Chemisorption of CO on ultrathin films of Pd on Mo(100)

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Received 21 February 1992; accepted for publication 7 April 1992

The altered bonding that exists at bimetallic interfaces can affect the properties of metal monolayers and thin films. We have probed the chemisorptive properties of ultrathin films of Pd on Mo(100) by studies of CO adsorption on these surfaces. Our investigations were carried out using Auger electron spectroscopy (AES), low energy electron diffraction (LEED), temperature programmed desorption (TPD), and high resolution electron energy loss spectroscopy (HREELS). The heat of adsorption of CO is reduced from 36.5 kcal/mol on Pd(100) single crystal surfaces to 20 kcal/mol on the pseudomorphic Pd monolayer. In addition, a 34% reduction in the initial sticking probability of CO occurs on the Pd monolayer at 150 K relative to thick (20 layers) Pd films. Both the heat of adsorption and the sticking probability of CO increase with Pd film thickness indicating that the chemistry of these surfaces can be "tuned". However, the origin of this tuning is not clear. On the Pd monolayer, HREELS shows that hollow and bridging sites are populated first, followed by atop sites at higher CO coverages. This is consistent with the site preference on bulk Pd(100) surfaces. The bonding of CO at bridging sites is clearly destabilized on the Pd monolayer and to a lesser extent on thicker films. The vibrational spectra of chemisorbed CO are shown to be a sensitive probe of the structure of Pd films of this type. The alterations in CO adsorption on the Pd monolayer and thin films on Mo(100) compared with that on bulk Pd surfaces are consistent with those observed for ultrathin Pd films on other early transition metal substrates such as Nb, Ta, and W. CO bonding on the pseudomorphic monolayer of Pd on Mo(100), which has a highly strained Pd–Pd lattice, is not weakened as much as on the relatively less strained Pd monolayers on Nb(110) and Ta(110), indicating that lattice strain is not sufficient to account for the origin of the weakened CO interactions.

1. Introduction

Metal monolayers and ultrathin (bilayer, trilayer, etc.) films often have altered electronic structure and chemisorption properties relative to the bulk metals. Some of the largest effects have been seen on thin films of Pd on refractory metal substrates. For example, photoemission studies of Pd films on Nb(110) and Ta(110) show a reduction in the density of states (DOS) at the Fermi level and a narrowing of the d-band, which is also shifted to higher binding energy [1–5]. Early UPS studies of CO chemisorption on a Pd monolayer on Ta(110) indicated a greatly reduced sticking coefficient for CO at room temperature [6]. Ruckman et al. [7] also found evidence of a weak CO–metal interaction by a decreased shift of the CO 5σ orbital energy in low temperature adsorption experiments. More recently, the Pd–CO bond strength has been measured to be 14.4 kcal/mol [8] using TPD on Pd/Ta(110). This can be contrasted with the value of 35.5 kcal/mol for the heat of adsorption of CO on the (111) surface of bulk Pd [9].

Discovering the origin of the altered properties of ultrathin Pd films on early transition metals is an important goal for designing surfaces with specific chemical and physical properties. Several proposals can be put forth to explain the observed effects including lattice strain and direct, local bonding interactions. On all of the refractory metal substrates studied thus far, a large lattice mismatch exists between the substrate and bulk Pd. This could reduce the Pd–Pd interactions in the thin Pd films, rehybridizing the Pd and causing the Pd to be more "atomic-like",...
and thus perturb the bonding of CO to Pd. Another explanation is that charge transfer [10] or rehybridization [11] of Pd occurs as a result of the Pd–substrate interaction. It is clear that a firm understanding of the relationship between the physical and electronic structure and the chemical properties of these altered surfaces is still forthcoming. Experiments on the properties of Pd films on different metal substrates aid in this endeavor.

In a previous paper [12], we have described the growth and thermal stability of Pd films on Mo(100). A Pd monolayer can be formed at 150 K that is pseudomorphic with the substrate lattice and Pd films can be grown at this temperature with a small amount of layer disorder and/or non-ideal layering. The monolayer is stable to 1200 K, but Pd in excess of one monolayer agglomerates into 3D crystallites upon annealing. The average crystallite thickness was estimated to be four layers for Pd films annealed to 450 K. There is also evidence of the formation of a Pd–Mo alloy for thicker Pd films upon heating to 1200 K, but the temperature for the onset of alloying is not clear and could be as low as 600–800 K.

Previous chemisorption measurements on Pd films formed on the (110) face of bcc substrates have been compared to the Pd(111) surface, but we feel that it is more appropriate to compare our experiments on Pd/Mo(100) with the Pd(100) surface due to structural considerations [12]. We briefly review below some pertinent aspects of CO adsorption on bulk Pd(100). This is by no means intended to be a comprehensive review, but is intended to aid the reader in comparing our results on Pd thin films with those obtained on Pd single crystals.

