

Ethene Adsorption, Dehydrogenation and Reaction with Pd(110): Pd as a Carbon ‘Sponge’[†]

Michael Bowker,* Chris Morgan, Neil Perkins, Richard Holroyd, Elodie Fourre, Federico Grillo, and Alexander MacDowall

Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff CF10 3TB, Wales, U.K.

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The interaction of ethene with the Pd(110) surface has been investigated, mainly with a view to understanding the dehydrogenation reactions of the molecule and mainly using a molecular beam reactor. Ethene adsorbs with a high probability over the temperature range 130 to 800 K with the low-coverage sticking probability dropping from 0.8 at 130 K to 0.35 at 800 K. The adsorption is of the precursor type, with a weakly held form of ethene being the intermediate between the gas phase and strong chemisorption. Dehydrogenation begins at ~300 K and is fast above 350 K. If adsorption is carried out at temperatures up to ~380 K, adsorption saturates after about 0.25 monolayer have adsorbed, but above ~450 K, adsorption continues at a high rate with continuous hydrogen evolution and C deposition onto the surface. It appears that, in the intermediate temperature range, the carbonaceous species formed is located in the top layer and thus interferes with adsorption, whereas the C goes subsurface above 450 K, the adsorption is almost unaffected, and the C signal is significantly attenuated in XPS. However, the deposited carbon can easily be removed again by reaction with oxygen, thus implying that the carbon remains in the selvedge, that is, in the immediate subsurface region probably consisting of a few atomic layers. No well-ordered structures are identified in either LEED or STM, though some evidence of a $c(2\times 2)$ structure can be seen. The Pd surface, at least above 450 K, appears to act as a “sponge” for carbon atoms, and this effect is also seen for the adsorption of other hydrocarbons such as acetaldehyde and acetic acid.

Introduction

The adsorption and reaction of ethene with transition metal surfaces is of importance in several ways. First of all, it is the simplest of the alkenes and as such is something of a model for alkene behavior in general. Second, it is an important industrial intermediate chemical that is produced from crude oil via catalytic cracking and is then used in a wide variety of other processes. One of our particular interests at present is in the synthesis of vinyl acetate, which takes place industrially on Pd surfaces. Industrial catalysts nowadays are rather more complex than simple supported Pd, and one of the best systems comprises a Au/Pd alloy catalyst, with promoters such as KOAc.^{1–5} These catalysts operate at around 440 K and 4 bar pressure. In previous publications we have examined the adsorption and reaction of acetic acid with the surface of Pd(110),^{6,7} and also the adsorption of oxygen.⁸ Ethene, then, is the third component comprising the feed for vinyl acetate synthesis and is the subject of this paper.

Although there is a significant body of work relating to ethene adsorption on Pt surfaces, and on Pt(111) in particular,⁹ there is much less work on Pd surfaces. Madix et al. carried out work on the ethene interaction with Pd(100) in the 1980s using EELS and TPD.^{10,11} The conclusions were that ethene bonds in two forms at low temperature, namely, π and di- σ , and that the former desorbs at up to 300 K, whereas the latter is dehydrogenated. They further concluded that there was mainly methyldiyne ($-\text{CH}$) present at 300 K and that this species dehydrogenated between 350 and 500 K. At about the same time Chesters et al.¹² carried out EELS studies on Pd(110) and again

focused on the low-temperature (110 K) state of ethene, which they reported to be predominantly π , but with a small amount of di- σ at high coverages. Nishijima et al.^{13,14} have carried out work previously on Pd(110) using EELS, LEED, and TPD. They found that the layer saturates at close to half a monolayer of ethene molecules at low temperature and is present in the π form. Much of this desorbs by 260 K to leave approximately 0.38 monolayer of molecules that dehydrogenate upon heating to 300 K. The dehydrogenated form is cited to be the ethynyl, C_2H , in which both C atoms are proposed to interact with the surface and to be hybridized as sp^2/sp^3 , though this latter point is a little uncertain. This species dehydrogenates at ~480 K to leave C on the surface. Several more recent publications by Kawai et al. focus on the low-temperature, low-coverage form of ethene, which is considered to be π -bonded.^{15–19} They identified a $c(2\times 2)$ structure for ethene at 250 K using STM.¹⁹

In some ways the paper most relevant to what we report here is the recent work of Shaikhutdinov et al.²⁰ who worked on model nanoparticulate catalysts of Pd/ Al_2O_3 /NiAl(110). They stressed the importance of surface carbon as a product of ethene decomposition. They found that carbon deposits did not inhibit decomposition of ethene but deactivate the surface for dehydrogenation, which they propose occurs through a di- σ species. In this case the main surface intermediate was proposed to be the alkylidyne, formed on mainly (111)-type Pd facets.

In this work we have used a different kinetic technique from those used previously, namely, a molecular beam reactor, used in both isothermal and temperature-programmed modes. The advantage of such a reactor is that it can examine the interaction of ethene with the surfaces at temperatures above those for which TPD gives information. It can also measure any steady-state catalysis that may take place. Finally, in previous work

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* Corresponding author. E-mail: bowkerm@cardiff.ac.uk.

we have identified carbon deposition as an important factor in the reactivity of these systems, something not considered by the authors above, except for Shaikhutdinov et al.²⁰ We will show that, even with a significant amount of C present, the reactivity of Pd(110) can still be very high.

Experimental Section

The molecular beam system and methodology have been described in detail elsewhere.^{21,22} It comprises a stainless steel UHV chamber maintaining a base pressure of $\sim 2 \times 10^{-10}$ mbar (95% H₂), which increased to $\sim 6 \times 10^{-10}$ mbar during the course of some of the adsorption experiments. It consists of the molecular beam itself, which delivers a circular beam at the sample of 2.9 mm diameter, usually with a flux of 1.5×10^{17} molecules m⁻² s⁻¹, or about 0.015 monolayer of molecules s⁻¹ with respect to the number of surface atoms. The Pd(110) crystal was mounted on a custom-built holder in the chamber center. In the same horizontal plane is the molecular beam enclosure, a rear-view retarding field analyzer system with a coaxial electron gun (supplied by VG Microtech) for low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES), and a set of differentially pumped chambers that comprise an angle-resolved mass spectrometer. Also in the main UHV chamber is a quadrupole mass spectrometer (QMS) (Hidden Analytical Limited) employed for residual gas analysis (RGA). The QMS provides an indication of the angle-integrated partial pressure within the vacuum chamber, because no direct line of sight exists between the sample and detector; this mass spectrometer was used in the work reported here.

The Pd(110) crystal (5 N purity, Metal Crystals and Oxides Ltd), cut and polished in the (110) plane, could be cooled and heated in the chamber to between 110 and 1040 K. The sample was heated by direct contact with two tungsten wires, which passed through grooves in the edge of the crystal and were resistance heated. The heating rate was set at ~ 4 K s⁻¹ in the temperature range of interest for most of the experiments. Sample cooling was performed by close proximity of the sample mount to a liquid N₂ reservoir, connected by a Cu braid and a sapphire thermal switch. The temperature was recorded through a chromel–alumel thermocouple attached to the sample by a small hole drilled in the edge parallel with the surface plane. The surface was cleaned by cycles of Ar⁺ bombardment (500 eV, 6 μ A/cm², 30 min), annealing (850 K, 20 min), and flashing (1020 K, 2 min).

