# Chemisorption of hydrogen on ultrathin Pd films on Mo(100)

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The $H_2$ adsorption properties of ultrathin Pd films deposited on Mo(100) have been studied with Auger electron spectroscopy (AES) and temperature-programmed desorption (TPD). The pseudomorphic monolayer of Pd on Mo(100) has a greatly reduced $H_2$ uptake capacity at 150 K compared to bulk Pd. Desorption from the Pd monolayer occurs from a chemisorption state with a desorption temperature of about 290 K. Thicker Pd films also have a reduced $H_2$ uptake, until $\theta_{Pd} \geqslant 5.5$. $H_2$ desorption from the low-temperature hydride state that is characteristic of bulk Pd only occurs for Pd films with $\theta_{Pd} \geqslant 5.5$.

## 1. Introduction

The properties of thin metal films [1] and small metal clusters [2] have received a great deal of attention recently due in part to their potential for controlling reactivity at the atomic scale and to their importance in understanding heterogeneous catalysis. It is widely accepted that the properties of a catalyst are strongly influenced by the morphology and particle size of the active metal and this is therefore an important consideration in catalyst design. One interesting question is whether hydrogen is able to populate subsurface sites on very small metal clusters and the effect of cluster size. This is important since subsurface hydrogen can influence the binding energy and reactivity of adsorbates on the surface. While Leary et al. have shown that penetration of hydrogen into subsurface sites occurs for a silica-supported palladium catalyst [3] no information on the effect of particle size on this phenomenon is available.

In addition to their intrinsic interest, ultrathin Pd films (monolayer, bilayer, trilayer, etc.) can be used to probe some effects of cluster size on the penetration of hydrogen into subsurface sites by carefully

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controlling the Pd film thickness. Previous work by Strongin and co-workers [4–6] showed changes in the hydrogen uptake for thin Pd films on Nb and Ta due to Pd film thickness. Using resistivity measurements, they found that a Pd layer less than one monolayer thick either did not change or would inhibit hydrogen absorption in Nb and Ta. Pd films thicker than one monolayer enhanced the hydrogen uptake rate. More recently, preliminary TPD studies of hydrogen adsorption on thin Pd films on Nb(110) [7] and Ta(110) [8] have been made. A monolayer Pd film on Ta(110) decreased the $H_2$ uptake, while a Pd monolayer on Nb(110) had almost no effect when compared to the respective substrates. Hydrogen uptake increased as the Pd film thickness increased in agreement with previous observations [4–6]. The $H_2$ desorption temperature in TPD measured for a monolayer Pd film on Ta is 1400 K. By comparison, chemisorbed $H_2$ desorbs from bulk Pd(111) at about 310 K and a low-temperature hydride state desorbs at 190 K [9]. No desorption peaks characteristic of $H_2$ desorption from subsurface Pd sites were seen for monolayer Pd films on Nb and Ta. On W(110) a small TPD peak at $\approx 200$ K was observed for Pd films equal to or exceeding one monolayer and was attributed to hydrogen desorption from a hydride phase [10]. For W(100) no well developed Pd-hydride state was observed but a small shoulder at 200 K was attributed to Pd-hydride formation for a 4.8 monolayer thick film [10]. No pre-

vious work on these type of systems has clearly identified the hydride state characteristic of bulk Pd or identified the conditions for its existence.

We have recently described the growth and thermal stability of monolayer and ultrathin Pd films on Mo(100) [11]. These results will be briefly summarized here in the context of the present work. A Pd monolayer can be formed at 150 K that is highly strained and pseudomorphic with the substrate lattice. Pd films can be grown at this temperature with only a small amount of layer disorder and/or non-ideal layering. The monolayer is stable to 1250 K, but Pd in excess of one monolayer tends to agglomerate into three-dimensional (3D) crystallites upon annealing above 400 K. 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 upon heating to 1250 K for thicker Pd films, but the temperature for the onset of alloying is not clear and could be as low as 600–800 K. In this Letter we present results for an investigation of hydrogen adsorption on these ultrathin films of Pd on Mo(100).

