

# Chemisorption of Ethylene and Acetylene on Ultrathin Pd Films on Mo(100)

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Previous studies of the chemisorption properties of ultrathin (mono-, bi-, and trilayer) metal films have usually focused on CO adsorption. While the CO adsorption energy on these Pd films is often decreased, CO is one of the strongest  $\pi$ -acceptor ligands and probes mainly one aspect of the chemistry of these surfaces. We report here the first detailed study on ultrathin metal films of the chemisorption of two unsaturated hydrocarbons,  $C_2H_4$  and  $C_2H_2$ , which initially bond to the surface as  $\sigma$ -donors and can rehybridize to form strong metal-carbon bonds. The adsorption and dehydrogenation of ethylene and acetylene on monolayer and ultrathin Pd films on Mo(100) were investigated using Auger electron spectroscopy (AES), temperature-programmed desorption (TPD), and high-resolution electron energy loss spectroscopy (HREELS). The pseudomorphic monolayer of Pd on Mo(100) has greatly altered chemisorption properties for  $C_2H_4$ . Ethylene is weakly chemisorbed on the Pd monolayer, and the adsorbed species is much less rehybridized from  $sp^2$  in the gas phase toward  $sp^3$  on this surface compared to  $C_2H_4$  chemisorbed on the (100) surface of bulk Pd. In addition, a smaller fraction of the adsorbed ethylene dehydrogenates during TPD experiments on the Pd monolayer compared to thicker Pd films; i.e., the selectivity for reversible  $C_2H_4$  adsorption is increased on the Pd monolayer. The weaker  $C_2H_4$  chemisorption interaction of the Pd monolayer is consistent with previous CO adsorption studies, along with UV photoemission studies and electronic structure calculations showing a filled d-band. However, acetylene chemisorption is not affected like  $C_2H_4$ , and  $C_2H_2$  is strongly rehybridized from  $sp$  in the gas phase toward  $sp^3$  on the Pd monolayer as it is on bulk Pd(100). We propose that the  $C_2H_2$ -Pd interaction is strong enough to rehybridize Pd in the monolayer back toward its normal bulk electronic structure (with a partially filled d-band) in order to have the favorable energy change from a large heat of adsorption for  $C_2H_2$  and strong Pd-C bonding.

## Introduction

The properties of metal monolayers and ultrathin films have generated a considerable amount of interest in recent years due to observations of strongly altered behavior when compared with bulk metal surfaces. In the case of thin Pd films, most studies have focused on CO adsorption.<sup>1-11</sup> For example, the Pd-CO bond strength has been measured for the Pd/Nb(110),<sup>5,10</sup> Pd/Ta(110),<sup>7,11</sup> Pd/Mo(100),<sup>8</sup> Pd/W(110),<sup>6,9</sup> and Pd/W(100)<sup>6</sup> systems using TPD and was found to be  $\leq 21$  kcal/mol in all cases. This can be contrasted with the values of 35 and 36.5 kcal/mol found for the heat of adsorption on the (111)<sup>12</sup> and (100)<sup>13</sup> surfaces of Pd single crystals. While a fair number of experiments have studied CO,<sup>1-11</sup>  $H_2$ ,<sup>2,5-7,14-16</sup> and  $O_2$ ,<sup>1,17,18</sup> adsorbed on thin Pd films deposited on several early transition metal substrates, nothing is known about the interaction of other gases with these surfaces. Other molecules probe different aspects of the electronic structure of these surfaces, and additional adsorption studies would be helpful in exploring and understanding the rich chemistry of these interesting systems. To this end we have carried out experiments characterizing the chemisorption properties of  $H_2$ ,<sup>16</sup>  $C_2H_4$ , and  $C_2H_2$  on Pd/Mo(100) (this work) and  $H_2$ ,<sup>19</sup>  $C_2H_2$ ,<sup>20</sup> and  $NO$ <sup>21</sup> on Pd/Ta(110). The recent work of Lambert<sup>22</sup> on  $C_2H_2$  adsorption on Pd/Au(111) surfaces is notable also. However, since these films either have unaltered Pd properties<sup>23</sup> or form Pd-Au alloys,<sup>24</sup> the results do not bear directly on the early transition metal substrate systems of interest here.

In this paper we present results for ethylene and acetylene adsorption on a Pd monolayer and thin films of Pd on Mo(100). We show that these Pd films exhibit reduced reactivity with  $C_2H_4$  compared to bulk Pd(100) surfaces. The Pd monolayer does not

rehybridize ethylene as strongly and has a decreased propensity for dehydrogenation. These effects are not observed for  $C_2H_2$ . Presumably, acetylene is so strongly adsorbed that it rehybridizes the Pd electronic structure in an effect that is similar to the chemisorption-induced reconstruction of the surface layers seen for other single-component metal systems.

## Experimental Information

The experimental apparatus has been described previously.<sup>25</sup> The instrumentation includes a double-pass cylindrical mirror analyzer (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.