Park and Madden [13] were among the first to study CO adsorption on the (100) face of Pd. Using LEED, these authors proposed that one CO molecule adsorbs to every two Pd atoms in an alternating bridge-bonded arrangement forming a \((2 \times 4)R45^\circ\) pattern at 300 K. This was followed by papers by Tracy and Palmberg [14,15] who extended the LEED observations to higher coverages to reveal a compression structure and who determined the binding energy of CO at zero coverage to be 36.5 kcal/mol. Bradshaw and Hoffmann [16] used IR reflection-absorption spectroscopy and followed the CO stretching frequency, \(\nu_{\text{CO}}\), as a function of CO coverage. Initially \(\nu_{\text{CO}}\) occurs at 1895 cm\(^{-1}\), but continuously shifts to higher frequencies at higher \(\theta_{\text{CO}}\), reaching 1949 cm\(^{-1}\) at \(\theta_{\text{CO}} = 0.5\) for CO exposure at 300 K. In agreement with LEED studies, this was attributed to CO adsorbed in two-fold bridge sites. A further shift to higher frequency was found during the compression stage so that \(\nu_{\text{CO}} = 1983\) cm\(^{-1}\) for \(\theta_{\text{CO}} = 0.6\). If the compression stage was reached by exposing the surface to \(1 \times 10^{-7}\) Torr of CO at 300 K, a second band appeared at 2096 cm\(^{-1}\). This second band disappeared upon heating to 400 K and re-cooling to 300 K in \(1 \times 10^{-7}\) Torr of CO or pumping the CO away and was assigned to atop-bonded CO. They postulated [16] that some CO molecules initially adsorb in energetically unfavorable atop sites due to the “fast compression” and reduced mobility at high \(\theta_{\text{CO}}\). Ortega et al. [17] in IR investigations of CO adsorption at 80 K, found a similar behavior of the C–O stretching frequency although \(\nu_{\text{CO}} = 1997\) cm\(^{-1}\) at \(\theta_{\text{CO}} = 0.81\) at this temperature. They proposed a model in which all of the CO molecules are equivalent in the compression stage (although only a small fraction of the CO molecules can sit in crystallographically distinct bridge sites) and the large shift in \(\nu_{\text{CO}}\) is due to both static lateral interactions and vibrational coupling. No atop CO was observed in their study. Behm and co-workers [18] have carried out similar experiments using HREELS. Their results are in general agreement with those of Bradshaw and Hofmann [16] with the exception of a lower initial CO stretching frequency of 1774 cm\(^{-1}\). It was proposed that this was possibly due to CO in a highly coordinated site, i.e., a four-fold hollow. TPD of CO adsorbed at 125 K on the Pd(100) surface results in a three peak structure with maxima at 258, 378 and 515 K [19] with an initial adsorption energy between 36.5 [14] and 38.5 kcal/mol [20]. The adsorption energy is constant up to \(\theta_{\text{CO}} = 0.45\) [20], but decreases rapidly above this coverage possibly due to repulsive interactions between the CO molecules.
In the present paper we discuss CO chemisorption studies on ultrathin Pd films on a Mo(100) single crystal substrate using AES, LEED, TPD and HREELS. The Mo(100) surface has a larger lattice mismatch with bulk Pd than the bcc (110) surfaces studied thus far [21]. If lattice strain is an important factor in the altered chemistry of Pd thin films, then a larger effect might be expected for Pd/Mo(100). We will show that Pd films on Mo(100) do have altered CO chemisorption properties relative to bulk Pd(100) and that the size of the effects is comparable to those seen on W(110) and W(100) [22], but are not as dramatic as Pd films on Nb(110) [23] and Ta(110) [8]. Thus, lattice strain is not sufficient to explain our results and some direct interaction between the Pd adlayers and the substrate is implicated.

2. Experimental methods

The apparatus used has been described previously [24]. The instrumentation included a double-pass CMA with a coaxial electron gun, LEED optics, a quadrupole mass spectrometer and an HREELS spectrometer. The base pressure of the chamber was $5 \times 10^{-11}$ Torr. The Mo(100) single crystal (Atomergic Chemical Corp.) was cleaned by heating in O$_2$ followed by repeated flashes in vacuum to 2000 K. The temperature of the sample was measured by a W-5%Re/W-26%Re thermocouple spot-welded to the side of the sample. Pd was deposited on Mo(100) by resistively heating a 10 mil tungsten wire which was wrapped with 5 mil Pd wire (Aesar 99.99% pure). Research purity CO (Matheson, 99.99%) was passed through a liquid nitrogen trap, but was used without any further purification.

