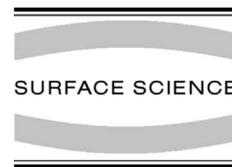




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# Tuning the chemistry of metal surfaces: II. Acetylene cyclotrimerization on ultrathin Pd films on Ta(1 1 0)

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## Abstract

Chemisorption of acetylene ( $C_2H_2$ ) and benzene ( $C_6H_6$ ) on ultrathin Pd films (monolayer, bilayer, trilayer, etc.) deposited on Ta(1 1 0) is weaker than on bulk-terminated Pd surfaces, but it is not as strongly perturbed as was seen for  $H_2$ , CO, NO, and  $C_2H_4$ . Thus, the well-known alterations of the chemical properties of ultrathin metal films deposited on refractory metal substrates can be modified by strongly adsorbed species.  $C_2H_2$  is predominately reversibly adsorbed on the Pd monolayer ( $\theta_{Pd} = 1$ ) at 91 K, with thermal desorption peaks at 180 and 265 K.  $C_6H_6$  is formed via cyclotrimerization of  $C_2H_2$  and desorbs in a single peak at 407 K, but the yield is small (1% of an adsorbed benzene monolayer on that surface). Bilayer and trilayer Pd films ( $\theta_{Pd} = 2-3$ ) have similar  $C_2H_2$  chemistry to that from thicker films. On a thick film ( $\theta_{Pd} = 5$ ) at 175 K,  $C_2H_2$  adsorption leads to  $C_2H_2$  desorption in a very broad peak near 330 K, and to benzene desorption at 250 and 500 K, with a yield of twice that on the Pd monolayer. Benzene chemisorption on the Pd monolayer is only slightly weaker than that on a thick Pd film ( $\theta_{Pd} = 5$ ) or on Pd(1 1 1), (a reduction of 6 kcal/mol) but is completely reversibly adsorbed. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Thermal desorption spectroscopy; Catalysis; Chemisorption; Thermal desorption; Palladium; Tantalum; Alkynes; Metallic films; Single crystal surfaces

## 1. Introduction

Cyclotrimerization of acetylene to benzene is a rather unique C–C coupling reaction that occurs in UHV on Pd(1 1 1) surfaces [1–5]. The reaction mechanism involves a sequential  $C_2 \rightarrow C_4 \rightarrow C_6$  process without any C–C or C–H bond cleavage. There is a threshold  $C_2H_2$  coverage necessary for this reaction to occur, and the maximum amount of acetylene-to-benzene conversion is less than

25% on a clean Pd(1 1 1) surface. However, the conversion can be increased by the addition of coadsorbates [6,7]. Reactively-formed  $C_6H_6$  desorbs from the Pd(1 1 1) surface in peaks at 250 and 500 K in TPD. These have been attributed to benzene bonded in “tilted” and “flat-lying” orientations, respectively [2,4].

$C_2H_2$  cyclotrimerization has also been observed on Cu(1 1 0) [8], Pd films on Au(1 1 1) and Pd–Au surface alloys [9], two Pt–Sn surface alloys [10] and Pd films on W(2 1 1) [11]. For Pd films on Au(1 1 1), the extent of reaction depended on the Pd film morphology, with the reaction occurring to a larger extent on smooth films than on rough films.

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However, Pd films on Mo(1 0 0) do not show C<sub>2</sub>H<sub>2</sub> cyclotrimerization activity [12]. This may be due to the larger Pd–Pd separation (expansive strain) or lower symmetry for Pd films on Mo(1 0 0). This reaction is known to be structure-sensitive on Pd, with a much lower C<sub>6</sub>H<sub>6</sub> yield from the Pd(1 0 0) surface than from the Pd(1 1 1) surface [5,6].

In this paper, we present results for C<sub>2</sub>H<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> chemisorption, and the cyclotrimerization of acetylene to form benzene, on ultrathin Pd films deposited on Ta(1 1 0). The Pd monolayer is less reactive than bulk Pd surfaces, binding C<sub>2</sub>H<sub>2</sub> more weakly with increased reversible adsorption. C<sub>6</sub>H<sub>6</sub> desorption from the cyclotrimerization reaction occurs in a single peak in TPD on the Pd monolayer, but two peaks are seen for thicker ( $\theta_{\text{Pd}} = 5$ ) Pd films just as for Pd(1 1 1) crystals. The Pd monolayer completely reversibly adsorbs benzene and the chemisorption bond is weaker than on thick ( $\theta_{\text{Pd}} = 5$ ) Pd films and bulk Pd(1 1 1) crystals, where benzene desorbs at 500 K in competition with decomposition.

## 2. Experimental information

The UHV chamber used in this work has been described previously [13]. The instrumentation included a double-pass CMA with a coaxial electron gun, LEED optics, and a UTI 100C quadrupole mass spectrometer. The base pressure of the chamber was  $1 \times 10^{-10}$  Torr.

The Ta(1 1 0) single crystal was cleaned by Ar<sup>+</sup> ion sputtering followed by repeated flashes to 2500 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 Ta(1 1 0) by resistively heating a 0.5-mm tungsten wire which was wrapped with 0.1-mm Pd wire (Aesar 99.99% pure).

C<sub>2</sub>H<sub>2</sub> (Matheson, 99.6%) was purified using standard fractional distillation procedures on a glass vacuum line to remove traces of acetone, and was stored at pressures less than one atmosphere in a glass bulb. Dosing of all gases was carried out using a glass, microcapillary array doser attached to a leak valve. This doser had a flux enhancement

factor of 50 over the measured background pressure. Exposures are reported in units of Langmuirs ( $1 \text{ L} = 1 \times 10^{-6}$  Torr s) and are corrected for ionization gauge efficiency and doser enhancement factor.

Pd coverages reported in this paper were derived from AES and LEED observations, consistent with our previous study [18]. All C<sub>2</sub>H<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> experiments were performed on Pd films which had been annealed to 400 K, unless otherwise specified, in order to avoid (as much as possible) changes in the Pd film structure during TPD experiments. The heating rate used during TPD experiments was 5 K/s.

The growth and structure of Pd films formed by vapor-deposition on Ta(1 1 0) has been studied previously [14–17]. With the substrate at 300 K, Pd film growth is best described by a Frank-van der Merwe (layer-by-layer) mechanism. The first Pd layer initially grows in a two-dimensional, pseudomorphic structure, probably as islands. Pseudomorphic growth continues up to  $\theta_{\text{Pd}} = 0.65$  (defined relative to the atomic density of the (1 1 1) surface of bulk Pd, i.e.,  $\theta_{\text{Pd}} = 1$ ). Subsequent deposition of Pd causes a “beat” pattern to appear in LEED, with the new spots aligned parallel to the short axis of the distorted hexagon of the substrate. The deposition most likely causes a structural phase-transition to occur within the monolayer and the beat pattern has been attributed to the formation of fcc(1 1 1) islands [16–18]. Further deposition leads to the formation of an fcc(1 1 1)-Pd monolayer with  $\theta_{\text{Pd}} = 1$ . The film continues to grow with an fcc(1 1 1) structure as more Pd is deposited. The beat pattern observed in LEED fades and a symmetric hexagon pattern appears that is characteristic of the fcc(1 1 1) structure. The growth of Pd films a few layers thick on Ta(1 1 0) at 125 K is nearly identical to that at 300 K, with only a small deviation from the layer-by-layer mode.

The bcc(1 1 0) pseudomorphic monolayer is very stable (up to 1350 K), but the fcc(1 1 1) monolayer is stable only up to temperatures of 550–600 K. At these temperatures the beat pattern in LEED disappears and the (1 × 1) pattern appears due to the pseudomorphic Pd monolayer structure with  $\theta_{\text{Pd}} = 0.86$ . This coverage is obtained by removal of Pd

from the monolayer to form clusters on top of the pseudomorphic Pd monolayer. Films thicker than this agglomerate into three-dimensional clusters that are two or three-layers thick at temperatures as low as 370 K. In particular, annealing a  $\theta_{\text{Pd}} = 2$  film to 350–450 K causes a decrease in the Pd AES signal, and heating to 850 K reduces the Pd AES signal to about 85% of its initial value at 125 K. The formation of Pd crystallites with an average cluster-thickness of two layers can account for these changes [18]. At 550–600 K, the beat pattern begins to fade and then disappears completely as a new pattern forms with elongated spots. This new pattern disappears completely at about 850 K and a  $(1 \times 1)$  LEED pattern is observed. The new LEED structure is associated with two or three-layer thick Pd-clusters, with a structure very close to that of a bulk Pd(100) crystal surface, on top of the pseudomorphic Pd monolayer on Ta(110). This structure induces a 4% lattice strain in the Pd clusters compared to the 20% lattice strain in the [110] direction induced by formation of the pseudomorphic structure. For the initial Pd film with  $\theta_{\text{Pd}} = 3$ , the changes that occur in the Pd and Ta AES annealing curves and the behavior of the LEED pattern are similar to that for  $\theta_{\text{Pd}} = 2$ . However, the beat pattern disappears at a temperature of 650 K instead of 600 K.

