THE ADSORPTION OF CO ON Pd THIN FILMS ON Ta(110)

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The heat of adsorption of CO on Pd overlayers on a Ta(110) single crystal substrate has been measured using temperature programmed desorption (TPD). We find that the Pd monolayer film has a dramatically altered chemistry, weakly chemisorbing CO with an adsorption energy of only 14.4 kcal/mol. This can be contrasted with the value of 34 kcal/mol for the heat of adsorption of CO on the bulk Pd(111) surface. The CO adsorption energy increases with Pd film thickness, returning to the value for bulk Pd for a 3 ML Pd film. The Pd adlayers were characterized using AES, LEED, and Pd TPD to accurately determine the Pd coverage on Ta(110). Pd was shown to grow in a layer-by-layer mechanism at 775 K. The first monolayer adopts a pseudomorphic structure with the Ta(110) surface. Pd films annealed to 1075 K resulted in extensive alloy formation. However, the alloy is capped by a Pd monolayer that has a structure and surface chemistry identical to the as-deposited 1 ML Pd film formed at lower temperatures.

1. Introduction

Thin transition metal films on metal substrates have been shown to have remarkably altered electronic structure and chemical properties [1–21]. Much of the available information concerns thin Pd films on Nb(110) [1–10] and Ta(110) [1,2,10–13] substrates. For example, on Pd/Ta(110), Ruckman et al. [10,11] observed using UPS that a Pd monolayer had a greatly reduced CO sticking coefficient at room temperature. In low temperature adsorption experiments using UPS, they found a weak CO–metal interaction as evidenced by a decreased shift of the 5σ CO orbital and an increase in the 4σ shake-up intensity. However, little is known quantitatively about the reduction in CO

adsorption energy on these thin metal films. This information is critically needed for a complete understanding of the mechanism responsible for the alteration of the electronic structure and chemisorption properties and for progress in the development of the ability to carefully tailor surface chemistry.

In this paper, we present results for CO adsorption on Pd overlayers on a Ta(110) single crystal substrate. Using TPD of Pd, AES, and LEED, we characterize the growth mechanism and structure of the Pd overlayers. We show directly using CO TPD that the Pd monolayer only weakly adsorbs CO. In addition, we explore the CO–Pd interaction as a function of film thickness and structure.

2. Experimental

The UHV chamber used for these studies has been described previously [21]. This apparatus was

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equipped with AES, LEED, and TPD instrumentation. AES data was obtained using a 3 kV incident beam and 6 V modulation of the double-pass CMA.

The Ta(110) crystal was mounted on the sample holder using two 0.020″ Ta wires spot-welded across the back of the crystal to two 0.165′ nickel posts. This allowed resistive heating of the sample for TPD to 1800 K using about 60 A. An electron beam heater which could deliver 280 W (700 V, 400 mA) to the crystal was constructed for high temperature annealing and cleaning of the crystal. The temperature of the crystal was monitored by a W/5%Re–W/26%Re thermocouple spot-welded onto the edge of the crystal. The sample holder was liquid nitrogen cooled and could reach temperatures of 100 K.

The Ta crystal was cleaned by successive annealing cycles at 2300–2500 K, followed by AES. After about 2.5 hours, the O(505)/Ta(210) AES ratio reached a steady value of 0.05, corresponding to approximately 0.025 ML oxygen atoms. Following this extensive initial cleanup, clean Ta(110) surfaces could be regenerated by one minute anneals to 2300 K. All experiments were performed with an O(505)/Ta(210) AES ratio below 0.07.

Pd was deposited on the Ta(110) crystal by a Pd evaporator made by wrapping 0.005″ Pd wire around a 0.012″ W wire. Heating the W wire with 5–6 A resulted in a Pd deposition rate of about 1 ML in 1.5 minutes. Thick Pd films were deposited using a faster Pd evaporation rate, so that all Pd films were prepared in less than 5 min.

