Cu titration of tilted CO on a Mo(110) surface

J.-W. He, W.K. Kuhn and D.W. Goodman

Department of Chemistry, Texas A&M University, College Station, TX 77843-3235, USA

Received 2 November 1990; in final form 28 November 1990

Upon CO exposure to a Mo(110) surface at 95 K, the initial ~0.3 monolayer (ML) of CO does not exhibit a vibrational frequency in the 1800–2200 cm⁻¹ region, implying that the C–O axis is tilted with respect to the surface normal. Upon subsequent deposition of ~0.9 ML Cu at 95 K followed by heating, infrared-reflection-adsorption-spectroscopy (IRAS) shows that a portion of the tilted CO molecules diffuses onto the Cu overlayer and assumes an upright bonding geometry, with the remainder dissociating on the Mo(110) surface into atomic C and O.

1. Introduction

Recently, unusually low vibrational frequencies (≈1065–1600 cm⁻¹) have been reported for CO adsorbed on Mo(100) [1], Mo(110) [2], and Fe(100) [3,4] surfaces. These low frequencies have been shown to arise from unique CO adsorption states which are precursors to CO dissociation. It has been proposed that the CO in these low-frequency states assumes a “tilted” chemisorption geometry, i.e., the C–O bond has a large angle with respect to the substrate surface normal [1–4]. This bonding geometry is believed to result in an increase in the metal d electron backdonation into the CO 2π* orbital, and, consequently, in a weakening of the C–O bond [1–4]. The tilted CO can either dissociate into atomic C and O upon heating to ≈230 K or can be converted into upright CO by the pre-adsorption of oxygen [2]. Furthermore, theoretical work [5] has predicted that tilted CO is energetically more stable than upright CO on a Ru(001) surface.

In this Letter, we present the results of studies on tilted CO on Mo(110) using infrared-reflection-adsorption-spectroscopy (IRAS), Auger electron spectroscopy (AES), as well as Cu titration. As will be seen, the present work shows that at initial CO coverages of ~0.3 monolayer (ML), CO adsorbs on Mo(110) but exhibits no vibrational frequencies in the 1800–2200 cm⁻¹ region which are typically observed for upright CO on metal surfaces. It is further shown that upon deposition of ~0.9 ML Cu at 95 K and subsequent heating to between 95 and 290 K, the tilted CO undergoes two competitive surface processes; (a) diffusion onto the Cu overlayer with an upright configuration; and (b) dissociation into atomic C and O on the Mo(110) surface.

2. Experimental

The experiments were performed in an ultrahigh vacuum chamber equipped with infrared spectroscopy, Auger electron spectroscopy (AES), and low-energy-electron-diffraction (LEED). This chamber has been described in detail previously [6]. The Mo(110) sample was cleaned using a relatively simple procedure: oxidation in oxygen (2×10⁻⁷ Torr, 1600 K) and anneal in vacuum (1800–2000 K). After this procedure, AES indicated a clean surface, with C, O, and S impurities less than 1 at%, and LEED exhibited a sharp substrate pattern. The infrared spectra were obtained in the single-reflection mode at an 85° incident angle with 4 cm⁻¹ resolution.

Cu was evaporated from a copper wire wrapped around a W filament. Prior to each deposition, the source was degassed extensively. The copper coverage was determined using the relationship of the AES
ratio, \( \text{Cu(60 eV)}/\text{Mo(186 eV)} \), versus the TPD area of Cu from ref. [7], where one monolayer coverage was defined to be \( 1.428 \times 10^{15} \) atoms/cm\(^2\), the Mo(110) surface density.

3. Results and discussion

Fig. 1 shows IR spectra of CO as a function of CO exposure on a Mo(110) surface. CO dosing and spectral collection were carried out at a sample temperature \( (T_\text{s}) \) of 95 K. This figure shows that at an exposure of 2 L (1 L = \( 10^{-6} \) Torr s), no CO features are observed in the 1800–2200 cm\(^{-1}\) region, whereas at 3 L, three peaks at 1993, 1927, and 1885 cm\(^{-1}\) are evident. As the exposure is increased to 6 L, the spectrum exhibits only one peak at 2029 cm\(^{-1}\) which saturates at \( 2040 \text{ cm}^{-1} \) at \( \approx 8 \) L exposure. The three peaks at 3 and 4 L CO exposure suggest either multiple states for the linear CO, or the coexistence of linear and bridging CO.

Fig. 2 presents the correlation between the integrated CO IR intensity and the C(273 eV)/Mo(186 eV) AES ratio as a function of CO exposure. This figure shows that by a 2.5 L CO exposure, considerable carbon is detected on the surface, yielding the AES ratio, C(273 eV)/Mo(186 eV) = 0.14. Previous thermal desorption data of CO from Mo(110) indicate that \( \approx 0.3 \) ML CO dissociates into atomic C and O upon heating to 280–500 K, assuming the CO saturation coverage on Mo(110) at 115 K to be 1.0 ML [7]. Dissociated CO at 0.3 ML is found to correspond to a C(273 eV)/Mo(186 eV) AES ratio of 0.13. We conclude then that a 2.5 L CO exposure at \( T_\text{s} = 95 \) K results in the adsorption of \( \approx 0.3 \) ML CO. This CO shows no vibrational frequencies in the 1800–2200 cm\(^{-1}\) region where linear and bridge-bound CO on a metal surface are typically found [8].
Upon flashing the 2.5 L CO/Mo(110) to \(\approx 300\) K and re-cooling to 90 K, we detected no CO features in the 1000–2000 cm\(^{-1}\) region. Further heating to \(> 400\) K leads to the dissociation of CO into atomic C and O [2,7].

