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 (α_1), whereas it adsorbs normal to the surface at higher coverages (α_2). 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 β-state): TDS shows first order desorption kinetics. The core and valence level spectra of O/W(110) and those of β-CO/W(110) are different. Most importantly, the 4σ molecular orbital of CO can be identified in the valence level spectra of the β-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.[1] 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.[2] A similar conclusion was drawn by Gomer and others, who used thermal desorption spectroscopy (TDS) and field ionization microscopy (FIM).[3-6]

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 at around 1500 K, and the dissociative chemisorption of CO was suggested.[7-9] The chemisorption state below 600 K was assigned to molecular chemisorption, whereas the higher-temperature-state (which is called the β-state) to dissociative chemisorption. Wang *et al.* also used TDS to study CO chemisorption on W(100), concluding that CO is dissociatively adsorbed in the β-state.[10] Umbach *et al.* used photoelectron spectroscopy, suggesting dissociative chemisorption of CO in the β-state.[11,12] In the works of Umbach *et al.* transition from virgin- to dissociated-CO was proposed to take place at around room temperature.[11,12] In the recent literature, the dissociative chemisorption of CO on W surfaces has been more generally proposed than non-dissociative adsorption based on experimental and theoretical results.[13-17]

Spectroscopic determination of the structure of CO in the β-state is non-trivial: for example, using vibrational spectroscopy, the absence of the C-O stretching mode can be attributed to its dissociative chemisorption; however, according to the surface selection rule, a lying down species with a C-O bond axis parallel to the surface may not be active.[16] In the valence band spectra, the 4σ state of CO cannot be found due to its very low cross section in the lying-down structure. The 5σ and 1π states of CO cannot be clearly discriminated from the O 2p state.

In contrast to these previous works, we found some evidence for the non-dissociative chemisorption of β-CO on W(111) surfaces using TDS in combination with photoelectron spectroscopy.[18,19] Using the atomic superposition and electron delocalization molecular orbital (ASED-MO) method, the non-dissociative chemisorption of CO on W(111), (110) and (100) surfaces was proposed.[20,21] 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 β-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 1×10^{-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 2×10^{-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 α, β_1 and β_2, respectively. It is noticeable that the temperatures corresponding to the maximum desorption rate for the α and β_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 (β_1) appears.

Considering the previous data in the literature, it is reasonable to suggest that the α-state corresponds to the molecular CO species adsorbed perpendicular to the surface, with the carbon atom directly attached to the W surface.[17-19] Gomer *et al.* and Umbach *et al.* used the term "virgin-CO" for the low-temperature species, which is dented as α-CO in the present work.[6,11,12]

As mentioned in the introduction, the structure of β-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 β_2 state forms. Our TDS spectra are more suggestive of the molecular chemisorption of CO in the β_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.[22] 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 β_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]

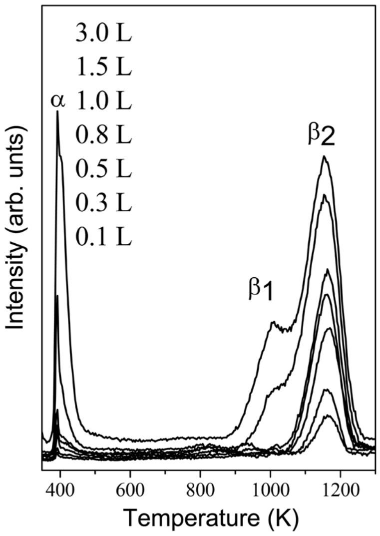

Figure 1. Thermal Desorption Spectra of CO obtained after exposing W(110) to various amounts of CO at room temperature. The heating rate was 6 K/s.