The use of a molecular beam reactor system allows sticking and kinetic information to be obtained and is described in more detail in previous literature.^{21–24} The system relies on principles originally presented by King and Wells,²³ which removes problems associated with mass spectrometer calibration and enables sticking probabilities to be measured to within ± 0.01 , depending on conditions and the particular system involved.

The purities of gaseous Ar (99.999%, Argo Ltd.), ethene (99.7% Argo Ltd.), and O₂ (99.6%, Argo Ltd.) were considered to be of a suitable level for direct use.

Results and Discussion

1. Ethene Sticking and Dehydrogenation. Ethene adsorbs with a high probability at all temperatures, as shown in Figures 1 and 2. Figure 1 shows the coverage dependence of the sticking probability, S , at several temperatures, and Figure 2 shows the temperature dependence of the initial sticking probability, S_0 . In Figure 1 the sticking is characterized by a plateau of constant reactivity at the start and then a drop of the adsorption at high coverages. This plateau diminishes somewhat as the adsorption

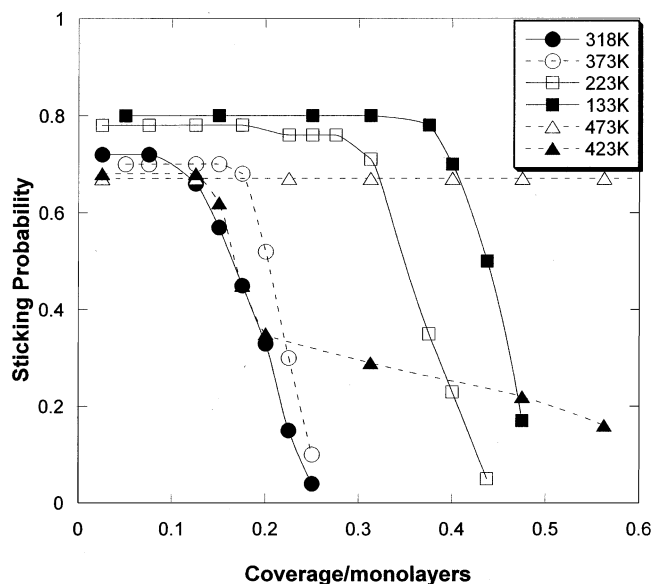


Figure 1. Sticking probability (S) for ethene adsorption as a function of amount adsorbed on the surface at several adsorption temperatures. The lines are interpolated curve fits.

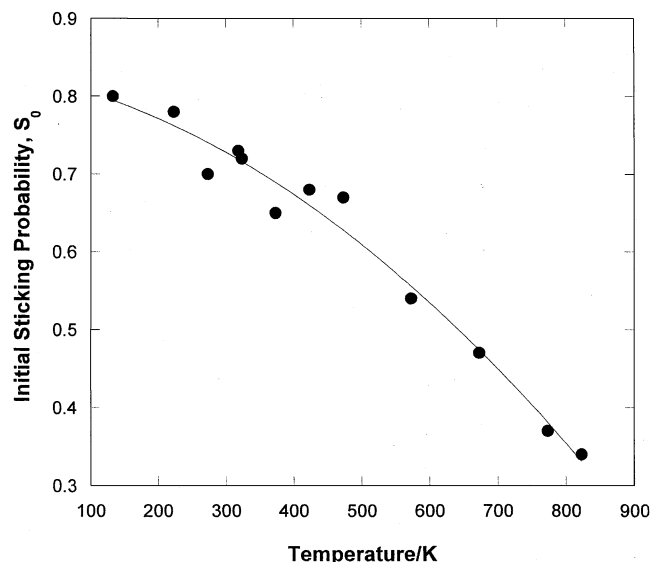


Figure 2. Dependence of the initial sticking probability (S_0) upon adsorption temperature.

temperature increases but is always present. This behavior is extremely non-Langmuirian but is typical of that expected from the influence of an intermediate state in the adsorption process, as delineated by a number of authors.^{24–30} This intermediate species is mobile in the physisorbed state and it can diffuse over filled sites. The important point about such diffusivity is that the adsorption continues at a high rate, even as sites at the surface are filled, because of the high diffusivity of the weakly held state on the surface, even though it has a short lifetime.³⁰ Such effects have been shown to be of great significance in catalysis, for instance, by enhancing the rate of CO oxidation via “reverse-spillover” of weakly held CO on a support to the active metal sites.³¹ The data in Figure 2 can be plotted in an Arrhenius fashion to elucidate something about the energetics of the adsorption process. The details of this are given elsewhere²⁴ but relate to the following equation

$$\ln\{(\alpha/S_0) - 1\} = (A_d/A_a) \exp(-(E_d - E_a)/RT)$$

Here α is the low-temperature limit of the initial sticking

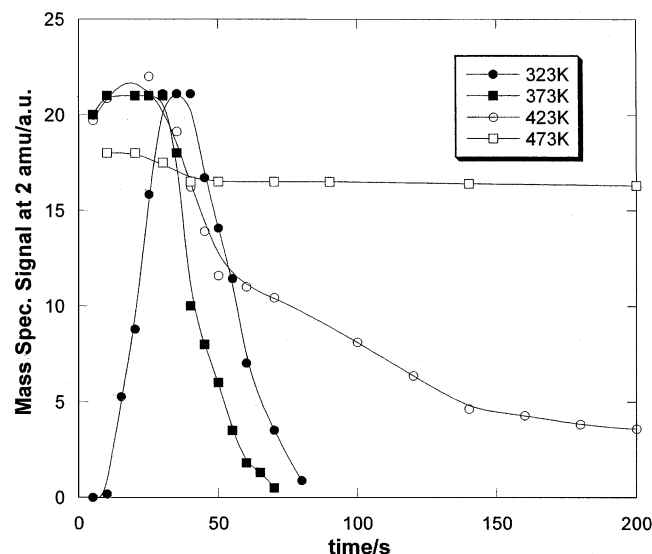
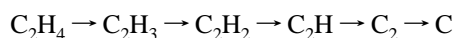


Figure 3. H_2 evolution during the adsorption of ethene at several temperatures. There is no hydrogen evolution below 270 K. All of the curves are for continuous exposure of the surface to the beam (which begins at time zero). The lines are smoothed curve fits.

probability S_0 and E_d and E_a are activation barriers for desorption from the precursor state back into the gas phase and adsorption from the precursor into the final state. This value from the Arrhenius plot, assuming the ratio of preexponential factors is unity, is 10 kJ mol^{-1} . Thus there is no NET barrier to adsorption, E_a being 10 kJ mol^{-1} lower than E_d . In turn, this dictates the decrease in sticking as the temperature goes up (Figure 2), because the *relative* rate of desorption increases as temperature goes up.

