The adsorption and desorption of CO on the W(111) surface

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(Received 28 September 1999; accepted 1 May 2000)

The adsorption and desorption of CO have been studied on the W(111) surface in the temperature range of 300 and 1100 K by x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and thermal desorption spectroscopy. Saturation adsorption of CO at 300 K reveals four desorption states at 410, 850, 1000, and 1150 K, called \( \alpha, \beta_1, \beta_2, \) and \( \beta_3 \) states, respectively. The desorption kinetic order of CO in the \( \beta_3 \) state is followed by the first order, indicating that CO in the \( \beta_3 \) state seems to be nondissociative, rather than dissociative. The inequalities of XPS and UPS obtained following adsorption of CO and O\(_2\) under the same condition support a nondissociative adsorption of CO in the \( \beta_3 \) state. Based on calculations for CO adsorbed on W\(_{43}\) cluster models using atom-position and electron delocalization molecular orbit, the changes in binding energy and in intensity of XPS and UPS can be attributed to a lying-down species of nondissociatively adsorbed CO in the \( \beta_3 \) state. As a result, the binding energies of O(1s) and C(1s) for adsorbed CO in the \( \alpha \) state is characterized by 529.8 and 282.7 eV, respectively, whereas those for nondissociatively adsorbed CO in the \( \beta_3 \) state is characterized by 530.1 and 282.4 eV, respectively. © 2000 American Vacuum Society.

I. INTRODUCTION

The interaction of carbon monoxide (CO) with transition metal surfaces is not only of enormous technological importance in the field of heterogeneous catalysis such as the Fischer−Tropsch synthesis and the exhaust gas purification, but also as part of the core knowledge of surface chemistry. For example, it has been shown that elements to the left of a line connecting cobalt (Co) and tungsten (W) on the periodic table are able to dissociate a portion of chemisorbed CO prior to desorption while those on the right side display multiple desorption states. Over the last 30 years, the interaction of CO with W has been studied extensively with a wide variety of techniques, and several excellent reviews\(^1\)−\(^5\) have been published in leading journals. Despite extensive studies of the system, however, a number of questions regarding structure and kinetics still remain unresolved.

Thermal desorption spectra (TDS) of CO desorbed from the W surfaces have shown two main desorption states; one of them, called the \( \alpha \) state, desorbs at about 400 K; the other, called the \( \beta \) state, show two or three desorption features in the range of about 800 to 1300 K, depending on surface conditions and surface plane. Regarding the \( \alpha \) state, it has been firmly thought that it is due to molecular species of an end-on type on the surface, based on the experimental data of TDS, vibrational spectroscopy, and photoelectron spectroscopy. On the other hand, the structure of the \( \beta \) state has been the subject of controversy for a long time. Even until early 1970, nondissociative adsorption of CO had been accepted, generally on the basis of the fact that no pattern by contamination of carbon and oxygen on the surface of field emission tips was observed, even after repeated adsorption/desorption. Also, the diffusion of CO in the \( \beta \) state does not occur below 700 K, which is quite different from adsorbed pure oxygen, which is mobile even below 400 K.\(^1\) Moreover, the desorption of CO from the \( \beta \) as well as the \( \alpha \) state follows first-order kinetics.\(^1\) Goymour and King\(^6\)−\(^8\) observed, however, that desorption spectra for the \( \beta_2 \) state appeared near 1500 K, shifted to lower temperature with increasing coverage, and they proposed a dissociative model. Using this model, they explained completely not only their results of TDS for the \( \beta \) state, but also, previous results on the isotope exchange.\(^9\) Many experimental data obtained by photoelectron spectroscopies,\(^10\)−\(^12\) vibrational spectroscopies,\(^13,14\) and electron-stimulated desorption\(^6,15,16\) have been explained on the basis of the dissociative model. It is now widely accepted that the adsorption of CO in the \( \beta \) state is dissociative. Up to now, however, it has not been explained well why C and/or O are not observed on the surface after repeated desorption. Also not explained is why the diffusion of the oxygen atom formed by dissociation of CO occurs only at higher temperature, compared to the dissociatively adsorbed oxygen by pure oxygen molecules.