### 3. Results

#### 3.1. $\text{C}_2\text{H}_2$ chemisorption on a monolayer Pd film, $\theta_{\text{Pd}} = 1$

Fig. 1 shows TPD spectra following  $\text{C}_2\text{H}_2$  exposures on a  $\theta_{\text{Pd}} = 1$  film at 91 K.  $\text{C}_2\text{H}_2$  adsorption under these conditions is nearly reversible, with a very small amount of  $\text{C}_6\text{H}_6$ ,  $\text{C}_2\text{H}_4$  and  $\text{H}_2$  desorption observed. A small exposure of 0.005-L  $\text{C}_2\text{H}_2$  leads to a single desorption peak of  $\text{C}_2\text{H}_2$  at 265 K with a small shoulder on the low temperature side (Fig. 1(a)). Doubling the exposure to 0.01-L  $\text{C}_2\text{H}_2$  increases the size of the peak at 265 K and gives rise to a second peak at 180 K. Further increases in  $\text{C}_2\text{H}_2$  exposure causes the peak at

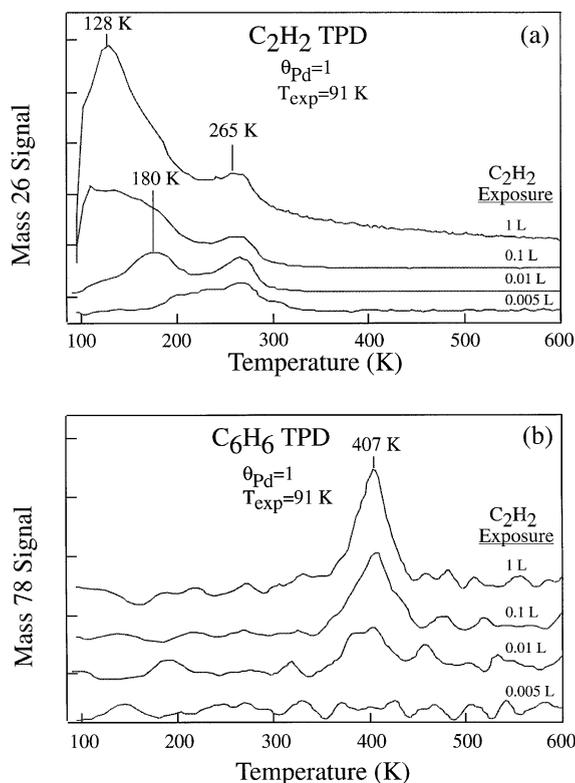


Fig. 1. TPD spectra from  $\theta_{\text{Pd}} = 1$  films as a function of  $\text{C}_2\text{H}_2$  exposure at 91 K: (a)  $\text{C}_2\text{H}_2$  TPD spectra and (b)  $\text{C}_6\text{H}_6$  TPD spectra.

180 K to increase in size and broaden toward lower temperature prior to saturation.

Fig. 1(b) shows  $\text{C}_6\text{H}_6$  TPD spectra following  $\text{C}_2\text{H}_2$  exposures. No  $\text{C}_6\text{H}_6$  desorption occurs following a 0.005-L  $\text{C}_2\text{H}_2$  exposure, but a small  $\text{C}_6\text{H}_6$  desorption peak is seen at 407 K when the  $\text{C}_2\text{H}_2$  exposure is doubled to 0.01 L.  $\text{C}_2\text{H}_2$  exposures up to 1 L, increase the amount of  $\text{C}_6\text{H}_6$  desorption. A small amount of  $\text{C}_2\text{H}_4$  was observed in a broad desorption peak for a 0.005-L exposure. For higher exposures, a small peak grows in near 200 K which broadens and shifts down to 177 K for a 1-L exposure.

Unfortunately,  $\text{H}_2$  TPD spectra cannot be used to quantify  $\text{H}_2$  and other product desorption yields because H atoms are absorbed by the Ta crystal. Thus, there is no desorption of  $\text{H}_2$  over the range 100–600 K that would be attributable to

chemisorbed hydrogen or decomposition of reaction intermediates on the Pd monolayer film. At much higher temperatures (not shown), a substantial amount of  $H_2$  is evolved from H atoms in the bulk of the crystal, but this also contains a contribution from the decomposition of  $C_2H_2$  on the clean edges and back of the Ta crystal.

Much of the previous work on Pd(111) single crystals [1–4] was done using  $C_2H_2$  exposures on the Pd substrate at 175 K. We performed analogous experiments at this temperature to allow direct comparisons to these studies. TPD spectra after  $C_2H_2$  exposures on a  $\theta_{Pd} = 1$  film at 175 K are shown in Fig. 2.  $C_2H_2$  desorption occurs initially in a peak at 265 K following a 0.005-L exposure, with a second peak at 215 K growing in after the exposure is doubled to 0.01 L. Both peaks

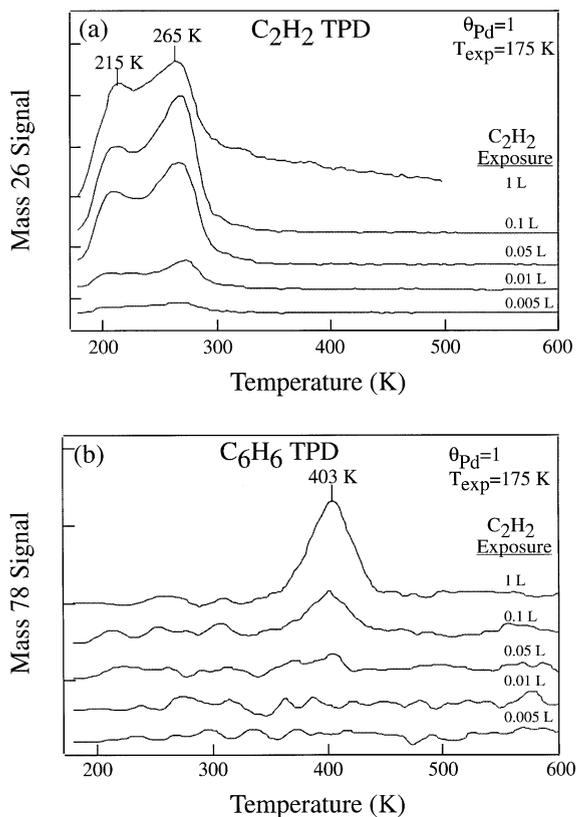


Fig. 2. TPD spectra from  $\theta_{Pd} = 1$  films as a function of  $C_2H_2$  exposure at 175 K: (a)  $C_2H_2$  TPD spectra and (b)  $C_6H_6$  TPD spectra.

grow in size as the  $C_2H_2$  exposure is increased, reaching a maximum after a 1-L  $C_2H_2$  exposure. A 0.1-L  $C_2H_2$  exposure is required before  $C_6H_6$  desorption is observed, which is a ten-fold increase relative to the  $C_2H_2$  exposures required to initiate benzene formation with the substrate at 91 K. A single  $C_6H_6$  desorption peak occurs at 403 K. Only trace amounts of  $C_2H_4$  were observed after  $C_2H_2$  exposures and no  $H_2$  desorption was detected other than that desorbing from the bulk of the Ta crystal.