## 2. Experimental methods

The experimental apparatus has been described previously [12]. The instrumentation includes a double-pass CMA with a coaxial electron gun, LEED optics, and quadrupole mass 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 to 2000 K. The temperature of the sample was measured by a W-5%Re/W-26%Re thermocouple spotwelded to the side of the sample. Pd was deposited on Mo(100) by resistively heating a 0.5 mm tungsten wire, which was wrapped with 0.1 mm Pd wire (Aesar, 99.99% pure). All Pd coverages $\theta_{Pd}$ 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 ($1.01 \times 10^{15}$ atoms/cm$^2$), as described in our previous paper [11]. $H_2$ was used as supplied (Matheson PP Grade, 99.9%) without further purification. Reported $H_2$ exposures have not been corrected for ion gauge sensitivities nor doser enhancement factor. All $H_2$ adsorption experiments

were performed on Pd films which had been pre-annealed to 450 K in order to minimize any changes in the Pd film structure during subsequent annealing or TPD measurements. $H_2$ TPD experiments were carried out in line-of-sight of an apertured mass spectrometer ionizer and used a heating rate of 6 K/ s.

## 3. Results

$H_2$ TPD spectra obtained after 2.4 L $H_2$ exposures on several thin Pd films on Mo(100) at 150 K are shown in fig. 1. For comparison, $H_2$ desorption after the same $H_2$ exposure on clean Mo(100) at 150 K
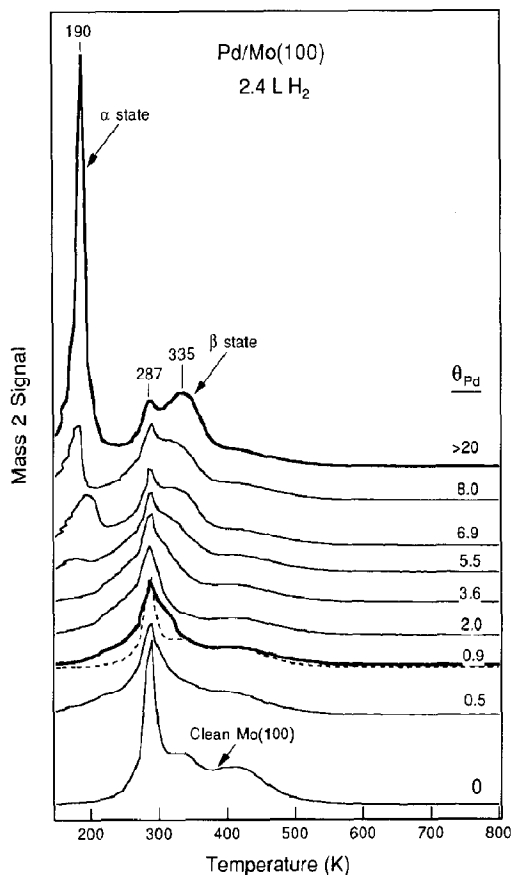


Fig. 1. $H_2$ TDP spectra as a function of Pd film thickness on Mo(100). The $\theta_{Pd}=0.9$ film and the $\theta_{Pd} \geqslant 20$ film are shown by the thick lines. The dashed line represents a scaled TPD spectrum from clean Mo(100).