The product evolution for these reactions is shown in Figure 3; the only products are hydrogen and surface carbonaceous species. No hydrogen evolves for the reactions carried out at the lowest temperatures, up to $\sim 273 \text{ K}$. It can be seen that hydrogen evolution is relatively slow at first at 320 K and lags the uptake of ethene considerably. From experiments that involved chopping the beam partway through the adsorption, the decay appears to follow first-order kinetics, with a rate constant of $\sim 0.2 \text{ s}^{-1}$ and a half-life of $\sim 3 \text{ s}$. This implies that the rate limiting step is the decomposition of a surface intermediate and not hydrogen desorption (which should be second order³²). The normal desorption peak temperature for hydrogen evolution from the clean surface is approximately 310 K , both from this work and from that of others, and the desorption shows second-order characteristics.^{13,14,32} At 420 K the hydrogen evolution rate is immediately high, showing that decomposition and desorption are instantaneous and that, therefore, there is a very low coverage of the hydrogen-evolving species, which is achieved soon after admission of the beam to the surface. The possible reactions involved can be written as follows, many of the hydrogenated intermediates having been identified on various surfaces,



It is not possible to directly assess the stability of all these intermediates from this work. Further, when it comes to TPD from the beam experiments, it is difficult to assess the exact degree of dehydrogenation due to low levels of background H_2 adsorption on the crystal outside the beam area (which accounts for 90% of the total crystal area), which strongly affects subsequent desorption integrals. Experiments with TPD after

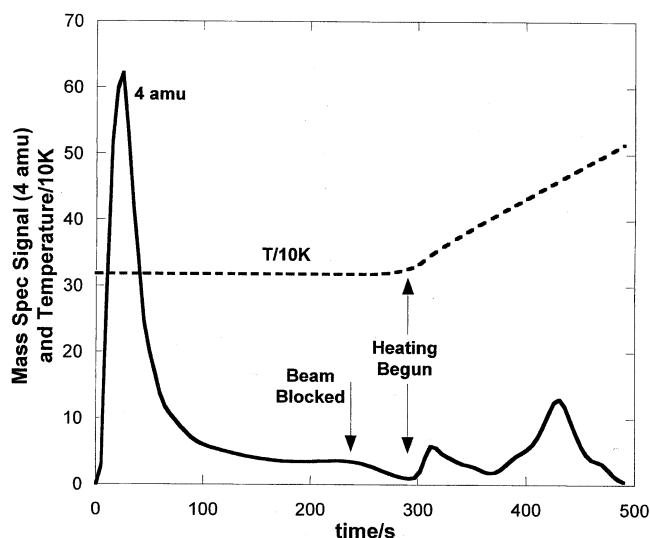


Figure 4. Adsorption experiment at 318 K for C_2D_4 on $\text{Pd}(110)$, showing D_2 evolution during isothermal adsorption and subsequent temperature-programmed desorption, heating beginning at $\sim 300 \text{ s}$.

background dosing of ethene are not shown here because they are essentially the same as those presented before by Nishijima et al.^{13,14} However, some experiments were carried out with C_2D_4 in the molecular beam to clarify the nature of the surface intermediate formed after adsorption at 320 K (that is, how much hydrogen is lost from the ethene molecule during adsorption, and how much is left associated with the adsorbed species?) and to assess the amount of background H_2 adsorption. The results for D_2 production are shown in Figure 4. These showed several interesting features. There was some hydrogen contamination of the surface before the ethene adsorption begins (from the ratio of $\text{HD}:\text{D}_2$ desorption, which was $\sim 1:8$, this contamination was approximately 0.05 monolayer of H atoms). There was no measurable desorption of H_2 during this period of beam impingement on the surface, implying that the HD was a product of the reaction, and indeed, the HD peak evolved to a maximum rate slightly earlier than that for the D_2 , due to loss of H from the beam area by reaction. To test the level of dehydrogenation during sticking at 320 K , the surface was then heated, and only a small amount of further D_2 was evolved, a small peak just after heating, followed by a bigger peak at $\sim 460 \text{ K}$. The first peak is merely the remnant of the tail of the decomposition peak seen during adsorption, whereas the second peak is due to the remaining D associated with the adsorbed layer. If we assume the latter is associated with the carbon in some way, then we can estimate the maximum C:D ratio associated with this layer. The ratio of deuterium lost during adsorption to that evolved at 460 K is $5.3(\pm 0.5):1$, which indicates a hypothetical formula for the remaining layer of approximately $\text{C}_2\text{D}_{0.7}$. Clearly then, the molecule has become very largely dehydrogenated by reaction at 320 K . It appears, however, to be a mix of carbon and a hydrogenated intermediate, presumably the ethynyl identified by others,^{13,14} or an extremely dehydrogenated oligomeric species (e.g., C_6D_2). This disagrees with Nishijima et al.^{13,14} who identify the state of the layer at $\sim 400 \text{ K}$ as purely the ethynyl, largely by vibrational spectroscopy and TPD. However, it is interesting to examine some of the published data for the H_2 desorption from the ethene layer. In Nishijima's work, if the relative desorption integrals for the low T (P1) and high T (P2) are measured, varying ratios of P1:P2 are obtained, varying between a value of $\sim 3.3:1$ to $\sim 4.5:1$, with an average value of about $3.8:1$. In our own background-dosed TPD the ratio was about $4.2 (\pm 0.4):1$. This compares

with the expected value of 3:1; clearly the stoichiometry is not right but is closer to the expected value than our results with C_2D_4 , which give nearly half of the expected amount. Nevertheless, it may be that, even in Nishijima's work the average surface species is more dehydrogenated than C_2H . Unfortunately, no estimates of the coverage of the ethynyl were given from the other works. Extra adsorbed carbon would probably not be noted in Nishijima's EELS data, though there is some intensity in the expected region after heating to only 350 K, but this also includes the Pd–C stretch of the ethynyl.^{13,14} Clearly this is an area for more detailed work.

Returning to the data of Figure 1, it appears that the adsorption of ethene saturates at a coverage of around 0.25 monolayer at ambient temperature and so leaves about 0.5 monolayer of carbon on the surface after heating. This is supported, though to a limited degree, by the LEED data. We found that a generally disordered surface was formed after adsorption of ethene at a variety of temperatures, but especially at room temperature, with a significant broadening of the integral order spots of the surface and an increase in background intensity. However, we did occasionally manage to identify a faint $c(2 \times 2)$ structure (after ethene dosing and taking LEED at 473 K), indicative of a half monolayer of adsorbate. Reasons for the lack of a well-ordered structure are given below.

More ethene adsorbs at low temperatures, but upon heating part of this layer desorbs as ethene at low temperatures, with peaks at ~ 220 and 300 K, leaving around 0.25 monolayer of ethene on the surface. From the beam measurements the coverage of ethene at 140 K is about one-third of a monolayer. Above 400 K adsorption temperature the situation begins to change and hydrogen evolution is seen to occur continuously at 473 K, which proceeds, at least within the time scale of these experiments, at steady state. This means that there is a continuous uptake of carbon onto the surface, and in the most extreme experiment, carried out for 60 min, ~ 20 monolayers of carbon were deposited onto the surface. However, the surface was not coated in carbon, because the Auger signal for carbon was very small, although the exact Auger ratio for small coverages is very difficult to determine in Auger with an RFA, due to the severe overlap between C and Pd(MNN) peaks at ~ 275 eV electron energy. Thus it is likely that most of the carbon has gone subsurface and has dissolved into the crystal (this is discussed more in relation to separate XPS studies below). It has not formed a carbide with all of this carbon in the surface region because an Auger signal ratio of about 1:1 would be expected, whereas the ratio is very small. Thus it appears that most of the carbon has left the immediate surface region. This effect of apparently continuous carbon uptake at high temperatures has been reported by us before for alkenes³³ and has also been reported by Raval et al. for CH_2Cl_2 adsorption.³⁴ Further support for the loss of carbon from the surface region is the high value for the sticking probability of ethene, which is similar to that on the clean surface. The nature of this extraordinary C deposition will be discussed further below in relation to carbon clean-off experiments with oxygen.