Research purity H$_2$ (99.999%) and CO (99.99%) were supplied by Matheson and used without further purification. Gas dosing was carried out using a stainless steel needle with a local pressure enhancement of about 25 : 1, and the reported gas exposures have been corrected for this flux enhancement. Gas dosing was always carried out at 100–120 K. Pd dosing for growing the evaporated Pd films was also carried out at 120 K, but all films were flash annealed to 775 K prior to analysis or chemisorption experiments.

TPD of gases or Pd was always carried out at 10 K/s.

3. Results

3.1. Growth and structure of Pd films on Ta(110)

AES spectra of the clean Ta(110) surface and those of evaporated Pd films of two thicknesses are shown in fig. 1. The spectra of clean Ta(110) and the thick Pd film agree well with previously reported spectra for Ta [22] and Pd. In these film growth studies, it is critical to exclude adsorbed oxygen that can alter the film growth mechanism and structure. It is clear from fig. 1 that the Ta substrate can be prepared free of adsorbed oxygen and that Pd films can be deposited without coadsorbed oxygen. Comparison of the Pd AES ratios also indicates that the Pd films are formed without codeposited carbon. At submonolayer coverages
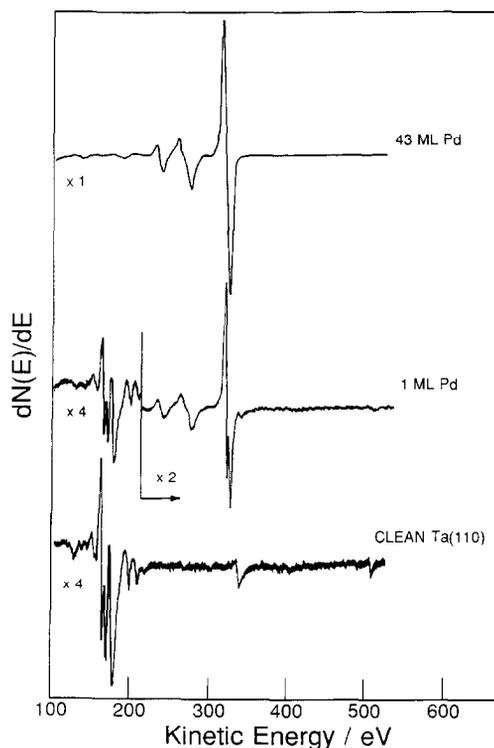

Fig. 1. AES spectra of Pd adlayers deposited on the Ta(110) crystal surface at 120 K, after annealing to 775 K. Bottom curve is for clean Ta(110) prior to Pd deposition; middle curve is for 1 ML Pd on Ta(110); top curve is for 43 ML Pd on Ta(110).
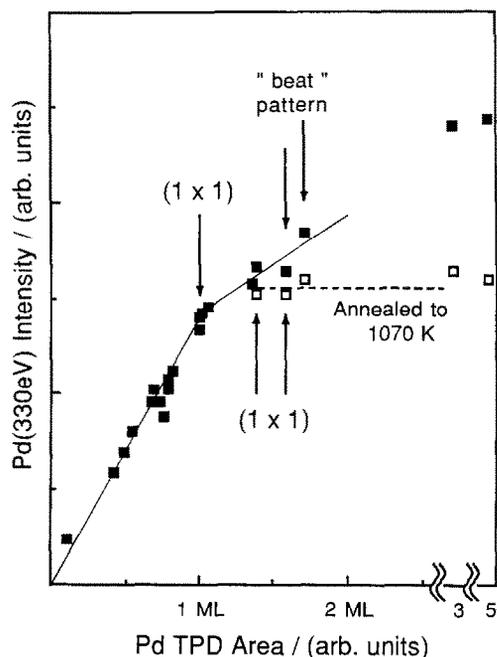
Fig. 2. Detail of the growth of the first Pd monolayer obtained by plotting the Pd(330) AES signal (filled squares) versus the amount of deposited Pd (as determined by integrated Pd TPD areas). Deposition of Pd was carried out at 120 K followed by annealing to 775 K. The dashed line indicates the Pd(330) AES signal (open square) obtained for annealing thick Pd films to 1070 K for 30 s. The LEED patterns observed for several Pd adlayers are indicated.

of Pd, the Pd Auger lineshape is altered from that of bulk Pd. This observation has been made previously for Pd films on several substrates [12,23,24], and has been studied in some detail on Nb(110) [25]. The Pd lineshape evolves fairly rapidly to that of the bulk, so that after about three layers the lineshape closely resembles that of bulk Pd.

