

## CO Adsorption on Mo(110) Studied Using Thermal Desorption Spectroscopy (TDS) and Ultraviolet Photoelectron Spectroscopy (UPS)

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Received March 25, 2009, Accepted May 4, 2009

This study examined the adsorption of CO on a Mo(110) surface by Thermal Desorption Spectroscopy (TDS) and synchrotron-radiation based photoemission spectroscopy (SRPES). CO desorption was observed at approximately 400 K ( $\alpha$ -CO) and > 900 K ( $\beta$ -CO). When CO was exposed to Mo(110) at 100 K, it showed a tilted structure at low CO coverage and a vertical structure after saturation of the tilted CO. After heating the CO-precovered sample to 900 K, a broad peak at 12 eV below the Fermi level was identified in the valence level spectra, which was assigned to either the 4 $\sigma$ -molecular orbital of CO, or 2s of dissociated carbon. TDS results of the  $\beta$ -CO showed a first order desorption. These results are in a good agreement with the observations of CO adsorption on W(110) surfaces.

**Key Words:** Chemisorption, CO, Mo(110), Photoemission spectroscopy

### Introduction

The elementary steps in heterogeneous catalysis consist of the chemisorption of gas molecules on solid surfaces.<sup>1,2</sup> Understanding of the chemisorption of reactants on the atomic scale is essential for examining the mechanism of heterogeneously catalyzed reactions. CO chemisorption on transition metal surfaces has been studied extensively over the last 50 years due to its structural simplicity and technological importance in heterogeneous catalysis.<sup>3,4</sup>

In particular, the CO adsorption structure on W and Mo has been debated for a considerable time. The dissociative and non-dissociative chemisorption of CO on both surfaces have been suggested using a variety of experimental and theoretical methods.<sup>3,5-24</sup> Experimentally, identifying the dissociative chemisorption of CO on a solid surface is not trivial. Electron stimulated desorption (ESD) and Thermal Desorption Spectroscopy (TDS) are useful in obtaining information about adsorbate geometries; however, these methods are often regarded as rather destructive techniques, providing only indirect information.<sup>5-13</sup> Vibrational spectroscopy, such as high-resolution electron energy loss spectroscopy (HREELS) and infra-red absorption spectroscopy (IRAS), can be useful but the selection rules prohibit the detection of some molecular structures, e.g. it is difficult to observe molecularly bound CO placed parallel to the surface.<sup>21-22</sup> Ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS) and Auger-electron spectroscopy (AES) can also provide important information on chemisorption geometry of CO on the surface.<sup>14-20,23-25</sup> A combination of surface analysis techniques is required to fully understand the chemisorptions structure of CO.

Previous studies on CO chemisorptions on W(110) in our group suggested that CO is bound molecularly in a tilted form at low CO coverage at 100 K, and forms a vertically chemisorbed structure after saturation of the tilted structure.<sup>23,24</sup> The vertical CO desorbs below 400 K, whereas the tilted one

desorbs at above 900 K.<sup>23,24</sup> Most of the previous studies suggested a dissociative chemisorption of CO on W(110) above 400 K; however, a first order desorption kinetics was found for the  $\beta$ -state (desorption state above 900 K) of CO, which does not reconcile associative desorption of dissociated C and O.

This study examined CO adsorption on Mo(110) using synchrotron-radiation based photoemission spectroscopy (SRPES) with a range of photon energies. The adsorption properties of CO on Mo(110) and W(110) surfaces are almost identical. In particular, the first order desorption for the  $\beta$ -CO was also found on Mo(110) surfaces. In order to clarify origin of the first order desorption of  $\beta$ -CO on both W and Mo surfaces, further studies should be performed.

### Experimental

The experiments were carried out 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 spectroscopy (QMS).

The Mo(110) samples were cleaned by a thermal treatment at 1700 K under an O<sub>2</sub> atmosphere at  $2 \times 10^{-8}$  torr, and heated to 2300 K. This procedure was repeated until no impurities could be observed by 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 connected to the sample using a Cu wire. For CO chemisorption, the UHV chamber was backfilled with CO.

