

A survey of acetylene cyclization on single crystals, supported particles and bimetallic surfaces: new cyclization studies on bimetallic Pd/W(211)

Ihab M. Abdelrehim^a, Kalman Pelhos^a, Theodore E. Madey^{a,*}, Joseph Eng Jr.^b,
Jingguang G. Chen^b

^a *Laboratory for Surface Modification, Department of Physics and Astronomy, Rutgers University, Piscataway, NJ, 08855, USA*

^b *Corporate Research Laboratories, Exxon Research and Engineering, Amundale, NJ, 08801, USA*

Received 16 June 1997; accepted 17 September 1997

Abstract

A review of acetylene cyclotrimerization to form benzene is presented. This structure-sensitive catalytic reaction is of particular interest because C–C bonds can be formed readily on certain surfaces under ultra high vacuum (UHV) conditions. In addition, we present new results for acetylene cyclotrimerization on a bimetallic surface, Pd deposited on W(211). Pd on W is chosen because it is a morphologically unstable system and W(211) facets develop after annealing Pd/W(111) to ≥ 700 K. Temperature programmed desorption (TPD) data reveal negligible amounts of benzene detected from acetylene adsorption on clean W(211). A monolayer (ML) Pd film on W(211) decreases the high reactivity towards acetylene decomposition and catalyzes the cyclotrimerization reaction; benzene desorbs with TPD peaks at 210 K and ~ 470 K. The use of high resolution electron energy loss spectroscopy (HREELS) has shown the desorption of benzene products to be reaction rate-limited on the ~ 1.0 ML Pd/W(211) surface. © 1998 Elsevier Science B.V.

Keywords: Bimetallic; Cyclotrimerization; Acetylene

1. Introduction

Acetylene cyclization to form benzene ($3\text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6$) is an important reaction that has been investigated on a variety of single crystal surfaces under UHV conditions for over a decade [1–32]. In addition, acetylene cyclization has been observed to occur in high pressure [9] and homogeneous organometallic [10,11] catalytic studies. The correlation between UHV, high pressure and organometallic studies makes

this an important reaction to analyze. The motivation for studying acetylene cyclization (also called cyclotrimerization) under UHV conditions is its extreme structure sensitivity: certain single crystal surfaces with specific crystal plane orientations such as Pd(111) [1–9,12–21,24–27] and Cu(110) [22,23] are highly active, whereas the reaction is virtually inactive on the Pd(110) surface [4,9]. The specificity of this reaction to the surface conditions of well-ordered single crystals (i.e., Pd(110) and Cu(110)) gives it a distinct quality for probing the effects of surface electronic and geometric structure.

* Corresponding author.

A significant aspect of this reaction is the remarkable efficiency of making C–C bonds under UHV conditions on Pd(111). In addition, isotopic studies reveal that the reactants do not undergo C–C or C–H bond scission [24]. Further investigations have provided evidence that the reaction on Pd(111) is a stepwise process, with the rate determining step being the addition of acetylene to a C_4H_4 intermediate [2,13–18,26,30,33]. On the other hand, Pt(111) (a metal in the same group as Pd) results in acetylene decomposition, with very little desorption of benzene following adsorption of acetylene [34]. The Pt(111) surface does not facilitate the cyclization reaction, apparently due to stronger carbon–metal interactions than are present on the Pd(111) surface.

In addition to the plethora of acetylene cyclization studies on elemental single crystal metal surfaces [1–32], there have also been reports of acetylene cyclization studies on bimetallic surfaces [34–40] and supported metals [33,41]. Model bimetallic surfaces include Pd/Au(111) [36,37], Au/Pd(111) [38], Pd/Mo(100) [39], Pd/Ta(110) [40] and Sn/Pt(111) [34]; of these, the Pd/Au [36–38], Pd/Ta [40] and Sn/Pt [34] systems were the only bimetallics observed to catalyze the cyclization reaction. Pierce and Barteau also reported acetylene cyclotrimerization on reduced $TiO_2(001)$ [42]. Bertolini et al. [41] were the first to observe acetylene cyclization to benzene on supported Ni catalysts, while the only reported acetylene cyclization studies on high surface area Pd materials (i.e., actual catalytic turnovers) were performed by Ormerod and Lambert [33]. Kinetic and mechanistic studies of the acetylene/Pd system were also conducted by Tysoe et al. [2] and Patterson and Lambert [24,25] and Abdelrehim et al. [26,27] in order to understand the cyclization process in more detail.

The understanding of chemical reactivities of bimetallic systems is of practical importance since numerous industrial catalysts consist of bimetallics and alloys [43–47]. A detailed un-

derstanding of metal–metal interactions with respect to physical (i.e., structural and electronic) properties of the bimetallic system is needed prior to initiating investigations of reaction processes. It is understood that a bimetallic system can exhibit chemical and catalytic properties that are different from those observed on the individual pure metal surfaces. In some cases these systems provide improved catalytic activity as well as selectivity. For instance, cyclotrimerization of acetylene does not occur on a pure Au(111) surface, but as little as one monolayer (ML) of Pd activates the reaction [36,37]. On the other hand, depositing Au on Pd(111) also catalyzes the cyclization reaction [38], even though pure Au does not, indicating that ligand or electronic effects are significant [48]. The adsorption of acetylene and subsequent formation of benzene and butadiene on Sn/Pt(111) further support the claim that a pure, highly reactive metal (i.e., Pt(111)) on which reactants and products can dissociate readily, can be changed to a less reactive bimetallic surface [34]. In addition, high pressure investigations on Sn/Pt(111) demonstrate the presence of a C_4 species as well as a distribution of C_6 products which include linear and cyclic hydrocarbons [49]. The varied C_6 product distribution was not observed under UHV conditions indicating that the reactant pressure is also an important factor that influences the reaction pathway to product formation.

Several outstanding issues need to be addressed for a better understanding of acetylene cyclization. For instance, the observation that the row-and-trough type surfaces of some metals catalyzes acetylene cyclotrimerization with high efficiency (e.g., Cu(110) but not Pd(110)), is still not understood. In addition, it would be of interest to know if the C_4H_4 intermediate believed to be present on hexagonal substrates (e.g., Pd(111), Sn/Pt(111), etc.) is also seen on surfaces of different symmetry. Furthermore, the effects of bimetallics and additives on reaction rates needs to be further investigated. The

goal of this paper is 2-fold: (1) to review briefly important studies relevant to acetylene cyclization with emphasis on results that have appeared since the Lambert and Ormerod reviews [21,50], and (2) to present new preliminary results for acetylene cyclization over a bimetallic surface (Pd/W(211)). The Pd/W(211) studies are the first investigations of acetylene cyclotrimerization to benzene on a bimetallic surface having 2-fold symmetry with a row-and-trough structure.