AES spectra similar to those of fig. 1 were used to construct a Pd uptake curve in order to determine monolayer coverage and to investigate the film growth mechanism. We show this uptake curve of the data obtained near 1 ML Pd in fig. 2 as a plot of the Pd(330) AES signal (following annealing to 775 K) versus the amount of Pd deposited in the film, as determined by integrating the area of Pd peaks in TPD [26]. The sharp change in slope of the curve in fig. 2 defines the point at which a monolayer of Pd is formed. The uptake curve over the first two monolayers can be

fit well by computer simulations using a layer-by-layer (Frank–van der Merwe) growth mechanism, showing that this film growth mode occurs under our deposition conditions. This plot, a plot of the Ta(179) AES signal, and a plot of the Pd(330)/Ta(179) AES ratio versus the amount of Pd deposited in the film (not shown) are all consistent with a layer-by-layer growth mechanism for larger Pd coverages also. We note here that the plot of the Pd(330)/Ta(179) AES ratio versus the amount of Pd is not a very reliable method for determining the monolayer coverage; this point will be discussed in a future publication [27].

Observations of the LEED pattern for several Pd films are also given in fig. 2. The (1 × 1) pattern observed at the monolayer break point indicates that the first Pd layer grows pseudomorphically with the Ta(110) substrate. A complicated "beat" pattern [8,12] was observed at 1.6 ML Pd. This LEED pattern has been attributed to two possible origins. First, an ordered defect structure, with a large unit cell, could occur in the formation of the second layer [28] as a mechanism to relieve some of the enormous lattice strain in the Pd layer due to the large (18% in one direction) lattice mismatch between Pd and Ta. This defect structure continues in the Pd film until the accumulation of enough layers to provide the relaxation to allow the Pd to go into the more stable, epitaxial Pd(111) structure. A second hypothesis proposes that a phase transition from a commensurate Pd*(110) structure (pseudomorphic with Ta(110)) to an incommensurate Pd(111) structure occurs *within* the first monolayer of Pd. This model has been discussed in detail elsewhere [2,12]. Unfortunately, our preliminary data reported here do not conclusively rule out either of these proposals. However, the observation of the (1 × 1) pattern at monolayer coverage (the break point in fig. 2) certainly would argue against a phase transition *within* the monolayer. Further work on this important point is planned.

A final observation concerning fig. 2 should be noted. Multilayer Pd films that have been annealed to 1075 K give nearly the same Auger signals irrespective of the initial film thickness and always have the (1 × 1) LEED pattern. These results are shown in fig. 2 as the dashed line. This
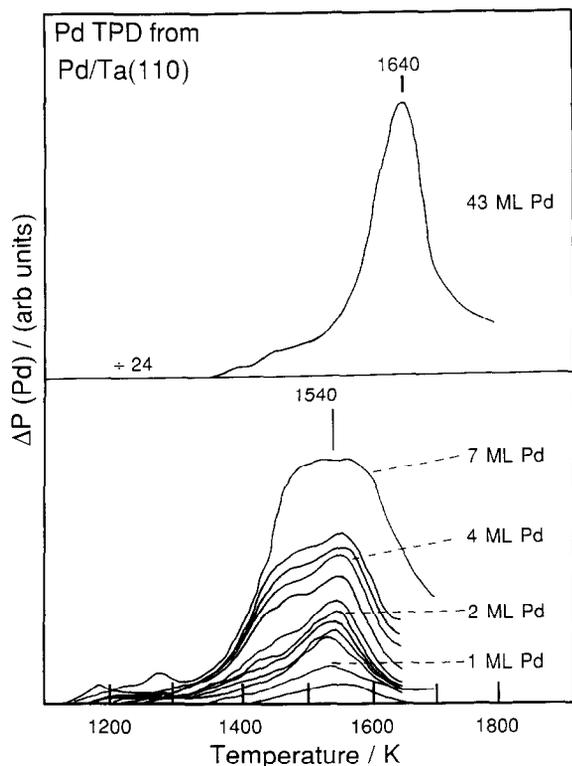
Fig. 3. Pd TPD spectra from Pd on Ta(110). The heating rate was 10 K/s. The top curve shows the spectrum obtained for a very thick (43 ML) Pd film, while the lower curves show spectra obtained as a function of the Pd coverage for thicknesses below 7 ML.