The heating rate used during TPD experiments was 6 K/s. All Pd coverages are referenced to the clean Mo(100) surface, with $\theta_{Pd} = 1$ corresponding to a Pd coverage equal to the Mo(100) surface atom density, as described in our previous paper [12]. All CO adsorption experiments were performed on Pd films which had been annealed to 450 K in order to avoid as much as possible any changes in the Pd film structure during subsequent annealing of CO adlayers or TPD experiments.

3. Results

3.1. CO chemisorption on a monolayer Pd film, $\theta_{Pd} = 1$

3.1.1. CO TPD

A CO TPD spectrum after a 0.1 L CO exposure on a pseudomorphic Pd monolayer film at 150 K is shown in fig. 1. This exposure resulted in a TPD area which was 13% of the TPD area for saturation exposures. If we arbitrarily define the CO saturation coverage as $\theta_{CO} = 1$, then the 0.1 L exposure produces a coverage of $\theta_{CO} = 0.13$. The main desorption peak for this CO coverage is observed at 329 K, with much smaller desorption features seen at 920 and 1018 K. The smaller peaks occur at temperatures where CO desorption from clean Mo is observed by us and others [25] and we attribute them to desorption from the back and edges of the Mo crystal [26]. Thus, only one desorption state is observed at $\theta_{CO} = 0.13$ on
the Pd monolayer and it is approximately 175 K below that observed on bulk Pd(100) [17,19,20] for a similar $\theta_{\text{CO}}$. A TPD spectrum after a saturation exposure (48 L) of CO on a one monolayer Pd film at 150 K is also shown in fig. 1. There is a single, low temperature peak at 319 K due to CO desorption from the pseudomorphic Pd monolayer and a high temperature peak due to desorption from the back and edges of the Mo(100) crystal. Comparison to the 0.1 L CO exposure TPD experiment shows a slightly lower peak maximum for saturation CO exposure and a broadening of the desorption peak towards lower temperatures. This is characteristic of a decreased energy of desorption as $\theta_{\text{CO}}$ is increased due to lateral interactions and population of more weakly bound sites.

Fig. 1 can be contrasted with CO desorption from Pd(100) after saturation CO exposures which results in a three peak structure with peak maxima at 258, 378, and 515 K [19]. Using the Redhead analysis [27], the activation energy for CO desorption is found to be approximately 20 kcal/mol assuming first-order kinetics and a pre-exponential factor of $10^{13}$ s$^{-1}$. This is the adsorption energy since CO adsorption proceeds with only a small (if any) activation energy. Comparison with the CO adsorption energy on the (100) surface of bulk Pd, where $E_{\text{ads}} = 36.5$ kcal/mol [14,15], shows a 45% reduction in the CO-Pd chemisorption bond strength on the Pd monolayer.

### 3.1.2. CO HREELS

HREELS experiments were conducted as a function of CO coverage in order to determine the sequence of population of adsorption sites for CO on the Pd monolayer. This is shown in fig. 2 for a Pd thickness of $\theta_{\text{Pd}} = 1.0$. Small CO exposures (0.1 L) on this film at 150 K lead to peaks at 310, 1745, 1920, and a small shoulder at 1850 cm$^{-1}$. The peak at 310 cm$^{-1}$ is attributed to the Pd-CO stretching mode, $\nu_{\text{Pd-CO}}$, and the peaks at higher frequencies are assigned to CO stretching modes, $\nu_{\text{CO}}$, for CO adsorbed in various sites. The peak observed at 1745 cm$^{-1}$ is due to CO adsorbed in Pd four-fold hollow sites. Occupation of the hollow site is expected to shift $\nu_{\text{CO}}$ to a lower vibrational energy relative to CO adsorbed in the two-fold bridge sites and has been proposed by Behm et al. [18] to explain their HREELS peak at 1774 cm$^{-1}$. The peak at 1920 cm$^{-1}$ is due to a two-fold bridging CO species as has been previously observed on Pd(100) [16–19]. Additional intensity near 1850 cm$^{-1}$ shows that there is a range of bonding environments for CO at these low coverages. As the CO exposure is increased to 0.6 L, the $\nu_{\text{CO}}$ peak due to the hollow site disappears and the peaks for the bridging species merge into one peak and shift up in energy to 1995 cm$^{-1}$. This shift to higher energies with increasing $\theta_{\text{CO}}$ has been attributed to vibrational coupling and static lateral interactions [17]. An atop site with $\nu_{\text{CO}} = 2110$ cm$^{-1}$ is also populated at this CO coverage. This is surprising since population of an atop site would not be expected under these conditions for Pd(100) single crystals even at saturation CO coverages.
CO exposures up to 48 L on the \( \theta_{\text{Pd}} = 1.0 \) film produce no further changes in the vibrational spectrum.

