

# The interaction of ethylene, acetylene and butadiene with a clean tungsten (100) surface

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## Abstract

The interactions of ethylene, acetylene and butadiene with a W(100) surface at 300 K have been investigated using photo electron spectroscopy, work function measurement and thermal desorption techniques. The course of the interaction is shown to be coverage dependant. At low coverage, acetylene is initially decomposed on the surface to its constituent atoms carbon and hydrogen, followed by the formation of a molecular species (I) as the coverage is increased. Further exposure results in the displacement of adsorbed hydrogen atoms by (I) and then the formation of a second adsorbed species (II) at the expense of (I). At saturation, all four species are present to some extent. With butadiene, all three adsorption regimes are again observed, but with ethylene only the first two are apparent. The nature and bonding of the adsorbed species (I and II) are discussed. © 1998 Elsevier Science B.V.

*Keywords:* Adsorption; Hydrocarbons; Tungsten (100); Polymerisation

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## 1. Introduction

Metal catalysts can exhibit diverse reactions with hydrocarbon feedstock depending upon the nature of the metal, the geometric characteristics of the metal surface and the specific chemical interactions involved. The surface chemistry of specific metal surfaces towards small unsaturated hydrocarbons is therefore of some importance and it is interesting to compare properties both between and within the groups of the periodic table. Group VIII metals, for example, are effective hydrogenation cata-

lysts and the adsorption of ethylene or acetylene is accompanied generally by the breaking of carbon–hydrogen bonds. Within the group, however, Ir(111) is found to be more active than Rh, Pd or Pt(111) surfaces. Several types of reaction intermediate have been identified, according to the identity of the metal and the reaction temperature. Rh(111) for example, is found to form vinylidene ( $-\text{C}-\text{CH}_2$ ) species at 270 K but CCH and CH species above 400 K [1]. Vinylidene species have been identified on Pt(111) with acetylene [2] while Pd(111) is found to catalyse the cyclotrimerisation of acetylene to benzene [3]. The ethylidene species has been identified on Ir(111) at 180 K after the

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adsorption of acetylene or ethylene [4]. Interestingly, the possibility of polymerisation has been discussed for ethylene on Ir(111) at 500 K [5] and with acetylene on Ni(755) at high coverage [5].

Carbon–carbon bond breaking is not commonly found at low temperatures with group VIII metals, although it has been reported for iron(100) [6] and cobalt above 500 K [7]. There is however much more evidence for low temperature C–C bond breaking with group VI metals. These metals are effective catalysts for olefin metathesis and hydrogenolysis as well as hydrogenation [8]. The interactions of ethylene and acetylene with Mo(100) have been reported by Wang et al. [8,9]. In the case of tungsten(100) the interactions with some cyclic hydrocarbons have been reported [10,11]. The adsorption of ethylene and acetylene has been previously investigated by ultraviolet photoelectron spectroscopy (UPS) [12], high resolution electron energy loss spectroscopy (HREELS) [13] and Auger spectroscopy [14,15]. The conclusions drawn from the early work on tungsten were based on a rather limited range of adsorption conditions and tended to be technique specific, but nevertheless some measure of agreement was achieved. However significant differences concerning the nature of the adsorbed intermediates remain. In this paper we draw on the results, methods and conclusions of earlier work, but we extend the range of hydrocarbons to include butadiene and we undertake a systematic study of the coverage dependence of the interaction. UPS, thermal desorption spectroscopy (TDS) and work function measurements ( $\Delta\phi$ ) are used for the experimental study. By investigating the adsorption process as a function of exposure, we are able to show that the surface reactions are more complex than previously reported and to resolve some of the discrepancies concerning the nature and bonding of the surface intermediates. In addition the possibility of polymerisation under conditions of high coverage is discussed and the behaviour of tungsten compared with that of molybdenum.