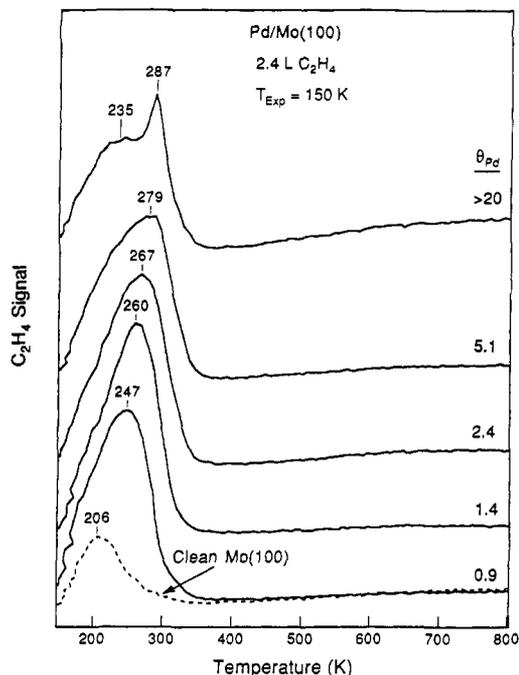
The Mo(100) single crystal (Atomergic Chemical Corp.) was cleaned by heating in  $O_2$  followed by repeated flashes to 2000 K. The temperature of the sample was measured by a W-5% Re/W-26% Re thermocouple spot-welded to the side of the sample. Pd was deposited on Mo(100) by resistively heating a 0.5-mm-diameter tungsten wire which was wrapped with 0.1-mm-diameter Pd wire (Aesar, 99.99% pure). 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.<sup>26</sup>

$C_2H_4$  was obtained from Scientific Gas Products (99.9%) and  $C_2D_2$  from Cambridge Isotope Laboratories (99 atom % D); both were used without further purification.  $C_2H_2$  was supplied by Matheson (99.6%) and was purified using standard glass vacuum line fractional distillation procedures to remove traces of acetone and was stored at pressures less than 1 atm in a glass bulb.  $C_2H_4$  and  $C_2H_2$  ( $C_2D_2$ ) exposures were carried out with the aid of a glass capillary array doser. Exposures are reported in units of langmuirs (1 langmuir =  $1 \times 10^{-6}$  Torr s) but have not been corrected for ion gauge sensitivities nor doser enhancement factor.

The heating rate during TPD experiments was 6 K/s. HREELS experiments were performed in the specular direction

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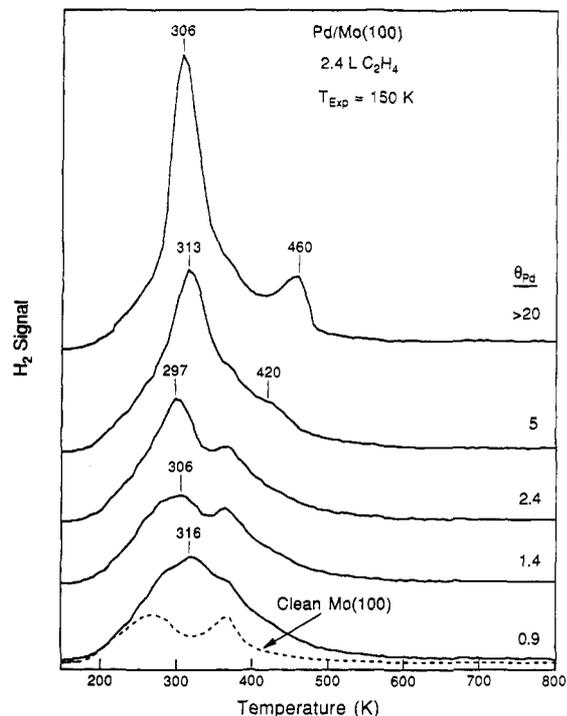
**Figure 1.**  $C_2H_4$  TPD spectra from several Pd films following 2.4-langmuir  $C_2H_4$  exposures at 150 K. The dashed curve is a  $C_2H_4$  TPD spectrum from clean Mo(100).

with a beam energy of 2.8 eV. The resolution varied between 68 and 86  $cm^{-1}$ . All HREELS spectra were recorded at 100 K. All adsorption experiments were performed on Pd films which had been annealed to 450 K in order to minimize any changes in the Pd film structure during subsequent annealing or TPD experiments.

We have recently described the growth and thermal stability of monolayer and ultrathin Pd films on Mo(100).<sup>26</sup> 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 pseudomorphic with the substrate lattice, and Pd films can be grown at this temperature with a small amount of layer disorder and/or nonideal layering. The monolayer is stable to 1250 K, but Pd in excess of one monolayer tends to agglomerate into three-dimensional crystallites upon annealing above 400 K. The average crystallite thickness was estimated to be four layers for Pd films annealed to 450 K. Due to this cluster formation, thicknesses reported for these films must be taken as indicating an average value since there will be a range of thicknesses present. The chemistry reported for these thicker films must be considered within this context. There is also evidence of the formation of a Pd–Mo alloy for thicker Pd films upon heating to 1250 K, but the temperature for the onset of alloying is not clear and could be as low as 600–800 K.