The population of a more weakly bonded atop site is reflected by the low temperature broadening in the TPD spectra of fig. 1. HREELS warm-up experiments were conducted to address this point. Fig. 3 shows a vibrational spectrum for a saturation CO exposure on a \( \theta_{\text{Pd}} = 1.1 \) film for CO dosed at 150 K and a vibrational spectrum acquired after heating to 450 K. At 150 K, both two-fold bridge and atop sites are populated for saturation CO coverages on the Pd monolayer. Heating to 450 K removes CO bonded at the atop sites and shifts \( \nu_{\text{CO}} \) for CO in the bridge site down to 1910 cm\(^{-1}\). The hollow site at 1790 cm\(^{-1}\) is also seen after the warm-up to 450 K. All of the CO desorbs above this temperature.

We can conclude from the uptake and warm-up HREELS experiments that the hollow and bridging sites have a higher binding energy than atop sites which leads to these sites being populated at low coverages (produced either by small exposure or by heating) on the Pd monolayer. Weakly bound atop sites are populated for CO exposures \( \geq 0.6 \) L.

3.2. CO chemisorption on Pd films of increasing thickness

While the Pd monolayer is quite well-characterized [12], films thicker than this are more complex in that a small amount of 3D clustering occurs and therefore, a small distribution of Pd thicknesses will be present. This in turn may complicate the interpretation of the chemistry which occurs on these films. However, the chemistry must be investigated to determine if Pd films thicker than \( \theta_{\text{Pd}} = 1 \) have interesting chemisorption properties (and therefore deserve better characterization efforts) and, in fact, the determination of CO adsorption sites may give insight into the Pd film structure.

3.2.1. CO TPD

CO TPD spectra after 0.1 L exposures of CO on Pd films at 150 K are shown in fig. 4 as a
function of Pd film thickness. As the Pd coverage increases, the Pd film thickness increases and the CO desorption state at 329 K for the one monolayer Pd film gradually shifts to higher temperature. The maximum CO desorption temperature is not yet reached for \( \theta_{Pd} = 7 \). For thick Pd films, \( \theta_{Pd} \geq 20 \), CO desorption with a peak at 499 K is in good agreement with previously reported CO desorption from bulk Pd(100) [17,19,28].

CO TPD spectra after saturation exposures of CO on Pd/Mo(100) at 150 K are shown in fig. 5 for several Pd coverages. CO desorption is characterized by a peak at 319 K for the one monolayer Pd film. As the Pd coverage increases to \( \theta_{Pd} = 2.2 \), the centroid of the peak shifts to 375 K and a shoulder appears at 261 K. This shoulder evolves into a peak at 235 K on the \( \theta_{Pd} = 5 \) film and another new state also appears at 462 K. At this point the desorption spectra look very similar to desorption from bulk Pd(100), albeit with slightly shifted peak maxima. At Pd coverages \( \geq 17 \text{ ML} \) CO desorption is again in good agreement with previously reported CO desorption from Pd(100) [19].

We can quantify the CO coverages obtained in the uptake of CO on the Pd films by using the CO TPD area in the experiments shown in figs. 4 and 5. For small CO exposures (0.1 L) on the Pd monolayer, a reduction in the amount of CO adsorbed is observed when compared to equivalent CO exposures on thick Pd films. Fig. 6a shows the CO TPD area as a function of Pd film thickness for constant CO exposures of 0.1 L. This CO dose produces only 66% of the CO coverage on the monolayer Pd film as the thickest Pd film studied (< 20 ML). A much smaller (only 10%) reduction in the saturation coverage is seen...
for saturation CO exposures on the Pd films, as would be expected, and also indicates the number of adsorption sites is nearly independent of film thickness, i.e., no large change occurs in the geometric surface area of the sample due to gross changes in Pd film morphology and roughness. This data is presented in fig. 6b. This indicates the small TPD area observed for the ultrathin Pd films in fig. 6a is not due mainly to a decrease in the number of sites available for adsorption. So, we can infer that a significant drop occurs in the sticking probability of CO on ultrathin Pd films, even at 150 K, with the largest effect observed on the monolayer Pd film.

3.2.2. CO HREELS

HREELS experiments were also carried out for two CO exposures as a function of Pd coverage on Mo(100). Fig. 7 shows these results for small CO exposures (0.1 L). The Pd monolayer shows CO stretching modes at 1745, 1925, and a small shoulder at 1850 cm\(^{-1}\) as discussed above. The \(\nu_{\text{CO}}\) mode at 1745 cm\(^{-1}\) disappears by \(\theta_{\text{Pd}} = 3.1\). Since the CO sticking probability increases slightly as the Pd film thickness increases, the disappearance of the four-fold hollow site mode may be due to an increase in the CO coverage. (A similar behavior is seen on Pd(100) single crystals with increasing CO coverage [18].) Two closely spaced \(\nu_{\text{CO}}\) modes are observed at 1890 and 1925 cm\(^{-1}\) on the \(\theta_{\text{Pd}} = 3.1\) film. These peaks are due to two-fold bridge-bonded CO species. The two modes merge into a single peak at 1950 cm\(^{-1}\) on the \(\theta_{\text{Pd}} > 20\) film. No atop species are seen on any of the Pd films at small CO coverages.