## 2. Experimental

The apparatus used in the present investigation, the geometry employed to record photoelectron (pe) spectra with He I (21.2 eV) radiation and the method of cleaning the (100) oriented crystal are as described previously [16]. For thermal desorption studies the crystal was heated radiatively at a constant rate of 12 K s<sup>-1</sup>. The work function values for the surfaces of interest were determined from the low photoelectron cut-off to  $\pm 0.05$  eV. The hydrocarbon adsorbates were derived from spec. pure sources and the purity verified by mass spectroscopy in the UHV chamber. In the generalised experiment, the hydrocarbon of choice was adsorbed onto the previously cleaned crystal to a defined coverage, the appropriate measurement performed and the experiment repeated as a function of coverage.

## 3. Results

When thermal desorption experiments were carried out with each of the hydrocarbons, hydrogen was the only desorption product observed over the temperature range investigated although the possible presence of other desorption products was investigated by mass spectrometry. Fig. 1 shows a series of hydrogen desorption spectra obtained after the adsorption of acetylene at 300 K. For comparison, a desorption curve is also shown for ethylene at one coverage and the spectrum obtained from W(100) saturated with hydrogen is also included. Ethylene and butadiene behaved in a somewhat similar fashion; for a given exposure the normalised peak areas decrease in the order: C<sub>2</sub>H<sub>4</sub> > C<sub>4</sub>H<sub>6</sub> > C<sub>2</sub>H<sub>2</sub>.

For each adsorbate the spectra at low exposures covered the same temperature range as with pure hydrogen and showed similar desorption states. However, at higher exposures (Fig. 1d) hydrogen desorption from both the acety-

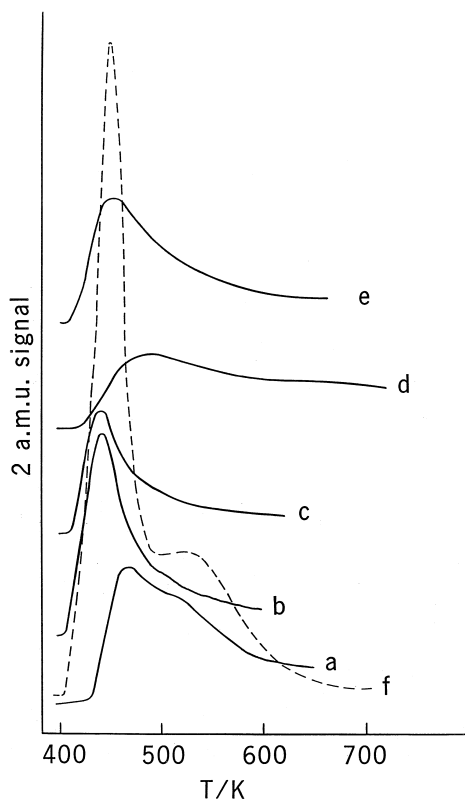


Fig. 1. Hydrogen thermal desorption spectra from a W(100) surface after various exposures to acetylene at 300 K: (a) 0.5 L; (b) 0.75 L; (c) 1.0 L; (d) 3.0 L. For comparison, the desorption spectra are shown for (e) ethylene at 5 L and (f) hydrogen at saturation.

lene and butadiene adsorbates continued to much higher temperatures than was observed for pure hydrogen, the desorption traces did not return to the baseline within the temperature range investigated and the desorption curves exhibited some structure. This effect was observed to be much less pronounced with ethylene at equivalent coverages (Fig. 1d, e).

The changes in work function of the W (100) surface as a result of sequential exposure to each of the hydrocarbons are given in Fig. 2 as a function of coverage (clean surface value 4.6 eV). In each case the work function rises initially to a maximum and then decreases. These maxima occur at an exposure of 0.75 L for acetylene and ethylene and 1 L for butadiene