2. Overview

2.1. Single crystal investigations

The most widely used technique for the detection of benzene from acetylene cyclization is TPD. A central question is, at what temperature does the product form on the surface? For a desorption-limited process, the formation temperature for benzene from acetylene can be much lower than the actual desorption temperature observed with TPD. The use of spectroscopic or laser desorption techniques is therefore needed to detect the benzene species on the surface, prior to desorption. Using laser induced thermal desorption spectroscopy (LITD) coupled with Fourier transform mass spectrometry (FTMS), the onset of acetylene cyclization to form benzene has been observed at ~ 150 K on a clean Pd(111) surface [26]. Using LITD [51–55], the laser rapidly heats (~ 1000 K in ~ 10 ns) a small spot on a surface, ~ 1 mm in diameter. This fast heating ($\sim 10^{11}$ K/s) causes entropic factors to be favored [56] and, in most cases, results in the desorption of intact surface species [57–60]. Thus, for example, employing TPD, a low temperature benzene desorption peak appears at 210–250 K (assigned to the desorption of a tilted benzene species) while a high temperature peak appears at 500 K (assigned to the desorption of flat lying benzene) [1–5,21]. Furthermore, for C_2H_2 on Pd(111) the approximate yield for benzene formation using TPD is

$\sim 25\%$ [61]. In contrast, benzene is detected at ~ 50 K lower with $\sim 100\%$ conversion efficiency on the surface using LITD [26], demonstrating that reaction pathways that lead to benzene decomposition are present prior to or during conventional thermal desorption. In addition, the lower yield of reactively formed benzene in TPD may also be associated with the saturation of reaction sites required for cyclization to take place. Based on TPD measurements, Cu(110) is the only single crystal surface studied to date which catalyzes the cyclotrimerization reaction at very high efficiency ($\sim 85\%$) [23]. Since the hexagonal symmetry generally believed to be necessary for proper acetylene orientation is not present on this surface, then reactant mobility as well as surface electronic structure may play crucial roles in the formation of benzene on the Cu(110) surface.

A number of investigations have focused on identifying the intermediates of the cyclotrimerization mechanism [2,13–18,26,30,62]. A variety of evidence points to the role of a C_4H_4 intermediate formed by the coupling of two C_2H_2 species. Evidence for the presence of C_4H_4 in acetylene cyclization is based on molecular beam [2] and LITD/FTMS [26,27] measurements. The molecular beam investigations showed the desorption of benzene and C_4H_x species when Pd(111) was exposed to a beam of acetylene [2]. In addition, the C_4H_4 intermediate was also observed in the form of 1,3-butadiene (C_4H_6) when an acetylene covered Pd(111) surface was resistively heated to ~ 300 K and exposed to a Nd:YAG laser [26]. The LITD results favor a stepwise reaction mechanism with the rate determining step being the addition of acetylene to a C_4H_4 surface species [26,27]. Other studies have focused on the surface chemistry of C_4H_4 -containing precursor molecules, or on the desorption of C_4H_4 -containing products. For example, near-edge X-ray absorption fine structure (NEXAFS) studies have indicated that the C_4H_4 intermediate produced after $C_4H_4Cl_2$ adsorption is a tilted metallocycle [30]. Other studies have

drawn conclusions by using $C_4H_4Cl_2$ as a precursor to form benzene [17,24], furan (C_4H_4O) [17] and thiophene (C_4H_4S) [13]. Further evidence of a stepwise mechanism and the existence of a C_4 surface species is indicated by formation of furan [17,62] and thiophene [13–16,18] when acetylene is co-adsorbed with oxygen or sulfur on Pd(111), respectively.

A detailed kinetic study of benzene formation from acetylene was also performed using LITD/FTMS [26,27]. The activation barrier and pre-exponential factor for benzene formation have been observed to be coverage dependent [27]. It was concluded that the increase in the activation energy for benzene formation as a function of acetylene exposure was a consequence of an increasing barrier to C–Pd bond breaking resulting from stronger interactions at higher acetylene coverages [27]; the corresponding increase in the pre-exponential factor with respect to activation energy can be explained by a compensation effect [63,64].

2.2. Investigations on supported metals

In an effort to understand the Pd/acetylene system under high temperatures and pressures, studies of Pd supported on silica, titania, alumina and charcoal were performed by Ormerod and Lambert [33]. Benzene was observed only when temperatures exceeded 480 K. The initial benzene yield was high and dropped to a steady state level after a short time; evidence of coking was also reported [33].

The simultaneous observation of 1,3-butadiene and butene and the absence of C_3 and C_5 species provides evidence that a C_4H_4 intermediate is involved under these reaction conditions. The lack of C_3 and C_5 fragments also indicates no C–C bond breaking occurs, similar to the behavior observed in UHV single crystal Pd studies [24]. In addition, 1,3-butadiene and butene products have the same time profile as benzene, supporting the fact that the C_4 intermediate plays a key role in the reaction pathway toward acetylene cyclization. The results ob-

served by Ormerod and Lambert [33] support the argument that the cyclotrimerization reaction proceeds via a C_4 intermediate under conditions of true catalytic turnover.

Structure sensitivity has also been addressed by using different Pd loadings. Greater Pd loadings resulted in a higher steady-state level of benzene formation. The higher steady-state levels of benzene can be attributed to the presence of large, thermodynamically stable, fcc(111) close packed planes on the larger area particles. This agrees with single crystal investigations showing that the acetylene cyclization reaction proceeds readily on Pd(111) under UHV conditions [4,9].

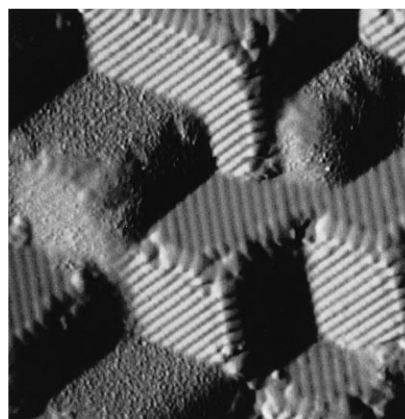
2.3. Bimetallic studies

Pd/Au [36–38], Pd/Ta [40] and Sn/Pt [34] are the only bimetallic systems investigated which have shown benzene formation from acetylene. The highest selectivity toward cyclization has been observed on Pd/Au surfaces with the catalytic efficiency reaching $\sim 100\%$ [37,38]. The conversion of acetylene to benzene decreases dramatically to $\leq 25\%$ on the Pd/Ta [40] surface and $\sim 10\%$ on Sn/Pt [34] surface. The benzene desorption pathway is preferred over decomposition on Pd/Au surface alloys. These alloys are more effective than pure Pd(111) in acetylene cyclization due to decreased interactions between Pd and acetylene, allowing the alkyne bond character to be better preserved, facilitating the cyclotrimerization reaction. In addition, the strength of the benzene–Pd bond is also reduced, enhancing the possibility of desorption. On the other hand, the presence of Sn in Sn/Pt(111) decreases the tendency toward adsorbate decomposition while activating the benzene desorption process [34]. The Sn/Pt system is more effective than pure Pt(111) in benzene desorption because of weaker interactions between adsorbate and substrate. The use of Sn to reduce the high reactivity of Pt(111) slightly in order to observe benzene desorption is another application of bimetallic

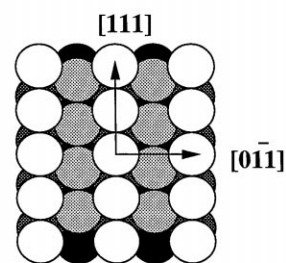
catalysts [34]. In addition to benzene desorption, butadiene, a C_4 product from a C_4H_4 intermediate involved in the production of benzene, is also observed from the Sn/Pt(111) surface [34]. An increase in both benzene and butadiene TPD signals is observed when increasing the amount of Sn in the Sn/Pt alloy, further confirming the increased selectivity toward desorption.