HREELS experiments shown in fig. 8 for saturation doses (48 L) of CO on Pd/Mo(100) at 150 K as a function of \(\theta_{\text{Pd}}\) show both bridge-bonded and atop CO on Pd films up to \(\theta_{\text{Pd}} = 5\). On the thick (\(\theta_{\text{Pd}} \geq 20\)) film, \(\nu_{\text{CO}}\) appears at 2010 cm\(^{-1}\)
with a small shoulder at 2100 cm\(^{-1}\). This is attributed to CO adsorbed in two-fold bridging sites with a very small amount of CO in atop sites. The overlap of these two peaks can account for the slightly higher frequency observed for the two-fold bridging species in our work (2010 cm\(^{-1}\)) compared to that observed by Ortega et al. [17] (1997 cm\(^{-1}\)). While TPD results show nearly bulk behavior for a Pd film thickness of 5 layers, HREELS experiments reveal that at this thickness there is still some perturbation in the population in CO adsorption sites compared to bulk Pd(100).

3.3. LEED

LEED observations as a function of CO exposure on various Pd films on Mo(100) were conducted at 150 K. Exposure to CO caused an increased background intensity. The background intensity increased with CO coverage and no new ordered patterns due to CO were ever observed. This is consistent with the absence of the formation of an ordered CO overlayer at low temperature on Pd(100) [17].

3.4. Consideration of the activation energy of desorption of CO

In section 3.1.1, we discussed a rough determination of the activation energy for desorption, \(E_a\), of CO from a Pd monolayer film. Using Redhead analysis [27] and assuming a pre-exponential factor of \(10^{13}\) s\(^{-1}\) and first order desorption kinetics we arrived at \(E_a = 20\) kcal/mol. A useful check of the accuracy of the results obtained from Redhead analysis, or for that matter any procedure which attempts to get energetic and kinetic information from TPD data, is to calculate or simulate a spectrum from the derived parameters and compare it to the actual experimental data. Fig. 9a shows the results of this comparison for CO desorption following a small (0.1 L) CO exposure from a \(\theta_{Pd} = 1\) film using the values from Redhead analysis. While the temperature of the peak maximum and the leading edge of the simulated spectrum agree well with the experimental data, the overall shape of the spectra are quite different, with the simulated spectrum being approximately twice as high and half as wide as the experimental peak. Figs. 9b–9d

![Fig. 9. Comparison of experimental CO TPD spectra from several Pd films with simulated TPD spectra. The thick solid lines represent the experimental data. The dashed lines correspond to simulated TPD spectra using values of \(E_a\) which were derived from Redhead analysis while the thin solid lines correspond to simulated TPD spectra using values of \(E_a\) and \(v\) derived from plots of \(\gamma\) versus \(1/T\). \(\theta_{Pd} = 1\) (a), 2.3 (b), 3.8 (c), \(\geq 20\) (d).]
show similar comparisons for thicker Pd films. For these Pd films, while the temperature of the peak maximum of the simulated spectra from Redhead analysis and experimental data agree, the agreement at low temperature gets progressively worse as the Pd film thickness increases. Overall, the simulated spectra are all much narrower than the corresponding experimental TPD spectrum similar to the observations for the $\theta_{\text{Pd}} = 1$ film. These comparisons show that while the activation energy derived from the Redhead analysis may be approximately correct, a satisfactory fit to the entire TPD spectrum requires more complicated kinetics than simple first-order desorption with constant activation energy.

As a second means of analyzing the TPD data, plots of $[\ln(-d\theta/dt)-n \ln(\theta)]$ versus $1/T$ were constructed for several of the TPD spectra of fig. 4. A parameter, $\gamma$, defined as

$$\gamma = \ln(-d\theta/dt) - n \ln(\theta_{\text{CO}})$$

is convenient to use in this discussion [29,30]. The desorption rate of CO is $-d\theta/dt$, $n$ is the kinetic order of desorption, $\theta_{\text{CO}}$ is the CO coverage, and $T$ is the temperature. Plots of this type yield a straight line for the entire desorption peak with a slope of $-E_a/R$ and an intercept of $\ln(\nu/\beta)$ ($R$ is the ideal gas constant and $\beta$ is the heating rate) when $n$ is chosen correctly and simple desorption kinetics ($E_a$, $\nu$, and $n$ are not functions of $\theta$) are observed [29]. Fig. 10a shows the results of this treatment for the experimental TPD spectrum shown in fig. 9a using $n = 1$. At low temperatures there is an initial linear segment which begins to “roll over” near the TPD peak maximum. The curve then goes through a small minimum and increases again as the last CO molecules desorb. While this analysis does not yield a straight line for the entire desorption spectrum, fitting a straight line to the initial linear segment yields $E_a = 23.5$ kcal/mol and $\nu = 3.2 \times 10^{15}$ s$^{-1}$. The simulated spectrum which results from using these parameters is shown by the thin solid line in fig. 9a. It can be seen that this treatment does not result in a significantly better fit than that obtained using $E_a$ derived from the Redhead analysis, but a slightly higher value of $E_a$ is obtained.