The situation at 423 K seems to be intermediate between the low-temperature and high-temperature regimes, that is, although there is significant extra uptake of ethene at this temperature compared with lower temperatures, the uptake saturates. Although some C goes subsurface, the amount is limited. There appear to be, then, two processes taking place, possibly in competition with each other, at this temperature. The first process is the usual formation of a surface layer of carbon or carbonaceous species and the second is diffusion into some kind

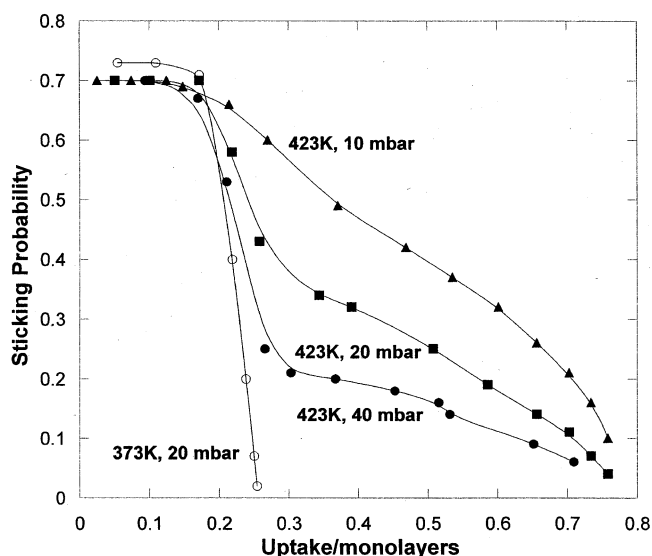


Figure 5. Sticking probability dependence on uptake of ethene at 423 K at three different beam pressures. The usual beam source pressure, and that used in the other beam experiments shown in this paper, is 20 mbar. Data at 373 K are shown for comparison. The lines are smoothed curve fits.

of subsurface site. This being the case we might expect the adsorption to be strongly pressure dependent at this temperature. Indeed, we did find this to be the case, as shown in Figure 5. Here, although the total uptake appears to be independent of the beam flux (which is proportional to pressure in the beam), the shape of the uptake curve is quite different for the different source pressures. When the pressure is high, the sticking drops fast to a low-sticking plateau, which continues with a slow decrease over time. However, at low pressure the sticking probability remains high during the saturation process. It would appear that, at the low pressure, the surface remains relatively unsaturated as adsorption proceeds, presumably due to sufficient loss of material from the surface to the subsurface region in the time scale of the adsorption. At the high pressure the surface layer has less time to diffuse into the bulk and so the surface layer builds up to a higher coverage while the subsurface diffusion takes place. It is somewhat strange that there appears to be saturation behavior of these bulk states at this temperature, independent of pressure, but this perhaps indicates a buildup of carbon in a well-defined selvage state, without too much diffusion into the "deep" bulk. The fact that the uptake appears to saturate after approximately 3 times the normal uptake, that is, at around 0.75 monolayer of molecules, or 1.5 monolayers of atoms, may imply that we have a half monolayer of surface carbon, plus either a full monolayer of, effectively, PdC below it, or two further half monolayers below the surface layer. To support this, it was interesting to observe that the oxygen sticking probability after such an experiment had decreased to 0.25 and slowly increased with time as the carbon was removed. In contrast to this behavior, at 473 K the ethene sticking remained constant and showed very little decrease, even after 6 monolayers of carbon atoms had been adsorbed onto the surface. This is presumably because diffusion deeper into the bulk becomes facile.

Limited XPS experiments were carried out in a separate system in an attempt to determine the nature of the carbon layer that is formed by ethene adsorption (Figure 6). Here it can be seen that the C(1s) binding energy is ~ 284.5 eV after adsorption at 323 K, and this shifts to slightly lower binding energy upon heating to 423 K. Indeed, there appears to be a change in the

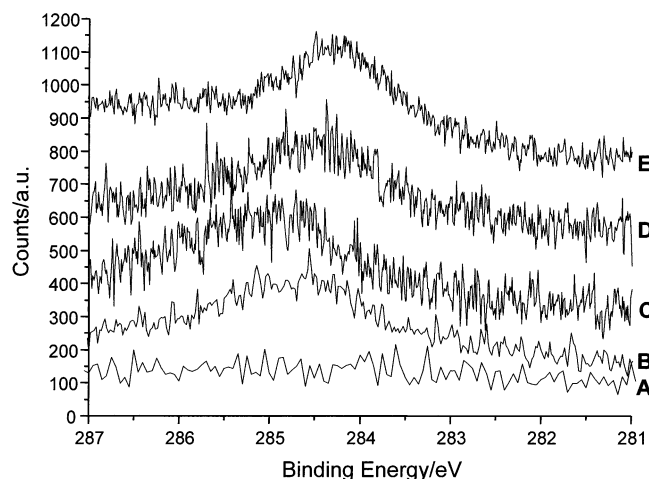


Figure 6. XPS C(1s) spectra before dosing ethene (lowest curve) and, from bottom to top, after ethene adsorption at 323 K, followed by heating to 373 and 473 K, together with the signal after adsorption at 423 K (top). Spectra C and D are multiplied by 3 compared with the others and each spectrum is offset vertically for clarity.

electronic state of the carbon between 373 and 473 K, because the peak shifts by ~ 0.4 eV to lower binding energy. The signal also diminishes considerably after heating to 373 K, which indicates that the carbon has already changed its site, and probably gone subsurface, under the top layer. If it was in the troughs of the surface, we would expect to see little change in the signal, because the electrons are sampled normal to the surface and so would not be "shadowed" by any Pd atoms in that position. Upon adsorption at 423 K a bigger signal is observed, presumably due to some buildup of carbon in the subsurface region, as suggested by the data of Figure 5. The binding energy is ~ 284.3 eV. The binding energies observed are not so useful for chemical identification, because they are in the region typical of what might be expected for surface carbon, though it is difficult to unambiguously identify the exact form of carbon. Adsorbed ethene and graphite appear at about this energy, amorphous carbon is around 284.5 eV, whereas carbides vary between ~ 282 and 284 eV (Ni_3C , for instance, being 283.9 eV). We have not found a reference value for palladium carbide.

Further experiments were carried out with ethene adsorption, involving temperature-programmed adsorption (TPA). A result is given in Figure 7 and shows the usual isothermal uptake curve at 320 K, for which the saturation uptake was 0.25 monolayer of ethene molecules (here shown in terms of total C atoms taken up), at which point adsorption ceased. Upon heating above 400 K, uptake of ethene recommenced, hydrogen was evolved, a maximum reaction probability of ~ 0.55 was attained at 570 K, and thereafter it decreased in a nearly identical fashion to the dependence shown in Figure 2, though in this case the sticking is onto a surface which has already taken up carbon. It is quite clear from all of these data that the presence of the adsorbed layer on the surface, although blocking ethene adsorption below 400 K, has almost no effect on the reaction with ethene above this temperature. The total uptake of carbon in the experiment of Figure 7 was around 3 monolayers, or 6 times the saturation coverage of carbon formed at ambient temperature with ethene.

