Adsorption and Desorption of CO on W(110) Surfaces

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The adsorption of CO on W(110) surfaces was studied using thermal desorption spectroscopy (TDS), and core and valence level spectroscopy. At 120 K, CO forms a tilted structure at lower coverages ($\alpha$), whereas it adsorbs normal to the surface at higher coverages ($\beta$). Tilted structures have been suggested to be precursors of dissociative chemisorption; however, experimental evidence is provided for the non-dissociative chemisorption of CO at temperatures above 900 K (which is referred to as the $\beta$-state). TDS shows first order desorption kinetics. The core and valence level spectra of O/W(110) and those of $\beta$-CO/W(110) are different. Most importantly, the 4$\sigma$ molecular orbital of CO can be identified in the valence level spectra of the $\beta$-CO.

Key Words: Tungsten, CO, Chemisorption, Photoelectron spectroscopy

Introduction

Information on the chemisorption of small gas molecules on transition metal surfaces is crucial to obtain a molecular-level understanding of the mechanism of heterogeneous catalysis and, thus, chemisorption on single crystal surfaces has been extensively studied in the past in surface chemistry and physics. In the case of CO on transition metal surfaces, which is one of the most extensively studied systems in surface chemistry due to its technological importance as well as its structural simplicity, a transition from dissociative to molecular chemisorption has been found in traversing from the left to the right side of the periodic table. W lies at the borderline between the molecular and dissociative chemisorption of CO, and it is a long-standing question as to whether CO is dissociated or not on W surfaces.

In the late 1950s, Ehrlich and coworkers found that no residual carbon or oxygen remained on W after repeated cycles of adsorption of CO and subsequent heating to 2300 K. It was concluded that CO is non-dissociatively bound to W surfaces. A similar conclusion was drawn by Gomer and others, who used thermal desorption spectroscopy (TDS) and field ionization microscopy (FIM).

In later studies, however, several experimental works suggested the dissociative chemisorption of CO on W surfaces. Goymour and King observed the second order desorption of CO/W(111), (110) and (100) surfaces was proposed. In the present work, CO chemisorption on W(110) surfaces was studied experimentally. In particular, synchrotron radiation was used to obtain higher quality valence band spectra. We found evidence for the molecular chemisorption of $\beta$-CO at temperatures above 900 K, which is quite in contrast to earlier reports.

Experimental

The experiments were performed in an ultrahigh vacuum (UHV) system with a base pressure of $1 \times 10^{-10}$ torr equipped for x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and quadrupole mass spectrometry (QMS).

The W(110) samples were cleaned by thermal treatment at 1700 K under an O$_2$ atmosphere of $2 \times 10^{-8}$ torr, and subsequent heating to 2300 K. This procedure was repeated until no impurities could be found using LEED and XPS.
The sample temperature was measured using a C-type thermocouple spot-welded on its side. For the TDS experiments, a heating rate of 6 K/s was used, which was controlled using a programmed integral differential (PID) controller. The sample was cooled using a He-cryogenic system, which was connected to the sample using a Cu wire. For CO chemisorption, the UHV chamber was backfilled with CO.

The O 1s and valence band spectra were collected in the Pohang Accelerator Laboratory (beam line 2B1). For the photoemission experiments in Pohang, the analyzer was placed normal to the sample surface, and the angle between the synchrotron radiation and the analyzer aperture was 45°. The sample temperature was measured by a pyrometer in Pohang.

**Results and Discussion**

**TDS results.** Figure 1 shows the TDS spectra collected after exposing the clean W(110) surface to various amounts of CO at room temperature. Three distinct features can be observed at ~400, ~1000 and ~1150 K, which are denoted as \( \alpha \), \( \beta_1 \) and \( \beta_2 \), respectively. It is noticeable that the temperatures corresponding to the maximum desorption rate for the \( \alpha \) and \( \beta_2 \) states are almost constant for a given amount of CO exposure. When the CO exposure exceeds 1.5 L (Langmuir = torr x sec.), an additional state at 1000 K (\( \beta_1 \)) appears.