Plots of $\gamma$ versus $1/T$ for thicker Pd films are shown in figs. 10b–10d. These curves also show an initial linear segment, but show a change in slope in the temperature range of 360–400 K.

![Fig. 10. Plots of $\gamma$ versus $1/T$ for several Pd films. $\theta_{\text{Pd}} = 1$ (a), 2.3 (b), 3.8 (c), $\geq 20$ (d).](image)
Fitting a straight line to the initial linear segment of these plots results in values of $E_a < 23$ kcal/mol and values of $\nu < 1.8 \times 10^{10}$ s$^{-1}$ for CO desorption from the thicker Pd films. Using these values of $E_a$ and $\nu$ in the calculation of simulated spectra gives the results shown by thin solid lines in figs. 9b–9d. While these simulated spectra very nicely fit the leading edge (low temperature portion) of the experimental data, they give a lower temperature for the peak maxima and are much too narrow compared to the experimental data. If we include all points up to the peak maximum instead of fitting the initial linear segment of the $\gamma$ versus $1/T$ plots the resulting simulated spectra (not shown) predict the temperature of the peak maximum much better, but are still more narrow than the experimental data and in particular do not match the trailing edge (high temperature).

The failure of these methods to accurately simulate the experimental TPD data implies that desorption of CO from these thin Pd films is more complex than simple first-order kinetics. This could possibly be due to coverage dependant kinetic parameters, or very likely, structural changes in the Pd film which occur during the TPD experiment. Small changes in the Pd film morphology such as three dimensional cluster formation could easily alter the bonding site and/or strength and affect the shape of the TPD spectrum. In either case, $E_a$ and/or $\nu$ would be expected to change as a function of $\theta_{CO}$ and/or temperature. If we assume that $\nu$ is constant and $E_a$ is a function of coverage, the desorption rate equation [31] can be written as:

$$\text{Rate} = \frac{-d\theta}{dt} = \frac{\nu}{T} \theta^n \exp\left(\frac{-E_a(\theta)}{RT}\right).$$

(2)

Taking the logarithm and rearranging yields

$$E_a(\theta) = -RT \left[ \gamma - \ln(\nu/\beta) \right],$$

(3)

which can be used to extract a value of $E_a$ for each point in a TPD spectrum as a function of coverage [30]. Fig. 11a shows the coverage dependence of $E_a$ using this method for the CO desorption spectrum shown in fig. 9a using the value of $\nu$ derived from fig. 10a. This shows that at the highest temperatures, very low $\theta_{CO}$, $E_a$ is close to the value seen on bulk Pd(100) [14,20] but rapidly drops off and approaches 23 kcal/mol by $\theta_{CO} = 0.13$. Using this coverage dependence of $E_a$ results in the simulated TPD spectrum (thin solid line) shown in fig. 11b. The quality of the fit of the simulated spectrum to the experimental data (thick solid line) is very good compared to the previous treatments. The leading edge of the desorption peak, temperature of the peak maximum and width of the simulated peak are now all very close to that of the experimental data. Spectra simulated with a coverage dependant $E_a$ for the thicker Pd films also showed good fits to the experimental data. Since it is rather unphysical for $E_a$ to simply have such a strong dependence
on small CO coverages, we suggest that CO can induce changes in the Pd film morphology at temperatures above 350 K. The simulations show that these effects are smallest on the monolayer Pd film and increase with Pd film thickness. Additionally, \( \nu \) and even \( n \) could also change as a function of \( \theta_{\text{CO}} \) and/or Pd film morphology and obviously further complicates the analysis. Clearly, much more careful studies (e.g. equilibrium measurements) of the desorption kinetics are required to determine the cause of the complex TPD spectra we observe.

4. Discussion

Our results obtained by using TPD and HREELS clearly show that ultrathin Pd films on the Mo(100) surface have strongly altered CO chemisorption properties when compared to bulk Pd surfaces. The Pd monolayer shows the largest effects, weakly adsorbing CO with an adsorption energy of about 20 kcal/mol. This is a 45% reduction in the adsorption energy when compared to Pd(100). In addition to this decrease, a large drop (34%) in the sticking probability is observed for CO on the Pd monolayer compared to thick Pd films on Mo(100). This is clearly not mainly due to a decrease in the number of binding sites for the Pd monolayer film, since \( \theta_{\text{CO}}^{\text{cat}} \) is nearly constant, but rather it is a manifestation of differences in the CO adsorption energy and adsorption kinetics.

