Photoemission studies of carbon monoxide on tantalum-supported palladium thin films

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We present experimental observations of the adsorption of carbon monoxide on tantalum-supported thin films of palladium. We find that for a palladium monolayer the adsorption produces a photoemission spectrum identical to that found for adsorption on the noble metals. For thicker films, which are shown by low-energy electron diffraction to grow parallel to the ⟨111⟩ direction, the photoemission spectrum is found to agree with previous studies on Pd(111) single crystals.

I. INTRODUCTION

Carbon-monoxide bonding to metal surfaces has been the subject of numerous theoretical[1] and experimental[2–4] studies in recent years. These studies have shown that in general the bonding of this adsorbate system falls into two classes:[5] strong chemisorption, characteristic of the bonding to transition metals, and weak chemisorption or physisorption, characteristic of the adsorption on noble metals.

The strong-chemisorption case is believed to be reasonably well undertsood. In general it is found that on transition metals carbon monoxide bonds linearly to the surface with the carbon atom down on the metal substrate.[2] Bonding between the molecular 5σ orbital and the unoccupied metallic d orbitals is compensated for by "back bonding" from the occupied d orbitals into the unoccupied molecular $2\pi^*$ level.[6,7]

Adsorption on the noble metals is believed to be similar although the photoemission spectra from these systems is less well understood. For example, while the photoemission spectra for carbon monoxide adsorbed on Cu(111) (Ref. 8) have features in common with those observed for carbon monoxide on Pd(111) (Ref. 9) it is found that on Cu(111) the molecular orbitals have shifted to higher binding energies and an additional feature identified as a "shake-up" satellite is observed.[10]

This shake-up structure is a many-body excitation caused by the readjustment of the valence electrons of the system to screen the photoinduced 4σ hole. In the case of carbon-monoxide adsorption it would require more unoccupied states in the $2\pi^*$ orbital and thus indicates a weaker bond.[11]

In the present paper we discuss a photoemission study of the adsorption of carbon monoxide on a Pd(111) surface compared with adsorption on a Pd monolayer grown on a Ta(110) surface. In an earlier study[12] similar behavior was found to previous work on the growth of thin films of Pd on niobium substrates.[13] At approximately one-monolayer coverage the Pd overlayer moved from a commensurate structure to an incommensurate structure producing a low-energy electron diffraction (LEED) pattern similar to the Pd(111) surface at Pd coverages exceeding several monolayers. Photoemission studies of the Pd monolayer revealed that the electronic structure of the complex was similar to that of a noble metal such as copper, in that the d band now appeared to be full with a consequent reduction of the density of states at the Fermi level. The noble-metal character of the Pd monolayers was confirmed by CO-uptake studies performed at room temperature[14] where it was found that the Pd monolayer in either the commensurate or incommensurate structure was inert to the uptake of carbon monoxide. This situation altered with increasing thickness of Pd and above three monolayers the films showed identical room-temperature adsorption characteristics to the Pd(111) surface.

Our investigation of the adsorption of carbon monoxide on these surfaces has now been extended to low-temperature adsorption studies. We find that carbon monoxide adsorbs on the Pd monolayer structure at liquid-nitrogen temperature and that the electronic structure is similar to that obtained following adsorption of carbon monoxide on a Cu(111) surface.

In Sec. II we describe the experimental procedures used in the present study. In Sec. III we elucidate the experimental observations and in Sec. IV we discuss these results in the context of theoretical models of the adsorption of CO on metal surfaces.

II. EXPERIMENTAL

All experiments described in this paper were performed in one of two UHV chambers. Each chamber capable of base pressures of the order of 10^{-10} Torr was equipped with LEED, Auger, and photoemission facilities to allow characterization of the surface under consideration. In one chamber the photoemission was conducted using a He resonance lamp and, in the other chamber, synchrotron radiation was used as the photon source. In both chambers photoelectron kinetic energies were measured with a PHI double-pass cylindrical mirror analyzer.

Palladium thin films were grown by evaporating palladium from a tungsten basket onto a tantalum (110) surface. This surface was previously prepared by recrystallization of a tantalum foil following partial melting of the foil by resistive heating. Sample cleaning and/or removal of adsorbed metal overlayers was accomplished using the same resistive heating technique used to prepare the sample.

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The film thickness was computed from the deposition time for evaporations performed at fixed Pd source current and calibrated by comparison of Auger spectra. It was found that indistinguishable palladium monolayers could be produced either by direct evaporation or by the annealing of Pd(111) thicker films. The tantalum foil was mounted at the base of a liquid-helium cryostat but the use of liquid nitrogen was sufficient to produce the temperatures required for this study.