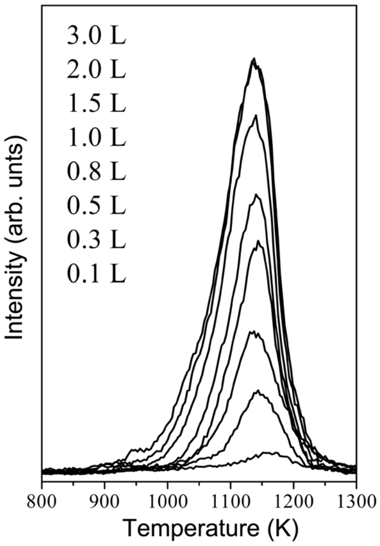

Figure 2. Thermal Desorption Spectra of CO obtained after exposing W(110) to various amounts of CO at 900 K. The heating rate was 6 K/s.

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 β_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 β_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,

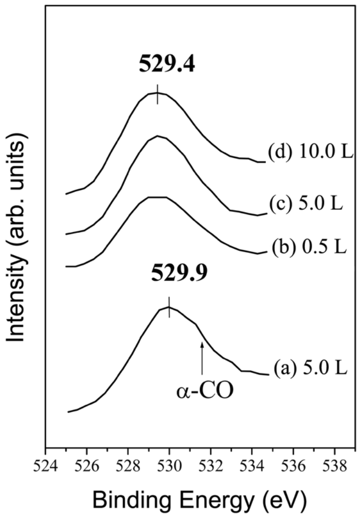

Figure 3. (a) O 1s spectra after exposing W(110) to 5.0 L of CO at room temperature. Synchrotron radiation with a photon energy of 770 eV was used. (b-d) After CO exposure at room temperature, the samples were heated to 900 K and then the O 1s spectra were collected. The CO doses are given in the figure.

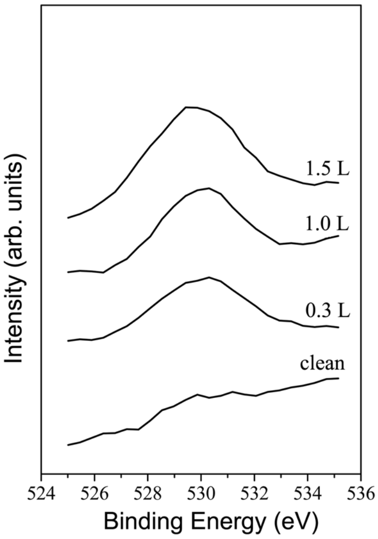

Figure 4. O 1s spectra taken after exposing W(110) to various amounts of O_2, followed by heating to 1500 K. A photon energy of 770 eV was used.

whereas the β_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 β_2-CO and that of oxygen can reveal whether CO is dissociated or not. As a function 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 β_2-CO in Figure 3, suggesting that CO is non-dissociatively chemisorbed in the β_2-state.

In general, the binding energy of the O 1s level of molecularly bound CO is centered at ~532 eV.[11] The O 1s binging energy of the β-CO state in the present work is 529.4 eV, which is much lower. In the next section, we will show that the β-CO is most likely a lying-down species, in which the π bond is broken. In this case, the chemical environments of oxygen in the β-CO should be much different from those of upright CO species, resulting in large core (O 1s) level shift between the α- and the β-CO.

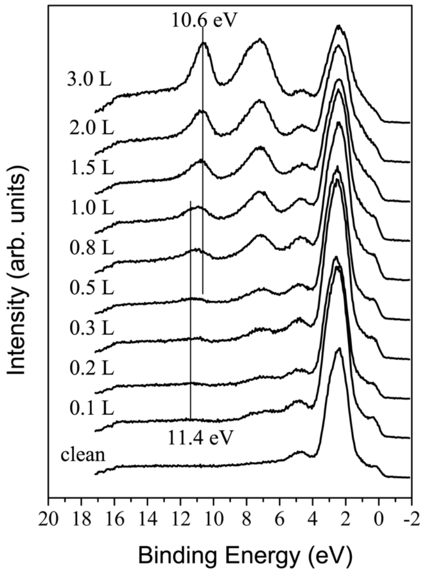

Figure 5. Valence band spectra obtained after exposing W(110) to various amounts of CO at 120 K. A photon energy of 90 eV was used.