Fig. 3 compares the product yields calculated from the TPD peak areas. The amount of reversibly adsorbed  $C_2H_2$ , and the amount of  $C_2H_4$  desorbed, is much larger when  $C_2H_2$  is dosed onto

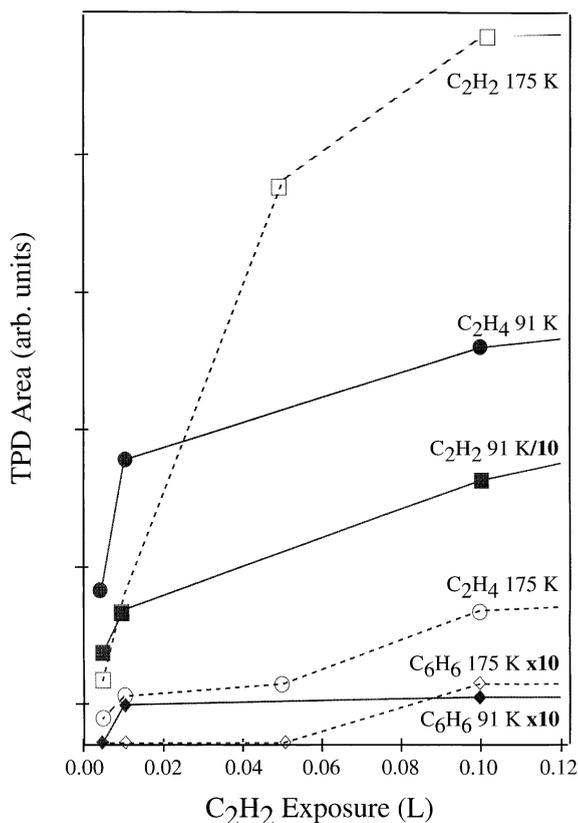


Fig. 3. Comparison of TPD areas for desorption products following  $C_2H_2$  exposures on  $\theta_{Pd} = 1$  films at 91 and 175 K. Note that the  $C_2H_2$  TPD area for exposure at 91 K has been divided by 10 while the benzene TPD areas for both exposure temperatures have been multiplied by 10.

the Pd monolayer film at 90 K than at 175 K. However, the amount of  $C_6H_6$  desorbed does not change, although much larger exposures are required to reach the cyclotrimerization reaction threshold. The additional  $C_2H_2$  adsorbed at 91 K does not affect the amount of  $C_6H_6$  desorbed and the total amount of  $C_6H_6$  desorbed is quite low, only 1% of the amount of the benzene monolayer on a  $\theta_{Pd} = 1$  film (vide infra).

### 3.2. $C_2H_2$ chemisorption on Pd films of increasing thickness

Fig. 4 shows TPD spectra following large, 1-L  $C_2H_2$  exposures onto Pd films of increasing

thickness at 175 K. As shown in Fig. 4(a), reversible  $C_2H_2$  adsorption is nearly eliminated on the  $\theta_{Pd} = 2$  film. For thicker films, ( $\theta_{Pd} = 3$  or 5) both  $C_2H_2$  desorption peaks observed on the monolayer are completely gone and a very broad desorption feature is observed between 300 and 500 K.

Fig. 4(b) shows  $C_6H_6$  TPD spectra following 1-L  $C_2H_2$  exposures onto several Pd films at 175 K. As the Pd film thickness is increased from the monolayer ( $\theta_{Pd} = 1$ ) film to the bilayer ( $\theta_{Pd} = 2$ ) film, the single desorption peak at 403 K disappears and two peaks at 300 and 480 K (with a shoulder at 430 K) are observed. For the trilayer ( $\theta_{Pd} = 3$ ) film,  $C_6H_6$  desorption peaks shift to 250

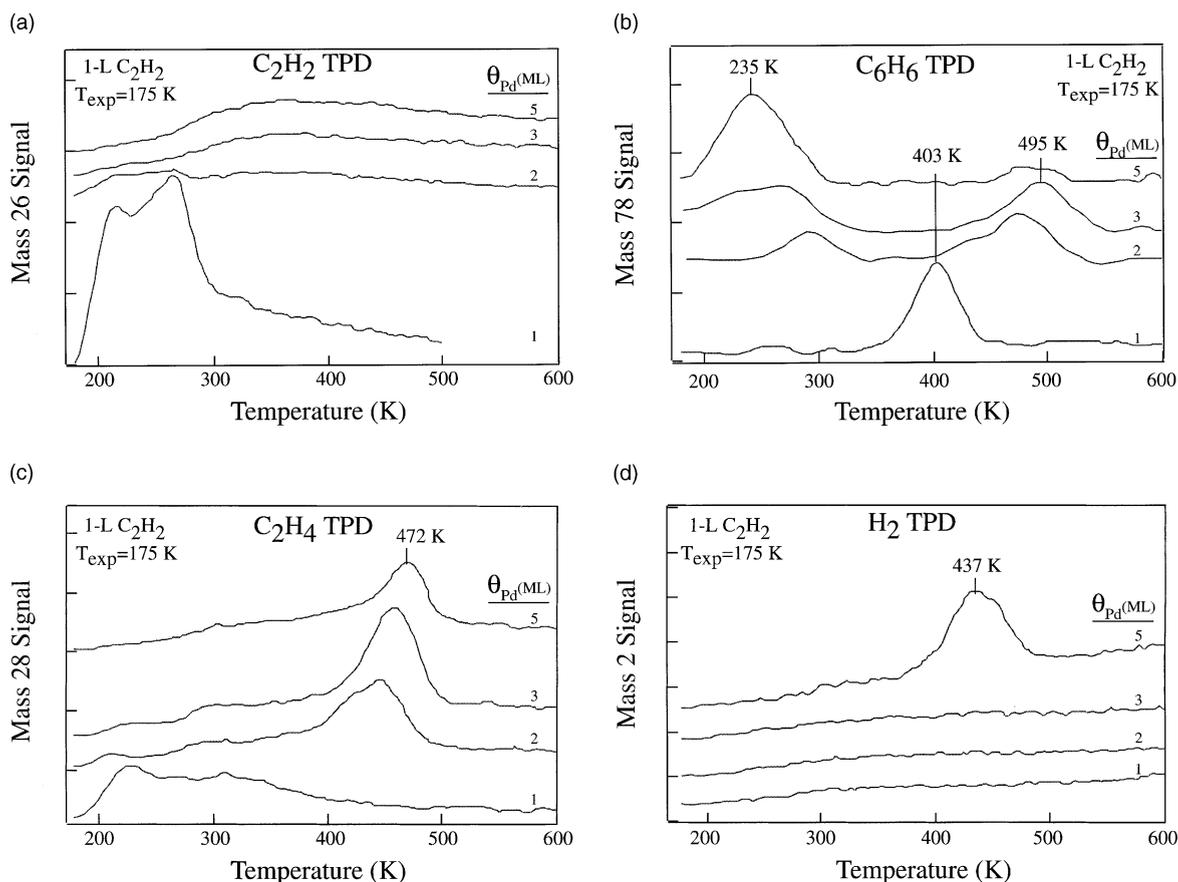


Fig. 4. TPD spectra following 1-L  $C_2H_2$  exposures at 175 K on several Pd films: (a)  $C_2H_2$  TPD spectra, (b)  $C_6H_6$  TPD spectra, (c)  $C_2H_4$  TPD spectra and (d)  $H_2$  TPD spectra.

and 495 K. With an additional increase in film thickness to  $\theta_{\text{Pd}} = 5$ , the  $\text{C}_6\text{H}_6$  desorption peak at 250 shifts to 235 K and increases in size while the peak at 495 K decreases.

As shown in Fig. 4(c), increasing the Pd film thickness from  $\theta_{\text{Pd}} = 1$  to  $\theta_{\text{Pd}} = 2$  resulted in a slight reduction in the amount of  $\text{C}_2\text{H}_4$  desorbed and a shift in desorption temperature from the two low-temperature features to a peak at 445 K. Increasing the Pd film thickness further eliminated low-temperature  $\text{C}_2\text{H}_4$  desorption and caused a shift in the high temperature peak to 472 K.

No  $\text{H}_2$  desorption below 600 K that would be attributable to chemisorbed hydrogen or to the decomposition of reaction intermediates on Pd films was observed for  $\theta_{\text{Pd}} = 1$ –3. For the  $\theta_{\text{Pd}} = 5$  film, a  $\text{H}_2$  desorption peak occurs at 430 K due to the decomposition of adsorbed hydrocarbon species. Unfortunately, even though some hydrogen desorbs from this Pd film,  $\text{H}_2$  TPD spectra cannot be used quantitatively because of competition with H absorption by the Ta crystal, as described above.