For the adsorption studies carbon monoxide was introduced into the chamber to a partial pressure of 10^{-6} Torr. CO-gas purity was monitored using a quadrupole mass spectrometer.

III. RESULTS

In Fig. 1(a) we show the change in the valence electronic structure as palladium overlayers are deposited on the tantalum (110) substrate. Note that in the region of one monolayer there is a decrease in the density of states at the Fermi level, characteristic of metallic monolayers. Figure 1(b) shows the measured photoemission spectra recorded following carbon-monoxide exposure at room temperature to these different palladium overlayers. On this clean tantalum (110) it is found that the carbon monoxide dissociates and adsorbs atomically while on the thick palladium overlayers it adsorbs as a molecule. In the region of one monolayer of palladium the surface appears to be inert with no photoemission structure indicative of either dissociative adsorption or molecular adsorption.

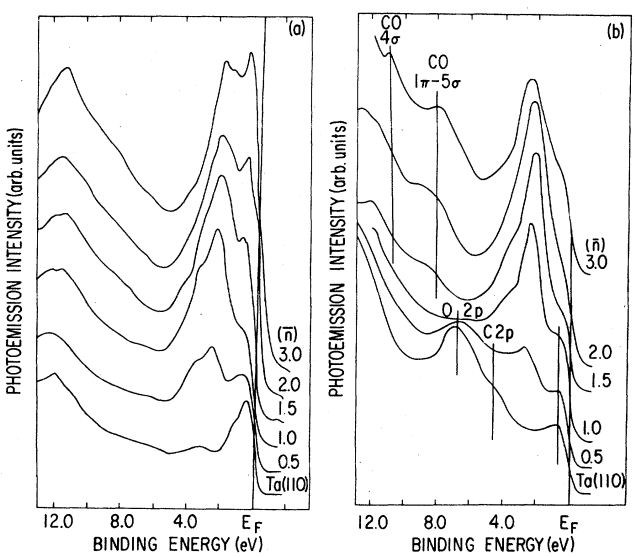

FIG. 1. (a) Angle-integrated photoemission spectra, taken using the HeI emission, obtained from a Ta(110) surface for various coverages of Pd; $\bar{n}$ is the estimated Pd coverage in monolayers. (b) Angle-integrated photoemission spectra taken after exposure to ≈ 21 L of CO as measured at the vacuum gauge. [1 langmuir (L) $\equiv 10^{-6}$ Torr sec.] Note that CO exposures were performed at room temperature.

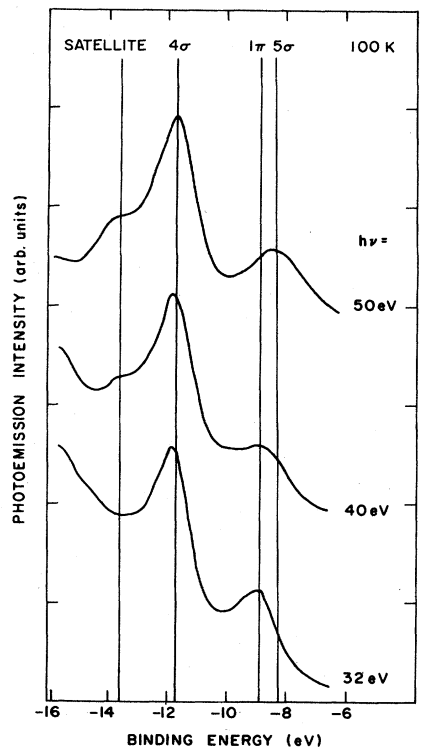

FIG. 2. Energy distribution curves of the CO-induced photoemission features on Pd*(110) supported on Ta(110) at 32, 40, and 50 eV photon energy. Note the appearance of a shoulder at -14-eV binding energy and the partial resolution of the photoemission feature at ≈ -9-eV binding energy into two peaks. CO exposures were performed on a liquid-nitrogen-cooled substrate.

However, at liquid-nitrogen temperatures carbon monoxide is found to adsorb on this Pd monolayer as shown in Figs. 2 and 3(b). From Fig. 2 it will be seen that carbon-monoxide-induced features occur at 8.9, 11.6, and 13.6 eV with respect to the Fermi level. Examination of the spectra as a function of photon energy show that the peak at approximately 9 eV is probably composed of two features as would be expected for carbon-monoxide adsorption. These peaks would be identified as the 1π and 5σ orbitals and because of its p-like as opposed to s-like character the 1π orbital is expected to have a higher cross section at lower photon energies.[15] We therefore suggest that the 1π orbital has a binding energy of 8.9 eV and the 5σ orbital a binding energy of 8.2 eV. The peak at 11.6-eV binding energy we identify with the 4σ orbital and that at 13.6 eV we suggest is a shake-up satellite.