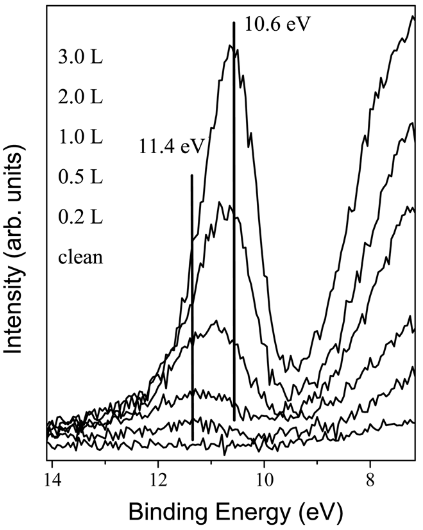

Figure 6. A magnified view of some spectra in Fig. 5 is shown in order to clearly see the evolution of the 4σ state as a function of CO exposure.

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.

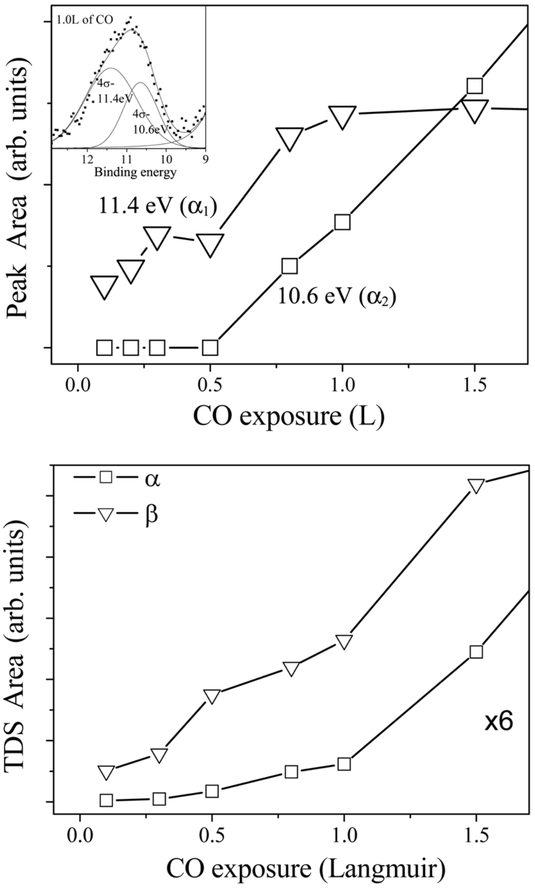

Figure 7. Top: Each spectrum in Fig. 5 was fitted by four Gaussian functions, two of them for the $1\pi + 5\sigma$ state, and the other two for the 4σ state, and the relative intensity ratios of the two different 4σ states are summarized. In the inset, a magnified view of a fitted valence band spectrum is shown as a representative example, which was taken after a CO exposure of 1.0 L. Bottom: the relative intensity ratios of the α- and β-CO in the TDS spectra in Fig. 1 are summarized.

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.[24-29]

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 (α_1) and 10.6 eV (α_2), and the results are summarized in Figure 7.[30,31] 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 α_1-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 â-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.*[6] The CO exposure dependent behavior of the β-state in the TDS spectra is quite analogous to that of the α_1-peak in the valence band spectra, whereas the α-peak in the TDS spectra to that of the α_2-peak in the valence band spectra. This result is in line with the previous data of Gomer *et al.*[6] This result suggests that the α_2-state at 120 K desorbs at ~400 K (the α-state in TDS), whereas the α_1-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 (α_1).[30-32] After the saturation of the α_1-state, additional CO adsorbs with an upright structure (α_2-state). Upon heating, the CO molecules with an upright geometry desorb at ~400 K, whereas the tilted CO molecules desorb at temperatures above 900 K.