3. Acetylene cyclotrimerization over a model bimetallic surface: Pd/W(211)

The surface and interface properties of bimetallic and alloy systems have been the subject of many investigations because of their unique physical and chemical properties [65,66]. The impetus for the present study is the morphological instability of ultrathin metal films deposited on refractory metals [67,68]. For instance, atomically rough bcc W(111) and Mo(111) coated with a single monolayer of metals having Pauling electronegativities > 2.0 (Pt, Pd, Ir, Rh, Au) undergo massive reconstruction to form a highly faceted surface upon annealing to ≥ 700 K [67,69,70]. Pyramidal facets with $\{211\}$ orientation and nanometer scale dimensions are observed when ≥ 1 ML Pd/W(111) is heated above 700 K [68,69,71]. An atomic resolution STM image of the pyramidal facets that form on ~ 1.2 ML Pd/W(111) heated to ~ 1075 K is shown in Fig. 1a. The sides of the pyramids consist of faces with the $\{211\}$ orientation, characterized by a row/trough configuration. Butane hydrogenolysis investigations on Pt/W(111) have shown that the planar surface has a higher selectivity towards ethane production and higher reaction rates while methane formation is dominant on the faceted surface [72]. In addition, increasing facet size decreases the concentration of 4-fold coordination (C_4) sites, simultaneously reducing ethane production [72]. These studies suggest that the catalytic activity and production of intermediates responsible for product formation are af-



(a)



W(211)

(b)

Fig. 1. (a) An atomic resolution STM image of a ~ 1.2 ML Pd/W(111) surface annealed to ~ 1075 K ($150 \text{ \AA} \times 150 \text{ \AA}$) is shown [68]. (b) A hard sphere model of the W(112) facets showing the row-and-trough geometry seen on the sides of the pyramids in (a).

ected by surface morphology. To study the structure–reactivity relationship of the morphologically-unstable Pd/W system further, acetylene cyclization has been chosen as a probing reaction.

The surface geometrical structure of clean W(211) is similar to that of an fcc(110) row/trough type configuration. Since little or no acetylene converts to benzene on Pd(110), whereas Cu(110) has $\sim 85\%$ selectivity to benzene formation [23], it is interesting to see if the Pd/W bimetallic system can catalyze the cyclotrimerization reaction. More specifically, the use of W(211) maintains the row-and-trough type geometry (see Fig. 1b); our goal is to

determine whether or not vapor-depositing thin films of Pd perturbs the electronic structures of both metals sufficiently to enhance the reactivity toward cyclotrimerization. In our studies we examine the cyclization reaction on Pd thin films ranging from submonolayer to multilayers deposited on W(211) surfaces. It is interesting to note the palladium/tungsten surface does not form an alloy at monolayer Pd coverages, as confirmed by low energy ion scattering (LEIS) of Pd/W(111) [73]. Rather, the Pd remains in the topmost layer of the bimetallic surface. As will be demonstrated later, TPD and HREELS results exhibit different reaction processes for acetylene on clean W(211) as compared with Pd/W(211).

4. Experimental

The TPD experiments are performed at Rutgers in a previously described UHV chamber with a base pressure of 5×10^{-11} Torr [74,75], while the HREELS studies are conducted at the Exxon Corporate Research Laboratories in a UHV system with a base pressure of 2×10^{-10} Torr [76]. Both chambers are equipped with Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and a quadrupole mass spectrometer (QMS) used for monitoring background residual gas and detecting desorbed species during TPD. The HREEL spectrometer (LK 3000) was operated with a primary beam energy of 6 eV, impinging the surface at 65° from the surface normal. HREEL spectra were taken in the on-specular and -15° off-specular directions. The HREEL spectra reported here have a spectroscopic resolution (full-width at half maximum) of $30\text{--}40 \text{ cm}^{-1}$ and an elastic peak intensity ranging from 10^5 to 10^6 cps.

The W(211) sample was prepared from a ~ 8 mm diameter boule and aligned by X-ray diffraction to within a 0.5° of the (211) plane. The surface was polished to a mirror finish and spot welded to tantalum leads for support and

resistive heating. At Rutgers, the sample could be resistively heated to 1300 K and during cleaning, heated by electron bombardment to 2400 K, as measured using a W-5 %Re/W-26 %Re thermocouple junction. At Exxon, a type K thermocouple was used, since the sample temperature did not exceed 1200 K, due to different cleaning procedures, as described below. Both chambers have cryogenic capabilities to cool the sample to ~ 100 K.

The preparation of the surface differs between the Rutgers and Exxon chambers. At Rutgers the surface was cleaned by annealing at 1200 K in 5×10^{-8} Torr oxygen for 1–5 min to remove residual carbon, followed by flashing to 2200 K (heating rate $\cong 400$ K/s) to remove metal overlayers as well as chemisorbed oxygen. At Exxon the W(211) surface was cleaned by Ne^+ sputtering (5 kV, $\sim 8\text{--}10 \mu\text{A}$ sample current) for 10 min at 1000 K, followed by annealing at 1150 K for 5 min. Oxygen treatments to titrate residual carbon impurities were performed if needed [77]. The surface cleanliness and long range order were verified by AES and LEED, respectively.

The acetylene is spectral grade (99.96% pure) and was purified with a dry-ice/acetone cooled trap. The dry-ice/acetone bath was used to condense acetone impurities onto the walls of the trap, allowing purified acetylene to be collected in a separate vessel. The purity was checked with mass spectrometry prior to and during use in the UHV chambers. A glass flask with 1 atm of deuterated acetylene (99.9% purity) was purchased pre-purified. All acetylene dosing was performed using a sapphire sealed variable leak valve with the surface temperature at ~ 100 K. Acetylene exposures are not corrected for ion gauge sensitivities.

The metal evaporation sources at both Rutgers and Exxon consisted of high purity Pd wire wrapped around a larger diameter W wire. The evaporation rate was controlled by varying the current used to resistively heat the wire. In addition, the evaporation source was outgassed extensively prior to deposition. The purity of

the Pd overlayers on W(211) was always confirmed by AES prior to reaction experiments.

5. Results and discussion

5.1. TPD studies

The TPD spectra shown in Fig. 2 demonstrate that benzene formation occurs after dosing 3 L of acetylene on Pd/W(211) pre-annealed to 700 K for 3 min. The clean W(211) surface shows little or no benzene formation while ~ 0.5 ML Pd on the W(211) substrate facilitates the reaction (not shown). As the coverage increases from ~ 0.5 ML to ~ 1.0 ML Pd, 2–3 times more benzene is formed from acetylene. Two benzene TPD peaks are evident at 210 K and 470 K for the ~ 1.0 ML Pd coverage and a small shoulder is seen at 340 K. For comparison, a high temperature desorption peak (500 K) attributed to flat-lying benzene was observed in previous Pd(111) studies [1–5,21]. Furthermore, although a coverage of ~ 5.0 ML Pd deposited at 100 K will quench the reaction, producing no benzene, annealing the ~ 5.0 ML Pd/W(211) surface to 1050 K produces additional benzene desorption peaks (not shown). The appearance of several states may be associated with different bonding con-

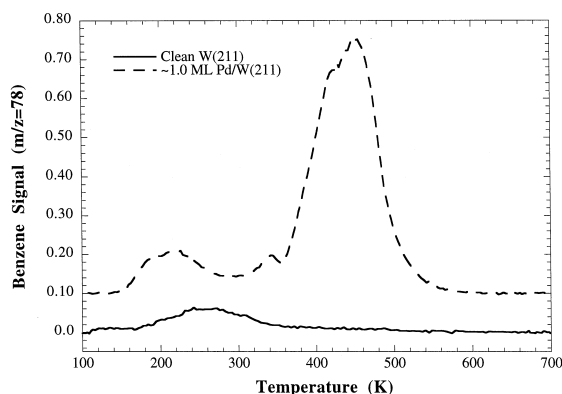


Fig. 2. The TPD spectra of reactively formed benzene ($m/z = 78$) from 3 L of acetylene on clean W(211) (solid line) and ~ 1.0 ML Pd/W(211) (dashed line) are shown for a heating rate of 5 K/s.