In Fig. 3 we compare spectra recorded at 40 eV for carbon-monoxide adsorption on (a) a Pd(111) surface and (b) the Pd monolayer. The former spectra, recorded at liquid-nitrogen temperature, contains two CO-induced features at 11- and 8.0-eV binding energy and was identical to that observed at room temperature. Similar features were observed from adsorption studies of CO on single-crystal palladium (111).[9] In those angle-resolved

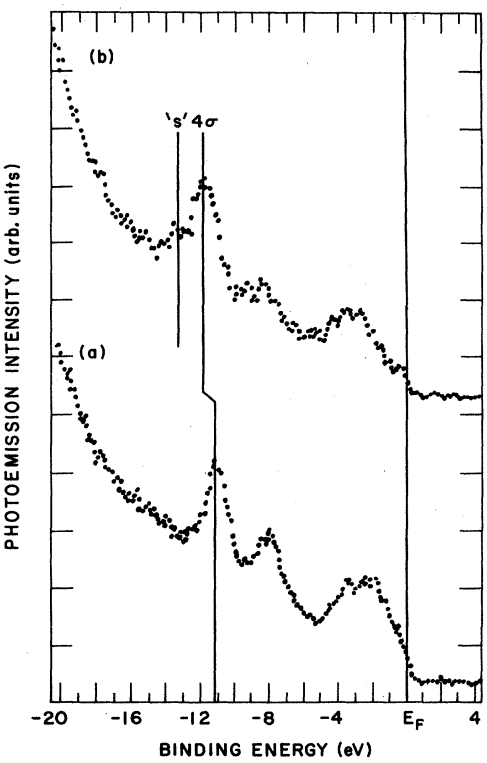

FIG. 3. Adsorption of CO on tantalum-supported palladium thin films: (a) saturation CO coverage ($\approx$24 L) on a thick (>3 monolayers) Pd(111)-like film at liquid-nitrogen temperature; (b) saturation CO coverage ($\approx$6 L) on a commensurate Pd*(110) monolayer at liquid-nitrogen temperature.

photoemission studies the peak at 11 eV was identified with the 4σ orbital and the peak at 8.0-eV binding energy was labeled the $5\sigma, 1\pi$ orbitals. Furthermore, the 5σ orbital was found to have a slightly higher binding energy, 8.2 eV, than the 1π orbital at 7.5 eV. In conclusion we find that CO adsorbs on a palladium monolayer at liquid-nitrogen temperatures with an electronic structure similar to that following adsorption on Cu(111). At thicker layers adsorption occurs at room temperature and the measured photoemission spectrum agrees with that observed in previous studies of CO adsorption on Pd(111) single crystals.

IV. DISCUSSION

In this study, we have compared the adsorption of carbon monoxide on the palladium surface of a thicker film and a monolayer which has a different electronic structures due to interactions with an underlying metallic substrate, in the present case tantalum. On the palladium monolayer the bond is found to be weaker and as a result adsorption occurs only at liquid-nitrogen temperatures. Electronic evidence for this weaker bond comes from the fact that the 1π and 5σ orbitals appear to reverse their relative binding energies in going from the Pd(111) surface to the Pd monolayer. Thus on the monolayer the bonding orbital, the 5σ level, is less tightly bound. Furthermore, the appearance of the shake-up satellite for adsorption on this monolayer would indicate that the other bonding orbitals, the 2π level, has a lower occupation than the equivalent orbital following adsorption on the Pd(111) surface.

The relative separation of the 4σ and 1π orbitals undergoes a slight reduction in moving from the Pd(111) system to the Pd monolayer. This reduction may be traced to two possible sources. One explanation is that the interatomic spacing between the carbon and oxygen atoms may be closer to the gas-phase value for the molecule weakly bound on the Pd monolayer. The alternative explanation relates to the observation of the satellite which is believed to be associated with excitation from the 4σ orbital. Application of the "sum rule"[8] for the different poles requires that the 4σ orbital moves to a lower binding energy than the calculated one-electron binding energy. This move will be compensated for by the appearance of the satellite at higher beinding energy.

In summary, while in previous work[14] it was shown that CO adsorption depends on the electronic structure of the surface, in this present work we have shown that the nature of the bonding between the CO molecule and the metallic surface also confirms the noble-metal-like character of the monolayer. In the monolayer case the satellite structure characteristic of weak bonding in a noble metal is observed, along with a shift to higher binding energies. In the thick-layer case the usual features of strong bonding in a transition metal was observed.

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