## Results

**Ethylene ( $C_2H_4$ ) Adsorption.** Ethylene TPD spectra following large  $C_2H_4$  exposures (2.4 langmuirs) at 150 K are shown in Figure 1 as a function of Pd film thickness. This exposure gave a saturation coverage of  $C_2H_4$  on the clean Mo(100) surface. Signals at 2, 27, and 28 amu were monitored during TPD experiments. A  $C_2H_4$  TPD spectrum from clean Mo(100) is shown in Figure 1 (dashed curve) in order to evaluate the contribution of the back and edges of the Mo(100) single crystal to the  $C_2H_4$  signal from the Pd films. Only a small amount of  $C_2H_4$  desorbs at 206 K from the clean Mo(100) surface.<sup>27</sup> The  $C_2H_4$  desorption signal from Mo will be reduced by more than a factor of 2 following deposition of a Pd monolayer film, resulting in a very small contribution to the  $C_2H_4$  TPD spectra for the Pd films. While it is likely that chemisorption-induced changes occur



**Figure 2.**  $H_2$  TPD spectra from several Pd films following 2.4-langmuir  $C_2H_4$  exposures at 150 K. The dashed curve is a  $H_2$  TPD spectrum from clean Mo(100) which has been scaled to estimate the maximum contribution of the Mo(100) crystal to the  $H_2$  TPD signal from the Pd films.

in the Pd films, it is not likely that these changes expose the Mo(100) substrate and result in contributions to the TPD spectra from the front face of the Mo(100) crystal. The contributions to the TPD spectra from Mo(100) are relatively constant for the desorption products seen in this work ( $C_2H_4$ ,  $H_2$ ,  $C_2D_2$ , and  $D_2$ ) as the Pd film thickness increases, and this would not be expected if these features were due to desorption from the front face of the Mo(100) crystal.

A single molecular  $C_2H_4$  desorption peak is seen at 247 K on the  $\theta_{Pd} = 0.9$  film. The activation energy for molecular  $C_2H_4$  desorption is estimated to be 15 kcal/mol using Redhead analysis<sup>28</sup> and assuming first-order kinetics and a preexponential factor of  $10^{13} s^{-1}$ . As the Pd coverage increases, this peak shifts to slightly higher temperature and appears at 279 K for  $\theta_{Pd} = 5.1$ . At a Pd thickness of greater than 20 layers, the TPD spectrum has  $C_2H_4$  peak temperatures close to that obtained for  $C_2H_4$  desorption from Pd(100), although the relative intensity of the low-temperature peak on the thick Pd film is somewhat larger than that obtained from  $C_2H_4$  desorption from bulk Pd(100).<sup>29</sup> Figure 1 clearly shows  $C_2H_4$  to be more weakly bound to the Pd monolayer than to the thick ( $\geq 20$  layers) Pd films, where some  $C_2H_4$  desorption occurs with an activation energy of 17 kcal/mol.

Figure 2 shows  $H_2$  TPD spectra following saturation  $C_2H_4$  exposures at 150 K as a function of Pd film thickness. These spectra were taken concurrently with the  $C_2H_4$  TPD spectra shown in Figure 1. We have included a  $H_2$  TPD spectrum following  $C_2H_4$  exposures on clean Mo(100) in Figure 2 (dashed curve). Since much more  $H_2$  desorption occurs on Mo(100), this spectrum has been scaled to estimate the maximum possible contribution of the Mo(100) crystal (back face and edges) to the  $H_2$  TPD spectra from the Pd films. The scaling was done by modifying the size of the  $H_2$  TPD spectrum from Mo(100) until the intensity was less than or equal to the intensity of the  $H_2$  signal from the Pd films at all points in the spectrum. The actual contribution to the  $H_2$  TPD signal by the back and edges of the Mo(100) crystal may in fact be smaller. On the  $\theta_{Pd} = 0.9$  film, a broad  $H_2$  desorption peak at 316 K is observed. The small shoulder or peak at 350 K in this curve and also for the thicker films is due

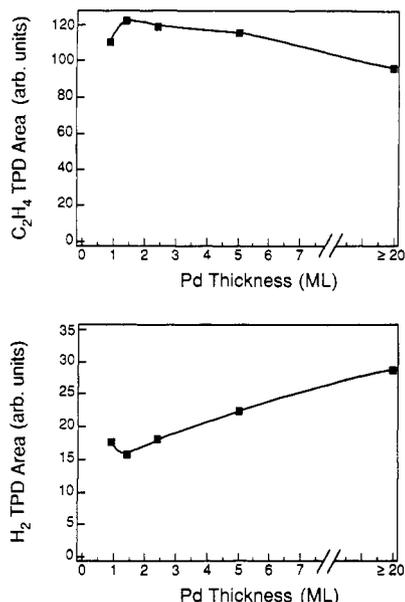


Figure 3. (a, top)  $C_2H_4$  TPD area as a function of Pd film thickness. (b, bottom)  $H_2$  TPD area as a function of Pd film thickness.

to desorption from the clean back and edges of the Mo(100) crystal. The peak at 316 K increases in size and shifts toward lower temperature as the Pd film thickness increases to  $\theta_{Pd} = 2.4$ . Upon increasing to  $\theta_{Pd} = 5$  this peak grows larger, and some higher temperature desorption is observed at 420 K. Hydrogen desorption from ethylene exposure on the 20-layer-thick film resembles that from  $C_2H_4$  exposure on bulk Pd(100).<sup>29</sup> Although the peak maxima appear at lower temperatures on the Pd film compared to Pd(100), the relative intensities of the two peaks are comparable. Since  $H_2$  desorption from hydrogen chemisorbed on the thin Pd films occurs in a temperature range from 200 to 400 K,<sup>16</sup> the  $H_2$  peak at 306 K could be due to a desorption rate-limited process from low-temperature decomposition of  $C_2H_4$ . The  $H_2$  TPD peak at 460 K is rate limited by decomposition of some hydrocarbon species on the surface.