The influence of Pd film thickness on the type and amounts of desorption products in TPD is illustrated in Fig. 5. About twice as much  $\text{C}_2\text{H}_2$  and one-half as much benzene is desorbed from the  $\theta_{\text{Pd}} = 1$  film than from the  $\theta_{\text{Pd}} = 5$  film at 175 K. There is also a slight reduction in the amount of  $\text{C}_2\text{H}_4$  desorbing from a thick film ( $\theta_{\text{Pd}} = 5$ ) compared to the thinner  $\theta_{\text{Pd}} = 1$ –3 films exposed at 175 K. An abrupt increase in  $\text{H}_2$  desorption was seen on the  $\theta_{\text{Pd}} = 5$  film at 175 K.

### 3.3. $\text{C}_2\text{H}_2$ chemisorption on a five-layer thick film, $\theta_{\text{Pd}} = 5$

Following small  $\text{C}_2\text{H}_2$  exposures on a  $\theta_{\text{Pd}} = 5$  film at 91 K,  $\text{C}_2\text{H}_2$  desorbs in a small spike in TPD which arises from prompt desorption from the heating wires (Fig. 6(a)). Large  $\text{C}_2\text{H}_2$  exposures cause a desorption peak at 140 K which broadens toward higher temperature with increased  $\text{C}_2\text{H}_2$  exposure. No  $\text{C}_6\text{H}_6$  desorption occurred in concurrent TPD spectra. As shown in Fig. 6(c), a small  $\text{C}_2\text{H}_4$  desorption peak at 465 K, along with a small amount at 250 K, was observed following

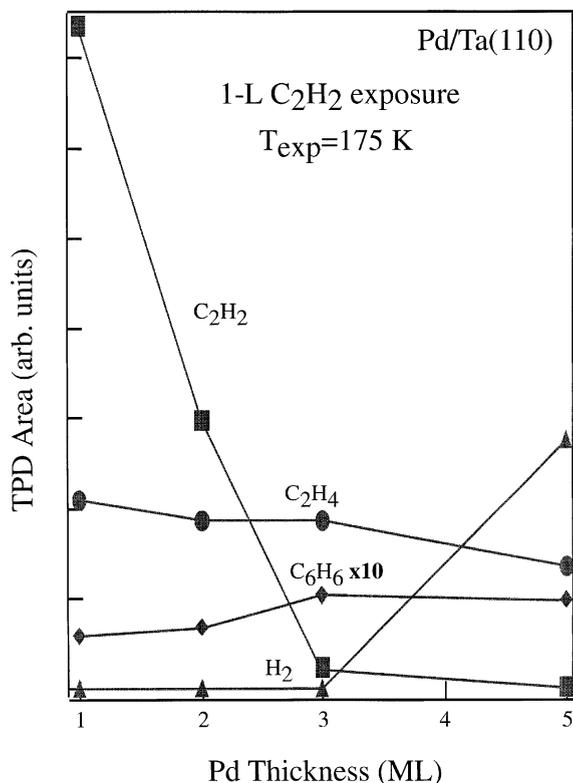


Fig. 5. Comparison of TPD areas of the desorption products as a function of Pd film thickness following 1-L  $\text{C}_2\text{H}_2$  exposures at 175 K. Note that the benzene TPD areas have been multiplied by 10.

a 0.01-L  $\text{C}_2\text{H}_2$  exposure. A broad desorption feature at 152 K emerged following large exposures. Accompanying  $\text{H}_2$  TPD spectra show that  $\text{H}_2$  desorbs in a small peak at 420–450 K for all exposures greater than 0.01-L  $\text{C}_2\text{H}_2$ .

$\text{C}_2\text{H}_2$  exposures were similarly made on a  $\theta_{\text{Pd}} = 5$  film at 175 K. Fig. 7 shows the resulting TPD spectra. No desorption of  $\text{C}_2\text{H}_2$  occurs following small exposures (0.05–0.1 L), but for larger exposures (1–2 L), a broad  $\text{C}_2\text{H}_2$  desorption feature is seen near 330 K. No benzene desorbed for 0.05-L  $\text{C}_2\text{H}_2$  exposures, but larger doses caused benzene desorption peaks at 250 and 500 K.  $\text{C}_2\text{H}_4$  desorbs in a peak at 470 K as shown Fig. 7(c).  $\text{H}_2$  desorbs in a peak at 420 K which shifts to 425–435 K after higher exposures.

Fig. 8 compares the desorption product yields following  $\text{C}_2\text{H}_2$  exposures on the  $\theta_{\text{Pd}} = 5$  film at 91

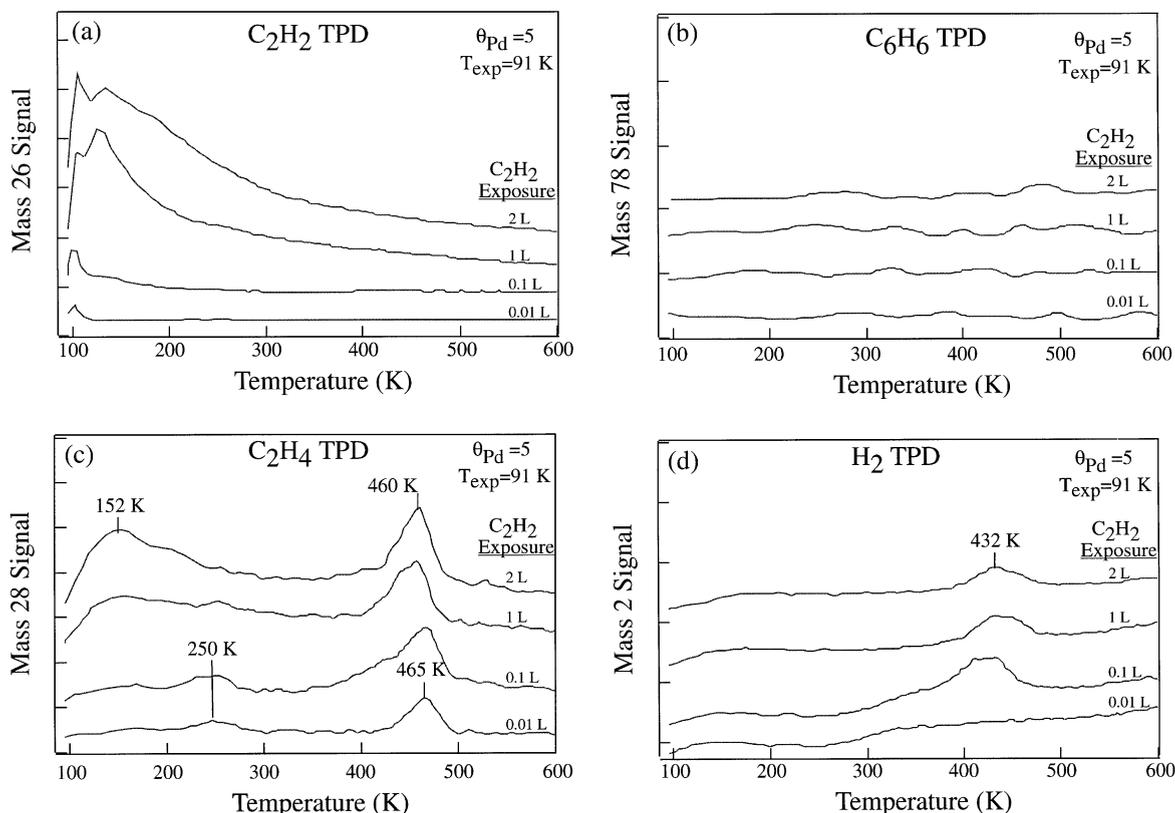


Fig. 6. TPD spectra from  $\theta_{\text{Pd}} = 5$  films as a function of  $\text{C}_2\text{H}_2$  exposure at 91 K: (a)  $\text{C}_2\text{H}_2$  TPD spectra, (b)  $\text{C}_6\text{H}_6$  TPD spectra, (c)  $\text{C}_2\text{H}_4$  TPD spectra and (d)  $\text{H}_2$  TPD spectra.

and 175 K. Dosing at 91 K leads to much larger  $\text{C}_2\text{H}_2$  desorption compared to that observed by dosing at 175 K, and completely eliminates  $\text{C}_6\text{H}_6$  desorption. The amount of  $\text{C}_2\text{H}_4$  and  $\text{H}_2$  desorbed was similar under both conditions.

Formation of an ordered  $\text{C}_2\text{H}_2$  layer exhibiting a  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  LEED pattern was necessary for the formation of benzene on Pd(111) [2,4]. One explanation for the decreased benzene yield for dosing  $\text{C}_2\text{H}_2$  on the  $\theta_{\text{Pd}} = 5$  film at 91 K is that steric interactions or disorder in the  $\text{C}_2\text{H}_2$  adlayer inhibits benzene formation. Unfortunately, no studies on Pd(111) single crystals below 130 K have been performed, and so we do not know if this behavior is unique to the Pd film.