A major question, then, is what determines that ethene adsorption recommences at around 400 K? It could be that, with carbonaceous species already present on the surface, the adsorption becomes activated, which is clearly not the case for the clean surface, because S_0 is high. However, we might expect a more gradual increase in rate with increasing temperature if

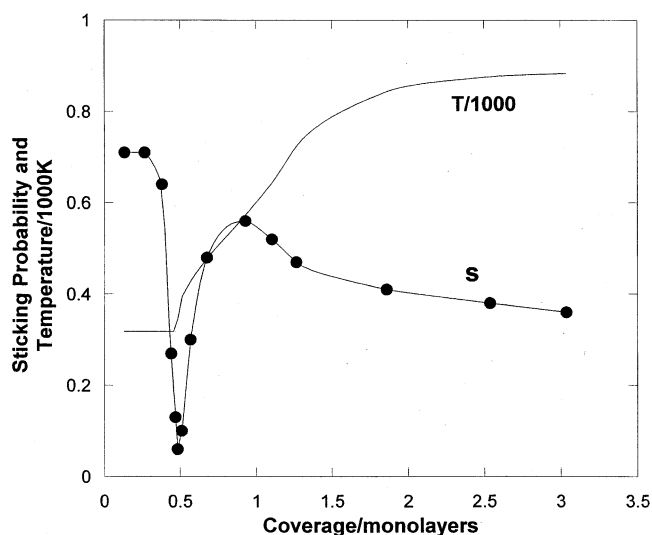


Figure 7. Temperature-programmed adsorption (TPA) measurement for ethene adsorption on the Pd(110) surface, with the beam on during heating. This shows the ethene sticking probability dependence upon coverage of carbon atoms for the isothermal period and the TPA period, with the temperature profile also.

this were the situation, whereas there appears to be a relatively sudden increase at ~ 400 K. Further, if the adsorption were activated, we would expect a significantly lower adsorption probability on the C-covered surface above 400 K than for the clean surface, which is also not the case. Thus it seems more likely that something critical happens to the C layer at ~ 400 K. This could be a change in surface structure or in the C location, or in the chemical nature of the surface species, or it may be that diffusion of C into subsurface regions only becomes possible at that temperature. The recommencement of the adsorption during temperature programming corresponds approximately with the beginning of the decomposition of the hydrogenated surface intermediate, and so the renewed uptake of ethene is presumably associated with that. As this state decomposes, so the C produced moves to different sites that unblock the adsorption sites at the surface. Those sites are probably sites in the $\langle 011 \rangle$ troughs or immediately beneath the surface layer, and these can in turn be freed by further diffusion of carbon into the deeper bulk, which appears to be more activated. The indication of a $c(2 \times 2)$ pattern from LEED at 473 K implies, however, that some carbon is left in the surface region (perhaps in the troughs of the (110) structure), or in the immediate subsurface (perhaps directly below the top layer ridge of atoms).

2. Oxygen Postadsorption. 2.1. Isothermal Carbon Clean-Off. A number of experiments were carried out by adsorbing oxygen following ethene uptake. For comparison purposes Figure 8a shows the sticking probability dependence upon coverage for ethene and for oxygen on the clean surface, together with sticking curves for oxygen after the adsorption of ethene. If oxygen was adsorbed at 573 K after the adsorption of ethene to saturation at 320 K, then the oxygen adsorbed very well on the carbon layer, with an uptake corresponding to approximately twice the uptake of ethene, that is, half a monolayer of oxygen molecules, or one monolayer of oxygen atoms, which is also twice the normal uptake of oxygen. Figure 8b gives the product evolution and shows that CO evolved immediately upon introduction of oxygen, followed by CO_2 , which peaks after the CO starts to diminish. This effect is presumably simply due to the changing balance of oxygen and carbon atoms on the surface; at the beginning there is little

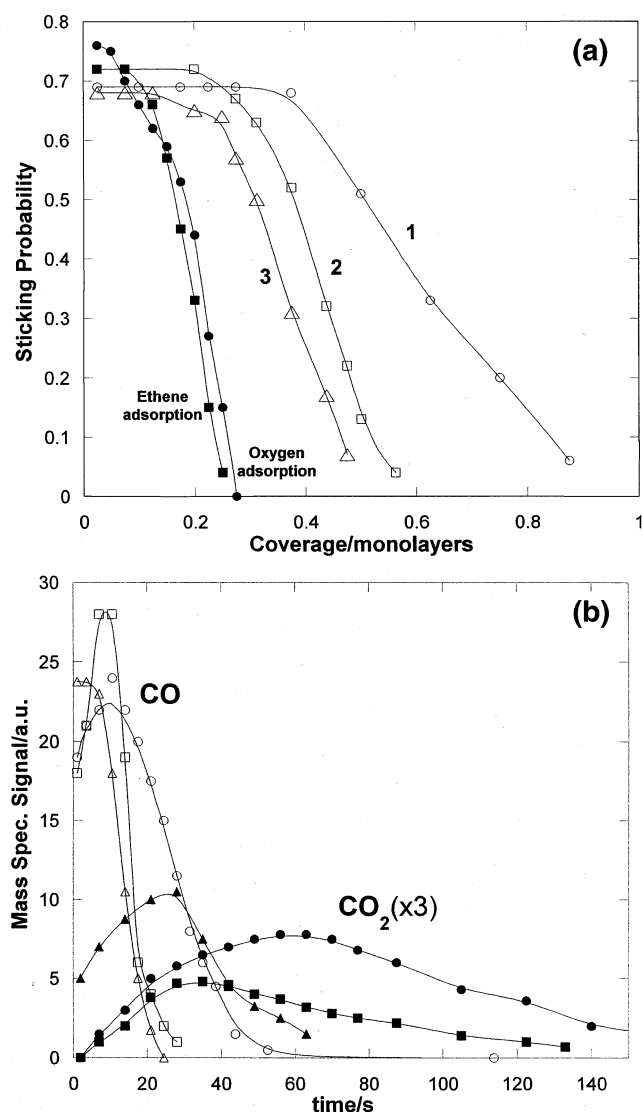


Figure 8. (a) Sticking probability curves for separate ethene and oxygen adsorption on Pd(110) at 318 K as a function of coverage, and for oxygen adsorption at 573 K after the dosing of ethene (curves 1–3): curve 1, oxygen adsorption after dosing ethene for 180 s at 573 K; curve 2, after ethene dosing for 90 s at 573 K; curve 3, after dosing ethene to saturation (0.25 monolayer) at 318 K. The lines are smoothed curve fits. (b) Product evolution as a function of temperature for the experiments of (a): filled data points, CO₂; open points, CO; circles, ethene dosed at 573 K for 180 s; squares, ethene dosed at 573 K for 90 s; triangles, ethene dosed at 318 K to saturation. The lines are smoothed curve fits.

oxygen on the surface, so CO forms and desorbs before it can encounter another oxygen atom, whereas at longer reaction times there is more oxygen than C on the surface and so CO, which is initially formed scavenges oxygen atoms before it desorbs, and so produces CO₂. During this part of the reaction there was a plateau of constant oxygen sticking probability, which contrasts with the behavior of oxygen on the clean surface. Further, this corresponds with the reaction period—when the oxygen sticking begins to drop, CO and CO₂ evolution have essentially finished, the sticking curve beyond this point looks like that for the clean surface, and about the same uptake (~0.5 monolayer of atoms) was obtained in that period.