The valence band spectra were collected at 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

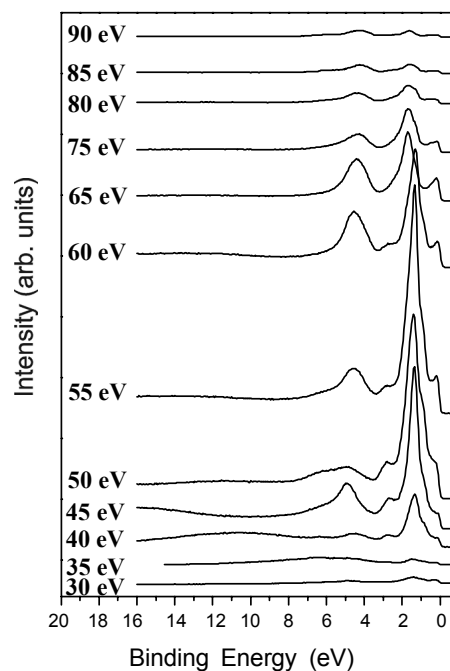
radiation and analyzer aperture was  $45^\circ$ . P-polarized light with different photon energies was used to collect the valence band spectra.

## Results and Discussion

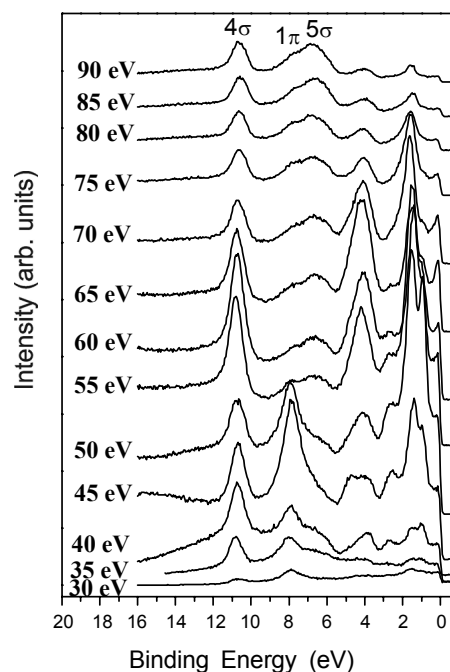
**Valence band spectra.** In order to shed light on the adsorption structures of  $\beta$ -CO on Mo(110) surfaces, the valence band spectra of clean and CO-covered Mo(110) surfaces were collected using a range of photon energies (Fig. 1 and 2). For the clean Mo(110) surface, the valence band spectra changed significantly as a function of the photon energy. The maximum intensity of the Mo-4d bands was observed at a photon energy of 55 eV. The 4d-peak intensity decreased gradually with increasing and decreasing photon energy from 55 eV. CO-induced features could be observed when the Mo(110) surface was exposed to 5.0 L (Langmuir  $1\text{L} = 10^{-6}\text{ torr} \times \text{sec}$ ) of CO at 100 K. A broad feature between 6–8 eV below the Fermi level, and another state at 10.7 eV was observed after CO adsorption, which were assigned to the  $(1\pi + 5\sigma)$  and  $4\sigma$ , respectively.<sup>26–30</sup> The CO  $4\sigma$ -peak showed its maximum intensity at a photon energy of 55 eV, whereas the peak at 7.9 eV corresponding to the  $5\sigma$ -state of CO at 45 eV. The  $5\sigma$ -state at 7.9 eV decreased in intensity with increasing photon energy from 45 eV, whereas the  $1\pi$ -peak increased. The  $1\pi$ - and  $5\sigma$ -states, which are located closely energetically, can be discriminated using a variety of photon energies.