However, our recent experimental results for CO/W(111) and CO/W(110) obtained using x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and thermal desorption spectroscopy (TDS) consistently indicate that CO in the \( \beta \) state is also nondissociative, which is quite different from the conclusions we held until now.

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Moreover, the $4\sigma$ peak was observed in the valence-band spectra for CO/W(110) using synchrotron radiation, even after heating the CO-adsorbed surface to about 900 K, which is direct evidence for the nondissociative state of CO. In this article, we present our recent experimental results for CO/W(111) obtained by using XPS, UPS, and TDS.

II. EXPERIMENT

The experiments were carried out in a stainless-steel ultrahigh vacuum (UHV) system with a base pressure of $2 \times 10^{-10}$ Torr. The UHV chamber is equipped with a Q-mass spectrometer, four-grid low energy electron diffraction (LEED) optics, and hemispherical energy analyzer for Auger electron spectroscopy (AES), UPS, and XPS. HeII and Mg($K\alpha$) were used as light sources for UPS and XPS. More details of the system are found in previous publications.

The tungsten single-crystal W(111) used in the experiments was approximately 10 mm in diameter and 1 mm in thickness. The crystal was spot welded onto a pair of parallel Mo rods (1.5 mm in diameter). The Mo rods were directly connected to a pair of Cu blocks, which were then connected to an electrical feedthrough to heat the crystal resistively. A W-5% Re/W-26% Re thermocouple was spot welded to the edge of the crystal for temperature measurement. The sample was cleaned using a cycle of oxygen treatment, Ar-ion bombardment, and annealing at 1300 K. The clean surface was identified by LEED and AES. For TDS, the sample was heated at a rate of 8 K/s by passing direct current through it.

III. RESULTS AND DISCUSSION

A. Thermal desorption spectra

Figure 1 shows thermal desorption spectra of CO on W(111) with increasing CO exposures. This exhibits an $\alpha$ state at 410 K and $\beta$ state in the range of 800 to 1200 K. The three peaks at 850, 1000, and 1150 K in the $\beta$ state are distinguished, and we labeled these peaks as $\beta_1$, $\beta_2$, and $\beta_3$, respectively. The $\beta_3$ peak started to grow from low CO exposure and was saturated at an exposure of about 1.5 L. But, although the $\alpha$ state was observed even at low CO coverages, its peak increases markedly only after saturation of the $\beta_3$ state with increasing CO exposures. These thermal desorption spectra are similar to those obtained previously for W(111).

Because the desorption kinetic order and the desorption temperature of the $\alpha$ state agree with previous works, we believe that the $\alpha$ state consists of a molecular species with a linear configuration, which was also identified by interpreting the data of photoelectron spectroscopy. On the other hand, the peak maxima for the $\beta_3$ state shift to higher temperatures with increasing CO exposures. This suggests that the adsorbed CO can exist nondissociatively and interact attractively toward each other. Our detailed analysis of TDS for the $\beta_3$ state by simulation using quasichemical approximation suggested a nondissociative character of adsorbed CO in the $\beta_3$ state.