is also shown ($\theta_{Pd}=0$ curve). This exposure resulted in a saturation coverage of adsorbed hydrogen on the Mo(100) surface ($\theta_H^{sat}=2.12\times10^{15}$ H atoms/cm$^2$ [13]). Three distinct H$_2$ desorption peaks can be seen on the Mo(100) surface at 287, 325 and 410 K in good agreement with previous work [13,14]. These peaks begin to decrease in magnitude as Pd is deposited on the surface with the state at 325 K disappearing by $\theta_{Pd}=0.5$ and the states at 287 and 410 K reaching a constant size for the nearly monolayer Pd film ($\theta_{Pd}=0.9$) shown in fig. 1. Only a small H$_2$ desorption feature near 290 K can be attributed to the monolayer Pd film and we designate this state $\beta$ in fig. 1. This feature overlaps the desorption state at 287 K which is due to desorption from the clean edges and back of the Mo(100) crystal. The desorption state seen at 410 K for the $\theta_{Pd}=0.9$ film can also be attributed to desorption from the back and edges of the crystal. This is reasonable in spite of their relatively large contribution to the TPD signal since they are thoroughly cleaned by the electron beam heating technique. Since no desorption from Pd occurs at 410 K we have attempted to estimate the contribution from the Mo(100) crystal back and edges by normalizing a TPD spectrum from clean Mo(100) to that from the $\theta_{Pd}=0.9$ film, as shown by the dashed curve in fig. 1. We can make a crude estimate of the activation energy, $E_a$, for H$_2$ desorption from the monolayer film by using Redhead analysis [15]. Assuming second-order kinetics and a pre-exponential of $1\times10^{-2}$ cm$^2$ s$^{-1}$, we estimate that $E_a=18$ kcal/mol. A small increase in the size of this peak is observed as $\theta_{Pd}$ increases to 3.6. The $\beta$ state increases in size and broadens towards higher temperatures for $\theta_{Pd}=5.5$. As $\theta_{Pd}$ increases further, this peak continues to shift towards higher temperature, and has a distinct peak temperature at 335 K for thick films ($\theta_{Pd}\geqslant20$). We estimate that $E_a=20$ kcal/mol for desorption from the $\beta$ state on the thick ($\theta_{Pd}\geqslant20$) Pd film using the same assumptions as above.

A striking change in the TPD spectra occurs at $\theta_{Pd}=5.5$ with the appearance of a new low-temperature desorption peak near 190 K designated as $\alpha$ in fig. 1. The $\alpha$ state increases in size with Pd and takes on a peak shape characteristic of zeroth order desorption and eventually becomes the dominant H$_2$ desorption channel for thicker Pd films. The desorption states at 190 and 335 K can be assigned to

desorption of hydrogen from a hydride phase and from chemisorbed hydrogen on the Pd films, respectively. These peaks correspond well to the H$_2$ desorption states from bulk Pd [9,16].

Fig. 2 shows the H$_2$ TPD area of the $\beta$ state, the H$_2$ TPD area of the $\alpha$ state, and the total H$_2$ TPD area as a function of Pd film thickness. Due to the desorption from Mo, it is difficult to accurately quantify the amount of chemisorbed H$_2$ on the Pd films. However, by assuming that the peak at 410 K is due solely to desorption from Mo we can scale the TPD spectrum from the clean Mo(100) surface as described above and subtract its TPD area from the values obtained for the $\beta$ state. The values shown in fig. 2 have been obtained in this manner. The H$_2$ TPD area of the $\beta$ state is a minimum at $\theta_{Pd}=0.9$. This state slowly increases in size and saturates at a Pd thickness of $\theta_{Pd}=5.5$. At this Pd coverage the $\alpha$ state begins to be populated. As the Pd film thickness increases further, the H$_2$ TPD area of the $\alpha$ state continues to increase. At $\theta_{Pd}\geqslant20$, the total H$_2$ TPD area is more than two times larger than the H$_2$ TPD area from clean Mo(100).