Figure 3a,b shows the  $C_2H_4$  and  $H_2$  TPD areas from Figures 1 and 2 as a function of Pd film thickness. The first data point is for the  $\theta_{Pd} = 0.9$  film (essentially a monolayer of Pd). Clean Mo(100) values are not shown since they are irrelevant to the point at hand, which is to see how the chemisorption properties of Pd are changed with increasing Pd film thickness. The  $C_2H_4$  curve in Figure 3a has a maximum at  $\theta_{Pd} = 1.4$  and then slowly decreases with Pd film thickness. About 20% more  $C_2H_4$  desorbs from the Pd monolayer than the thick Pd film. The corresponding  $H_2$  TPD area in Figure 3b has a minimum at a Pd film thickness of 1.4 layers and slowly increases with Pd film thickness in a complementary fashion to the molecular  $C_2H_4$  TPD area.

An HREELS spectrum of ethylene adsorbed on the Pd monolayer at 100 K is shown in Figure 4. Peaks in the loss spectrum are observed at 2980, 1525, 1235, and 865  $cm^{-1}$ . These peaks are due to the  $\nu(CH)$ ,  $\delta(CH_2)$ ,  $\nu(CC)$ , and  $CH_2(def)$  modes, respectively. The energy loss assignments were made from comparisons with gas-phase ethylene<sup>30</sup> and ethylene adsorbed on bulk Pd(100)<sup>29</sup> and Pt(111)<sup>31</sup> as listed in Table I. Also included in this table are values for Zeise's salt<sup>32</sup> and  $C_2H_4Br_2$ ,<sup>33</sup> since they are model compounds for  $\pi$ -bonded and di- $\sigma$ -bonded ethylene, respectively. In comparing these values, the vibrational frequencies of ethylene adsorbed on the Pd monolayer most closely resembles the vibrational frequencies of Zeise's salt; ethylene is  $\pi$ -bonded on the Pd monolayer. Two discrepancies in the vibrational spectra hint that things may be more complicated than this simple picture. The  $CH_2(def)$  and  $\nu(CH_2)$  frequencies differ from Zeise's salt by about 100  $cm^{-1}$ . The  $\nu(CH_2)$  peak is

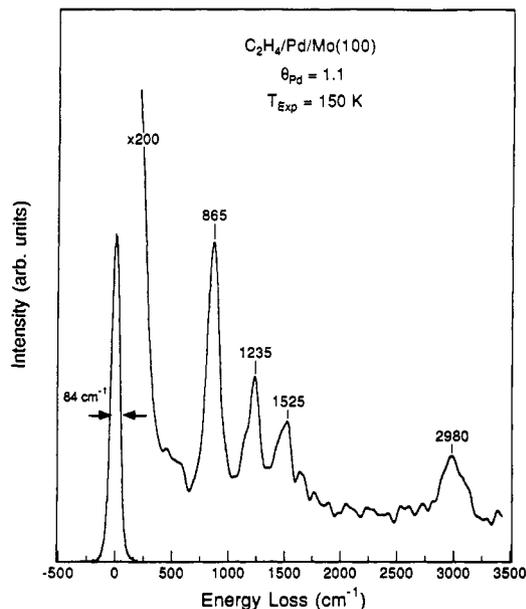


Figure 4. HREELS spectrum of  $C_2H_4$  adsorbed on a  $\theta_{Pd} = 1.1$  film at 150 K.

TABLE I: Comparison of Vibrational Frequencies ( $cm^{-1}$ ) for Adsorbed  $C_2H_4$ ,  $C_2H_4Br_2$ , and Zeise's Salt

mode	Pd monolayer	bulk Pd(100) <sup>a</sup>	Zeise's salt <sup>b</sup>	$C_2H_4Br_2$ <sup>c</sup>	$C_2H_4/Pt(111)$ <sup>d</sup>	gas <sup>e</sup>
$\nu(CH_2)$	2980	2980	3079	3005	3000	3026
$\delta(CH_2)$	1525	1455	1515	1420	1430	1342
$\nu(CC)$	1235	1135	1243	1019	1050	1623
$CH_2$ def	865	920	975	1278	980	1023
$\nu(PdC)$	439	390			470	

<sup>a</sup> Reference 29a. <sup>b</sup>  $K[(C_2H_4)PtCl_3]$ ; ref 32. <sup>c</sup> Gauche form, A modes only; ref 33. <sup>d</sup> Reference 31. <sup>e</sup>  $A_1$  modes only, ref 30.