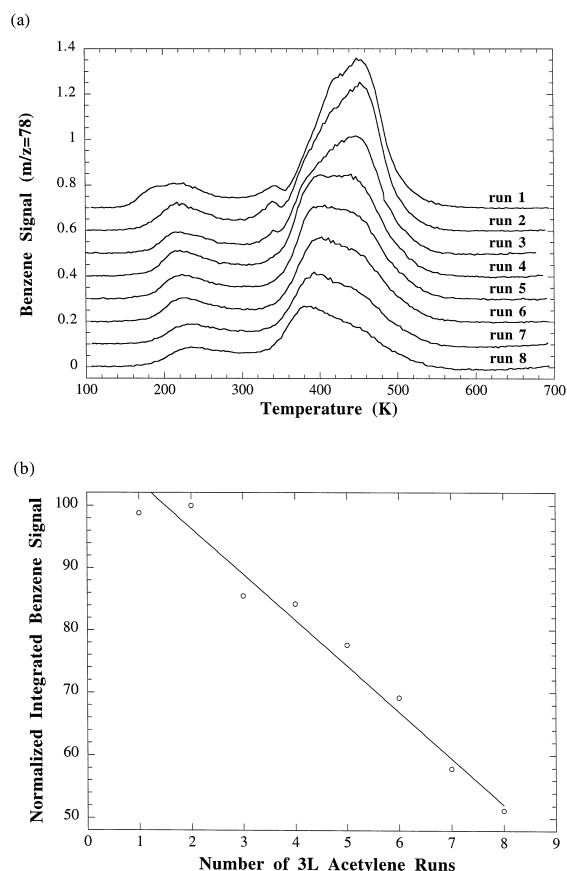


Fig. 3. The effects of carbon contamination on benzene yields are shown. (a) TPD spectra of reactively formed benzene ($m/z = 78$) from the cyclization of consecutive 3 L of acetylene on ~ 1 ML Pd/W(211). (b) Integrated benzene signal as a function of the number of 3 L acetylene runs.

figurations. TPD studies indicate that the inactivity of the as-deposited Pd/W surface may be related in part to the presence of surface hydrogen or CO adsorbed during metal deposition. The role of CO and hydrogen inhibition on acetylene cyclization will be addressed in a future paper [78].

The role of carbon contamination of metal surfaces is an important process to understand since coking deactivates catalytic surfaces. Fig. 3a shows the TPD spectra of eight consecutive 3 L acetylene exposures on ~ 1 ML Pd/W(211) pre-annealed to 700 K for 3 min prior to the initial run. As a function of consecutive acety-

lene TPD experiments, the activity of the surface decreases very gradually, without immediate complete poisoning. In addition, Fig. 3b depicts a linear relationship between integrated benzene signal area and the number of 3 L acetylene runs. Furthermore, Fig. 3b also confirms that the surface remains relatively reactive toward acetylene cyclization even after multiple cycles by exhibiting only a $\sim 50\%$ reduction in the yield of reactively formed benzene even after eight consecutive acetylene runs. This gradual decrease in benzene yield is caused by residual surface carbon blocking essential cyclization sites. In addition to the decrease in the overall benzene yield, a shift in the position of the dominant peak from 450 K to 380 K is observed. The 70 K shift to lower temperatures may be indicative of benzene desorption from

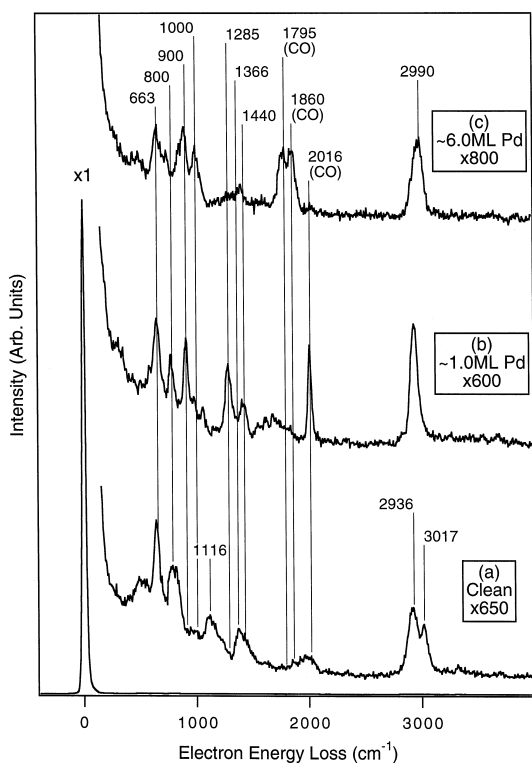


Fig. 4. A comparison of HREEL spectra of 1 L of acetylene on (a) W(211) (b) ~ 1.0 ML and (c) ~ 6.0 ML Pd/W(211) at 100 K. All spectra were taken in the specular direction with a primary beam energy of 6.0 eV.

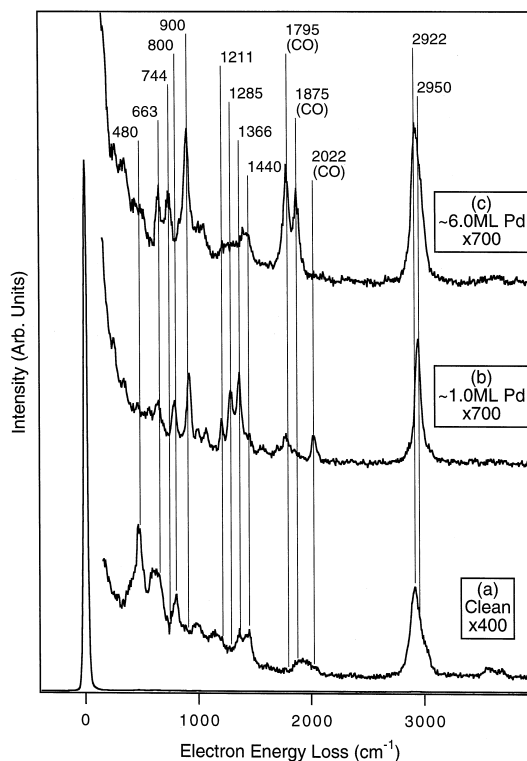


Fig. 5. The acetylene dosed (a) W(211) (b) ~ 1.0 ML and (c) ~ 6.0 ML Pd/W(211) surfaces prepared in Fig. 4 were annealed to 250 K and re-cooled to 100 K for subsequent HREELS measurements.

sites created by carbon contamination of reactive sites on clean Pd/W(211).