We estimate the amount of hydrogen desorbed from the chemisorption state on Pd increases by 48% as $\theta_{Pd}$ increases from $\theta_{Pd}=1$ to $\theta_{Pd}\geqslant20$. This increase is not likely due to increased surface roughness as our previous studies of CO adsorption on the
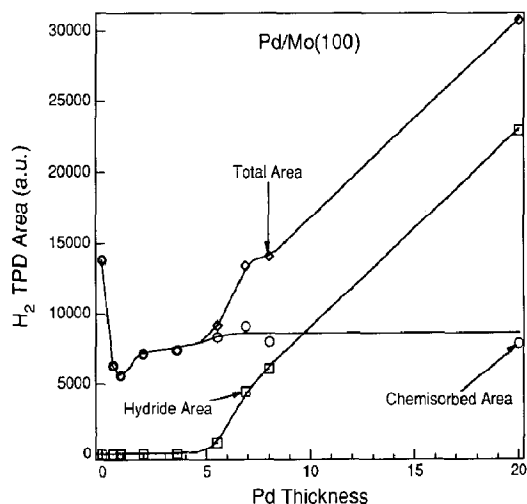


Fig. 2. H$_2$ TPD area of the $\alpha$ state, and $\beta$ state, and the total H$_2$ TPD area as a function of Pd film thickness. The data are taken from the curves shown in fig. 1.

same Pd films on Mo(100) show only a 10% increase in the CO TPD area for saturation exposures as the Pd film becomes thicker [17]. AES studies are also inconsistent with an extremely rough surface [11]. Instead, we propose that the dissociative sticking coefficient, $S$, for $H_2$ on Pd is decreased on the $\theta_{Pd}=0.9$ film relative to the $\theta_{Pd} \geqslant 20$ film.

## 4. Discussion

The $H_2$ chemisorption properties of a Pd surface can be changed extensively from that of bulk Pd crystals by preparing ultrathin Pd films on Mo(100). The pseudomorphic Pd monolayer shows the largest differences, and the $H_2$ chemisorption properties may be controlled by changing the Pd film thickness. Compared to bulk Pd, a Pd monolayer on Mo(100) has reduced $H_2$ adsorption at 150 K, populating a chemisorption state with a desorption temperature of about 290 K. This indicates that the H–Pd bond strength is only reduced slightly on the Pd monolayer relative to bulk Pd(100) [16]. The characteristic, low-temperature desorption of $H_2$ from the Pd hydride state, the α state, does not occur until much thicker Pd films are reached, i.e. $\theta_{Pd} \geqslant 5.5$. As the Pd film thickness increases, the $H_2$ TPD peak due to chemisorbed hydrogen gradually shifts up in temperature to 335 K and the amount of $H_2$ desorbing from the a state increases. When $\theta_{Pd} \geqslant 20$, the $H_2$ TPD spectra resemble $H_2$ desorption from bulk Pd [9,16].

Studies of Pd films on Mo(100) by AES indicate that the Pd monolayer is best viewed as being two dimensional [11]. Changes in the Pd film morphology occur upon annealing for Pd coverages beyond one monolayer. The observed changes in the Pd and Mo AES signal intensities are relatively small upon annealing to 450 K and do not support extensive intermixing of the two metals at this temperature. The changes in the AES signals have been interpreted as due to the formation of 3D crystallites. This implies that there will be an increased range of Pd thicknesses for the Pd films with $\theta_{Pd}>1$. Unfortunately, the exact size and shape of these crystallites is not known and we must rely on an average crystallite size determined by modeling of the growth mode. The morphology of these thicker films is best represented by a flat monolayer with clusters ap-

proximately 4 layers thick [11]. The model [18] used in ref. [11] proposes that clusters grow both vertically and horizontally as Pd is deposited, which leads to a coalescence of clusters. Thus, we do not expect tall columns of Pd but rather relatively flat clusters which coalesce to form complete layers as the Pd coverage increases. For thick films, $\theta_{Pd}$ represents some average thickness only. Based on this description, it appears that on Mo(100) clusters approximately 5 layers thick are required to begin to have subsurface hydrogen. As the Pd film thickness is increased, the effective cluster size is increased, leading to an increased population of the α state because more subsurface sites are available.