Considering the previous data in the literature, it is reasonable to suggest that the \( \alpha \)-state corresponds to the molecular CO species adsorbed perpendicular to the surface, with the carbon atom directly attached to the W surface. Gomer et al. and Umbach et al. used the term “virgin-CO” for the low-temperature species, which is dented as \( \alpha \)-CO in the present work.6,11,12

As mentioned in the introduction, the structure of \( \beta \)-CO is still under debate: either molecular or dissociative chemisorption has been suggested in the past. Figure 2 shows the TDS spectra of CO obtained after CO exposures at 900 K, at which only the \( \beta_2 \) state forms. Our TDS spectra are more suggestive of the molecular chemisorption of CO in the \( \beta_2 \)-CO: for the dissociative chemisorption of CO, the recombination of C and O should precede CO desorption, i.e. the desorption of CO is described by second order kinetics. In this case, the shape of the TDS spectra should be symmetric and the temperature corresponding to the maximum desorption rate should gradually shift toward the lower temperature range with increasing CO coverage. In contrast, for first order desorption (molecular chemisorption of CO), the temperature corresponding to the maximum desorption rate should be constant as a function of the amount of CO exposure, and an asymmetric peak shape should be observed.22 The asymmetric shape of the desorption peak of the \( \beta_2 \)-CO state suggests first order desorption kinetics, i.e. CO is molecularly chemisorbed in this state. There is a small peak shift as a function of the CO exposure, yet the coverage dependent shift of this peak can be rationalized by the existence of repulsive lateral interactions between adsorbates.23

It is, however, important to mention that one should scrutinize for drawing a conclusion about the adsorption structure CO only based on TDS data. Later, we will show that photoelectron spectroscopy can provide more clear evidence on the adsorption structure of the \( \beta_2 \)-CO.

**XPS results-core level spectra.** Figure 3 shows the O 1s spectrum obtained after exposing the W(110) surface to 5.0 L of CO at room temperature (spectrum a). In addition, the O 1s spectra of the \( \beta_2 \)-state with different coverages are compared. These specimens were prepared by exposing the W(110) surface to various amounts of CO, followed by subsequent heating to 900 K (b-d). For the surface exposed to 5.0 L of CO at room temperature, an O 1s state centered at 529.9 eV with a shoulder at ~531-532 eV can be found,
whereas the $\beta_2$-state shows a peak at 529.4 eV (Fig. 3).

For the sake of comparison, the O 1s spectra were collected from W(110) surfaces exposed to various amounts of oxygen and subsequently flashed to 1500 K. A comparison of the O 1s spectrum of the $\beta_2$-CO and that of oxygen can reveal whether CO is dissociated or not. As a function of oxygen exposure, the O 1s binding energy changes within 0.2 eV (Fig. 4). Assuming that CO is dissociatively chemisorbed, the O 1s spectrum of CO and that of oxygen on W(110) should be identical. The O 1s binding energies of Figure 4 are significantly different from that of the $\beta_2$-CO in Figure 3, suggesting that CO is non-dissociatively chemisorbed in the $\beta_2$-state.

In general, the binding energy of the O 1s level of molecularly bound CO is centered at ~532 eV. The O 1s binding energy of the $\beta_2$-CO state in the present work is 529.4 eV, which is much lower. In the next section, we will show that the $\beta$-CO is most likely a lying-down species, in which the $\pi$ bond is broken. In this case, the chemical environments of oxygen in the $\beta$-CO should be much different from those of upright CO species, resulting in large core (O 1s) level shift between the $\alpha$- and the $\beta$-CO.

**Valence band spectra.** In Figures 5 and 6, the valence band spectra are shown, which were obtained after exposing the W(110) surface to various amounts of CO at 120 K. At lower CO exposures, new CO-derived features appear at 7.0 eV and 11.4 eV below the Fermi level. As the CO exposure becomes larger, the peak at 7.0 eV becomes asymmetric.
The peak at 11.4 eV saturates in intensity at a CO exposure of 0.8 L. At even larger CO exposures, an additional shoulder appears at 10.6 eV. Signals below 5 eV correspond to the metallic d-states of W.

Based on the previous results, the peak at a binding energy of 7.0 eV can be assigned to the overlap of the 5σ and 1π orbitals of CO, whereas the feature at about 11 eV is ascribed to the 4σ orbital. This assignment is supported by previous calculations of the photoionization cross sections as well as angle-resolved ultraviolet photoelectron spectroscopy.