Previously, a similar experimental result to ours was obtained using high-resolution electron energy loss spectroscopy (HREELS).[16] In this previous work, the tilted state was preferentially occupied 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 C-O stretching frequencies of 1360 and 2000 cm^{-1}, respectively.[16]

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 α_2-state at 10.6 eV is much higher than that of the α_1-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 $4\sigma/(5\sigma + 1\pi)$ ratio upon heating was attributed to the gradual change of the adsorption structure from a vertical to a tilted geometry.[32] This is in line with our suggestion that the α_1-state corresponds to the tilted geometry of CO, whereas the α_2-state corresponds to the upright structure. Based on TDS results, one can estimated the relative amount of α_1- and α_2-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 α_1- and the α_2-CO. We estimate that the photoemission cross section of the 4ó of the α_1-state is larger than that of the α_2-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 that of the upright structure.[21,30-33] In our results, the binding energy of the 4σ orbital of α_1-CO is indeed higher than that of α_2-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

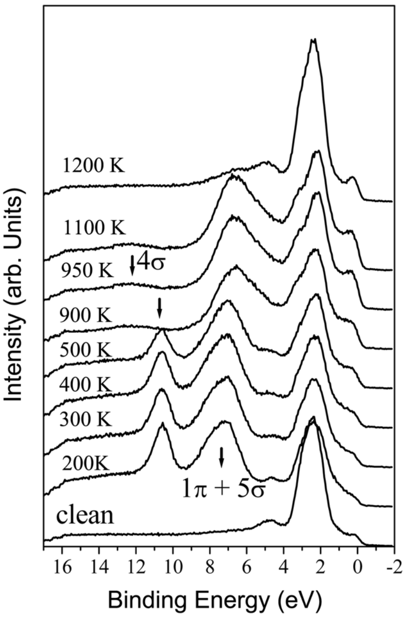

Figure 8. W(110) was exposed to 3.0 L of CO at 120 K and the valence band spectra were collected after stepwise heating. The heating temperature for each spectrum is given in the figure.

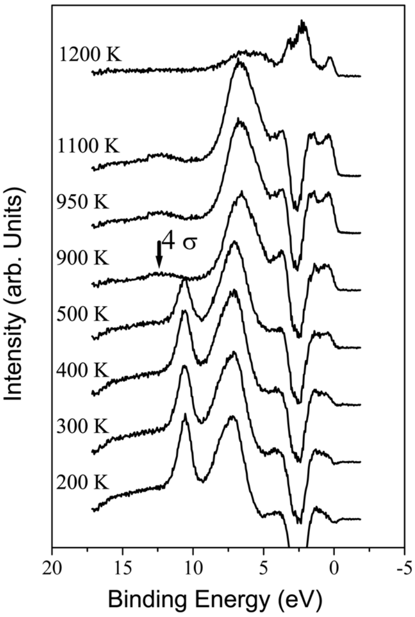

Figure 9. The clean surface spectrum was subtracted from each spectrum in Fig. 7 (difference spectrum). The heating temperature of each spectrum is denoted in the.

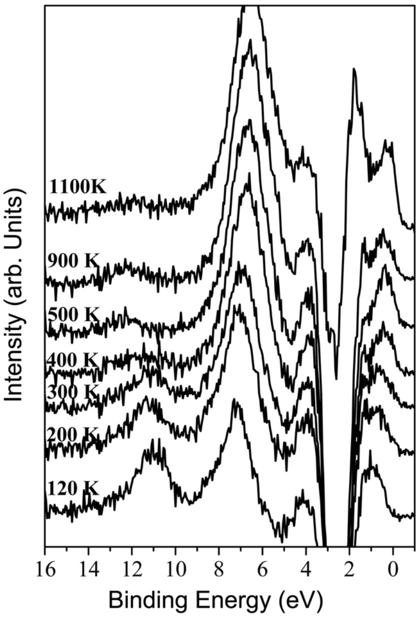

Figure 10. Difference spectra of valence band spectra collected after exposing W(110) to 0.8 L of CO at 120 K followed by stepwise heating. The heating temperature of each spectrum is given in the figure.