B. Photoelectron spectroscopy

Figure 2 shows O($1s$) with various exposures of CO at 315 and 1000 K. We also included here pure oxygen adsorbed at 315 K. This O($1s$) spectrum from adsorption of pure oxygen was taken after heating the oxygen-adsorbed surface to 1000 K to compare spectra of the adsorbed CO at 1000 K. The binding energies of O($1s$) obtained from adsorption of CO at 315 and at 1000 K do not change with adsorption coverage, and all their values are 529.8 and 530.1 eV. The binding energy of 529.8 eV can be attributed to the molecular species, as it has been identified by many experimental techniques that the adsorbed CO at room temperature is a molecular species with an end-on configuration. Although the difference in the binding energies between the two adsorption temperatures of 315 and 1000 K is only 0.3 eV, it indicates that the species in the $\beta_3$ state is different from the species at room temperature. The binding energy of 530.1 eV for the adsorbed CO also differs by 0.6 eV from that of the pure oxygen adsorption for 1.5 L exposure at room temperature. This implies that the adsorbed species in the $\beta_3$ state is not the dissociative atomic oxygen species obtained from oxygen adsorption. This is strong evidence for the nondissociative adsorption of CO. In the cases of tung-
sten surfaces other than (111), the oxygen binding energies for the \( \beta \) state of CO and oxygen adsorption were identical. So the dissociative adsorption of CO in the \( \beta \) state has been favored. However, we have found that we should be careful with such an interpretation, because binding energies of O\((1s)\) for adsorbed oxygen species may depend on their surface coverage. Figure 3 shows the XPS spectra of O\((1s)\) adsorbed on the W(111) surface with exposures of \( O_2 \); the binding energy of O\((1s)\) at 529.5 eV is constant until 1.8 L exposure, but it shifts to 529.5 eV for over 3 L exposure, which approaches that of the \( \beta_3 \) state within 0.15 eV. So, to compare the binding energies of oxygen from the adsorbed CO with that taken from oxygen adsorption, we must take XPS values obtained from the same surface concentration of CO and oxygen adsorption.

Figure 4 shows O\((1s)\) and C\((1s)\) spectra obtained after stepwise heating of the CO-saturated sample at 315 K to the indicated temperatures. The binding energy of O\((1s)\) shifts continuously to higher values, from 528.5 eV at 315 K to 530.1 eV at 1000 K. This figure also shows that the intensity decreases with increasing temperature, as well as the shift of binding energy. It indicates that the room-temperature species convert to other states with increasing temperature even though some of them desorb. In contrast to O\((1s)\), the binding energy of C\((1s)\) shifts continuously to lower values with increasing temperatures, from 282.75 eV at 315 K to 282.45 eV at 1000 K. Its intensity also decreases in parallel to that of O\((1s)\) with increasing temperature. The results indicate not only some desorption of CO, but also, a change of adsorbed states, in agreement with the O\((1s)\).

The binding-energy shift of C\((1s)\) and O\((1s)\) to lower and higher sides, respectively, can be explained qualitatively by theoretical calculations based on models of the end-on and lying-down orientations of CO on the W(111) surface. The calculations were performed for CO adsorbed on \( W_{43} \) cluster models using the atom-position and electron delocalization molecular orbital (ASED-MO)\(^{23} \). Some of the calculated results are represented in Table I. According to this table, when CO converts from the end-on species to the lying-down orientation, the positive charge of the carbon atom decreases, while the charge of the oxygen atom changes from negative to positive values. This suggests that the binding energy of C\((1s)\) for the lying-down orientation is lower, whereas that of O\((1s)\) is higher, compared with the end-on orientation. It is consistent with our observed results. Therefore, the binding energy shifts of C\((1s)\) and O\((1s)\)
suggest the lying-down species of CO nondissociatively adsorbed in the $\beta_3$ state.

Figure 5 shows He(II) UPS difference spectra obtained after stepwise heating of the CO-saturated sample at 315 K to the indicated temperatures. We also included here the spectrum of pure oxygen adsorbed at 315 K. This spectrum was taken after heating the oxygen-adsorbed surface to 1300 K, to compare those of the adsorbed CO at 1000 K. At room temperature, a broad band reveals a peak maximum at 6.3 eV. It seems to be overlapped with a shoulder around 7 eV. Based on results of TDS and XPS, the peak maximum could be most likely due to levels of $5s^1p^1$, even though it is in lower energy than that observed at about 7 eV in other tungsten surfaces.3,10 Unfortunately, however, in this experiment an emission peak corresponding to the $4s$ level could not be observed at room temperature because we did not have a low-temperature control system. It is well known that the intensity of the $4s$ peak is very low at room temperature in the CO/W(110) system. 11