In order to shed light on the coverage-dependent change in the electronic structure of CO on Mo(110), the valence band spectra were collected from CO-covered Mo(110) surfaces with various CO coverages (Fig. 3). CO was adsorbed at 100 K, and a photon energy of 80 eV was used to collect the valence band spectra. As mentioned above, the adsorption of CO induces the appearance of peaks at approximately 11 eV and 6–8 eV below the Fermi level. A close inspection of the  $4\sigma$ -state shows that there should be two components in the  $4\sigma$ -state of CO (one centered at 10.6 and the other at 11.4 eV). At lower CO coverage, only the 11.4 eV-peak was observed, whereas the 10.6 eV-peak increased in intensity after saturation of the peak centered at 10.6 eV. A similar result was previously observed for CO chemisorption on Cr and W surfaces at similar temperatures. In these cases, it was concluded that the 11.4 eV-peak should correspond to the CO molecules tilted away from the direction normal to the surface, whereas the 10.6 eV-peak should correspond to the vertical CO.<sup>23,24,31,32</sup> It is possible that CO should be tilted at lower coverage, whereas vertical CO forms at higher coverage. The higher binding energy of the  $4\sigma$ -state of the tilted CO with respect to that of the vertical one is also supported by theoretical calculations.<sup>33,34</sup>

In previous studies on CO chemisorption on W(110), it was reported that the vertical CO desorbs below 400 K, whereas the tilted one transforms to a ‘lying-down’ species or dissociated C and O upon heating.<sup>23,24</sup> In order to shed light on the CO adsorption properties on Mo(110) in the  $\beta$ -state, the CO-precovered sample was heated to 900 K, and the valence band spectra were collected using a range of photon energies (Fig. 4). Using a photon energy of 55 eV, the broad feature at 12 eV was assigned to the  $4\sigma$ -state of CO, or 2s of dissociated C, *i.e.*



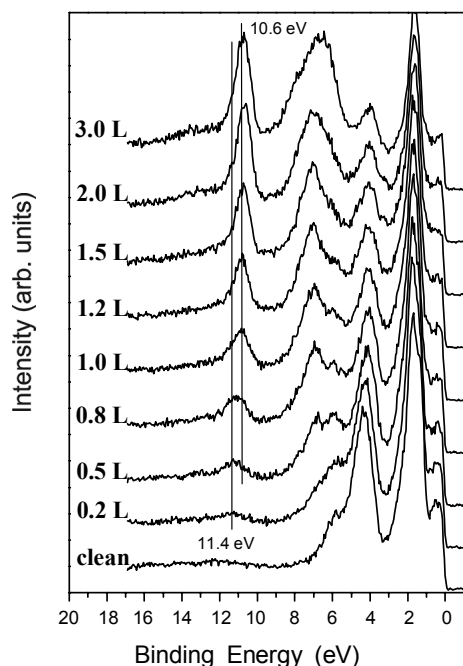
**Figure 1.** Valence band spectra of clean Mo(110) surfaces using a range of photon energies. The photon energies used to take the spectra are given in the figure.



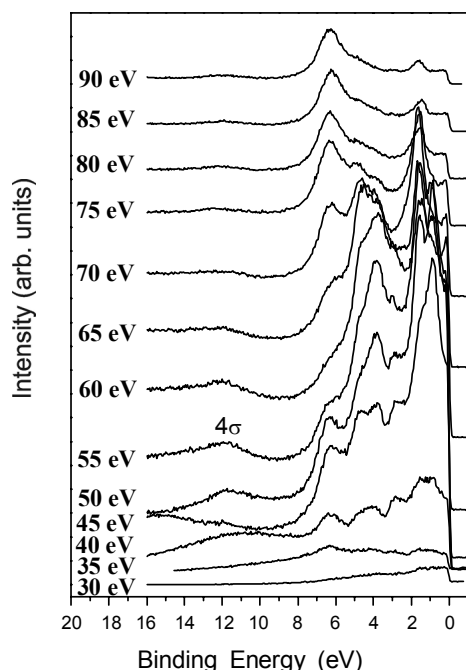
**Figure 2.** Valence band spectra of CO covered Mo(110) surfaces using various photon energies. The samples were exposed to 5.0 L of CO at 100 K. The photon energies used to take the spectra are given in the figure.