the desorption of CO. It is important to note that the relative intensity of the 4σ peak with respect to that of the $(5\sigma + 1\pi)$ state becomes smaller with increasing heating temperature. As mentioned above, a smaller 4σ 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 4σ 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 4σ feature is still observable after heating the sample to 900 K, indicating the molecular chemisorption of CO rather than dissociative chemisorption in the β_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 4σ 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 4σ and $(5\sigma + 1\pi)$ peaks (Fig. 8-10). Compared to the binding energy of the 4σ state of the α_1-CO at 120 K, heat treatment at 900 K increases the binding energy of the 4σ state, implying that upon heating there is a structural transition of the α_1-CO from a less to a more stable structure, *i.e.*, CO is tilted in the α_1-state at 120 K and, upon heating to higher temperatures, it tilts more and more, finally becoming a lying-down species. The 4σ peak of the β_2-state is centered at 12.5 eV, which is shifted by 2 eV with respect to the α-CO. Theoretical calculations predict a positive shift of the 4σ 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

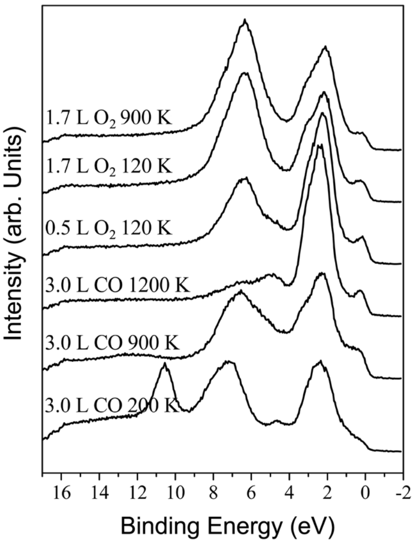

Figure 11. Valence band spectra collected after exposing W(110) to various amounts of CO and O_2 at different temperatures. The details of the gas exposure and temperature are given in the figure.

difference between Cr(110), Fe(100) and W(110) regarding their CO chemisorption behaviors: the tilted species was found to be a precursor state of CO dissociation on Cr(110) and Fe(100); however, on W(110) surfaces, we show that the tilted species does not dissociate upon heating.[30-32]

Previously, the C-O stretching frequency could not be detected upon heating the CO pre-covered W(110) surfaces above 250 K and, thus, dissociation of the intramolecular bond of CO upon heating was suggested.[16] It is, however, important to note that, based on the surface selection rule, the detection of the C-O bond of a lying-down species using HREELS under specular conditions is impossible, and, thus, the absence of the C-O 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 collected (Fig. 11). An oxygen-induced state at 6.4 eV can be observed without any additional peak above 10 eV, which is apparently different from the results of the β-CO, again suggesting that the structure of the β-CO cannot be explained by dissociative chemisorption, but only by molecular chemisorption.

Conclusion

At 120 K, we could identify two different CO adsorption states, which we attribute to the tilted (α_1) and upright (α_2) structures, respectively. The tilted CO was previously suggested to be a precursor of the dissociated state; however, we show that the tilted CO maintains its C-O bond until its desorption takes place. The following experimental data of the β_2-state (desorbing at ~1150 K) support the non-dissociative chemisorption of CO on W(110) surfaces: TDS shows first order desorption kinetics and XPS shows different O 1s binding energies of CO from those of oxygen atoms chemisorbed on the same surface. In the valence band spectra, molecular chemisorption can be identified by the state at ~11 eV below the Fermi level, which is assigned to the 4σ orbital of CO.

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