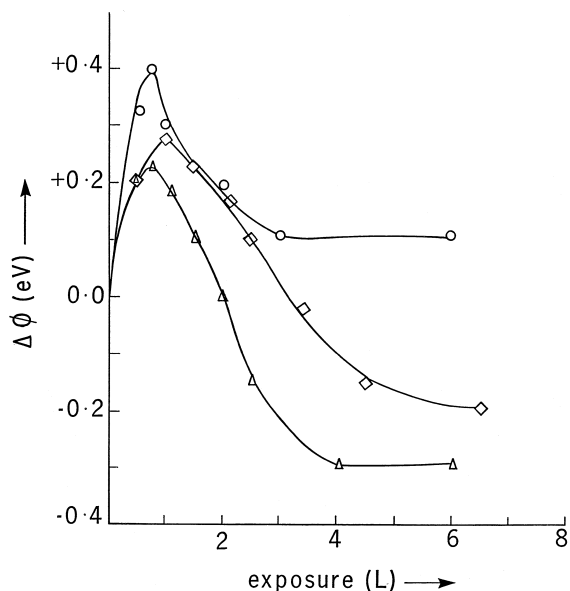


Fig. 2. Plot of  $\Delta\Phi$  as a function of exposure of clean W(100) surface to various adsorbates: (a) acetylene  $\Delta$ , (b) butadiene  $\diamond$ , (c) ethylene  $\circ$ .

and they decrease in magnitude in the order:  $C_2H_4 > C_4H_6 > C_2H_2$ .

The values of the change in work function of the saturated surfaces with respect to the clean surface also rank in this order.

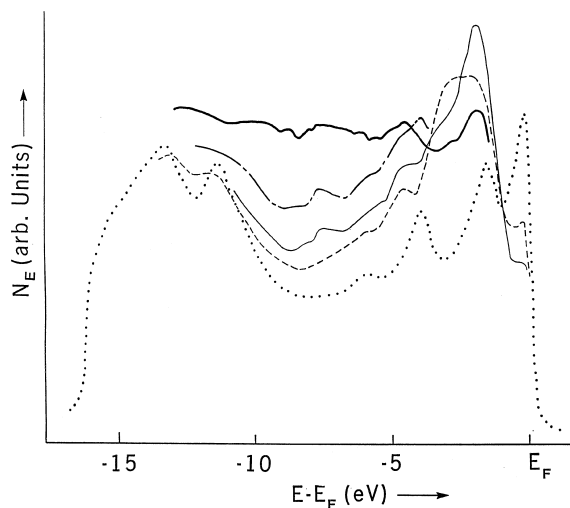


Fig. 3. He(I) photoelectron spectra of a W(100) surface after various exposures to acetylene at 300 K: (a) ( $\cdots$ ) clean surface; (b) ( $---$ ) 0.5 L; (c) ( $—$ ) 1 L; (d) ( $---$ ) 2 L; (e) ( $---$ ) 8 L.

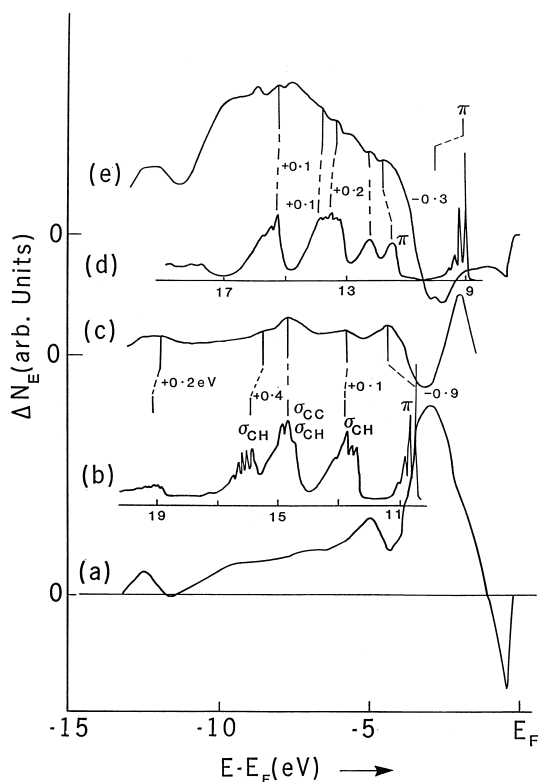


Fig. 4. Photoemission difference curves for varying exposures of a clean W(100) surface to acetylene at 300 K; (a) 0.5 L; (c) 1 L–0.5 L and (e) 8 L–0.5 L. For comparison, gas phase photoelectron spectra for (b) ethylene and (d) butadiene are also shown.