The absence of CO IR features in the 1800–2200 cm\(^{-1}\) region at a CO exposure of less than 2.5 L indicates that the CO is either dissociated or significantly tilted from the Mo(110) surface normal. Previous studies have reported that low coverages of CO on Mo(100) [1] and Mo(110) [2] exhibit vibrational frequencies in the 1065–1600 cm\(^{-1}\) region. No Mo–O bond feature, however, was found for this low frequency CO [1,2], indicating that the CO adsorbs on the surfaces non-dissociatively. The low C–O stretch frequencies are consistent with a tilted-CO bond geometry [1,2]. Similar results have been reported for CO adsorbed on Fe(100) surfaces [3,4].

In the present work, no peaks in the 1100–1600 cm\(^{-1}\) frequency range could be definitively identified; however, Cu evaporation was utilized to titrate the tilted-CO molecules. The results of these experiments are presented in figs. 3 and 4. The spectra in fig. 3 were obtained as follows: The Mo(110) surface was dosed with 2.5 L CO at \(T_s=95\) K (spectrum 1); \(\approx 0.9\) ML Cu was then deposited at \(T_s=95\) K (spectrum 2); the surface was then heated to the indicated temperature and the IR spectrum acquired (spectra 3–7). For the data in fig. 4, the Mo(110) surface was given the indicated CO exposure, covered with \(\approx 0.9\) ML Cu at 95 K, heated to 185 K, and the IR spectrum then acquired.

Figs. 3 and 4 show that upon Cu deposition onto the CO predosed Mo(110) surface, a peak at \(\approx 2100\) cm\(^{-1}\) emerges. This feature corresponds to linear CO on an unannealed monolayer of Cu on Mo(110) [9]. The appearance of CO on Cu is a clear indication of the presence of molecular CO on the Cu-free Mo(110) surface.

Fig. 3 shows that as the surface is heated to 145 K, the integrated intensity of the CO peak increases. The CO coverage corresponding to spectrum 3 in fig. 3 is estimated to be 0.14 ML, assuming a CO saturation coverage on monolayer copper to be 1 ML [9]. It is also found that upon flashing the 0.9 ML Cu/2.5 L CO/Mo(110) surface to 290 K, the C(273 eV)/Mo(186 eV) AES ratio was reduced to half its original value. Thus, it is estimated that 0.15 ML CO (half of the original 0.3 ML tilted CO) has diffused onto the Cu overlayer, in excellent agreement with the coverage (0.14 ML) estimated from the IR spectra. As \(T_s\) is increased from 185 to 290 K, fig. 3 shows that the intensity of the CO–Cu peak decreases due to desorption of CO from the Cu film [7,9].

Although the present IR spectra do not provide direct evidence of the fate of the 0.15 ML of tilted CO remaining, it is believed that it decomposes into atomic C and O near room temperature. Previous studies have shown that CO dissociates on Mo(110) [2] or Mo(100) [1] at \(T_s>230\) K.

Fig. 4 shows that the amount of CO diffusing onto the Cu overlayer increases as the CO exposure increases. At zero CO exposure (spectrum 1), no CO on Cu was observed. This blank experiment rules out the possibility that the CO on Cu in figs. 3 and 4 is due to the adsorption of background CO. In addition, upon covering a Mo(110) surface predosed with \(\approx 0.3\) ML of atomic C and O with 0.9 ML Cu, no CO appeared on the Cu overlayer. Thus, the CO on Cu

![Fig. 3. CO IR spectra acquired as follows: The Mo(110) surface was dosed with 2.5 L CO at a sample temperature \((T_s)\) of 95 K (1); the CO/Mo(110) surface was covered with \(\approx 0.9\) ML Cu at \(T_s=95\) K (2); this surface was heated to the indicated temperatures for the collection of the spectra (3–7).](image-url)
Fig. 4. CO IR spectra from a Mo(110) surface that was dosed to 0 L (1), 1.5 L (2), 1.9 L (3), and 2.5 L (4) CO at a sample temperature ($T_s$) of 95 K, covered with $\approx 0.9$ ML Cu at $T_s = 95$ K, and then heated to 185 K for spectral collection.

4. Summary and conclusions

The present work has shown that upon initial exposure of Mo(110) to CO at a sample temperature of 95 K, AES indicates the presence of $\approx 0.3$ ML carbon and oxygen. By means of Cu titration, at least 0.14 ML of this carbon and oxygen is identified as arising from molecularly adsorbed CO. The absence of a vibrational frequency in the 1800–2200 cm$^{-1}$ region, characteristic of upright CO on metal surfaces, strongly suggests that this CO is bound to the surface with the C–O axis tilted with respect to the surface normal. The present study further shows that upon the deposition of $\approx 0.9$ ML Cu and subsequent heating, the $\approx 0.3$ ML of tilted CO undergoes two competitive processes: half of it diffuses onto the Cu overlayer with an upright configuration and the remainder dissociates into atomic C and O.

Acknowledgement

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

References