TABLE II: Comparison of the  $\pi\sigma$  Parameter for  $C_2H_4$  Adsorbed on Several Surfaces

system	$\pi\sigma$	ref	system	$\pi\sigma$	ref
$C_2H_4Br_2$	1.0	30	Pd/Mo(100)	0.39	this work
Pt(111)	0.92	31	Zeise's salt	0.38	32
Ni(100)	0.83	50	Cu(100)	0.21	51
Pd(100)	0.78	34	Ag(110) + O	0.14	52
Pd(111)	0.43	37	$C_2H_4(g)$	0.0	30
Pd(110)	0.39	42			

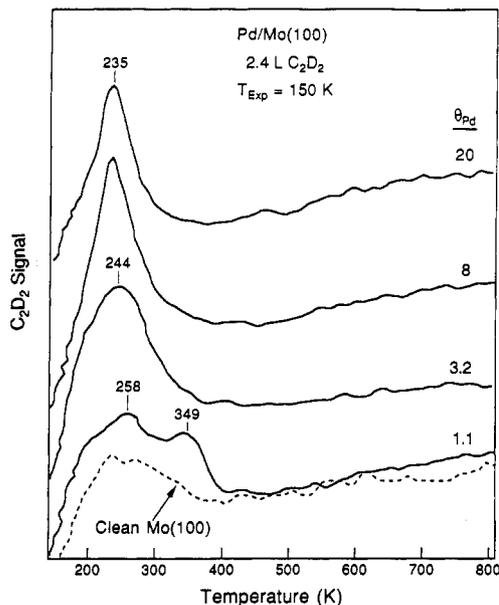
very broad, with an appreciable intensity near 3100  $cm^{-1}$ , and might be due to the presence of two types of adsorbed  $C_2H_4$  species.

A measure of the hybridization of  $C_2H_4$  adsorbed on metal surfaces is the  $\pi\sigma$  parameter<sup>34</sup> defined by

$$\pi\sigma(C_2H_4) = \frac{\frac{(1623\text{-band I})}{1623} + \frac{(1342\text{-band II})}{1342}}{0.366} \quad (1)$$

where band I refers to the higher frequency and band II to the lower frequency of the  $\nu(CC)$ - $\delta(CH_2)$  pair. Table II lists the  $\pi\sigma$  parameter for  $C_2H_4$  adsorbed on several surfaces. This parameter is 0 for gas-phase  $C_2H_4$ , 0.38 for Zeise's salt, and 1 for  $C_2H_4Br_2$ . For ethylene adsorbed on the Pd monolayer,  $\pi\sigma(C_2H_4) = 0.39$  whereas on bulk Pd(100)  $\pi\sigma(C_2H_4) = 0.78$ .<sup>34</sup> This indicates that considerably less rehybridization of  $C_2H_4$  from  $sp^2$  to  $sp^3$  occurs on the monolayer relative to bulk Pd(100).

**Acetylene ( $C_2H_2$  and  $C_2D_2$ ) Adsorption.** Acetylene TPD spectra following large  $C_2D_2$  exposures (2.4 langmuirs) at 150 K are shown in Figure 5 as a function of  $\theta_{Pd}$ . This exposure resulted in a saturation  $C_2D_2$  coverage on the clean Mo(100) surface.  $C_2D_2$  is seen to desorb from clean Mo(100) in a broad peak

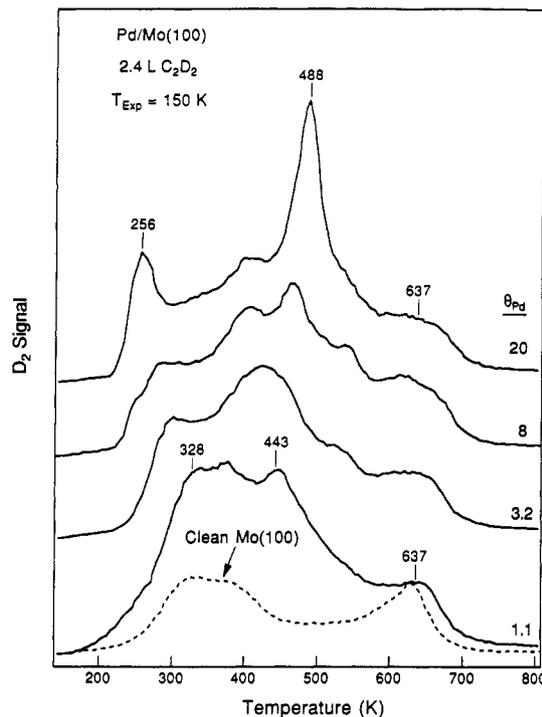


**Figure 5.**  $C_2D_2$  TPD spectra from several Pd films following 2.4-langmuir  $C_2D_2$  exposures at 150 K. The dashed curve is a  $C_2D_2$  TPD spectrum from Mo(100).