The broad spectrum at room temperature changes gradually both in shapes, as well as in intensity, with increasing temperature. The peak maximum at 6.3 eV decreases clearly above 1000 K, whereas the shoulder peak around 7 eV exhibits a marked maximum peak even at 1100 K. The peaks above 1000 K clearly correspond to the $\beta_3$ state. All the spectra of CO are inconsistent with oxygen spectra of 1.5 L exposure. Like O(1s) in XPS for the adsorption of pure oxygen, notice that UPS for adsorbed oxygen also depend on surface coverages. Figure 6 shows the UP spectra with exposures of O$_2$ adsorbed on the W(111) surfaces. The maximum peak at 5.5 eV for 1.5 L shifts to higher binding energies with increasing exposures, and for exposure of 8 L it shows the binding energy of 6.5 eV, with a shoulder around 7.5 eV. Its shape in spectrum seems to be similar to the band obtained at 315 K for 5 L of CO, but its intensity is very high. Therefore, to compare spectra of the adsorbed CO with that taken from oxygen adsorption, we must take spectra obtained from the same surface concentration of oxygen for CO and oxygen adsorption.

All the spectra show that their binding energy of 6.3 eV at room temperature shifts to higher binding of 7.1 eV at 1000 K. This result could probably be attributed to some mixing of bonding orbitals of CO with the surface band by the conver-

<table>
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<th>Model</th>
<th>BE(eV)</th>
<th>ROP$^a$</th>
<th>$R_{\text{CO}}$($\text{Å}$)</th>
<th>$R_{\text{WC}}$($\text{Å}$)</th>
<th>$\bar{h}^p$(C)</th>
<th>$\bar{h}^p$(O)</th>
<th>$\theta^c$</th>
<th>$Q_C^d$</th>
<th>$Q_O^d$</th>
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$^a$ROP, reduced overlap population between C and O.
$^b$h(C) and h(O), the height of C and O.
$^c$Tilt angle.
$^d$Q$_C$ and Q$_O$ are charges on C and O, respectively.
$^e$Relative to the surface normal.
$^f$The (m,n) denotes the orientation of CO that C coordinates tungsten atom in the mth layer and O in the nth layer.
$^g$Relative to the surface plane.

FIG. 5. Difference spectra of He(II) UPS obtained after stepwise heating the CO-saturated sample at 315 K to the indicated temperatures.
tion of CO from the $\alpha$ state to the $\beta_3$ state. Based on calculations for CO adsorbed on W$_{43}$ cluster models using ASED-MO, the main difference between the electronic structure of the lying-down and end-on configurations arises in the $5s$ state of the adsorbed CO. The $5s$ state is more strongly mixed with the metal $sp$ band in the lying-down configuration than in the end-on configuration, thus becoming much more scattered. This agrees with the experimental observations. This indicates CO in the $\beta_3$ state in the $\beta_3$ state is nondissociative and a lying-down species. Decrease of the total intensities at 1000 K, compared to those at room temperature, can be attributed to some desorption, as well as to changes of adsorbed states. It agrees with the results of XPS.

IV. CONCLUSIONS

In the TDS for CO adsorption on the W(111) surface, the $\alpha$ state was observed at a low temperature near 410 K, whereas $\beta_1$, $\beta_2$, and $\beta_3$ states were observed at 850, 1000, and 1150 K, respectively. The desorption kinetic order of CO in the $\beta_3$ state follows the first order, indicating that CO in the $\beta_3$ state seems to be nondissociative, rather than dissociative. The inequalities of XPS and UPS obtained following adsorption of CO and O$_2$ under the same condition support a nondissociative CO in the $\beta_3$ state. Based on calculations for CO adsorbed on W$_{43}$ cluster models using ASED-MO, the changes in binding energy of spectrum and in intensity can be attributed to a lying-down species of nondissociatively adsorbed CO in the $\beta_3$ state.

ACKNOWLEDGMENT

Support of this research by the Ministry of Education, Korea, under project of BSRI (Grant No. 1998-015-D00138) is gratefully acknowledged.