1560 K. Redhead analysis of this curve assuming first-order desorption kinetics gives 97 kcal/mol for the desorption activation energy, which is also the bond dissociation energy of the Pd–Ta substrate bond. The Pd peak temperature decreases slightly to 1540 K with increasing coverage up to 1 ML. This high temperature Pd desorption state then shifts slightly to higher temperature with increasing film thickness, so that it occurs at 1550 K for a 4 ML film. Deposition of Pd films thicker that 1 ML also lead to the formation of a new, low temperature desorption state with a peak temperature of 1480 K. For these intermediate Pd coverages, some additional Pd desorption can be observed with an onset near 1200 K. This is most clearly seen in the Pd TPD spectra for the 4–7 ML films. The most noticeable effect in these higher Pd coverages (> 2 ML) is that they show extensive tails to higher temperatures. Thus, to desorb all of the Pd for a 5 ML film the temperature must be held at 1700 K for a substantial time (several tens of seconds). This high temperature desorption tail is clearly seen in the top of fig. 3, which shows a TPD spectrum obtained for a thick (43 ML) Pd film. The peak temperature here is 1640 K, with a substantial desorption rate at 1800 K. Interestingly, the low temperature states that

line intersects the Auger uptake curve slightly above the monolayer break point. Based on the Pd TPD data that is presented below, we propose that significant alloying of Pd into the bulk of Ta occurs at this temperature. It is believed that all of the Pd in excess of the pseudomorphic monolayer of Pd dissolves into the Ta substrate, leaving a pseudomorphic monolayer of Pd "capping" the surface. This surface has a higher Pd AES signal than the monolayer due to some contribution from dissolved Pd. These results confirm that Ruckman et al. [10–13] were, in fact, studying the pseudomorphic monolayer (as they reported in their work), but prepared by high temperature annealing.

Pd TPD spectra from Ta(110) are shown in fig. 3. Pd desorption from submonolayer films initially occurs near 1400 K, with a peak temperature of
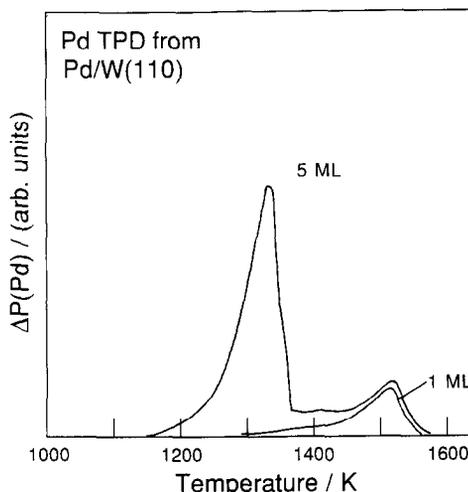

Fig. 4. Pd TPD spectra from Pd on W(110), adapted from ref. [20]. The heating rate was 10 K/s. The top curve shows the spectrum obtained for a thick (5 ML) Pd film and the lower curve shows the spectrum obtained for a 1 ML Pd coverage.

were formed during the deposition of the 2–3 monolayer films are not visible on this scale, and Pd desorption has an apparent onset at about 1330 K, similar to that of the monolayer film.