Fig. 9 compares the relative product yields following  $\text{C}_2\text{H}_2$  exposures on  $\theta_{\text{Pd}} = 1$  and  $\theta_{\text{Pd}} = 5$  films at 91 K. Initially, the amount of  $\text{C}_2\text{H}_2$  de-

sorbed from the  $\theta_{\text{Pd}} = 1$  film is more than ten times larger than that from the  $\theta_{\text{Pd}} = 5$  film. However, this difference decreases with increasing  $\text{C}_2\text{H}_2$  exposures, and the amount of  $\text{C}_2\text{H}_2$  desorbed from the two surfaces is nearly equal after a 4-L dose. Benzene desorption following  $\text{C}_2\text{H}_2$  exposures on the  $\theta_{\text{Pd}} = 1$  film at 91 K occurs in a single peak at 400 K and yields approximately 1% of the benzene that desorbs after a benzene monolayer is dosed on that surface. In contrast, no benzene desorbs from the  $\theta_{\text{Pd}} = 5$  film exposed at 91 K. Since nearly equivalent amounts of benzene desorbed from the  $\theta_{\text{Pd}} = 1$  film at 91 and 175 K, additional acetylene adsorbed at 91 K cannot account for the elimination of the cyclotrimerization pathway on the  $\theta_{\text{Pd}} = 5$  film. The amount of  $\text{C}_2\text{H}_4$  desorbed from the  $\theta_{\text{Pd}} = 1$  film was much larger than that for the  $\theta_{\text{Pd}} = 5$  film and there was no  $\text{H}_2$  desorption due to

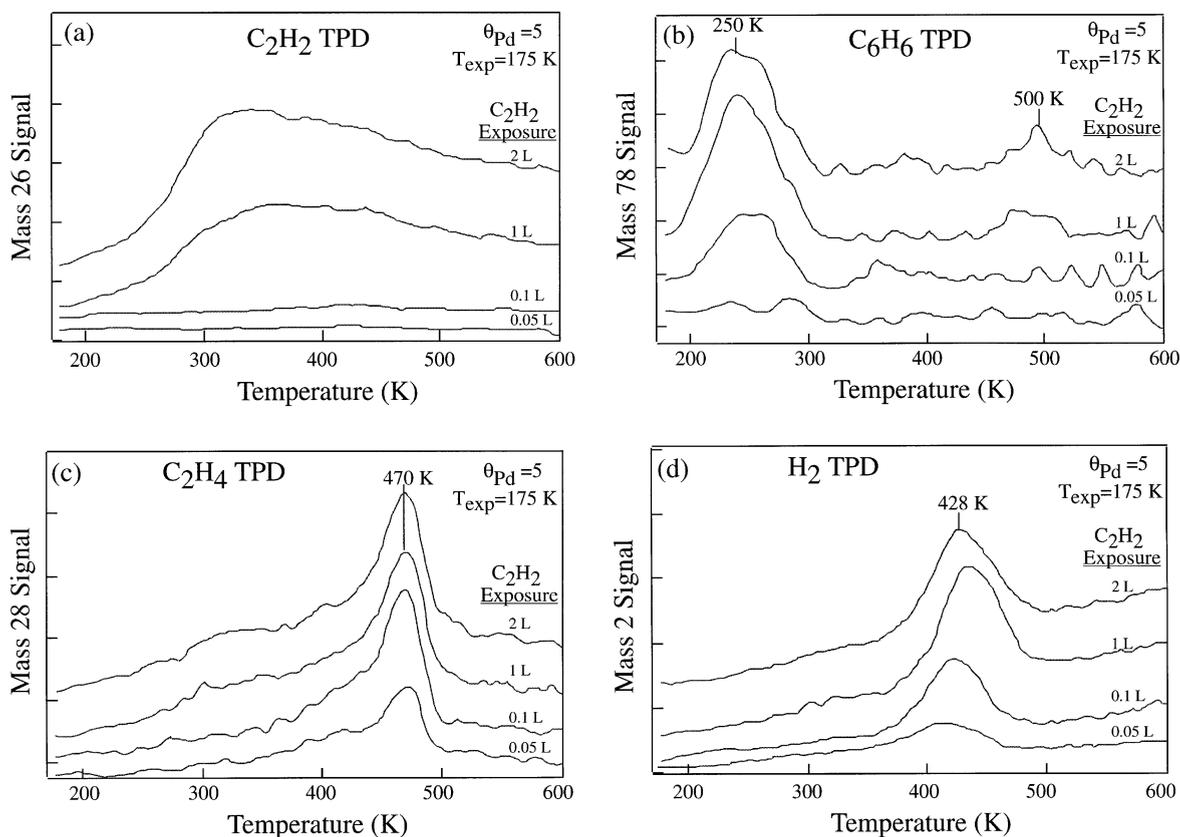


Fig. 7. TPD spectra from  $\theta_{\text{Pd}} = 5$  films as a function of  $\text{C}_2\text{H}_2$  exposure at 175 K: (a)  $\text{C}_2\text{H}_2$  TPD spectra, (b)  $\text{C}_6\text{H}_6$  TPD spectra, (c)  $\text{C}_2\text{H}_4$  TPD spectra and (d)  $\text{H}_2$  TPD spectra.

hydrocarbon decomposition on the  $\theta_{\text{Pd}} = 1$  film. It is possible that only a small amount of  $\text{C}_2\text{H}_2$  decomposition occurs on the  $\theta_{\text{Pd}} = 1$  film. Alternatively, C–H bond cleavage could occur followed by hydrogen absorption into the bulk of the crystal (the heat of solution of H in Ta is larger than the heat of adsorption of H on Pd).

Fig. 10 compares the relative product yields following exposures on  $\theta_{\text{Pd}} = 1$  and  $\theta_{\text{Pd}} = 5$  films at 175 K. For small  $\text{C}_2\text{H}_2$  exposures, more  $\text{C}_2\text{H}_2$  is desorbed from the  $\theta_{\text{Pd}} = 1$  compared to the  $\theta_{\text{Pd}} = 5$  film, but the amount of  $\text{C}_2\text{H}_2$  desorption from the  $\theta_{\text{Pd}} = 5$  film continues to increase for larger  $\text{C}_2\text{H}_2$  exposures. About twice as much benzene desorbed from the  $\theta_{\text{Pd}} = 5$  film as for the  $\theta_{\text{Pd}} = 1$  film for  $\text{C}_2\text{H}_2$  exposures at 175 K. In contrast, the amount of  $\text{C}_2\text{H}_4$  desorption from the  $\theta_{\text{Pd}} = 5$  film was about half that from the  $\theta_{\text{Pd}} = 1$  film.

### 3.4. Consecutive TPD experiments on a $\theta_{\text{Pd}} = 1$ and $\theta_{\text{Pd}} = 5$ film

From the preceding discussion, we conclude that very little  $\text{C}_2\text{H}_2$  decomposition occurs on the  $\theta_{\text{Pd}} = 1$  film while a substantial amount of decomposition occurs on the  $\theta_{\text{Pd}} = 5$  film. To further test this hypothesis, we conducted consecutive TPD experiments following 1-L  $\text{C}_2\text{H}_2$  exposures on  $\theta_{\text{Pd}} = 1$  and  $\theta_{\text{Pd}} = 5$  films at 175 K.

No changes were observed for consecutive TPD experiments for  $\text{C}_2\text{H}_2$  dosed on the Pd monolayer film at 175 K. These results confirm our assertion that decomposition is not occurring on this surface to any great extent since, otherwise, one would expect to observe changes in the product distributions due to the presence of reactively formed coadsorbates.