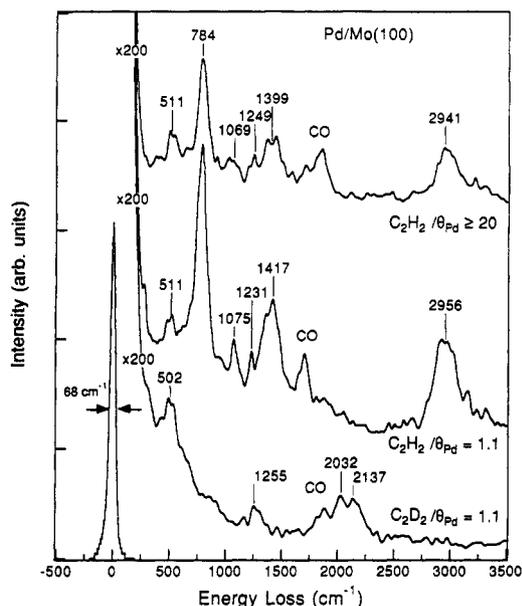
centered at 260 K as shown by the dashed curve in Figure 5. As in Figure 1, we estimate that the contribution of this spectrum to those from Pd is more than a factor of 2 smaller than shown by the dashed curve. On the monolayer Pd film, desorption of acetylene has a broad two peak structure with peak maxima at 258 and 349 K. This is similar to acetylene desorption from bulk Pd(100) where a broad plateau extending from 188 to 350 K is observed.<sup>35</sup> On the film with  $\theta_{Pd} = 3.2$ , the high-temperature peak is gone and a broad peak occurs at 244 K. This peak shifts down in temperature and narrows somewhat for thicker Pd films.

$D_2$  desorption was also monitored during the previous TPD experiments following saturation  $C_2D_2$  exposures (2.4 langmuirs) on the Pd films. This is shown in Figure 6. The dashed curve in Figure 6 is a  $D_2$  TPD spectrum from clean Mo(100) following  $C_2D_2$  exposure. This spectrum has been scaled to estimate the maximum possible contribution of the Mo(100) crystal (back face and edges) to the  $D_2$  TPD spectra from the Pd films by using the same procedure as was used for the  $H_2$  TPD spectra following  $C_2H_4$  exposures. Looking at the peak near 630 K reveals that the actual contribution to the  $D_2$  TPD signal is likely to be much smaller than that shown. The TPD spectrum of  $D_2$  from the Pd monolayer has a broad plateau with maxima at 328 and 443 K and a long tail extending to 700 K. This has the general shape and temperature range for hydrogen desorption from bulk Pd(100) surfaces following acetylene exposures.<sup>35</sup> Differences are observed in the onset temperature for hydrogen desorption, which is lower on the Pd monolayer, and the result that there is only one peak at 418 K followed by a long plateau on bulk Pd(100). The  $D_2$  TPD spectra change continuously as the Pd thickness increases. The onset of desorption becomes sharper as the peak initially at 328 K shifts down to 256 K, and new peaks are seen at 399 and 488 K. The final temperature for liberation of  $D_2$  from the surface due to complete dehydrogenation of adsorbed hydrocarbon species is not dependent on  $\theta_{Pd}$ .

Several groups have investigated the cyclotrimerization of  $C_2H_2$  to benzene on Pd surfaces (see ref 22 and the references therein). This reaction occurs readily on the Pd(111) surface, but to a much smaller extent on the Pd(110) surface. Benzene desorption was monitored during our experiments to see whether the cyclotrimerization reaction would occur on Pd films deposited on Mo(100). No  $C_6H_6$  desorption was observed for any of the Pd films studied. This is probably due to the reaction being highly structure sensitive. Evidently, distortions in the Pd-Pd distances



**Figure 6.**  $D_2$  TPD spectra from several Pd films following 2.4-langmuir  $C_2D_2$  exposures at 150 K. The dashed curve is a  $D_2$  TPD spectrum from clean Mo(100) which has been scaled to estimate the maximum contribution of the Mo(100) crystal to the  $D_2$  TPD signal from the Pd films.



**Figure 7.** HREELS spectrum of  $C_2H_2$  adsorbed on a  $\theta_{Pd} = 1.1$  film and a  $\theta_{Pd} \geq 20$  film at 150 K. Also shown is an HREELS spectrum of  $C_2D_2$  on a  $\theta_{Pd} = 1.1$  film (bottom spectrum).

or the overall geometric structure for these Pd films deposited on Mo(100) cause benzene formation to be suppressed.

In summary, regarding the  $C_2D_2$  and  $D_2$  TPD curves after  $C_2D_2$  exposure, the Pd monolayer resembles Pd(100) bulk single crystal surfaces while thicker films have  $D_2$  TPD spectra "richer" in structure than that seen on Pd(100) surfaces, obviously due to several Pd sites being exposed for reaction. The  $D_2$  peaks show that discrete dehydrogenation reactions occur, pointing to different surface species and possible changes in the dehydrogenation mechanism with increasing  $\theta_{Pd}$ .

Figure 7 shows vibrational spectra of  $C_2D_2$  and  $C_2H_2$  following saturation exposures (2.4 langmuirs) on a Pd monolayer at 150