If the oxygen treatment followed the continuous uptake of ethene at 573 K for 3 min (during which time approximately 5 times the room temperature uptake of ethene was obtained; that is, around 2.5 monolayers of carbon was deposited with a

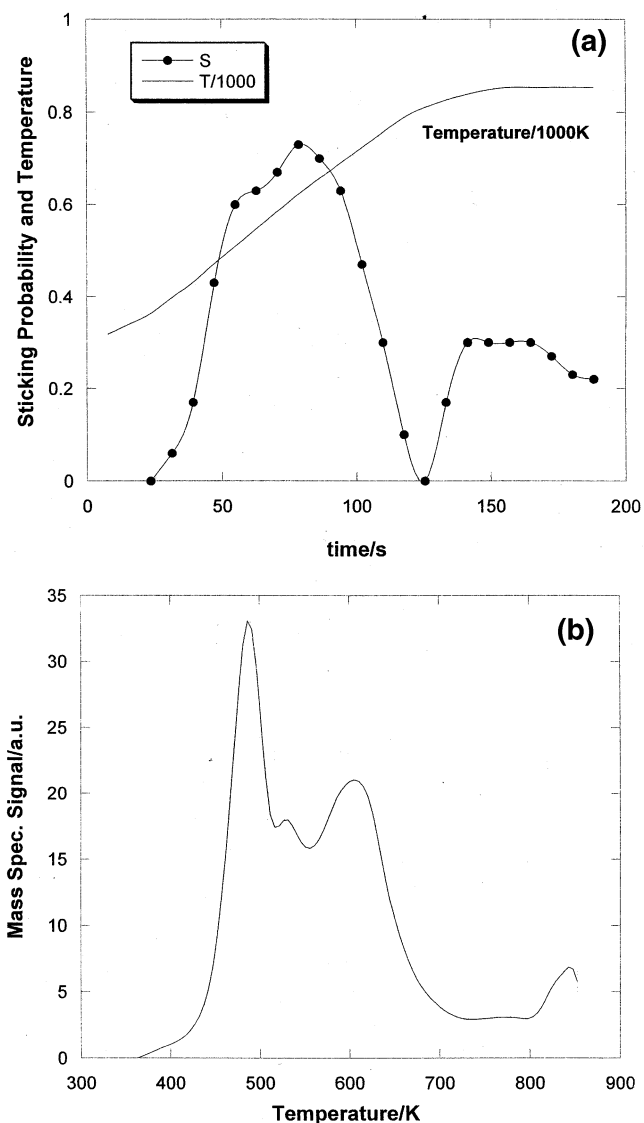


Figure 9. (a) Temperature-programmed reaction (TPR) in oxygen after the adsorption of ethene at 318 K, shown in terms of the sticking probability of oxygen as a function of time, together with the temperature profile. (b) Evolution of CO as a function of temperature during the experiment of Figure 9a. Only a small amount of CO₂ was evolved and is not shown here for clarity.

constant ethene sticking probability of 0.55), then the oxygen uptake was significantly increased to around 3.5 times the 320 K ethene uptake (that is, about 0.9 monolayer of oxygen molecules, adsorbed in atomic form); see Figure 8a. Thus, although the uptake of oxygen was significantly higher, it did not account for all the carbon deposited because, if we assume that 0.5 monolayer of oxygen atoms were actually left adsorbed on the surface, then only about 2.5 times the normal ethene uptake, or 1.25 monolayers of carbon was recovered in this experiment. About 6 times the oxygen uptake on the clean surface might have been expected (that is, 5 times the room temperature uptake of ethene, corresponding with the clean-off of 2.5 monolayers of carbon, plus a half monolayer of oxygen atoms). Again, the major product is CO early in the oxygen adsorption, followed by some CO₂, as shown in Figure 8b. Parts a and b of Figure 8 also show an experiment in which half the amount of ethene was deposited at 573 K (that is 2–2.5 times the normal uptake, equivalent to 1–1.25 monolayers of carbon deposited). In this case the oxygen uptake was between 2 and 2.5 times the normal value, that is, around 1–1.25 monolayers