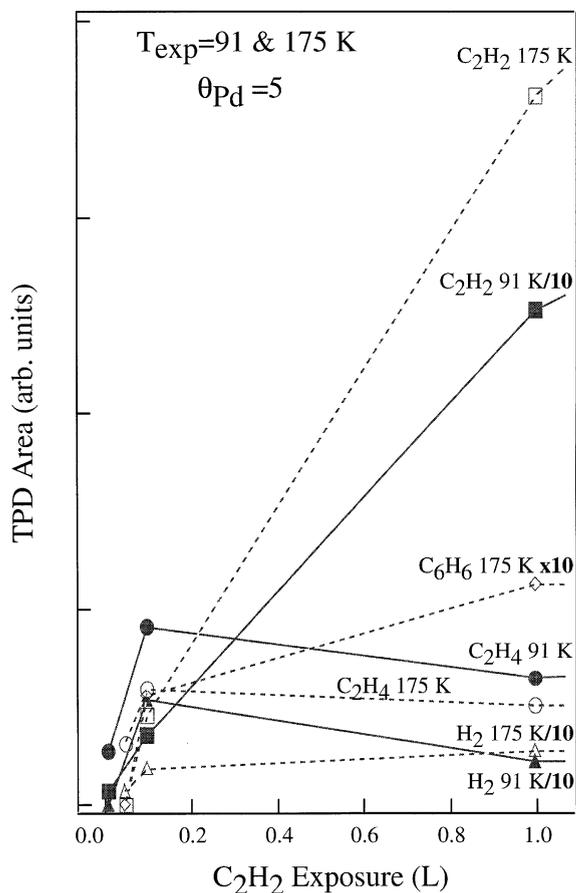


Fig. 8. Comparison of TPD areas for desorption products following  $C_2H_2$  exposures on  $\theta_{Pd} = 5$  films at 91 and 175 K. Note that the  $C_2H_2$  TPD area for exposure at 91 K and the  $H_2$  TPD areas for both exposure temperatures have been divided by 10, while the benzene TPD areas for both exposure temperatures have been multiplied by 10.

A similar consecutive TPD experiment was performed on the  $\theta_{Pd} = 5$  film at 175 K as shown in Fig. 11(a)–(d). No changes were observed in the  $C_2H_2$  desorption spectra as the TPD experiments were repeated. However, repeating the TPD experiment caused the  $C_6H_6$  peak at 250 K to broaden toward higher temperatures and the peak initially at 500 K to shift down to 450 K and increase in size. Repeating for a third time eliminated  $C_6H_6$  desorption from the high temperature state and significantly reduced the size of the 250 K peak. The size of this peak decreased further after

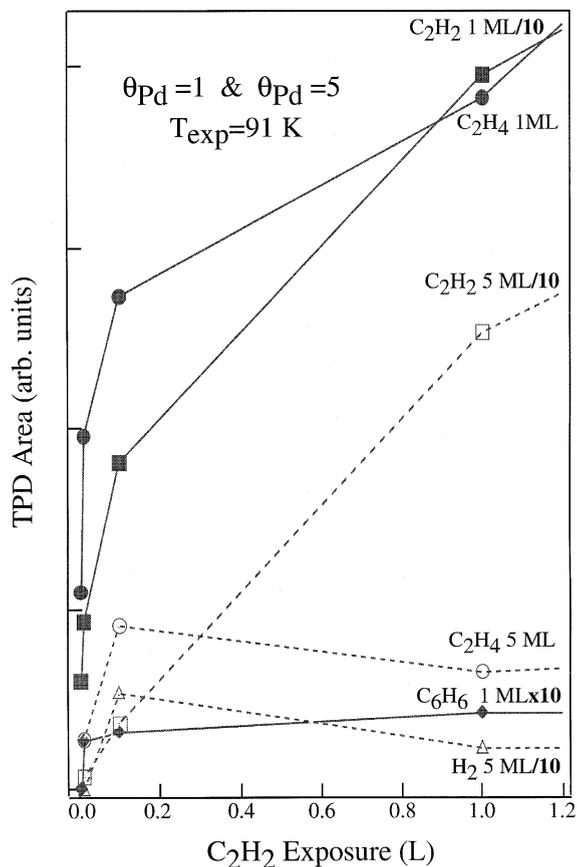


Fig. 9. Comparison of TPD areas for desorption products following  $C_2H_2$  exposures on  $\theta_{Pd} = 1$  and  $\theta_{Pd} = 5$  films at 91 K. Note that the  $C_2H_2$  TPD areas and the  $H_2$  TPD areas for both film thicknesses have been divided by 10, while the benzene TPD areas for both film thicknesses have been multiplied by 10.

the fourth TPD experiment. The  $C_2H_4$  desorption peak decreased in size in the second TPD spectra and disappeared following the third. Repeating the TPD experiment eliminated any  $H_2$  desorption at 420 K, and TPD showed only  $H_2$  desorption from the bulk of the Ta crystal.

For both films, the amount of  $C_2H_2$  desorption remained nearly constant as the TPD experiments were repeated, with twice as much  $C_2H_2$  desorbing from the  $\theta_{Pd} = 1$  film compared to the  $\theta_{Pd} = 5$  film. For the  $\theta_{Pd} = 1$  film, the amount of benzene desorbed was unchanged as TPD experiments were repeated. In contrast, benzene desorption from the  $\theta_{Pd} = 5$  film doubled for second TPD experiment

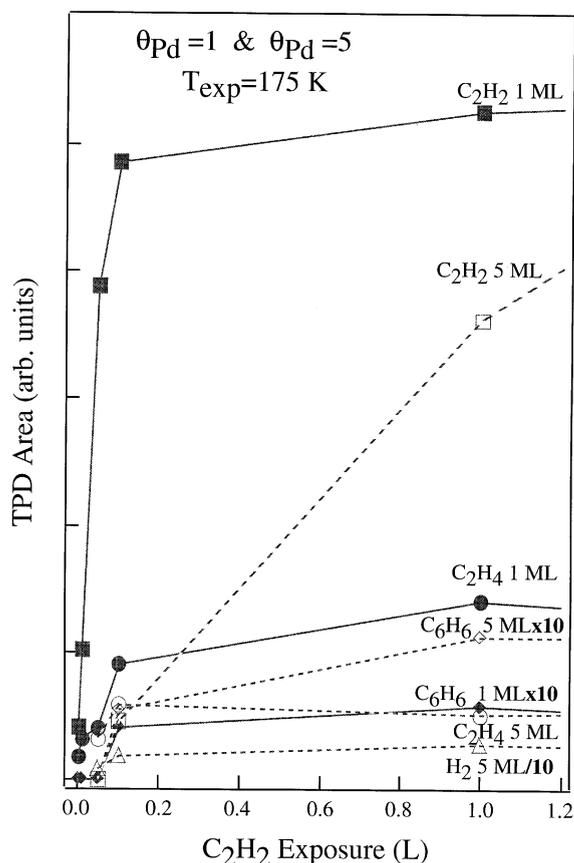


Fig. 10. Comparison of TPD areas for desorption products following  $C_2H_2$  exposures on  $\theta_{Pd} = 1$  and  $\theta_{Pd} = 5$  films at 175 K. Note that the  $H_2$  TPD area for the  $\theta_{Pd} = 5$  film has been divided by 10, while the benzene TPD areas for both film thicknesses have been multiplied by 10.

compared to the first one. The amount of benzene desorbed decreased for the third TPD experiment, and almost no benzene desorption was observed during the fourth experiment. We explain this trend on the  $\theta_{Pd} = 5$  film by suggesting that the small amount of residual carbon adsorbed on the surface following the first TPD acts much like other additives [6,7] to promote cyclotrimerization. However, as the coverage of adsorbed carbon increases in each subsequent TPD experiment, benzene formation is eventually eliminated due to site-blocking.

The amount of  $C_2H_4$  and  $H_2$  desorbing in consecutive TPD experiments for the  $\theta_{Pd} = 1$  film did

not change. However, for the  $\theta_{Pd} = 5$  film, both  $C_2H_4$  and  $H_2$  desorption was nearly eliminated in the second TPD experiment and was completely absent in the third. The decrease in the  $C_2H_4$  desorption occurred concurrently with a large increase in benzene desorption.

### 3.5. Benzene $C_6H_6$ chemisorption on $\theta_{Pd} = 1$ and $\theta_{Pd} = 5$ films

Fig. 12 shows that a small  $C_6H_6$  exposure on a  $\theta_{Pd} = 1$  film at 91 K leads to a  $C_6H_6$  desorption peak at 400 K. No other desorption products were observed. Redhead analysis, [19] assuming a desorption order of one and a value of  $10^{13} s^{-1}$  for the pre-exponential factor, was used to estimate a desorption activation energy  $E_d$  of 24 kcal/mol. With increasing coverage,  $C_6H_6$  desorption shifted toward lower temperatures and broadened, indicating that more weakly bound benzene is adsorbed at higher exposures. A tilted benzene species has been proposed on Pd(111) [2,4]. An exposure of 0.14-L  $C_6H_6$  initiates the formation of a multilayer which initially desorbs in a peak at 165 K.