Fig. 3 reproduces the pe spectra of a clean W(100) surface on sequential exposure to acetylene at 300 K and the difference curves are shown in Fig. 4. The spectra may be best described by considering two regions: a) 0 to  $-4$  eV; b) beyond 4 eV below the Fermi level ( $E_f$  used as the reference point for peak positions). In the first region an exposure of 0.5 L (1 L =  $1.33 \times 10^{-4}$  Pa s) produced a broad peak at  $-3$  eV and the intensity of photoemission increased with exposure. With an exposure of 0.75 L there was a sharp intense peak at  $-1.9$  eV and a shoulder at  $-3.3$  eV. Further exposure caused the photoemission in this region to decrease. In the second region, three adsorption regimes may be distinguished according to coverage:

(i)  $< 0.5$  L, peaks at  $-5.0$  eV and  $-12.5$  eV plus other minor features.

(ii) 0.5 L to 2.0 L, a new set of peaks (designated as (I)) at  $-4.4$ ,  $-5.7$ ,  $-7.7$ ,  $-8.5$ ,  $-12.0$  and  $-12.5$  eV.

(iii)  $> 2.0$  L, decreased intensity of the  $-4.4$  eV peak and the appearance of a new set of small peaks (designated as (II)) at  $-4.7$ ,  $-5.25$ ,  $-6.25$ ,  $-6.7$  and  $-8.15$  eV on top of a broad background and a peak at  $-3.1$  eV in the first region.

The spectra obtained for ethylene and butadiene adsorption at 300 K were found to be broadly similar, but with the following differences:

(a) for a given exposure below 0.75 L, the intensity of photoemission in the first region below 4 eV decreased in the order  $C_2H_4 > C_2H_6 > C_2H_2$ .

(b) the intensity maximum in the first region occurred for acetylene and ethylene at 0.75 L and for butadiene at 1.0 L.

(c) butadiene exhibited all three adsorption regimes identified for acetylene, but ethylene saturated after the first two stages and also produced only low intensity below 5 eV.

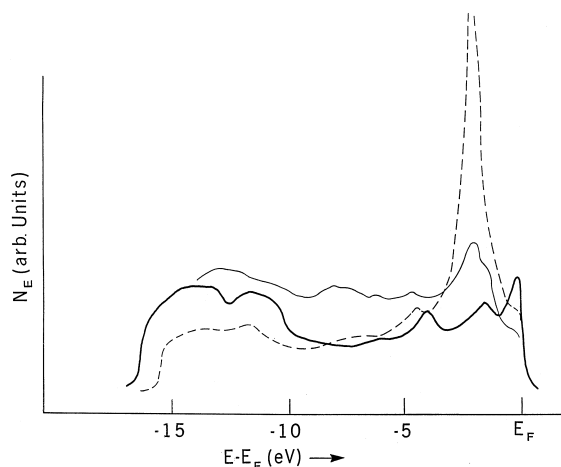


Fig. 5. Helium (I) photoelectron spectra of a W(100) surface following co-adsorption of hydrogen and acetylene at 300 K: (a) (—) clean surface; (b) (---) from (a) after saturation with hydrogen and (c) (.....) from (b) after exposure to 20 L of acetylene.

When a clean W(100) surface was presaturated with hydrogen and then exposed to acetylene the *pe* spectra given in Fig. 5 were obtained. Again ethylene and butadiene behaved similarly. Exposure of the hydrogen saturated surface to acetylene, butadiene or ethylene caused a work function change from +0.8 eV to -0.1, -0.2 and +0.1 eV respectively.