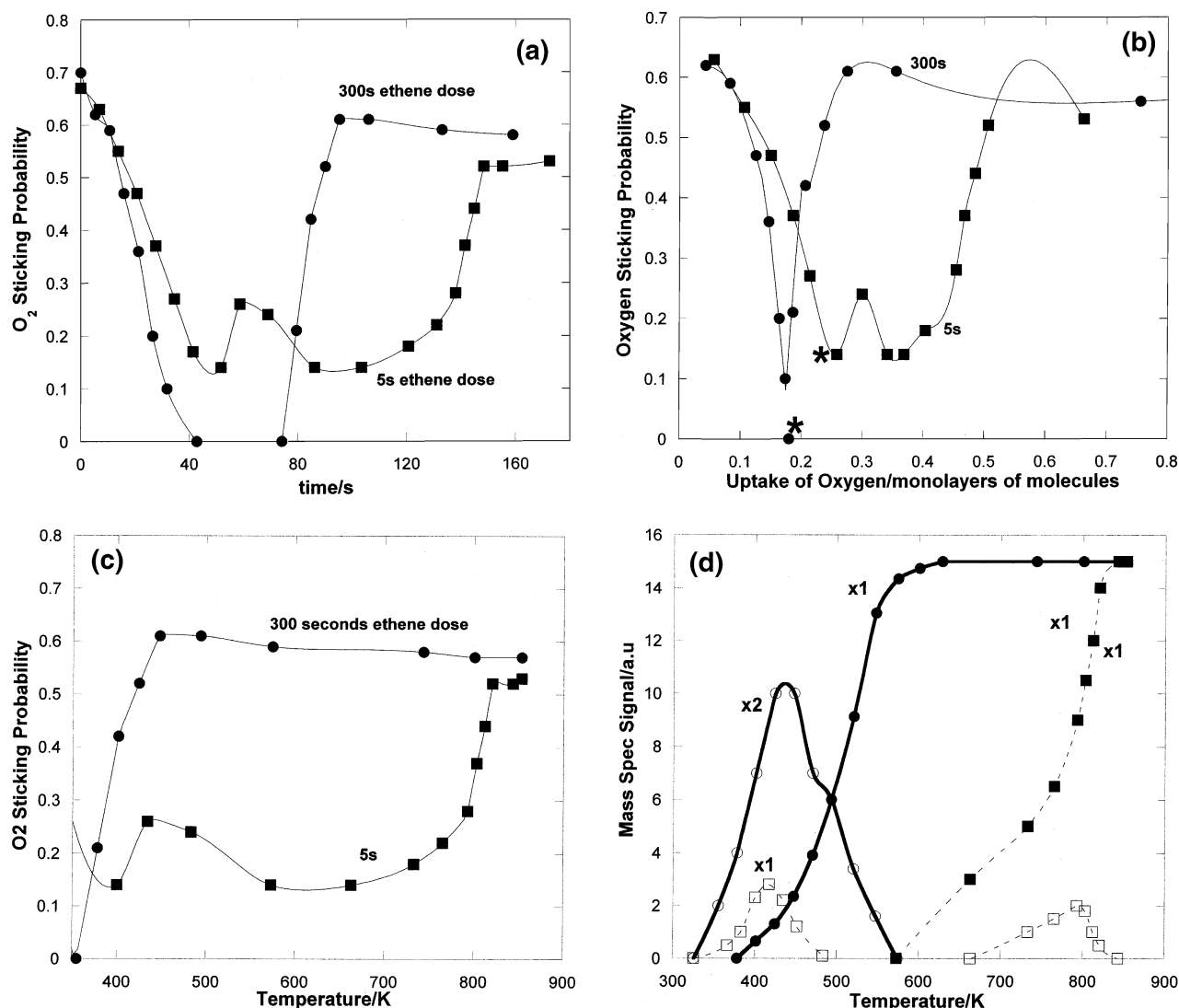


Figure 10. (a) TPR in oxygen after the adsorption of ethene at 573 K for various ethene adsorption times, showing the sticking probability for oxygen as a function of time. The asterisks note the time at which heating was begun for the different experiments; before this point the surface was held at 318 K. The lines are interpolated curve fits for all four parts of Figure 10. (b) Same data as (a), represented in terms of oxygen uptake onto the surface. The uptake has only been shown until 0.8 monolayer for clarity, but for this experiment to total oxygen uptake for the 300 s dose was 1.35 monolayers and for the 20 s dose 0.9 monolayer. (c) Data for (a) represented as a function of temperature during heating. (d) Product evolution as a function of temperature for the same experiments shown in (a)–(c). Filled points are for CO, and open points for CO₂; otherwise the symbols are as for (a)–(c). Data with the solid curve fit are for the 300 s ethene predose at 573 K; the dotted curve fit is for the 5 s predose.

of oxygen atoms, presumably including 0.5 monolayer of adsorbed oxygen atoms. Thus, again, the full amount of carbon does not appear to have been recovered in such an experiment.

2.2. Carbon Clean-Off by Temperature-Programmed Reaction. Another type of experiment was attempted, as shown in Figure 9, that is, a temperature-programmed reaction (TPR) of oxygen in the beam with ethene predeposited at 318 K. This blocked the oxygen sticking at 318 K. The uptake of oxygen begins at ~400 K, soon after heating begins, together with a rapid increase in CO₂ evolution, followed by CO, which is the dominant product. Two peaks are seen for both products, at ~500 and ~600 K for CO. The uptake of O₂ appears to diminish at ~720 K, but this is probably due to desorption of O₂ from the surface, and indicates that, at this point the surface is essentially clean of carbon. This is the correct temperature for desorption seen in other experiments.^{8,35} With decreasing amounts of ethene predeposited, the ratio of CO:CO₂ decreases considerably and CO₂ becomes the dominant product, desorbing in two peaks at 440 and ~500 K. The CO desorption then appears to be largely associated with the second peak. When

even less ethene was dosed, only one peak is seen for CO₂ at 440 K, with CO at ~500 K. For these latter two experiments it is clear that oxygen sticks very well to the surface even at 318 K but that no products evolved until the surface was heated, when extra uptake was also observed. In all of these experiments a small increase in the CO production was seen at the highest temperatures (~800 K), together with a net uptake of O₂. We believe that this is due to diffusion of some subsurface C back to the surface followed by reaction with oxygen to produce CO (no CO₂ was produced here because the surface lifetime and coverage of CO and oxygen are both low at high temperature). However, for ethene dosed at 318 K this high-temperature evolution was small and not very reproducible in intensity.

This latter effect was much more obvious for adsorption of ethene at elevated temperatures Figure 10a–d. Part a–c of Figure 10 represent these data in different forms for clarity—in terms of sticking probability dependence on time, uptake, and temperature, and here only two extremes of ethene dosing times are shown. Here ethene was adsorbed for varying times at 573 K, followed by cooling to ~320 K and by heating in a beam of

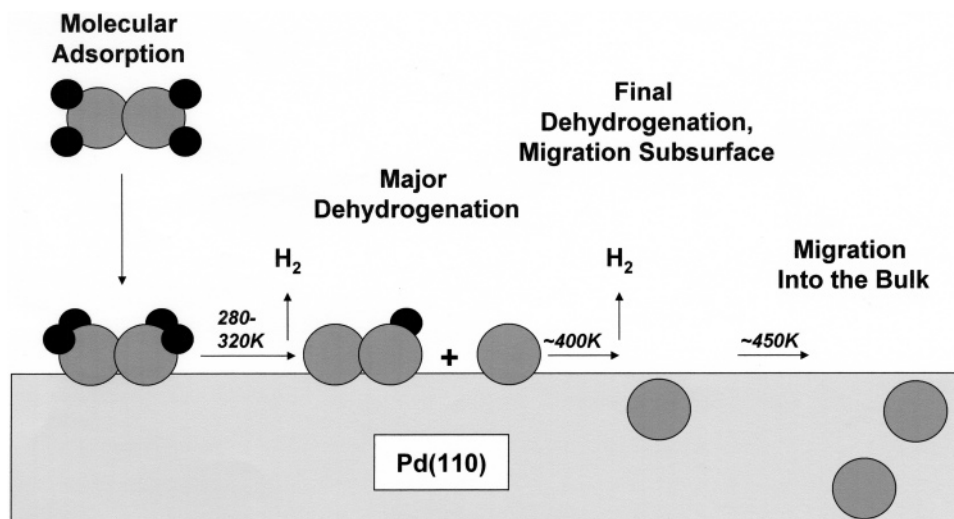


Figure 11. Schematic model summarizing the adsorption and dehydrogenation of ethene on Pd(110).

oxygen. The overall behavior is a little different from that in Figure 9 above—sticking was not impeded by the preadsorbed ethene, even for the highest dose of ~ 6 monolayers equivalent of carbon in these experiments. CO_2 was the first product to evolve upon heating (at ~ 350 – 500 K, Figure 10d), but the most noticeable difference from the curves above is that much more CO was evolved at high temperature. This, we believe, is due to reaction of oxygen at the surface with C from the subsurface region. Clearly this is not possible below ~ 700 K for the lowest doses, whereas for the highest dose CO evolves from much lower temperatures, due to the presence of much more C in the subsurface region. The time scale for adsorption at the lower doses means that less than 0.5 monolayer of carbon is adsorbed and this appears to remain near the surface, because there is relatively little desorption at the highest temperatures. Indeed, some of that which does desorb may be from deep carbon deposited from earlier experiments. For the long dose of 300 s there is much more subsurface carbon and therefore much more CO is evolved, and it begins at much lower temperature (~ 400 K for the 300 s dose vs ~ 600 K for the 5 s dose).