5.2. HREELS investigations

5.2.1. Acetylene on clean W(211) and Pd/W(211)

HREELS measurements have been performed for acetylene adsorbed on clean W(211) as well as ~ 1.0 ML and ~ 6.0 ML Pd/W(211). The studies provide insight into the bonding characteristics of acetylene on these surfaces, as well as supplying information about the surface intermediates present at different temperatures. Figs. 4 and 5 are HREEL spectra of 1 L of acetylene on clean W(211) and Pd/W(211) surfaces at 100 K and 250 K, respectively, while Fig. 6 shows a detailed study of the thermal behavior of 1 L of acetylene on ~ 1.0 ML Pd/W(211). Fig. 7 is shown for

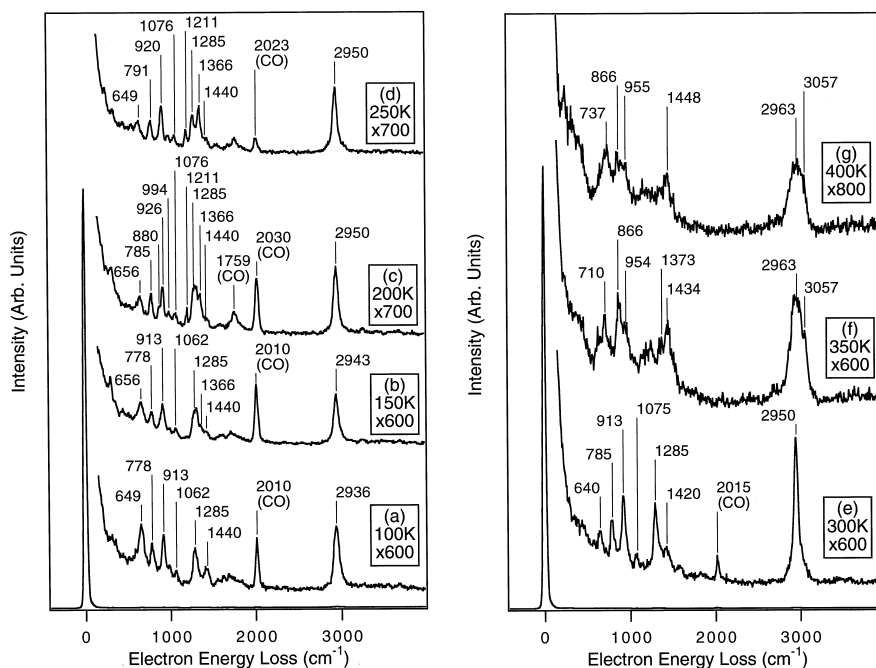


Fig. 6. A detailed thermal sequence of chemisorbed 1 L of acetylene on ~ 1.0 ML Pd/W(211) is shown. All annealed surfaces were re-cooled to 100 K prior to HREELS measurements.

comparison to illustrate the absence of benzene formation on the clean W(211) and the Pd/W(211) surfaces.

Fig. 4 shows HREEL spectra of 1 L of acetylene on clean W(211) and Pd/W(211) at 100 K. The discussion of the spectra begins with clean W(211) (Fig. 4a), then proceeds to the ~ 6 ML and ~ 1 ML Pd/W(211) surfaces (Fig. 4c and b, respectively). At this temperature and exposure, the majority of the adsorbed acetylene rehybridizes on the clean W(211) surface to form a di- σ/π bonded species. The features observed in Fig. 4a at 2936 and 3017 cm^{-1} correspond to the $\nu_s(\text{CH})$ and $\nu_{as}(\text{CH})$ modes of chemisorbed acetylene, respectively. The peak at 1366 cm^{-1} can be assigned to a $\nu(\text{CC})$ mode, while the relatively strong features at 800 and 663 cm^{-1} result from the $\rho_s(\text{CH})$ and $\rho_{as}(\text{CH})$ modes, respectively. Additionally, the feature at 1116 cm^{-1} is a $\delta_s(\text{CH})$ mode. These assignments have been confirmed by isotopic labeling experiments and are summarized in Table 1. Also shown in Table 1 is a

comparison of the vibrational modes of acetylene on clean Ru(001) [80], Fe(110) [81] and Mo(110) [82] surfaces.

After depositing ~ 6.0 ML of Pd onto the W(211) surface, annealing to 700 K for 1 min to improve the surface order and dosing 1 L of acetylene at 100 K, the vibrational spectrum of adsorbed acetylene (Fig. 4c) shows similar features to the spectrum obtained for acetylene on clean Pd(111) [8]. In particular, a strong indication that fcc(111) planes may be present is demonstrated by the $\delta_s(\text{CH})$ at 1000 cm^{-1} . For example, $\delta_s(\text{CH})$ features have been observed on Pd(111) [8] (cf. Table 2) and Ni(111) [84] at 1034 and 1080 cm^{-1} , respectively. The other features in Fig. 4c such as the $\rho_s(\text{CH})$ and $\rho_{as}(\text{CH})$ at 900 and 663 cm^{-1} , respectively and the $\nu(\text{CC})$ at 1407 cm^{-1} and $\nu(\text{CH})$ at 2990 cm^{-1} are also consistent with the presence of molecularly adsorbed acetylene on Pd(111) [8] (see Table 2).

The spectrum of 1 L of acetylene on a ~ 1 ML Pd/W(211) surface (Fig. 4b) shows sub-

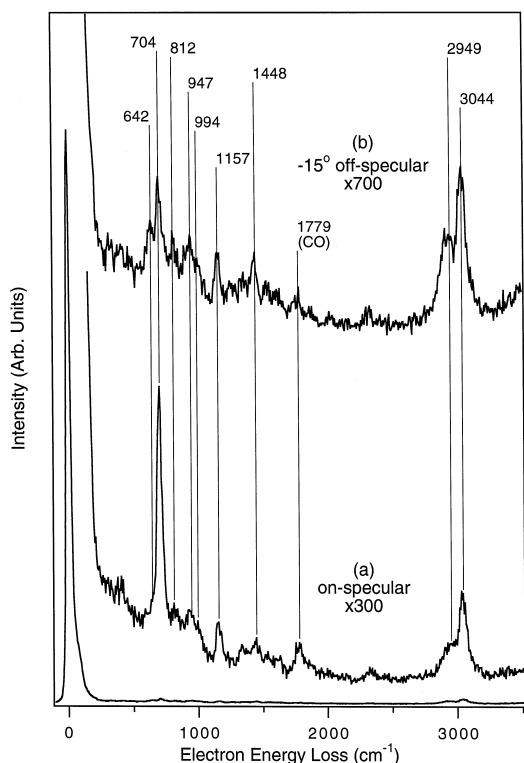


Fig. 7. The HREEL spectra of 1 L of benzene on ~ 1 ML Pd/W(211) at 100 K in the (a) on-specular and (b) off-specular directions.

stantially different features from the corresponding spectra seen for the clean W(211) and ~ 6.0 ML Pd/W(211) surfaces (Fig. 4a and c). For

example, the absence of the 1000 cm^{-1} feature observed with the ~ 6.0 ML Pd/W(211) suggests that different surface intermediates are formed. Furthermore, the intense features at 1285 and 1440 cm^{-1} seen in the ~ 1 ML Pd/W(211) spectrum (Fig. 4b) are not present in the clean W(211) spectrum (Fig. 4a). Additionally, the ~ 1 ML Pd/W(211) spectrum shows a relatively narrow and symmetric $\nu(\text{CH})$ mode at 2936 cm^{-1} , unlike what is observed for the clean W(211) surface and the Pd-multilayer covered (~ 6.0 ML) W(211) surface. These differences from the spectra shown in Fig. 4a and c reflect the different chemistry which occurs on ~ 1.0 ML Pd/W(211) surfaces, as compared with the clean and the ~ 6.0 ML Pd/W(211) surfaces. More detailed vibrational studies are underway to identify the surface intermediates which are present on these surfaces [85,86].