#### 4. Discussion

Although there are certain differences in detail, the experimental results on all three adsorbates have features in common which might indicate similarity in the surface interactions. At low coverages, the work function increases with all three adsorbates, hydrogen is the only thermal desorption product and changes in the *pe* spectra in the valence band region (between  $E_f$  and -5 eV) are typical of those produced by atomic carbon and hydrogen. Dissociative adsorption is therefore indicated at low coverages. Comparing Figs. 3 and 4 shows that the dominant peak due to hydrogen atoms is present on the surface exposed to acetylene, but that this peak decreases in intensity with increasing acetylene exposure. The hydrogen displacement experiment (compare Figs. 5 and 3) shows that acetylene readily displaces hydrogen at 300 K and that the heat of adsorption of hydrogen on W(100) is low. Adsorption of saturated hydrocarbons on tungsten normally increases the work function, while unsaturated hydrocarbons decrease it [17]. The decrease in work function observed at higher coverages (Fig. 1) is therefore consistent with the displacement of hydrogen atoms by unsaturated hydrocarbon species. The magnitude of the change in work function from the maximum value to that attained at saturation for the three adsorbates, increases as the ratio of carbon to hydrogen increases in the primary adsorbate. This suggests that, at saturation and 300 K, the degree of unsaturation in the adsorbed surface species increases: ethylene < butadiene < acetylene.

The spectra (I) and (II) cannot arise from adsorbed acetylene because there is no correlation with the gas phase spectrum of acetylene. There is however a relationship to the gas phase *pe* spectra of ethylene and butadiene respectively (Fig. 4b/c, d/e). A reasonable match of (I) to the spectrum of ethylene is achieved allowing for the work function of the clean surface (4.6 eV) and a relaxation shift of -2.36 eV if de stabilisation energies of +0.1, +0.4 and +0.2 eV for the  $\sigma_{CH}$  orbitals and a stabilisation energy of -0.9 eV for the  $\pi$  orbital are assumed. Organometallic clusters of di-substituted ethylene  $\sigma$  bonded to two metal atoms and  $\pi$ -bonded to a third metal atom are known [18], (Fig. 6). Replacement of two hydrogen atoms at 1,2 positions by more electropositive tungsten in the surface would de stabilise the  $\sigma$  orbitals and  $\pi$  orbitals involved in bonding to the surface should be stabilised by increased de localisation as is observed. (I) may therefore have 1,2 di- $\sigma + \pi$ -character. Similarly, organometallic clusters containing butadiene 1,4 di- $\sigma$ -bonded to two metal centres with two  $\pi$  orbitals bonded to a third metal centre are known [19] (Fig. 6) and a reasonable fit to the observed spectrum (II) is achieved with a relaxation shift of -2.5 eV,  $\sigma$  orbital bonding shifts of +0.2, +0.1 and +0.1 eV and  $\pi$ -orbital stabilisation of -0.9 and -0.35 eV.

A picture of the adsorption mechanism of acetylene, ethylene and butadiene on W(100) at room temperature as a function of coverage

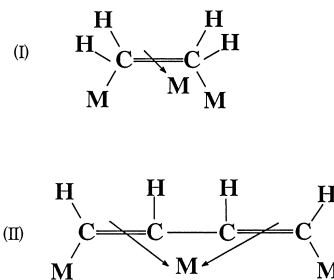


Fig. 6. Proposed adsorbed species (I) and (II).

which is consistent with the experimental evidence may therefore be summarised:

Stage 1: Dissociative chemisorption of the hydrocarbon to produce chemisorbed atomic carbon and hydrogen.

Stage 2: The adsorption of a molecular species (I) (corresponding to the set of peaks (I)) on a partially passivated surface and the consequent displacement and desorption of the adsorbed atomic hydrogen. Stage 2 overlaps with stage 1.

Stage 3: For acetylene and butadiene but not ethylene, further adsorption gives rise to a second type of molecular species (II) (corresponding to the set of peaks (II)) which adsorbs to a slightly greater extent for acetylene than butadiene.

The first two stages of adsorption described here are also consistent with the Auger [14] and HREELS [13] studies previously reported for the adsorption of acetylene on W (100). An analysis of the shapes of the carbon Auger lines obtained from a W (100) surface at different coverages led the authors [14] to propose a non sequential adsorption into two adsorption states  $\alpha$  and  $\beta$ . The  $\beta$  state obtained at low exposure was found to be dissociative and it was postulated that the  $\alpha$  state was either a C–H unit bound to a C atom or a  $C_2H_2$  unit. HREELS also indicated the initial dissociation of adsorbed acetylene, with two characteristic loss peaks for W–H and W–C bonds. Spectra obtained at higher exposures of acetylene and ethylene at 300 K were found to be identical and on the basis of the existence of a  $\nu CH$  loss peak at  $2976\text{ cm}^{-1}$  which was more intense for off-specular than specular reflection, the authors concluded that a  $C_2H_2$  species with a C–C–H angle of  $180^\circ$  was formed. However, features in the spectra below  $1600\text{ cm}^{-1}$  were poorly resolved, did not show the characteristic loss features of different types of adsorbed acetylene [10] and there was an unassigned weak loss feature at  $1800\text{ cm}^{-1}$ . The  $\nu CC$  and  $\nu CH$  frequencies expected for the three hybridisation states of carbon derived from the parent molecules acetylene, ethylene and ethane [20]