3. Ethene Adsorption, Decomposition, and Surface and Bulk Carbide Formation. The model for the reaction that evolves from this work is illustrated in Figure 11. At low temperatures ethene adsorbs molecularly and is intact, as described in the Introduction. Upon heating, the molecule begins to dehydrogenate. This probably happens at the same time as the second peak of ethene desorption, that is, around 270 K, though it is not clear from the current data whether other partially dehydrogenated intermediate species are formed at that point. The evidence certainly appears to be that, by 320 K, the molecule has almost completely dehydrogenated and may be a mix of ethynyl and surface carbon. It is clear that some kind of transformation in this layer takes place at ~ 400 K, because before that temperature this layer essentially blocks further adsorption of ethene or oxygen, whereas above this temperature further adsorption can take place surprisingly efficiently. This is probably due to both complete dehydrogenation of the remaining species and a change of site of the surface carbon, which could occur in a number of ways, such as, (i) surface reconstruction, (ii) loss of carbon from the immediate surface region, or (iii) a simple change in site position. Regarding (i) it is well-known that Pd(110) is prone to (1×2) reconstruction upon adsorption, forming alternate missing surface rows on the [001] direction. Thus, with oxygen a $c(2 \times 4)$ structure is seen, which consists of half the density of surface Pd atoms in the

(1×2) reconstruction, with zigzag arrays of oxygen atoms between them.^{35–37} This reconstruction tends to be lifted by CO clean-off reactions even at ambient temperature, and we found no evidence for this reconstruction from LEED. Regarding point ii above, it is clear that this process can indeed occur above 450 K, because many layers of C can be deposited, yet there appears to be no additional C at the surface. (iii) may occur at intermediate temperatures (~ 400 K) and may result in location of the surface carbon at the bottom of the troughs in the (110) surface, but it is clear that the carbon can diffuse further into the bulk from the very high levels of C that can be adsorbed and that are too high to be located at the surface. Further, multilayers of surface carbon are never identified in the Auger analysis.

Exactly where the C is located is not certain, but it would appear that, at least for the data at 423 K, the carbon is in a selvedge region, whereas for higher temperature adsorption, diffusion deeper into the lattice can occur. This can return to the surface at high temperatures, as evidenced by the high-temperature O_2 uptake and CO evolution in Figure 10. Although this carbon has diffused away from the immediate subsurface region, it has probably not been lost completely to the bulk on the time scale of these experiments, because it can be recovered by reaction with oxygen relatively quickly. On the other hand, as Figure 8 and the associated discussion show, at least some of this carbon cannot be recovered at 573 K in oxygen, presumably because it lies too deep in the bulk.

The reason it was very difficult to observe ordered structures in LEED probably relates to this varying surface composition. At ambient temperatures we may well have a mixed layer of largely dehydrogenated surface species, which are disordered; we did not see a good LEED pattern under these conditions, neither did others.^{12,13} Upon heating, loss of the remaining hydrogen from the adlayer occurs, beginning at ~ 400 K, but above ~ 450 K loss of carbon to the subsurface region occurs. Thus no well-ordered structure of rational coverage is ever obtained in these experiments, though after dosing at 473 K, a weak $c(2 \times 2)$ can be seen, implying the presence of ~ 0.5 monolayer of carbon somewhere in the surface region.

4. Effect of C Deposition on the Behavior of Other Organics. We have found that the adsorption of any organic molecule we have studied on Pd(110) results in C deposition, and the molecules we have investigated so far include a range of alkenes,³³ alcohols,^{38–40} acetaldehyde,^{33,41} acetic acid,^{6,7} and vinyl acetate.⁴² Although acetaldehyde decomposes catalytically

(at steady-state) at 300–400 K by decarbonylation to give methane and CO, nonetheless above 320 K some dehydrogenation takes place, leaving C on the surface.⁴³ This then extends the range for the steady-state decarbonylation to 400 K by stabilization of the methyl group on the surface. In this latter case a more well-defined $c(2\times 2)$ -C structure was obtained.^{33,41} Above 450 K, the reaction evolved to steady-state dehydrogenation, similar to the work here with ethene, but with continuous CO and hydrogen evolution and the deposition of many layers of carbon into the surface.

Acetic acid adsorption results in C deposition if adsorption is carried out above the stability range of the acetate on the clean surface (above about 400 K). This then results in considerable stabilization of the acetate, so that decomposition occurs at as high as 460 K. Furthermore, this carbon layer results in ordering of the acetate into structures that are mutually protective from decomposition, resulting in “explosive behavior” in TPD, which is manifested as a decomposition peak with very narrow half-widths (as narrow as 3 K for some acetate–metal systems^{43–45}).

Perhaps the most remarkable feature of this system is that the surface C present above 450 K appears NOT TO POISON any of these reactions, which all proceed at remarkably high reaction probability in a steady-state fashion under low-pressure conditions. This appears to be due to the fact that the surface remains essentially *clean*. However, because these reactions result in C deposition into the solid (especially alkene dehydrogenation), then carbon will build up over a long period of time in the bulk. When saturation of the bulk would occur is uncertain, but if we assume that the material is capable of complete conversion to PdC, then at our collision rate and reaction probability, and assuming that the latter does not decrease, it would take about 3×10^5 h (or about 30 years!) continuous running to reach this stage, when presumably C uptake would stop and the characteristics of the reaction would change, possibly for the better (e.g., for ethene, perhaps partial dehydrogenation in its various forms would take over). If the experiment could be run at atmospheric pressure, the time would be reduced to about 1 s. Now, when it comes to high-area catalysts, there is much less bulk relative to the surface to take up carbon. Thus, if we imagine a 3 nm hemispherical Pd catalyst particle, which would contain approximately 200 surface atoms, with the same conditions as in our molecular beam, it would take a much shorter time to saturate the particle to form PdC. In fact, it would take about 1000 s or 15 min. If this material were exposed to ethene at a more normal pressure of, e.g., 1 atm, then this time would be reduced to about 10^{-6} s. It would thus occur almost instantaneously, although under these circumstances the diffusion rate is likely to be rate-limiting and may slow the process somewhat. We thus propose that any organic reaction taking place under such conditions will produce significant C deposition onto the surface and into the bulk. Of course, many of the important commercial reactions of this type are hydrogenations and take place under conditions of high hydrogen pressure to force the reaction away from dehydrogenation conditions. However, the facility we have shown above for C deposition dictates that C formation may well occur and that, once formed, this C is unlikely to be removed as methane until high temperatures. However, all of this is clearly a subject for considerable debate, which we welcome.

Conclusions

The reaction of ethene with Pd(110) has been studied mainly using a molecular beam reactor. The molecule sticks efficiently

on the clean surface at all temperatures. At low temperature it adsorbs without product formation, above 270 K hydrogen is produced transiently during adsorption until the surface is saturated with 0.25 monolayer of adsorbate, whereas above 450 K hydrogen evolves continuously at steady-state and carbon is continuously deposited onto the surface. The surface carbon layer appears to saturate at about 0.5 monolayer, but above 450 K ethene still adsorbs efficiently on this layer, continuously depositing carbon, which apparently goes subsurface. At 320 K adsorption temperature the ethene is mainly dehydrogenated and probably exists as a mix of ethynyl and carbon, whereas the carbide is formed upon heating above 400 K or by adsorption above that temperature. The low-temperature form blocks further adsorption of ethene or oxygen at 320 K, but the carbide does not, presumably because the carbon is no longer at the surface and does not block the adsorption sites.

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