These results can be contrasted with those for Pd films on W(110) [20]. Fig. 4 reproduces an important result of this work. The monolayer Pd film on W(110) gives a similar high temperature Pd desorption peak at 1520 K. However, deposition of a 5 ML film leads to low temperature desorption of Pd with an onset just above 1100 K. This desorption has been analyzed using zero-order kinetics to give a desorption activation energy of 95 kcal/mol. Since this is essentially the bulk sublimation energy, the origin of this state has been attributed to the sublimation of Pd 3D crystallites formed on the surface by the high temperature heating that occurs during the TPD experiment. This explanation is also consistent with a large reduction in the Pd AES signal observed following heating thick films to 1000 K.

While the low temperature desorption features in fig. 3 indicate some small amount of Pd sublimation from Pd particles on the Pd monolayer on Ta(110), clearly formation of bulk-like Pd 3D crystallites are not responsible for the dramatic reduction in the Pd AES signal on Ta(110) that occurs from high temperature annealing. Rather, the shift of the Pd desorption peak to higher temperature and the extensive tailing of the high temperature side of the desorption peak with increasing Pd coverage indicates that Pd dissolution and alloy formation occurs during heating in TPD. Subsequently, Pd desorption kinetics are rate-limited by diffusion of Pd from the near surface region to the surface.

3.2. CO adsorption on Pd adlayers on Ta(110)

CO desorption spectra for saturation coverages of CO on Pd/Ta(110) as a function of Pd coverage are shown in fig. 5. At a Pd coverage of 1 ML, peaks are observed at 204 and 245 K. Below 1 ML Pd, these peaks correspond to the desorption of reversibly and molecularly adsorbed CO on the partial Pd monolayer, since the CO peak areas decreases nearly linearly with decreasing Pd coverage, at least to 0.5 ML Pd. This dramatic decrease
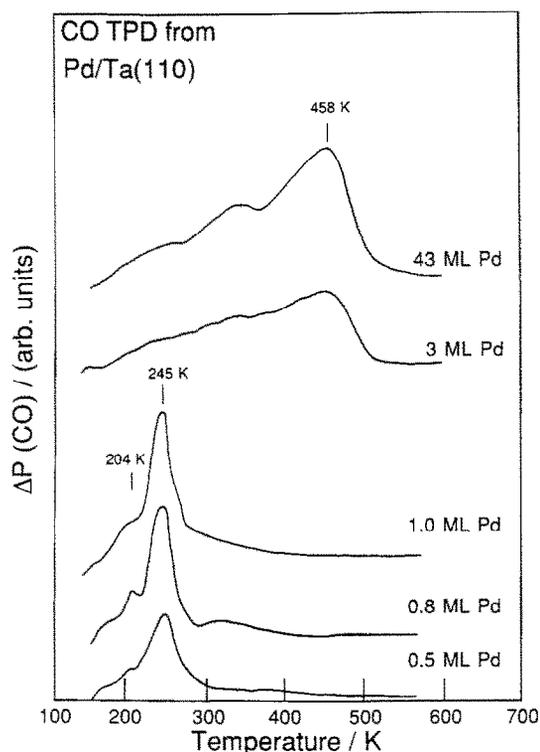

Fig. 5. CO TPD from Pd on Ta(110) as a function of the Pd coverage after a CO exposure of about 5 L at 120 K.

of 200 K in the desorption temperature of CO from the Pd monolayer compared to CO desorption from bulk Pd(111) surfaces, with a peak at 480 K [29], is responsible for the observation of Ruckman et al [10,11] previously that the Pd monolayer does not adsorb CO at 300 K. Using Redhead analysis, the desorption activation energy for CO according to first order kinetics was calculated to be 14.4 kcal/mol. Since CO adsorption proceeds with a negligible activation energy, the heat of adsorption of CO on the Pd monolayer on Ta(110) is determined to be 14.4 kcal/mol. This can be compared with the heat of adsorption of CO on bulk Pd(111) which has been determined previously [30] to be 34 kcal/mol. This is a dramatic reduction of nearly 60% of the CO chemisorption bond energy on the Pd monolayer compared to that on the (111) surface of bulk Pd. Weakening of the bonding of CO to Pd has been suggested previously for this system [11], but this represents the first quantification of the size of this effect.