Detailed analysis of the 4σ states in Figures 5 and 6 suggests that there are at least two different adsorption structures of CO at 120 K. The 4σ state of each spectrum was fitted by two different Gaussian functions centered at 11.4 (ασ) and 10.6 eV (βσ), and the results are summarized in Figure 7. As mentioned above, it can be seen that the peak at 11.4 eV rapidly grows at the initial stage of CO exposure and saturates at a CO exposure of 0.8 L, whereas the 10.6 eV-peak grows after the saturation of the ασ-state.

For comparison, the variation of the relative TDS peak areas of the different states is summarized in Figure 7. At lower CO coverages, the α-state is selectively occupied, and the α-peak starts to grow when the CO exposure exceeds 1 L. This result is in line with the previous data of Gomer et al. The CO exposure dependent behavior of the β-state in the TDS spectra is quite analogous to that of the ασ-peak in the valence band spectra, whereas the α-peak in the TDS spectra to that of the ασ-peak in the valence band spectra. This result is in line with the previous data of Gomer et al. This result suggests that the ασ-state at 120 K desorbs at ~400 K (the α-state in TDS), whereas the ασ-state desorbs at temperatures above 900 K (the β-state in TDS). Based on the previous results obtained for the chemisorption of CO on Cr(110) and Fe(100) surfaces, the following adsorption mechanism of CO can be suggested: at 120 K, CO adsorbs with a tilted geometry at lower CO coverages (< 0.5 ML), and the upright structure was formed after the tilted state had become nearly saturated at 90 K. The tilted and upright structures could be clearly identified by their CO stretching frequencies of 1360 and 2000 cm⁻¹, respectively.

In the TDS spectra, it is evident that the number of CO molecules in the α-state is lower than that in the β-state. However, the intensity of the 4σ orbital peak of the ασ-state at 10.6 eV is much higher than that of the ασ-state (11.4 eV). In a previous study of CO chemisorption on Fe(100) surfaces using HREELS in combination with ultraviolet photoelectron spectroscopy (UPS), the decrease of the 4σ/(5σ + 1σ) ratio upon heating was attributed to the gradual change of the adsorption structure from a vertical to a tilted geometry. This is in line with our suggestion that the ασ-state corresponds to the tilted geometry of CO, whereas the ασ-state corresponds to the upright structure. Based on TDS results, one can estimated the relative amount of ασ- and ασ-CO. By combining this information with the UPS results, one can roughly calculate the ratio of the photoemission cross sections of the 4σ-orbital of the ασ- and the ασ-CO. We estimate that the photoemission cross section of the 4σ of the ασ-state is larger than that of the ασ-CO by roughly two orders of magnitudes. In the tilted geometry, the 4σ orbital should be more stable due to the stronger chemical bond between W and CO, and therefore the binding energy of the 4σ orbital of the tilted CO should be higher that of the upright structure. In our results, the binding energy of the 4σ orbital of ασ-CO is indeed higher than that of ασ-CO.

In order to shed light on the structures of the various chemisorption states of CO on W(110), valence band spectra were taken after exposing the surface to 3.0 L of CO at 120 K followed by stepwise heating (Fig. 8). Upon heating, the CO-derived features gradually decrease in intensity due to
the desorption of CO. It is important to note that the relative intensity of the $4\sigma$ peak with respect to that of the $(5\sigma + 1\pi)$ state becomes smaller with increasing heating temperature. As mentioned above, a smaller $4\sigma$ peak intensity was found for the tilted geometry of CO compared to that of the upright structure, i.e., upon tilting, the cross section of the $4\sigma$ state for the photoelectron emission becomes smaller. The vertically adsorbed CO on W(110) desorbs first at lower temperatures, leaving only the tilted species above 500 K. Most importantly, the CO-derived $4\sigma$ feature is still observable after heating the sample to 900 K, indicating the molecular chemisorption of CO rather than dissociative chemisorption in the $\beta_2$-state. The existence of the CO-derived features above 900 K can be more clearly observed in the difference spectra (Fig. 9). When the initial CO exposure was changed from 3.0 L to 0.8 L (Fig. 10), the valence band spectra showed similar results to those of Figures 8 and 9. Upon heating at temperatures above 900 K, the $4\sigma$ peak is shifted to a higher binding energy, whereas the $(5\sigma + 1\pi)$ peak shifted to a lower binding energy, resulting in an increase in the separation between the $4\sigma$ and $(5\sigma + 1\pi)$ peaks (Fig. 8-10). Compared to the binding energy of the $4\sigma$ state of the $\alpha_1$-CO at 120 K, heat treatment at 900 K increases the binding energy of the $4\sigma$ state, implying that upon heating there is a structural transition of the $\alpha_1$-CO from a less to a more stable structure, i.e., CO is tilted in the $\alpha_1$-state at 120 K and, upon heating to higher temperatures, it tilts more and more, finally becoming a lying-down species. The $4\sigma$ peak of the $\beta_2$-state is centered at 12.5 eV, which is shifted by 2 eV with respect to the $\alpha$-CO. Theoretical calculations predict a positive shift of the $4\sigma$ state, as the upright structure becomes a lying down species; however, the experimentally observed shift is larger than the theoretically predicted values, which are below 1 eV.\(^{21,33}\)

