be significant and may represent a difference related to the two pressure/temperature regimes in which the respective measurements were made. The data of ref. [10] were from measurements within a much narrower pressure/temperature range ($3 \times 10^{-8}$ to $3 \times 10^{-5}$ Torr at 170 to 220 K), whereas the work here was carried out over significantly higher and wider pressure and temperature ranges ($1 \times 10^{-6}$ to 10 Torr, at 240 to 340 K).

It is noteworthy that at pressures $> 0.1$ Torr, the CO gas is in thermal equilibrium with the Cu surface, that is, the gas temperature is equal to the surface temperature [18]. At pressures significantly less that 0.1 Torr, the CO gas is essentially ambient ($\sim 300$ K). The data of fig. 3 at $\theta_{CO} > 0.2$ ML are a composite of data from both these pressure regimes, indicating that the sticking coefficients for CO are not significantly dependent on gas temperature within the 215–300 K temperature range.

The origin of the sharp reduction in $\Delta E_{\text{ads}}$ at 0.1 ML is not clear but may be due to surface heterogeneity, i.e., adsorption onto defect sites. These adsorption sites could be related to the small high-temperature shoulder observed in the thermal desorption spectra of CO/Cu(100) [19]. Another possible cause for the drop in $\Delta E_{\text{ads}}$ is a change in the nature of the Cu-CO interaction as the coverage of CO increases from 0 to 0.2 ML. Detailed LEED studies [10,16] indicate no long-
range order for CO on Cu(100) at low coverages; the c(2 × 2) structure develops rather abruptly at ~ 0.45 ML. Assuming that the CO grows via a 2D-island formation mechanism, where the CO molecules progressively adsorb onto energetically equivalent sites, then a coverage-independent $\Delta E_{ads}$ would be expected. However, as noted above, at the temperatures used in these experiments, the LEED data are not consistent with this island-growth mechanism. Rather it is more likely that the CO adsorption is via a random lattice gas where the CO–CO interaction is relatively small at coverages between 0.2 and 0.5 ML.

Our IR results for CO adsorbed on Cu(100) at temperatures above 200 K, show a significant increase in the stretch frequency (~ 20 cm$^{-1}$) as the adsorbate coverage varies from 0 to 0.5 ML. A simple interpretation of these results is that the blueshifts are a consequence of changes in the nature of the chemisorption bond, e.g., a reduction in electron donation from Cu into the CO ($2\pi^*$) orbital. This decrease in $\pi$-backbonding should be accompanied by a decrease in the heat of adsorption. In these cases, it is likely that the frequency shifts are not a consequence of changes in the chemisorption bond, but the results of dipole–dipole interactions between the CO molecules. Previous IR results for CO on Cu surfaces [20] have shown that dipole coupling can produce large upward shifts in the stretch frequency of the adsorbate.

These studies have shown the utility of IRAS for in situ, steady-state adsorption at elevated temperatures and pressures. For systems in which an adsorbate species has more than one bonding configuration (e.g., atop, bridged or three-fold hollow sites), IRAS may be less than ideal for elevated pressure studies because of the inherent difficulties in establishing a coverage/intensity relationship for each adsorbate species. An additional concern even for a single adsorbate species is the underlying assumption regarding the IR-intensity/coverage relationship. For this study, it has been assumed that the IRAS peak intensity for a given adsorbate coverage at high temperatures and pressures (i.e., at steady state) is essentially the same as the intensity found for the same coverage at ultrahigh vacuum conditions and at temperatures well below the onset of desorption. The linearity of the isosteric plots of fig. 3 sup-
port this assumption and is, in a sense, a self-proof that this relationship is valid for the CO/Cu(100) system.

Generalizations, however, cannot be made from these data to other adsorption systems regarding the equivalence of low temperature/low pressure data with high temperature/high pressure measurements. Recent work on the CO/Pd (111) system [21], for example, has shown that low temperature/low pressure adsorption data extrapolate to the high temperature/high pressure regime only if appropriate adsorption conditions are employed.

5. Conclusion

In summary this study has shown that:

1. IRAS can be used to study CO adsorption at relatively high pressures (≤ 10 Torr) and temperatures (≤ 340 K).
2. The CO heats of adsorption determined for data in the pressure range 10^{-6} to 10 Torr agree remarkably well with previous data acquired at < 10^{-4} Torr.
3. At substrate temperatures > 240 K and at pressures > 10^{-4}, significant bathochromic shifts of the CO stretch frequency to lower wavenumbers are observed.

Acknowledgement

We acknowledge with pleasure the support of this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

References