The dramatic alterations in CO bonding observed on the Pd monolayer are not present on the 3 ML Pd film. Fig. 5 shows that the CO TPD spectra from a 3 ML Pd film closely resemble that from a 43 ML Pd film and also bulk Pd(111) [29].

The CO TPD spectra from the stable Pd monolayer formed by annealing multilayer Pd films to 1075 K, shown in fig. 6, are the same as CO TPD spectra from the "as-deposited" Pd monolayer formed at much lower temperatures. This similar CO chemisorption bonding argues that high temperature annealing produces an extremely stable, pseudomorphic Pd monolayer structure rather than a surface alloy layer containing both Pd and Ta atoms.

3.3. H_2 adsorption on Pd adlayers on Ta(110)

Several experiments were carried out to explore the interaction of H_2 with these Pd films. One preliminary result is shown in fig. 7. H_2 TPD spectra from clean Ta(110) is compared to that from 0.75 ML Pd on Ta(110) for saturation exposures of H_2 at 120 K. The large reduction in the H_2 desorption peak area for the partial Pd monolayer indicates a dramatic reduction in the sticking coefficient of H_2 on this surface. Also, the absence

Fig. 7. H_2TPD from a clean Ta(110) surface and from 0.73 ML Pd on Ta(110). TPD was performed after a H_2 exposure of about 30 L at 120 K.

of low temperature H_2 desorption on the Pd monolayer surface indicates a large reduction in the Pd–H bond strength. Further work is planned to investigate the H_2–Pd interaction and the role of Pd interface states in inhibiting bulk absorption of hydrogen by Ta.

4. Discussion

Our results using AES uptake measurements clearly indicate a layer-by-layer growth mechanism for vapor-deposited Pd films on Ta(110) at 775 K. This result is in agreement with previous studies for Pd deposition on Ta(110) [12], and also Pd deposition on other refractory metals such as Mo(110) [14], Nb(110) [9] and W(110) [20]. The Pd monolayer on Ta(110) grows pseudomorphically up to at least one monolayer as indicated by our LEED observations. UPS studies [12] of this system have shown a considerable reduction in the d band density of states at the Fermi level, similar to that of the Group IB metals (e.g., Ag). Although previous LEED and UPS studies have

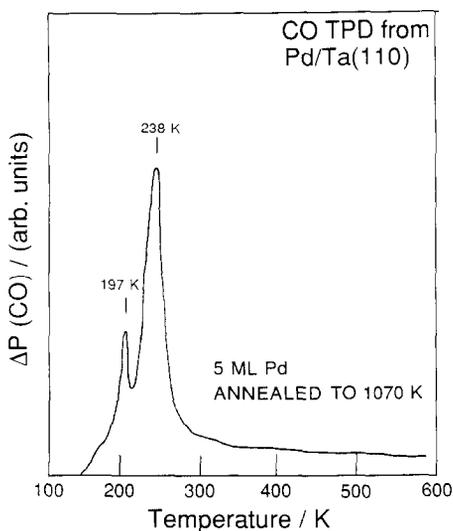Fig. 6. CO TPD from the stable monolayer of Pd on Ta(110) formed by annealing a thick Pd film to 1075 K after a CO exposure of about 5 L at 120 K.
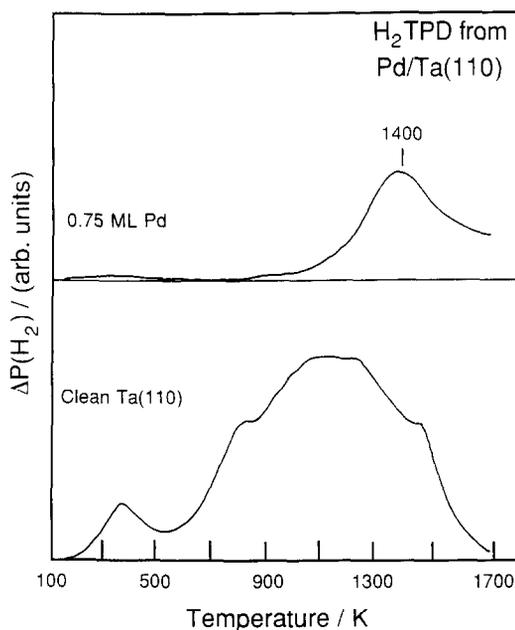
suggested that a two-dimensional phase transition from a commensurate to incommensurate structure occurs in the Pd monolayer and gives rise to a "beat" pattern in LEED, our data suggest that this pattern may be associated with the second Pd layer.