from the valence band spectrum, it is not clear, whether CO was dissociated or not upon heating to 900 K. It is worth mentioning that a similar result was found in a previous study, and in combination with C 1s level spectra, it was concluded that CO should be dissociated above 400 K.<sup>35</sup>

**TDS results.** Fig. 5 shows the TDS spectra of CO with

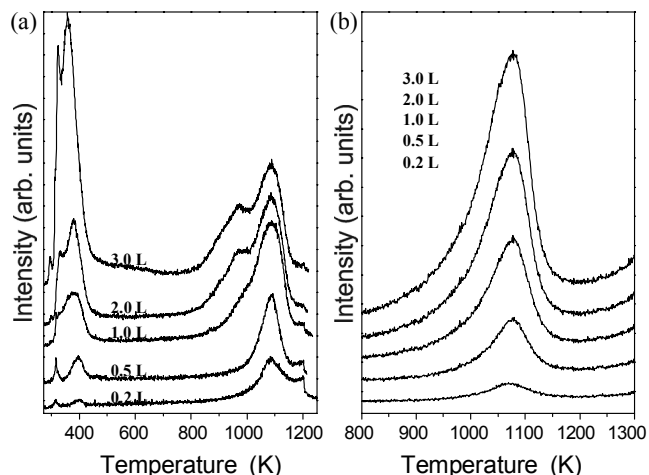


**Figure 3.** Valence band spectra of Mo(110) after stepwise exposure to CO at 100 K.



**Figure 4.** The valence band spectra were collected after heating the sample in Fig. 3 to 900 K. The photon energies used to take the spectra are given in the figure.

different initial coverages from a Mo(110) surface. Some of the CO molecules on the Mo(110) surfaces desorbed below 400 K ( $\alpha$ -state), which corresponds most likely to molecularly chemisorbed CO. Other desorption states were observed above 900 K, which are referred to as the  $\beta$ -CO. In order to examine the desorption characteristics of the  $\beta$ -state more in detail, the Mo(110) surface was exposed to CO at 900 K, and the TDS



**Figure 5.** a) TDS spectra of CO on Mo(110). CO was exposed at room temperature. b) TDS spectra of CO on Mo(110). The samples were exposed to CO at 900 K. CO exposures are given in the figure. (L= torr  $\times$  sec.)

spectra were collected (Fig. 5b). There was no change in the peak temperature when the amount of CO exposure was increased, which is indicative of first-order desorption. The asymmetric peak shape also indicates a first-order desorption of CO, which suggests a non-dissociative chemisorption of CO on Mo(110) surfaces above 900 K. This result is in contrast to the previous suggestions that CO is dissociated in the  $\beta$ -state on Mo(110).<sup>35</sup> Based on the TDS data, CO can be suggested to be molecularly bound the  $\beta$ -state. Alternatively, it is proposed there should be a substantial attractive interaction between O and C in the  $\beta$ -state, even when CO is dissociated, such that these atoms can readily recombine to a molecule without surface diffusion and can lead to the first order desorption kinetics.

## Conclusion

Using SRPES, the CO chemisorption structure on Mo(110) is quite similar to that on W(110) surfaces. The CO-induced peak centered at 12 eV below the Fermi level was observed in the valence level spectra after heating the CO/Mo(110) sample to 900 K, which can be attributed to the  $4\sigma$ -state of CO, or  $2s$  of dissociated C. TDS shows a first order desorption of CO above 900 K, implying that there should be formation of molecularly bound CO or a substantial attractive interaction between O and C above 900 K.

**Acknowledgments.** This study was supported by the SRC program (CNNC) of MOST/KOSEF (grant R11-2001-091-00000-0). The support from the BK 21 project of Ministry of Education, Korea, is gratefully acknowledged. The experiments at PLS were supported in part by MOST and by Dr. Ki-jeong Kim and Dr. Bongsoo Kim.

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