Initially CO adsorbs in four-fold hollow and two-fold bridging sites on the Pd monolayer. Atop sites are populated for higher \( \theta_{\text{CO}} \). This is the same site preference seen for bulk Pd(100), although atop sites can only be populated on bulk Pd(100) at 300 K if the compression stage is reached rapidly by exposure to \( 10^{-7} \) Torr of CO [16]. The maximum intensity ratio of atop to bridge-bonded CO on Pd(100) [16] was reported to be 1:3 and was difficult to reproduce. This was attributed to the difficulty of accurately controlling the rate at which the compression stage was reached. An interesting question is whether or not the population of the atop site on our ultrathin Pd films could possibly be due to defect sites, steps, or clusters in the films. Based on the nearly equal HREELS intensities of the atop and two-fold bridge sites, we feel that this is an unlikely explanation. Our previous work [12] is inconsistent with an extremely rough surface especially for the monolayer film. We propose that the population of atop sites is due to the destabilization of CO adsorption in the two-fold bridging sites as a result of weakened backbonding between Pd and CO. This creates a situation in which CO bonding to atop sites is only slightly less energetically favorable allowing atop sites to compete with two-fold bridge sites for CO molecules at high CO coverages.

Thicker films of Pd also show altered chemisorption properties. Due to difficulties in preparing “flat” films (some clustering occurs at 450 K) and characterizing these films, \( \theta_{\text{Pd}} \) probably represents some average thickness only. Nonetheless, the influence of Mo(100) on Pd chemistry probably extends through several Pd layers. The Pd–CO bond energy gradually increases as the Pd coverage increases and the films approach bulk Pd properties for \( \theta_{\text{Pd}} > 7 \). We are able to tune the Pd–CO bond energy between 20 and 36.5 kcal/mol by controlling the Pd coverage. The CO sticking probability and the CO adsorption site preference also gradually approach bulk Pd(100) characteristics as the Pd coverage increases and these can be tuned as well. A more complete unraveling of exactly how the Pd film electronic and geometric structure affect the chemistry at the surface must await additional (electronic and geometric) characterization of the film structure.

Comparison of our results to those from Pd films on Mo(110) would be valuable. One study of CO adsorption on Pd/Mo(110) has been carried out previously [32]. Their focus was on Pd films approximately six layers thick and they characterized CO thermal desorption behavior before and after ion bombardment. Because of the different preparation procedures and goals of that work from our studies, a direct comparison with this work is not possible.

We can compare our results to studies of CO adsorption on Pd films on W(100) [22] and W(110) [22,33]. The magnitude of the reduction in the
CO–Pd bond energy seen here for a Pd monolayer on Mo(100) is comparable to that seen for W(100) [22] and W(110) [22,33]. Zhao et al. [33] performed equilibrium adsorption experiments and obtained isosteric heats of adsorption for CO on the Pd monolayer on W(110). The heat of adsorption of CO, $\Delta H_{\text{ads}}$, is initially 20.5 kcal/mol and decreases with increasing CO coverage reaching 12.7 kcal/mol near saturation CO coverage. These authors also performed isothermal desorption experiments and obtained the desorption energy, $E_{\text{des}}$, for CO. At low coverages $E_{\text{des}}$ was larger than $\Delta H_{\text{ads}}$ but $E_{\text{des}}$ was smaller than $\Delta H_{\text{ads}}$ at higher CO coverages. For the high CO coverages, this was explained by decreases in the sticking probability with increasing temperature. At low CO coverage it was suggested that the high values of $E_{\text{des}}$ were due to non-equilibrium effects possibly due to changes in the surface morphology. This agrees with our results using TPD which also suggest changes in the Pd film structure for Pd films on Mo(100).

On W(110) and W(100), CO desorption from thick Pd films does not resemble CO desorption from bulk Pd(111) or Pd(100) [22]. This was attributed to the formation of three-dimensional Pd islands on W(110) since there is a low temperature CO TPD state representative of desorption from the monolayer and a high temperature shoulder. This was not the case for Pd/W(100) since the CO desorption peak maximum shift was only from 305 to 370 K for Pd films 1 to 4.8 layers thick. This is well below the peak temperature for CO desorption on Pd films 5 layers thick in our present work on Mo(100) and is also a much lower temperature than CO desorption from bulk Pd. We offer several proposals to explain this observation on W(100). First, the W(100) substrate may perturb the Pd overlayers over a longer distance than other substrates studied. Second, much larger crystallites may form and thus contribute little to the CO TPD spectra. Finally, the Pd coverage determination on W(100) may be inaccurate. These issues deserve further study.