K. On the basis of comparison with gas-phase  $C_2H_2$  ( $C_2D_2$ )<sup>30</sup> and adsorbed  $C_2H_2$  ( $C_2D_2$ ) on Pd(100),<sup>36</sup> and by utilizing isotope shifts, we assign the loss peaks in the  $C_2H_2$  spectrum at 2956, 1417, 1231, 1075, 784, and 511  $cm^{-1}$  as due to  $\nu(CH)$ ,  $\delta(CH)$ ,  $\nu(CC)$ ,  $\rho(CH)_{asym}$ ,  $\rho(CH)_{sym}$ , and  $\nu(PdC)$  modes, respectively.  $C_2D_2$  loss peaks at 2137, 2032, 1255, and 502  $cm^{-1}$  are assigned as due to  $\nu(CD)$ ,  $\nu(CD)$ ,  $\nu(CC)$ , and  $\rho(CD)$  modes, respectively. The observed vibrational frequencies of  $C_2H_2$  on the  $\theta_{Pd} = 1$  film on Mo(100) are attributed to strongly rehybridized acetylene as evidenced by the low  $\nu(CH)$  and  $\nu(CC)$  frequencies at 2956 and 1231  $cm^{-1}$ , respectively. The very broad ( $\approx 250$   $cm^{-1}$ )  $\nu(CH)$  mode suggests that there may in fact be more than one type of adsorbed  $C_2H_2$ . This is more evident in the HREELS spectrum for  $C_2D_2$  which has two  $\nu(CD)$  peaks which are resolved. However, there is no evidence of a  $\pi$ -bonded or slightly rehybridized  $C_2H_2$  species on the Pd monolayer. Only small shifts in the position of the HREELS peaks are observed when compared to bulk Pd(100).<sup>36</sup> This indicates that, unlike ethylene, the extent of rehybridization is nearly the same for  $C_2H_2$  on a Pd monolayer on Mo(100) as it is for  $C_2H_2$  on bulk Pd(100). An HREELS spectrum of a saturation exposure (2.4 langmuirs) of  $C_2H_2$  on a thick Pd film at 150 K is also shown in Figure 7. It is similar to that from the Pd monolayer and bulk Pd(100).

## Discussion

It is desirable to control the chemistry that occurs at metal surfaces for many applications. One method to achieve this goal is to chemically alter the surface properties of a metal by forming monolayer or thin films of the metal on a different metal substrate. The bonding interactions between the film and substrate can change the properties of the film. Pd monolayers on early transition metals have been shown to have altered (reduced) CO interactions, and now we have shown that the interaction of ethylene with Pd can be modified similarly from bulk Pd single crystal surfaces by making ultrathin Pd films on Mo(100). The Pd monolayer shows the largest changes and some of the chemisorption properties can be varied or "tuned" by changing the Pd film thickness, although the origin of this tuning is not clear as yet. The lower ethylene desorption temperature from a monolayer Pd film compared to that observed for ethylene desorption from bulk Pd indicates a slightly weaker Pd- $C_2H_4$  bond on the Pd monolayer surface. This is consistent with the observed vibrational spectrum which indicates that little rehybridization from gas phase ( $sp^2$ ) occurs upon chemisorption. The bilayer Pd film has properties similar to the monolayer, but a return to bulk Pd behavior is seen as the Pd coverage increases to about five monolayers.

Ethylene adsorption has been studied previously on the (111),<sup>37-39</sup> (100),<sup>29,34</sup> and (110)<sup>40-42</sup> surfaces of bulk Pd single crystals. Only 8% of the adsorbed ethylene dehydrogenates on Pd(111) for saturation coverages while approximately one-third dehydrogenates on Pd(100) and two-thirds dehydrogenates on Pd(110) for saturation  $C_2H_4$  coverages at exposure temperatures below 100 K. The amount of rehybridization from gas-phase  $C_2H_4$  also varies considerably among these Pd surfaces (see Table II). Ethylene is more rehybridized toward  $sp^3$  on the Pd(100) surface ( $\pi\sigma(C_2H_4) = 0.78$ ) than on the Pd(111) ( $\pi\sigma(C_2H_4) = 0.43$ ) or Pd(110) ( $\pi\sigma(C_2H_4) = 0.39$ ) surfaces. The  $\pi\sigma$  parameter observed for the Pd(110) surface is identical to the  $\pi\sigma$  parameter obtained for the Pd monolayer on Mo(100) and supports our claim that  $C_2H_4$  is  $\pi$ -bonded on the Pd monolayer. This should not necessarily be taken to indicate that the Pd monolayer has a geometric structure similar to Pd(110), since the Pd monolayer is pseudomorphic with the Mo(100) substrate and thus has an expanded Pd(100) lattice but, instead, indicates that the bonding of adsorbed  $C_2H_4$  is similar on the two surfaces.

The altered  $C_2H_4$  chemisorption properties of these thin Pd films may be explained in terms of their altered electronic

structure. It is generally believed that ethylene bonding to transition metal surfaces is similar to that which occurs between  $\pi$  acids and transition metals in organometallic complexes.<sup>43</sup> Within this context, the filled  $C_2H_4$   $\pi$  orbital donates its electrons to vacant  $d_\sigma$  orbitals of the metal while the empty  $C_2H_4$   $\pi^*$  orbital accepts electrons from filled  $d_\pi$  orbitals of the metal. The amount of back-donation is thought to be the dominating factor in determining the extent of rehybridization. It is clear from the value of the  $\pi\sigma$  parameter of 0.39 that  $C_2H_4$  is much less rehybridized on the Pd monolayer than on bulk Pd(100). This result is consistent with calculations of the electronic structure for a Pd monolayer on early transition metals.<sup>44</sup> The  $\sigma$ -donor bond formed by the interaction of the  $\pi$  orbital of ethylene is less effective since the d band of Pd in the monolayer is filled. Since the Pd band is fully occupied (or even if the d orbitals of Mo and Pd are extensively involved in bonding), the resulting Pd d band will have a lowering of energy overall and the energy gap between the Pd d band and the  $\pi^*$  orbital of  $C_2H_4$  will be increased leading to smaller overlap and less back-donation. Both of these effects weaken the  $C_2H_4$ -Pd bond and decrease the rehybridization upon adsorption. This interpretation suggests that the Pd monolayer has chemisorption properties similar to the group IB metals (Cu, Ag, and Au) which have filled d-bands. However, the desorption temperature for  $C_2H_4$  on the Pd monolayer is 100 K higher than observed for Ag(100),<sup>45</sup> and a significant amount of  $C_2H_4$  dehydrogenation occurs on the Pd monolayer while no dehydrogenation is seen on Ag(111).<sup>46</sup> Thus, while the chemisorption properties of ethylene on the Pd monolayer approach that of ethylene on Ag, it is clear that there are still significant differences.