The valence band spectra clearly show that CO adsorption on W(110) at 120 K results in two different adsorption structures with vertical and tilted geometries. The tilted species is occupied first and the vertical ones later. On Cr(110) surfaces, a similar result was found for CO adsorption at 100 K: CO first adsorbs with a tilted (or lying down) geometry, and then the vertical CO is formed after the saturation of the tilted CO.\(^{30,31}\) A similar phenomenon was found on Fe(100) surfaces.\(^{32}\) There is, however, a major

![Figure 8. W(110) was exposed to 3.0 L of CO at 120 K and the valence band spectra were collected after stepwise heating. The heating temperature for each spectrum is given in the figure.](image)

![Figure 9. The clean surface spectrum was subtracted from each spectrum in Fig. 7 (difference spectrum). The heating temperature of each spectrum is denoted in the.](image)

![Figure 10. Difference spectra of valence band spectra collected after exposing W(110) to 0.8 L of CO at 120 K followed by stepwise heating. The heating temperature of each spectrum is given in the figure.](image)
difference between Cr(110), Fe(100) and W(110) regarding 15 their CO chemisorption behaviors: the tilted species was 15 found to be a precursor state of CO dissociation on Cr(110) 15 and Fe(100); however, on W(110) surfaces, we show that 15 the tilted species does not dissociate upon heating.\cite{30,32}

Previously, the C-O stretching frequency could not 16 be detected upon heating the CO pre-covered W(110) 16 surfaces above 250 K and, thus, dissociation of the 16 intramolecular bond of CO upon heating was suggested.\cite{16} 16 It is, however, important to note that, based on the 16 surface selection rule, the detection of the C-O bond of a 16 lying-down species using HREELS under specular conditions is impossible, and, thus, the absence of the C-O 16 stretching frequency in the HREELS spectrum does not necessarily indicate the dissociative chemisorption of CO.

For comparison, a W(110) surface was exposed to various amounts of oxygen and the valence band spectra were 17 collected (Fig. 11). An oxygen-induced state at 6.4 eV can 17 be observed without any additional peak above 10 eV, which 17 is apparently different from the results of the $\beta$-CO, 17 again suggesting that the structure of the $\beta$-CO cannot be 17 explained by dissociative chemisorption, but only by mole- 17 cular chemisorption.

Conclusion

At 120 K, we could identify two different CO adsorption 20 states, which we attribute to the tilted ($\alpha_1$) and upright ($\alpha_2$) 20 structures, respectively. The tilted CO was previously sug- 20 gested to be a precursor of the dissociated state; however, we 20 show that the tilted CO maintains its C-O bond until its 20 desorption takes place. The following experimental data of 20 the $\beta_2$-state (desorbing at $\sim$1150 K) support the non- 20 dissociative chemisorption of CO on W(110) surfaces: TDS 20 shows first order desorption kinetics and XPS shows dif- 20 ferent O 1s binding energies of CO from those of oxygen 20 atoms chemisorbed on the same surface. In the valence band spectra, molecular chemisorption can be identified by the 20 state at $\sim$11 eV below the Fermi level, which is assigned to the 20 $\sigma$ orbital of CO.

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