Fig. 5 shows HREEL spectra of 1 L of acetylene on each of the surfaces shown in Fig. 4, taken after flashing to 250 K (heating rate = 3 K/s). Fig. 5a is different from the 100 K acetylene spectrum of the clean W(211) in several ways. The $\nu(\text{CH})$ region has lost the $\nu_s(\text{CH})$ and $\nu_{as}(\text{CH})$ characteristic of molecular acetylene and now has a single, broad feature at 2922 cm^{-1} . In addition, the features at 1366 and 1440 cm^{-1} which respectively occur in the

Table 1

The vibrational assignments of chemisorbed acetylene on several metals [b–d] and clean W(211)

Vibrational assignments (cm^{-1})	Gaseous $\text{C}_2\text{H}_2(\text{C}_2\text{D}_2)$ [a]	$\text{C}_2\text{H}_2(\text{C}_2\text{D}_2)$ on Ru(001) [b]	$\text{C}_2\text{H}_2(\text{C}_2\text{D}_2)$ on Fe(110) [c]	$\text{C}_2\text{H}_2(\text{C}_2\text{D}_2)$ on Mo(110) [d]	1 L $\text{C}_2\text{H}_2(\text{C}_2\text{D}_2)$ on W(211) at 100 K (this work)
$\nu_s(\text{CH})$	3287 (2427)	2940 (2210)	2940 (2210)	2900 (2170)	2922 (2185)
$\nu_{as}(\text{CH})$	3374 (2701)				3017 (2245)
$\nu(\text{CC})$	1974 (1752)	1135 (1085)	1240 (1235)	1130 (1090)	1366 (1366)
$\delta_s(\text{CH})$	729 (539)	980 (715)	1150 (935)	905 (710)	1116 (913)
$\delta_{as}(\text{CH})$	612 (505)		1415 (1140)		
$\rho_s(\text{CH})$	729 (539)	520 (–)	700 (550)	740 (–)	800 (630)
$\rho_{as}(\text{CH})$	612 (505)	765 (585)	870 (680)	(640)	663 (480)
$\nu(\text{CM})$		375 (350)	460 (420)	390 (400)	480 (475)

(a) See Ref. [79].

(b) See Ref. [80].

(c) See Ref. [81].

(d) See Ref. [82].

Table 2

The vibrational assignments of chemisorbed acetylene on several metals [b–d] and 6 ML Pd/W(211)

Vibrational assignments (cm ⁻¹)	Gaseous C ₂ H ₂ (C ₂ D ₂) [a]	C ₂ H ₂ (C ₂ D ₂) on Ni(110) [b]	C ₂ H ₂ (C ₂ D ₂) on Pd(110) [b]	C ₂ H ₂ (C ₂ D ₂) on Cu(110) [c]	C ₂ H ₂ (C ₂ D ₂) on Pd(111) [d]	1 L C ₂ H ₂ (C ₂ D ₂) on 6 ML Pd/W(211) at 100 K (this Work)
$\nu_s(\text{CH})$	3287 (2427)	2950 (2200)	2990 (2245)	2900 (2190)	2922 (2249)	2990 (2212)
$\nu_{as}(\text{CH})$	3374 (2701)					
$\nu(\text{CC})$	1974 (1752)	1350 (1205)	1400 (1274)	1305 (1280)	1402 (1359)	1407 (1340)
$\delta_s(\text{CH})$	729 (539)			940 (680)	1034 (850)	1000 (846)
$\delta_{as}(\text{CH})$	612 (505)			1140 (930)		
$\rho_s(\text{CH})$	729 (539)	675 (495)	690 (530)		673 (511)	900 (643)
$\rho_{as}(\text{CH})$	612 (505)	910 (685)	915 (700)		872 (621)	663 (480)
$\nu(\text{CM})$		470 (–)	obscured	470 (400)	500 (–)	obscured

(a) See Ref. [79].

(b) See Ref. [83].

(c) See Ref. [22].

(d) See Ref. [8].

frequency range of symmetric and asymmetric C–H deformations of CH₂ or CH₃ moieties, suggests that vinylidene (H₂C=C=M) or ethylidyne (H₃C–C≡M) is present. However, given the absence of the characteristic $\nu(\text{CC})$ feature of ethylidyne near 1100 cm⁻¹, the intermediate is more likely vinylidene. On the other hand, the presence of a small amount of acetylide (HC≡C–M) cannot be ruled out, since the vibrational features of acetylide are spectroscopically indistinguishable from those of vinylidene [80].

Unlike the behavior of acetylene on clean W(211), acetylene on the ~ 6.0 ML Pd/W(211) surface at 250 K yields a spectrum which is quite similar to that observed at 100 K (cf. Fig. 4c and Fig. 5c). This behavior indicates that acetylene has not decomposed and remains σ/π bonded to the surface. In contrast, the spectra of 1 L of acetylene on the ~ 1 ML Pd/W(211) surface, after flashing to 250 K, changes considerably (cf. Fig. 4b and Fig. 5b). The main region of interest falls between 1200 and 1500 cm⁻¹, where sharp, relatively intense features are observed. Such features indicate the formation and subsequent desorption and decomposition, of intermediates different from chemisorbed acetylene. A more detailed account regarding the vibrational assignments will be discussed in a separate paper [85].

5.2.2. Thermal sequence of chemisorbed C₂H₂ on ~ 1 ML Pd/W(211)

A detailed HREELS study of the thermal decomposition of 1 L C₂H₂ chemisorbed on ~ 1.0 ML Pd/W(211) is shown in Fig. 6. Major changes occur between 150–250 K, in Fig. 6b–d, particularly in the 1200–1500 cm⁻¹ regime, as described above. At temperatures above 250 K, these features disappear, indicating either a short-lived surface intermediate or the desorption of a product. Complementary multiplexing TPD experiments are underway to establish whether the disappearance of these features results from the desorption of a hydrocarbon product. Heating the surface to 350 and 400 K (Fig. 6f–g, respectively) induces another major change in the surface species. The $\nu(\text{CH})$ region shows a broad feature with a shoulder at 3057 cm⁻¹ denoting the presence of an sp²-hybridized carbon. Furthermore, a vibrational feature occurring at 710 cm⁻¹ may be characteristic of a $\gamma(\text{CH})$ (out-of-plane deformation) mode of an unsaturated ring compound. However, a comparison of the vibrational spectrum of 1 L of chemisorbed molecular benzene on ~ 1.0 ML Pd/W(211) (Fig. 7) with acetylene on ~ 1.0 ML Pd/W(211) heated to 350 K and 400 K (Fig. 6f–g) firmly indicates the absence of a strong $\gamma(\text{CH})$ denoting a lack of surface benzene. In particular, note that a comparison of the

on- and off-specular spectra in Fig. 7 shows that benzene has a flat-lying geometry on this surface, as indicated by the strong angle-dependent change in the intensity of the $\gamma(\text{CH})$ mode at 704 cm^{-1} . In contrast, an angle-dependent change is not observed with acetylene on ~ 1.0 ML Pd/W(211), in support of the conclusion that surface benzene is absent on this surface. Furthermore, comparing the TPD and HREELS results supports the speculation that the cyclotrimerization of acetylene to form gas-phase benzene may be a reaction-rate limited process on the ~ 1.0 ML Pd/W(211) surface. On the other hand, on the ~ 6.0 ML Pd/W(211) surface, the HREELS studies exhibit evidence for reactively formed benzene after flashing to 450 K [85]. This indicates different reaction pathways, possibly due to the presence of adsorption sites on the three-dimensional Pd clusters, which are different from those on the ~ 1.0 ML Pd/W(211) surface. A more detailed account of the reaction channels for the different coverages of Pd will be published later [85].