We also found that the pseudomorphic Pd monolayer could be obtained by annealing Pd multilayers to 1075 K. The Pd AES signals from monolayers prepared in this manner were independent of initial Pd film thickness, but were slightly larger than those of the "as-deposited" monolayer. This observation and the absence of Pd desorption at bulk Pd sublimation temperatures provides strong evidence that significant Pd dissolution into Ta occurs at 1075 K. Thus, even though similar changes were observed in Pd AES signals due to annealing for Pd films on W(110) [20], the explanation of this phenomenon for the two systems is completely different, with 3D crystallite formation indicated for Pd on W. One similarity for these two systems is the observation of an extremely stable pseudomorphic Pd monolayer in each case.

We report here the first determination of heat of adsorption of CO on the Pd monolayer on Ta(110), and find it to be 14.4 kcal/mol. This effect has been attributed to the dramatic alteration of the Pd electronic structure in the Pd monolayer on Ta(110) [11], with Pd characterized by an electronic structure similar to that of Ag. The Pd monolayer on Ta(110) has a small d density of states at the Fermi level and a narrow d band, characteristic of a completely filled 4d band. CO chemisorption bond strengths on the noble metals with filled d bands, such as Cu [31], Ag [32], and Au [33], are below 17 kcal/mol. Our experimental measurement of 14.4 kcal/mol for the heat of adsorption of CO on the Pd monolayer on Ta(110) agrees well with these values. It is interesting that Pd monolayers on all of the refractory metals studied to date, i.e. Mo(110) [14], Nb(110) [9] and W(110) [20], chemisorb CO weakly.

We believe that the origin of the altered electronic structure of Pd and the altered bonding to CO for these Pd monolayers is due to charge transfer to Pd or rehybridization of Pd as a result of the Pd–substrate interaction. Most of these substrate refractory metals are more electropositive than Pd and might donate charge to Pd. The bulk Pd alloys with these metals are formed exothermically, indicating extensive bonding interactions. Also, the bond dissociation energy for the Pd–substrate bond, as measured by the desorption activation energy for Pd from the monolayer (in those cases where it has been measured) is larger than the desorption activation energy for Pd from bulk Pd. This points to strong bonding interactions between the substrate and the Pd in the first monolayer. Since the electronic configuration of Pd is effectively $4d^{9.5} 5s^{0.5}$ in the bulk solid [7], little charge transfer to Pd or rehybridization of Pd has to occur in order to cause Pd to have a filled 4d band. This filling of the Pd 4d band would account for the large decrease in the heat of adsorption of CO on these Pd monolayers compared to bulk Pd. Small differences between Pd monolayers on several of the refractory metals could be due to the subtle differences in the Pd s and p band density of states due to differences in the Pd–substrate bonding.

Acknowledgements

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[33] The heat of adsorption of CO on Au(111) is very small, less than 6 kcal/mol; experiments in our laboratory showed no measureable adsorption of CO on Au(111) at 100 K under UHV conditions.