Fig. 13 shows benzene TPD curves following benzene exposures on a  $\theta_{Pd} = 5$  film at 91 K. Exposures larger than 0.025 L were required before  $C_6H_6$  desorption was observed. Initially, the  $C_6H_6$  desorption peak was at 495 K, just as on bulk-terminated Pd(111) surfaces [20]. Using Redhead analysis, we estimate that  $E_d = 30$  kcal/mol for this state. This peak broadens towards lower temperature at high  $C_6H_6$  exposures and eventually a multilayer peak occurs at 180 K.

Fig. 14 shows a direct comparison of the TPD spectra following a 0.1-L  $C_6H_6$  exposure onto both the  $\theta_{Pd} = 1$  and 5 films, illustrating the large difference in benzene desorption yield for the two films. The amount of reversibly adsorbed benzene on the  $\theta_{Pd} = 1$  film is more than 10 times that on the  $\theta_{Pd} = 5$  film.

## 4. Discussion

Monolayer and bilayer Pd films on Ta(110) have altered  $C_2H_2$  and  $C_6H_6$  chemisorption prop-

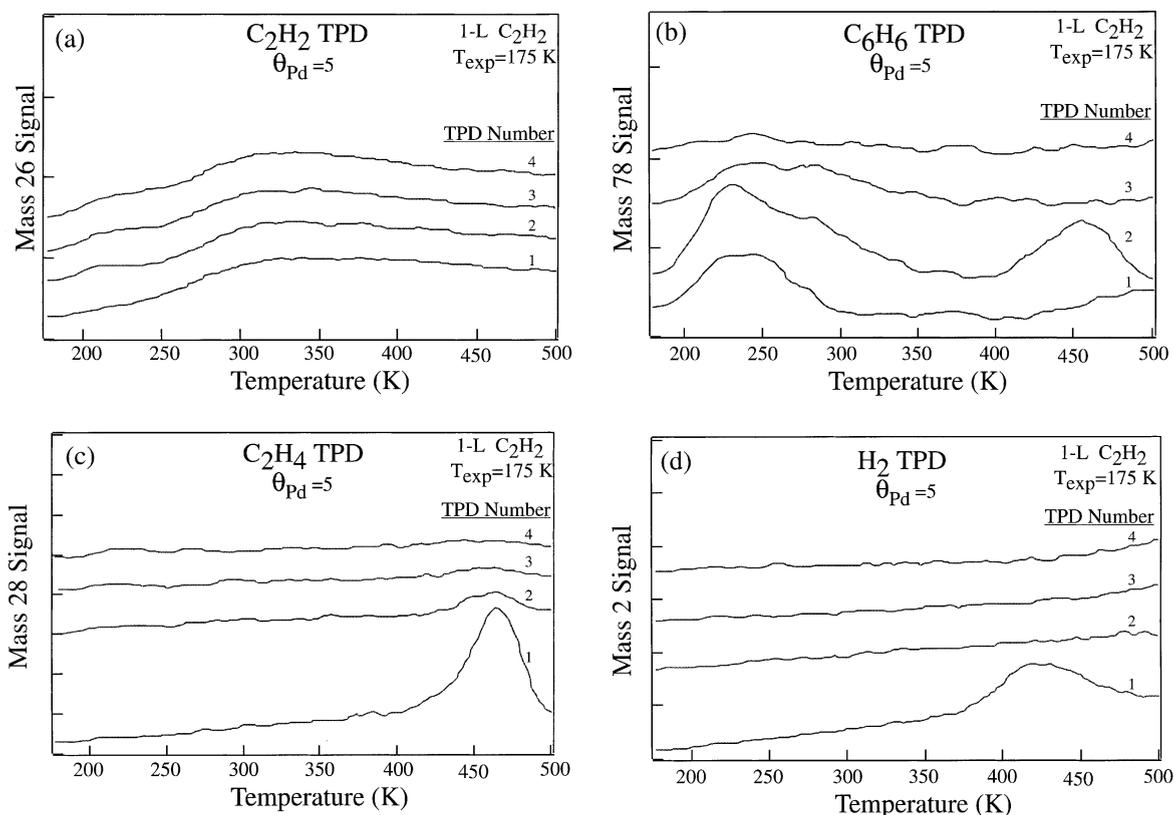


Fig. 11. Consecutive TPD spectra from a  $\theta_{\text{Pd}} = 5$  film following 1-L  $\text{C}_2\text{H}_2$  exposures at 175 K: (a)  $\text{C}_2\text{H}_2$  TPD spectra, (b)  $\text{C}_6\text{H}_6$  TPD spectra, (c)  $\text{C}_2\text{H}_4$  TPD spectra and (d)  $\text{H}_2$  TPD spectra.

erties compared to bulk Pd(1 1 1), with the largest differences observed on the  $\theta_{\text{Pd}} = 1$  film. The propensity for reversible adsorption of  $\text{C}_2\text{H}_2$  is greatly increased on the  $\theta_{\text{Pd}} = 1$  film relative to bulk Pd(1 1 1) and nearly all surface carbon is removed from the surface by 500 K (including reactions to desorb other products). In contrast, XPS data for  $\text{C}_2\text{H}_2$  adsorbed on Pd(1 1 1) at 300 K indicates that only 20% of the carbon on the surface is removed by 650 K [2]. Thus barriers to non-specific  $\text{C}_2\text{H}_2$  dehydrogenation are increased while barriers to hydrogenation and coupling reactions are the same or lower on the Pd monolayer compared to bulk Pd(1 1 1) surfaces.

In contrast to results for  $\text{H}_2$ , CO, NO, and  $\text{C}_2\text{H}_4$  chemisorption on the Pd monolayer on Ta(1 1 0), the strength of the  $\text{C}_2\text{H}_2$ -Pd chemisorption bond is not weakened substantially on the Pd monolayer

relative to bulk Pd(1 1 1).  $\text{C}_2\text{H}_2$  desorbs in peaks at 180 and 265 K on the Pd monolayer, while Gentle and Muettetier reported  $\text{C}_2\text{H}_2$  desorption peaks at 188 and 300 K on bulk Pd(1 1 1) [3].

We propose that this difference between  $\text{C}_2\text{H}_2$  and small molecules like CO and NO exists because of the strong  $\text{C}_2\text{H}_2$ -Pd chemisorption bond that can be formed if Pd electronic rehybridization occurs. Initially, Pd is rehybridized on Ta(1 1 0) to have a filled valence d-band (analogous to Ag) in order to maximize Pd-Ta bonding, but there is a competition between maximizing the Pd-adsorbate bonding and the Pd-substrate bonding in the presence of adsorbates. Strongly adsorbed molecules at the surface of the Pd film can change the balance to maximize the Pd-adsorbate bond and alter the Pd-substrate bond. We label this process “adsorbate-induced rehybridization”, and

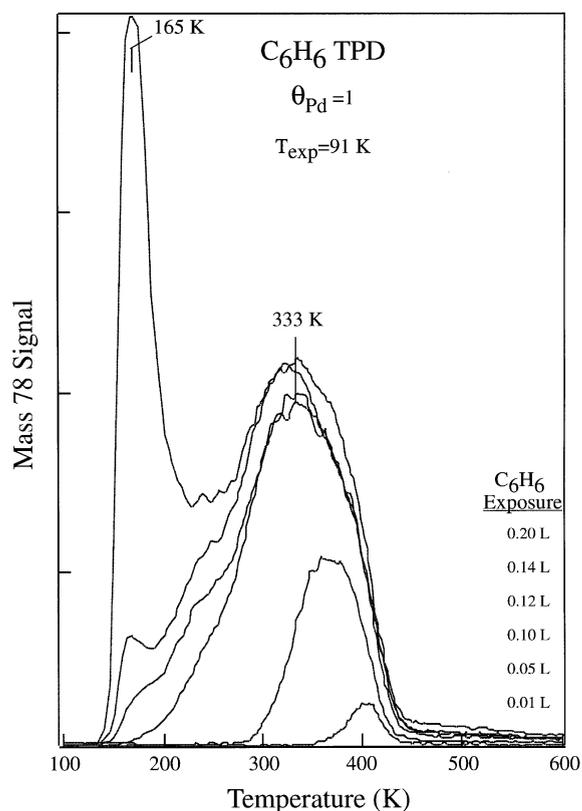


Fig. 12.  $C_6H_6$  TPD spectra following  $C_6H_6$  exposures on  $\theta_{Pd} = 1$  films at 91 K.

consider that it is analogous to adsorbate-induced reconstruction. This should be general behavior for bimetallic systems. For example, similar behavior was observed on Pd films on Mo(100), where  $C_2H_4$  chemisorption was weakened substantially, but not  $C_2H_2$  chemisorption [12].