Recent XPS data taken by Goodman and co-workers<sup>47</sup> have shown Pd monolayers on several early transition metal substrates to have Pd(3d) core levels shifted to higher binding energy when compared to the surface core levels of Pd(100). These shifts of the Pd(3d) core levels have been interpreted as being due to charge transfer from the Pd to the underlying substrate, leaving a partial positive charge on the Pd. Regardless of the origin of these shifts, the shift of the Pd valence d band to higher binding energy is consistent with previous UPS studies<sup>48,49</sup> and theoretical calculations.<sup>44</sup> This shift explains the chemistry which we have observed on a number of Pd monolayers on early transition metal substrates, i.e., a surface with a reactivity that approaches that of Ag.<sup>5,7,8,10,11,16,19-21,23</sup>

Somewhat surprisingly, the chemistry of acetylene on the Pd monolayer is similar to that observed on bulk Pd surfaces. We expected to see a reduced chemisorption interaction, similar to that for  $H_2$ , CO, and  $C_2H_4$ . However, both the TPD and HREELS spectra of acetylene on the Pd monolayer resemble those from acetylene adsorbed on Pd(100) single crystals. We propose that even though the Pd-Mo interaction alters or rehybridizes the Pd electronic structure in such a fashion that weak Pd- $C_2H_2$  bonding would occur, the energy gain due to strong bonding of acetylene to Pd is enough to rehybridize Pd in the monolayer back toward its normal bulk electronic structure; i.e., it is more exothermic to make strongly bonded acetylene with covalent Pd-C bonds (with somewhat weakened Pd-Mo interactions) than to have a weak  $\pi$ -bonded acetylene species on an unmodified Pd monolayer (with somewhat stronger Pd-Mo interactions). The initial bonding of acetylene on the thick Pd films (20 layers) is the same as on the Pd monolayer, and the HREELS spectra of chemisorbed  $C_2H_2$  at low temperature remain nearly constant as the film thickness increases. However, the TPD spectra change as  $\theta_{Pd}$  increases.  $H_2$  desorption occurs over a wider temperature range, and new desorption peaks are populated. This could be because the very strong chemisorption bonding of acetylene and the hydrocarbon fragments formed from decomposition cause additional changes in the morphology of the Pd film during the TPD experiments.

We have previously studied H<sub>2</sub><sup>16</sup> and CO<sup>8</sup> adsorption on monolayer and ultrathin Pd films on Mo(100). The interaction of H<sub>2</sub> and CO with these surfaces is strongly perturbed from that on bulk Pd(100). For example, the CO-Pd bond strength is reduced by 45% and the CO sticking probability is reduced by 34% on the Pd monolayer compared to bulk Pd(100) surfaces. CO adsorption properties characteristic of bulk Pd are reached only for  $\theta_{Pd} > 5$ . These results are similar to the results obtained in this work for C<sub>2</sub>H<sub>4</sub> although the alterations observed are larger for CO than for C<sub>2</sub>H<sub>4</sub>. This is understandable since CO is a stronger  $\pi$ -acceptor ligand and as such is expected to be more strongly affected by the reduction in back-bonding characteristics of the Pd monolayer.

### Conclusion

The Pd monolayer on Mo(100) has altered chemisorption properties relative to bulk Pd(100) for C<sub>2</sub>H<sub>4</sub>, but not for C<sub>2</sub>H<sub>2</sub>. The amount of irreversibly adsorbed C<sub>2</sub>H<sub>4</sub> and the extent of rehybridization of C<sub>2</sub>H<sub>4</sub> upon adsorption are both decreased relative to Pd(100). As the Pd film thickness is increased, the surface gradually acquires bulk Pd(100) properties. The changes in the chemistry of these films are consistent with a picture wherein the bonding interaction of Pd with the Mo(100) substrate causes a filling of the Pd d-band and a shift of the d-band to higher binding energies. This causes a decrease in the overlap of the C<sub>2</sub>H<sub>4</sub>  $\pi^*$  orbital with the Pd d-orbitals and results in  $\pi$ -bonded C<sub>2</sub>H<sub>4</sub> interacting more weakly with the Pd monolayer than bulk Pd(100). Unlike C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> chemisorption is not strongly altered on the Pd monolayer or thin films. This illustrates an important principle that the altered chemistry often observed on Pd monolayers may only occur for weakly adsorbed species, or hydrocarbon species which are not highly unsaturated, and is not a general property applicable to all molecules.

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