Somewhat larger reductions in the CO–Pd bond energy have been observed on a Pd monolayer on Nb(110) [23] and Ta(110) [8]. On these substrates the desorption energy is 15 and 14.4 kcal/mol, respectively. This is interesting since the pseudomorphic Pd monolayer on these substrates (bcc (110)) has less lattice strain than the pseudomorphic Pd monolayer on Mo(100) (bcc (100)). This indicates that the increase in strain does not correlate simply with the reduction in the CO–Pd bond energy. However, this does not necessarily imply that lattice strain is not important. Their may be some threshold Pd–Pd distance beyond which a large change in the Pd electronic structure, and thus a reduction in the CO–Pd bond energy, occurs. All of the systems studied thus far may be above this threshold, and little additional change occurs with increasing lattice strain. This possibility is also worth pursuing.

Photoemission studies of Pd monolayers on Nb(110) and Ta(110) have shown that the electronic structure of the Pd overlayer resembles a Group Ib metal (Cu, Ag, Au) in that the d-band is narrowed and shifted to higher binding energies and the DOS at the Fermi level is reduced [1–5]. Theoretical calculations by Kumar and Bennemann [34] predict that the Pd monolayer d-states are more filled relative to Pd(111). On Cu [35], Ag [36], and Au [37], CO desorption occurs with energies below 17 kcal/mol. The similarities between CO desorption energetics on the Pd monolayer and these noble metals suggest that the weakened CO bonding is due to the altered electronic structure of the Pd overlayer. According to the traditional Blyholder model [38,39], CO adsorption on transition metal surfaces involves donation of electron density from the CO $5\sigma$ orbital into empty d$_\sigma$ states of the metal and a back-donation of electron density from the occupied metal d$_\pi$-states to the CO $2\pi^*$ orbital. Fewer d-holes for Pd in the monolayer relative to bulk Pd makes donation from the CO $5\sigma$ orbital to the metal d-states less efficient. Additionally, the shift in the Pd d-band to higher binding energy increases the separation between the occupied d-states of the metal and the CO $2\pi^*$ orbital of CO, leading to a reduction in back-bonding to CO. Together, these effects will lead to an overall reduction in the CO–Pd bond strength on the Pd monolayer compared to bulk Pd.
While no photoemission studies have been carried out for the Pd/Mo(100) system, electronic structure changes similar to those above could be responsible for the observed effects on CO chemisorption properties. Nb, Ta, Mo, and W all form alloys with Pd [40] and these alloys may resemble intermetallic compounds. Thus, extensive bonding interactions can be expected between the Pd film and the substrate in all cases. In addition to lattice strain effects, direct Pd-substrate interactions may cause the surface electronic structure to be affected and perturb the bonding of CO as described above. However, more work needs to be done to elucidate the exact origin of the altered chemisorption properties of these thin Pd films. Clearly, the chemistry of ultrathin Pd films on Mo(100) is interesting and further study of both the electronic and geometric structure of these films is warranted.

5. Conclusions

Ultrathin Pd films on a Mo(100) substrate show modified CO chemisorption properties when compared to bulk Pd(100). The largest change occurs for the pseudomorphic Pd monolayer which has a 45% decrease in the CO adsorption energy, a 34% decrease in the CO sticking probability and also shows a facile adsorption of CO into atop sites. The CO chemisorption properties can be controlled by varying the Pd film thickness over a range of at least several layers. Pd films on W(110), W(110), Ta(110), and Nb(110) show similar reductions in the Pd–CO bond energy although the effect is somewhat larger on Nb(110) and Ta(110). The increased lattice mismatch for the Pd/Mo(100) system relative to Pd/Nb(110) and Pd/Ta(110) does not lead to any additional decrease in the Pd–CO bond energy on the Pd films.

Acknowledgements

The authors wish to acknowledge support of this work by the Analytical and Surface Chemistry Program in the Division of Chemistry, National Science Foundation. We would also like to thank Professor John Gland for the loan of the Mo(100) crystal sample. B.E.K. gratefully acknowledges the support of a Research Fellowship from the Alfred P. Sloan Foundation.

References

[21] The surface atom density of Pd(111) is 1.53 x 10^15, for Nb(110) and Ta(110) it is 1.30 x 10^15, for W(110) and Mo(110) it is 1.42 x 10^15, for Pd(100) 1.32 x 10^15, for W(100) it is 1.00 x 10^15, and for Mo(100) 1.01 x 10^15.
[26] It is possible that these states are due to defect sites in the Pd film. We believe that this is highly unlikely since (i) we know that the back of the crystal contributes an appreciable signal because it is highly cleaned by the electron beam heating procedure, and (ii) we find that Pd adatoms strongly modify the bonding of CO to Mo(100) at $\theta_{\text{Pd}} < 1$ and therefore defect sites would have shifted TPD peak positions.
[37] The heat of adsorption of CO on Au(111) is very small, less than 6 kcal/mol; experiments by J. Hrbek showed no measurable adsorption of CO on Au(111) at 85 K under UHV conditions (personal communication).