are:  $1970$  and  $3300\text{ cm}^{-1}$  for  $sp^3$ ,  $1600$  and  $2970\text{--}3100\text{ cm}^{-1}$  for  $sp^2$  and  $1000$  and  $2800\text{--}3000\text{ cm}^{-1}$  for  $sp$  hybridisation. The observed features at  $1800$  and  $2976\text{ cm}^{-1}$  are therefore consistent with bonding with more  $sp^2$  character. Furthermore, the plane of the proposed  $\sigma\text{-}\pi$  structure is far from perpendicular to the surface and the dipole associated with the CH stretch would have a large parallel component, giving rise to a weak  $\nu CH$  loss peak for specular reflection as observed.

The possible formation of polymeric surface species under conditions of high coverages of acetylene has been reported by Sheppard et al. [21]. They reported from an infra red study with nickel or platinum supported on silica that acetylene, unlike ethylene, formed dimers and to a lesser extent polymers on the surface and that subsequent hydrogenation produced n-butane and smaller amounts of higher hydrocarbons. On single crystal surfaces, polymer formation has been suggested for Ir(111) [4] and Ni(755) [5]. There is some evidence from the present work of similar reactions, but it is not conclusive. Polymers have bands of closely spaced molecular orbitals and solid state effects are expected to give rise to overlapping photo emission bands. The appearance of a broad background in the pe spectra (Fig. 3) following high exposures to acetylene is therefore consistent with this. Similarly, the wide range of temperature over which the thermal desorption of hydrogen was observed after high exposures of acetylene is consistent with the presence of a range of higher molecular weight species on the surface. The similarity in adsorption behaviour of acetylene and butadiene also suggests surface processes giving rise to a range of related surface species. In the case of butadiene, for example, adsorbate (I) would be formed by C–C bond scission and reaction with adsorbed hydrogen, while the proposed adsorbate (II) could be formed by molecular adsorption and C–H fission or by interaction between adjacent (I) species. The different behaviour observed with ethylene at high coverages is probably due to

the increased amount of hydrogen adsorbed in both the initial dissociative adsorption and in the subsequent molecular adsorption stage. Because hydrogen occupies a higher proportion of surface sites, the interaction between adjacent complexes would be inhibited so that species (II) is not formed; the work function data indicating a much lower coverage of the adsorbed molecular complex for ethylene than for acetylene or butadiene.

Consideration of our results and the work of Wang et al. [8,9] allows the relative reactivity of Mo and W(100) to unsaturated hydrocarbons to be compared. In general Mo appears to be more reactive, reaction occurring at lower temperatures and to a greater extent. Thus, with ethylene, on molybdenum at 80 K the adsorbate is substantially rehybridised to  $\sim sp^3$  and at 200 K decomposition to hydrogen and adsorbed acetylene occurs. Heating to 300 K produced C–C bond breaking and the formation of  $CH_x$  surface species. On W at this temperature C–C bond breaking is reported only at low coverages, and the proposed di  $\sigma$ – $\pi$  species predominates at high coverages. Acetylene adsorbed on Mo (100) at 80 K gave a mixture of molecular acetylene and an  $sp^2$  hybridised species. Heating to 180 K produced decomposition which was complete at 300 K to leave chemisorbed carbon. In contrast on W (100) at 300 K although a similar degree of C–H and C–C bond breaking occurs at low coverages there is evidence for re hybridisation to a species with more  $sp^2$  character at high coverages and the possibility of C–C bond formation.

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