6. Conclusions

A number of acetylene cyclization studies over various catalyst surfaces has been summarized, ranging from single crystals to supported catalysts, from UHV to high pressure studies. There is evidence from several studies that the reaction proceeds via an intermediate rate-determining step in which an acetylene molecule couples with a C_4H_4 surface intermediate to form benzene. In addition, the reaction is observed to take place without C–C or C–H bond scission. Furthermore, the desorption states for reactively formed benzene have been attributed to a tilted and flat-lying orientation. Studies on bimetallics have confirmed that mixed metal systems can result in reactions, such as acetylene cyclization, not achieved by the pure metal systems.

The unique reactivity of the 1.0 ML Pd/W(211) surface, as compared to the clean

W(211) and multilayer Pd/W(211) surface, is demonstrated by both TPD and HREELS experiments. For example, the evolution of benzene from the pre-annealed ~ 1.0 ML Pd/W(211) surface shows desorption features at 210 K and 480 K, while no benzene features are observed from the clean W(211) surface and multiple features are observed on the pre-annealed multilayer (~ 5.0 ML) Pd/W(211) surface. Furthermore, HREELS results indicate that the adsorption and the subsequent decomposition of acetylene are qualitatively different on the ~ 1.0 ML Pd/W(211) surface and the multilayer Pd/W(211) surface.

The results presented here for Pd/W(211) demonstrate that bimetallics change surface activity. For instance, acetylene cyclization does not occur on the clean W(211) surface, while the adsorption of Pd catalyzes the reaction. Furthermore, although the Pd(110) and Pd/W(211) surfaces both have row-and-trough structures, the Pd(110) surface does not catalyze the cyclotrimerization reaction, unlike the Pd/W(211) surface. This behavior indicates that the presence of the W substrate changes the electronic structure of the Pd adlayer, perhaps mimicking the electronic structure of Cu(110), rather than that of Pd(110) [87]. In order to understand further the correlation between morphology and chemical reactivity of these morphologically unstable surfaces, investigations using acetylene as a probing molecule will be performed on planar and faceted Pd/W(111) surfaces.

Acknowledgements

This work has been supported in part by the Division of Chemical Sciences, U.S. Department of Energy.

References

- [1] W.T. Tysøe, G.L. Nyberg, R.M. Lambert, *J. Chem. Soc., Chem. Commun.* (1983) 623.

- [2] W.T. Tysoe, G.L. Nyberg, R.M. Lambert, *Surf. Sci.* 135 (1983) 128.
- [3] W. Sesselmann, B. Woratschek, G. Ertl, J. Küppers, H. Haberland, *Surf. Sci.* 130 (1983) 245.
- [4] T.M. Gentle, E.L. Müeterties, *J. Phys. Chem.* 87 (1983) 2469.
- [5] C.H. Patterson, J.M. Mundenar, P.Y. Timbrell, A.J. Gellman, R.M. Lambert, *Surf. Sci.* 208 (1989) 93.
- [6] B. Marchon, *Surf. Sci.* 162 (1985) 382.
- [7] L.L. Kesmodel, G.D. Waddill, J.A. Gates, *Surf. Sci.* 138 (1984) 464.
- [8] J.A. Gates, L.L. Kesmodel, *J. Chem. Phys.* 76 (8) (1982) 4281.
- [9] T.G. Rucker, M.A. Logan, T.M. Gentle, E.L. Müeterties, G.A. Somorjai, *J. Phys. Chem.* 90 (1986) 2703–2708.
- [10] K.P.C. Vollhardt, *Acc. Chem. Res.* 10 (1977) 1.
- [11] P.M. Maitlis, *Acc. Chem. Res.* 9 (1976) 93.
- [12] H. Hoffman, F. Zaera, R.M. Ormerod, R.M. Lambert, J.M. Yao, D.K. Saldin, L.P. Wang, D.W. Bennett, W.T. Tysoe, *Surf. Sci.* 268 (1992) 1.
- [13] T.M. Gentle, C.T. Tsai, K.P. Walley, A.J. Gellman, *Catal. Lett.* 2 (1989) 19.
- [14] A.J. Gellman, *J. Am. Chem. Soc.* 113 (1991) 4435.
- [15] A.J. Gellman, *Langmuir* 7 (1991) 827.
- [16] A.J. Gellman, *J. Phys. Chem.* 96 (1992) 790.
- [17] R.M. Ormerod, R.M. Lambert, *Catal. Lett.* 6 (1990) 121–130.
- [18] I.M. Abdelrehim, N.A. Thornburg, J.T. Sloan, D.P. Land, *Surf. Sci. Lett.* 298 (1993) L169.
- [19] J.A. Gates, L.L. Kesmodel, *Surf. Sci.* 124 (1983) 68.
- [20] M.A. Logan, T.G. Rucker, T.M. Gentle, E.L. Müeterties, G.A. Somorjai, *J. Phys. Chem.* 90 (1986) 2709.
- [21] R.M. Lambert, R.M. Ormerod, in: R.J. Madix (Ed.), *Springer Series in Surface Science, Surface Reactions*, Vol. 34, Springer-Verlag, Berlin, 1994, 89–134.
- [22] N.R. Avery, *J. Am. Chem. Soc.* 107 (1985) 6711.
- [23] J.R. Lomas, C.J. Baddeley, M.S. Tikhov, R.M. Lambert, *Langmuir* 11 (1995) 3048.
- [24] C.H. Patterson, R.M. Lambert, *J. Phys. Chem.* 92 (1988) 1266.
- [25] C.H. Patterson, R.M. Lambert, *J. Am. Chem. Soc.* 110 (1988) 6871.
- [26] I.M. Abdelrehim, N.A. Thornburg, J.T. Sloan, T.E. Caldwell, D.P. Land, *J. Am. Chem. Soc.* 117 (1995) 9509.
- [27] I.M. Abdelrehim, T.E. Caldwell, D.P. Land, *J. Phys. Chem.* 100 (1996) 10265.
- [28] R.M. Ormerod, R.M. Lambert, D.W. Bennett, W.T. Tysoe, *Surf. Sci.* 330 (1995) 1.
- [29] A.F. Lee, C.J. Baddeley, C. Hardacre, R.M. Lambert, *J. Am. Chem. Soc.* 117 (1995) 7719.
- [30] R.M. Ormerod, R.M. Lambert, H. Hoffman, F. Zaera, J.M. Yao, D.K. Saldin, L.P. Wang, D.W. Bennett, W.T. Tysoe, *Surf. Sci.* 295 (1993) 277.
- [31] G. Pacchioni, R.M. Lambert, *Surf. Sci.* 304 (1994) 208.
- [32] A. Ramirez-Cuesta, G. Zgrablich, W.T. Tysoe, *Surf. Sci.* 340 (1995) 109.
- [33] R.M. Ormerod, R.M. Lambert, *J. Chem. Soc., Chem. Commun.*, 1990, 1421.
- [34] C. Xu, J.W. Peck, B.E. Koel, *J. Am. Chem. Soc.* 115 (1993) 751–755.
- [35] A.F. Lee, C.J. Baddeley, C. Hardacre, R.M. Ormerod, R.M. Lambert, *J. Phys. Chem.* 99 (1995) 6096.
- [36] R.M. Ormerod, C.J. Baddeley, R.M. Lambert, *Surf. Sci. Lett.* 259 (1991) L709.
- [37] C.J. Baddeley, R.M. Ormerod, A.W. Stephenson, R.M. Lambert, *J. Phys. Chem.* 99 (1995) 5146.
- [38] C.J. Baddeley, M. Tikhov, C. Hardacre, J.R. Lomas, R.M. Lambert, *J. Phys. Chem.* 100 (1996) 2189.
- [39] J.M. Heitzinger, S.C. Gebhard, B.E. Koel, *J. Phys. Chem.* 97 (1993) 5327.
- [40] J.M. Heitzinger, PhD. thesis, University of Southern California, 1993.
- [41] J.C. Bertolini, J. Massardier, G. Dalmai-Imelik, *J. Chem. Soc., Faraday Trans. 1* 74 (1978) 1720.
- [42] K.G. Pierce, M.A. Barteau, *J. Phys. Chem.* 98 (1994) 3882.
- [43] J.H. Sinfelt, *J. Catal.* 29 (1973) 308.
- [44] J.W. Sachtler, J.P. Biberian, G.A. Somorjai, *Surf. Sci.* 110 (1981) 43.
- [45] E. Bauer, in: D.A. King, D.P. Woodruff (Eds.), *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, Elsevier, New York, 1984.
- [46] I. Zuburtikudis, H. Saltsburg, *Science* 258 (1992) 1337.
- [47] K.H. Krauth, K.H. Lee, G.H. Bernstein, E.E. Wolf, *Catal. Lett.* 27 (1994) 43.
- [48] W.H.M. Sachtler, *Faraday Disc. Chem. Soc.* 72 (1981) 7.
- [49] J. Szanyi, M.T. Paffett, *J. Am. Chem. Soc.* 117 (1995) 1034.
- [50] R.M. Lambert, R.M. Ormerod, *Mater. Chem. Phys.* 29 (1991) 105.
- [51] J.P. Cowin, D.J. Auerbach, C. Becker, L. Wharton, *Surf. Sci.* 78 (1978) 545.
- [52] R.B. Hall, S.J. Bares, in: R.B. Hall, A.B. Ellis (Eds.), *Chemistry and Structure at Interfaces: New Optical Probes*, VCH, Deerfield Beach, FL, 1986, pp. 85–149.
- [53] S.M. George, A.M. DeSantolo, R.B. Hall, *Surf. Sci.* 159 (1989) L425.
- [54] J.L. Brand, S.M. George, *Surf. Sci.* 167 (1986) 341–362.
- [55] S.M. George, in: B.W. Rossiter, R.C. Baetzold (Eds.), *Investigations of Surfaces and Interfaces—Part A*, 2nd edn., Vol. IXA, Wiley, New York, 1993, pp. 453–497.
- [56] A.A. Deckert, S.M. George, *Surf. Sci.* 182 (1987) L215–L220.
- [57] R.T. McIver Jr., M.G. Sherman, D.P. Land, J.R. Kingsley, J.C. Hemminger, in: A. Benninghoven, R.J. Colton, D.S. Simons, H.W. Werner (Eds.), *Secondary Ion Mass Spectrometry: SIMS V*, Springer-Verlag, New York, 1986, 555 pp.
- [58] D.P. Land, C.L. Pettiette-Hall, R.T. McIver Jr., J.C. Hemminger, *J. Am. Chem. Soc.* 111 (1989) 5970.
- [59] D.P. Land, D.T.-S. Wang, T.-L. Tai, M.G. Sherman, J.C. Hemminger, R.T. McIver Jr., in: D.M. Lubman (Ed.), *Lasers in Mass Spectrometry*, Oxford Univ. Press, New York, 1990, 157 pp.
- [60] D.P. Land, C.L. Pettiette-Hall, J.C. Hemminger, R.T. McIver Jr., *Acc. Chem. Res.* 24 (1991) 42.
- [61] R.M. Ormerod, R.M. Lambert, *Surf. Sci.* 225 (1990) L20.
- [62] R.M. Ormerod, R.M. Lambert, *J. Phys. Chem.* 96 (1992) 8111.
- [63] A.K. Galwey, *Adv. Catal.* 26 (1977) 247.
- [64] W.C. Conner Jr., *J. Catal.* 78 (1982) 238.
- [65] J.H. Sinfelt, *Bimetallic Catalysts*, Wiley, New York, 1983.