$C_6H_6$  desorbs also during TPD of the  $C_2H_2$  monolayer on the  $\theta_{Pd} = 1$  film. However, cyclotrimerization is altered and appears to be only a minor reaction path on the  $\theta_{Pd} = 1$  film, accounting for only 1% of a  $C_6H_6$  monolayer ( $\sim 0.15$  ML).  $C_6H_6$  desorption appears to be desorption-rate limited, as on bulk Pd(111) [2] where it desorbs at the same temperature as does  $C_6H_6$  from  $C_6H_6$  exposures.

$C_6H_6$  desorption from cyclotrimerization on the  $\theta_{Pd} = 5$  film was very similar to that observed on bulk Pd(111). In both cases,  $C_6H_6$  desorption

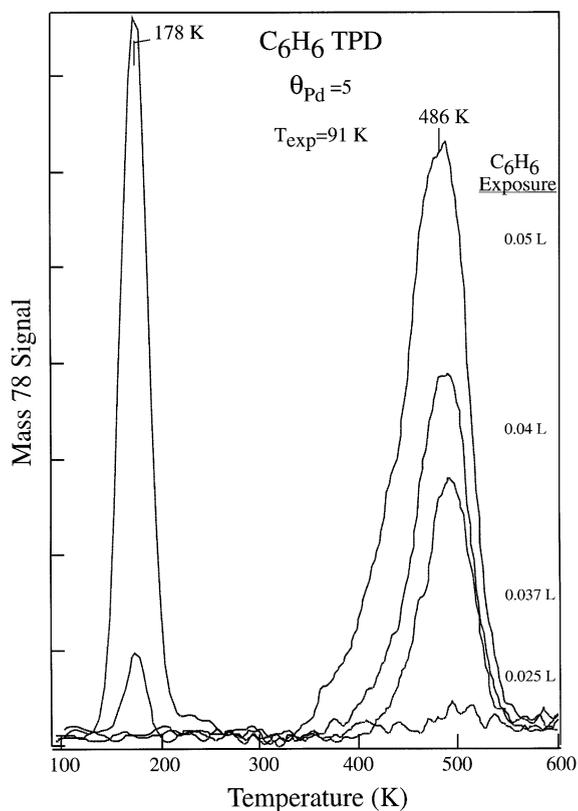


Fig. 13.  $C_6H_6$  TPD spectra following  $C_6H_6$  exposures on  $\theta_{Pd} = 5$  films at 91 K.

peaks were observed at 250 and 500 K. The main difference seen for the Pd film with  $\theta_{Pd} = 5$  was that most of the  $C_6H_6$  desorbs at 250 K, whereas nearly equal amounts were desorbed in both peaks on bulk Pd(111) [1–4]. The atomistic structure of the thin film may prevent the formation of flat-lying benzene or prevent its desorption from the surface. While  $C_2H_2$  desorption occurs at 188 and 300 K on bulk Pd(111) [3], the small broad  $C_2H_2$  desorption peak following  $C_2H_2$  exposures on a Pd film with  $\theta_{Pd} = 5$  at 175 K may indicate acetylene-induced morphology changes occurring as the surface is heated during a TPD experiment.

Films of intermediate thickness ( $\theta_{Pd} = 2$  and 3) appear to have some characteristics of both the  $\theta_{Pd} = 1$  and  $\theta_{Pd} = 5$  films for both  $C_2H_2$  adsorption and reaction. Benzene desorption from  $\theta_{Pd} = 2$  and  $\theta_{Pd} = 3$  films mostly resembles that from a

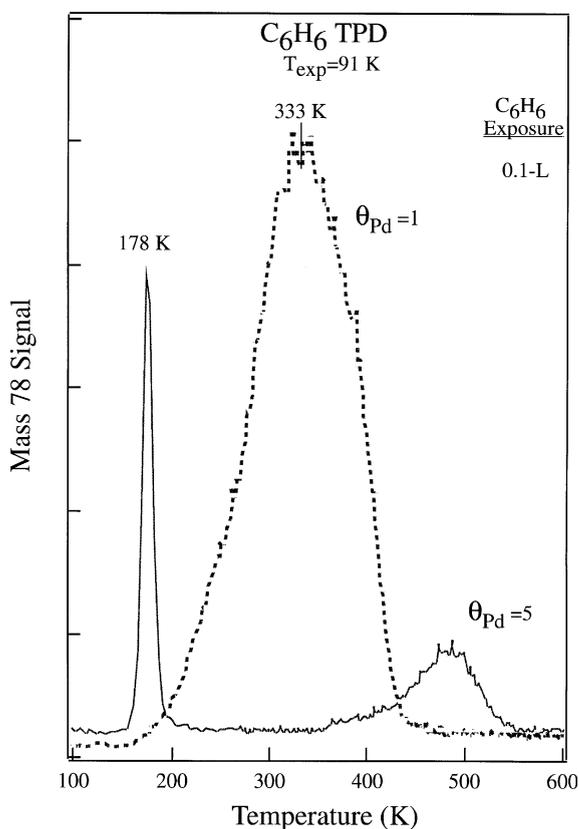


Fig. 14. Comparison of  $C_6H_6$  TPD spectra from  $\theta_{Pd} = 1$  and  $\theta_{Pd} = 5$  films.

$\theta_{Pd} = 5$  film. Thus, formation of the Pd monolayer on Ta(110) provides the ability for tuning the chemisorption properties of Pd. However, this tuning is limited to the first few monolayers of Pd film for strongly bound adsorbates.

$C_2H_2$  chemisorption studies have also been carried out on ultrathin Pd films on Mo(100) [2] and W(211) [11]. As for Pd/Ta(110), there was not a large change in the  $C_2H_2$ -Pd bond strength for  $C_2H_2$  adsorbed on the Pd monolayer film on Mo(100).

Benzene chemisorption is also altered on ultrathin Pd films on Ta(110). The most strongly adsorbed benzene is bound on the  $\theta_{Pd} = 1$  film about 6 kcal/mol less strongly than it is on the thick ( $\theta_{Pd} = 5$ ) Pd film or bulk Pd(111) [4,20]. Additionally, the propensity for reversible adsorption is greatly increased on the  $\theta_{Pd} = 1$  film. On the Pd

monolayer, benzene also forms more weakly bound species as evidenced by the desorption peak which extends to temperatures as low as 200 K. The  $\theta_{Pd} = 5$  film resembles bulk Pd with respect to benzene chemisorption.

## 5. Conclusions

Ultrathin Pd films deposited on Ta(110) have altered chemisorption properties for  $C_2H_2$  and  $C_6H_6$  when compared to bulk Pd(111). The propensity for reversible adsorption is greatly increased on the  $\theta_{Pd} = 1$  film for both molecules. The cyclotrimerization of  $C_2H_2$  to form  $C_6H_6$  was found to occur on the  $\theta_{Pd} = 1$  film, and the reactively formed  $C_6H_6$  desorbs from a single state at 400 K. In contrast, the same reaction on Pd(111) results in  $C_6H_6$  desorption at 250 and 500 K. The different desorption temperature for reactively-formed  $C_6H_6$  on the  $\theta_{Pd} = 1$  film is attributed to a more weakly bound, flat-lying benzene species. This is consistent with TPD spectra of  $C_6H_6$  following  $C_6H_6$  exposures on a  $\theta_{Pd} = 1$  film, which also show  $C_6H_6$  desorption at 400 K. Pd films two to three monolayers thick have some characteristics of the  $\theta_{Pd} = 1$  film as well as some characteristics of bulk Pd(111) while thicker ( $\theta_{Pd} = 5$ ) Pd films in general resemble bulk Pd(111).

We explain the differences observed between the interaction of  $C_2H_2$  with the Pd monolayer and that of other small molecules like CO and NO to arise because of the strong  $C_2H_2$ -Pd chemisorption bond that can be formed if Pd electronic rehybridization occurs. We label this process “adsorbate-induced rehybridization”, and consider that it is analogous to adsorbate-induced reconstruction. This should be general behavior for bimetallic systems.

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