A direct comparison between the $H_2$/Pd/Mo(100) and other similar Pd/substrate systems is complicated by the different film preparation procedures and $H_2$ exposure temperatures. Recent work in our laboratory has shown that these parameters are critical when studying the interaction of $H_2$ with Pd films [19]. In all previous studies, the Pd films were annealed to at least 700 K, whereas Pd films were only annealed to 450 K in our work. Structural changes are most certainly occurring in many of the systems of interest at these annealing temperatures. A reinvestigation of the Pd/Ta(110) system as a function of annealing temperature, $H_2$ exposure, and substrate temperature for $H_2$ exposure is currently underway in our laboratory. Despite these complications, a comparison can be made of these results to those of $H_2$ adsorption on Pd layers on Nb(110) [7], Ta(110) [8], W(110) [10] and W(100) [10] surfaces. $H_2$ TPD spectra from monolayer films on the different substrates are different. Hydrogen desorbs from the Pd monolayer with a peak maximum at 1400 K on Ta(110). This state is likely due to decomposition of Ta hydride at this high desorption temperature rather than Pd hydride or hydrogen chemisorbed on Pd. This is not surprising since it is well known that Ta can dissolve large amounts of hydrogen [20]. No chemisorbed hydrogen or Pd hydride state was seen for the pseudomorphic Pd monolayer on Ta(110). Very similar results have been obtained for Nb(110) [7]. On a W(110) surface, $H_2$ TPD from a monolayer Pd film showed the presence of a chemisorbed hydrogen state, which desorbed at a higher temperature (400 K) than the chemisorbed state for $H_2$ adsorbed on Pd(111), and

a high-temperature state (510 K) ascribed to interfacial hydrogen [10]. As the Pd film thickness was increased, the intensity of the chemisorbed $H_2$ state decreased and two new states were observed at 200 and 275 K. These were attributed to desorption of $H_2$ from a hydride phase and the surface of three-dimensional clusters of Pd, respectively. For a Pd monolayer on W(100) an interfacial $H_2$ desorption state was observed at 525 K and a chemisorbed state was seen at 350 K [10]. As the Pd film thickness increased, the chemisorption state shifted down in temperature to 300 K. No well developed Pd-hydride state was observed but a small shoulder at 200 K was attributed to Pd-hydride formation for films thicker than one monolayer.

It appears that an effective cluster thickness of 5 layers is not generally required to populate the α state. It is visible at one monolayer Pd coverage on W(110) [10] and we have recently observed it for an fcc(111) Pd monolayer film on Ta(110) [19]. We have also found the population of this state to be highly dependent on the temperature to which the Pd film was annealed, i.e. the Pd film morphology is critically important [19]. W(100) and Mo(100) may be similar in the need for a 5 layer Pd film to populate a Pd hydride state, however, the Pd film structure in these systems needs further investigation especially as a function of annealing temperature.

The reduced $H_2$ uptake observed for the $\theta_{Pd} = 1$ film compared to thick ($\theta \geqslant 20$) films is similar to the results obtained for Nb and Ta [4–8] although not as dramatic. Photoemission studies of monolayer 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 shifted to higher binding energy [21–25]. It has been suggested that the electronic structure of the Pd monolayer resembles that of a noble metal [22]. For Cu [26], Ag [27], and Au [28] it is known that $H_2$ chemisorption is an activated process which results in a low sticking coefficient. This is thought to be due to the lack of d holes for these metals which serve to reduce the Pauli repulsion through s–d transfer [29]. Because the d bands of Cu, Ag and Au are filled, s–d rehybridization cannot occur which causes the Pauli repulsion to be high and creates an activation barrier for chemisorption. A similar situation could be oc-

curring for the Pd monolayer films on these refractory substrates.

In summary, we show that thin Pd films on Mo(100) exhibit altered $H_2$ chemisorption properties when compared to bulk Pd(100). A small decrease in the bond energy for the Pd–H bond occurs for hydrogen chemisorbed on a Pd monolayer when compared to hydrogen chemisorbed on bulk Pd(100). Pd films less than 5 monolayers thick do not form a Pd hydride state characteristic of bulk Pd.

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