- [66] C.T. Campbell, *Ann. Rev. Phys. Chem.* 41 (1990) 775–837.
- [67] J. Guan, R.A. Campbell, T.E. Madey, *Surf. Sci.* 341 (1995) 311.
- [68] C.-H. Nien, T.E. Madey, *Surf. Sci.* 380 (1997) L527.
- [69] T.E. Madey, J. Guan, C.-Z. Dong, S.M. Shivaprasad, *Surf. Sci.* 287–288 (1993) 826.
- [70] J. Guan, R.A. Campbell, T.E. Madey, *J. Vac. Sci. Technol.* 13 (1995) 1484.
- [71] T.E. Madey, J. Guan, C.-H. Nien, C.Z. Dong, H.-S. Tao, R.A. Campbell, *Surf. Rev. Lett.* 3 (1996) 1315.
- [72] R.A. Campbell, J. Guan, T.E. Madey, *Catal. Lett.* 27 (1994) 273.
- [73] C. Dong, L. Zhang, U. Diebold, T.E. Madey, *Surf. Sci.* 322 (1995) 221.
- [74] D.W. Goodman, R.D. Kelley, T.E. Madey, J.T. Yates, *J. Catal.* 63 (1980) 226.
- [75] R.D. Kelley, D.W. Goodman, in: D.A. King, D.P. Woodruff (Eds.), *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, Vol. 4, Elsevier, Amsterdam, 1982, pp. 427–454.
- [76] B. Frühberger, J.G. Chen, *Surf. Sci.* 342 (1995) 38.
- [77] J.G. Chen, B. Frühberger, *Surf. Sci.* 367 (1996) L102.
- [78] I.M. Abdelrehim, K. Pelhos, T.E. Madey, J. Eng Jr., J.G. Chen, in preparation.
- [79] G. Herzberg, *Infrared and Raman Spectroscopy*, Vol. 2, Van Nostrand-Reinhold, New York, 1954.
- [80] J.E. Parmeter, M.M. Hills, W.H. Weinberg, *J. Am. Chem. Soc.* 108 (1986) 3563.
- [81] W. Erley, A.M. Baro, H. Ibach, *Surf. Sci.* 120 (1982) 273.
- [82] B. Frühberger, J.G. Chen, *J. Am. Chem. Soc.* 118 (1996) 11599.
- [83] B.J. Bandy, M.A. Chesters, M.E. Pemble, G.S. McDougall, *Surf. Sci.* 139 (1984) 87.
- [84] H. Ibach, S. Lehwald, *J. Vac. Sci. Technol.* 18 (1981) 625.
- [85] I.M. Abdelrehim, K. Pelhos, T.E. Madey, J. Eng Jr., J.G. Chen, in preparation.
- [86] J. Eng Jr., J.G. Chen, I.M. Abdelrehim, T.E. Madey, in preparation.
- [87] G.W. Graham, *J. Vac. Sci. Technol. A* 4 (3) (1986) 760.