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Surface Science 397 (1998) 197–208

surface science

The surface chemistry of 2-butenes adsorbed on Mo(100), oxygen-covered Mo(100) and MoO₂

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Received 12 May 1997, accepted for publication 5 September 1997

Abstract

2-Butenes adsorbed on Mo(100) and oxygen-covered Mo(100) can either thermally decompose to yield hydrogen and adsorbed carbon, desorb molecularly, self-hydrogenate to produce butane, or dissociate to form a C₂ species which can further decompose to desorb methane. 2-Butenes are proposed to completely thermally decompose on the four-fold sites on Mo(100) since the hydrogen yield decreases linearly with oxygen coverage and oxygen blocks the four-fold sites. The butene desorption and self-hydrogenation activation energy increases with increasing oxygen coverage suggesting that 2-butenes bond to Mo(100) predominantly by donation of π electrons to the molybdenum. Finally, methane is also formed. This is proposed to occur via the intervening formation of methylene carbenes formed by direct carbon–carbon double-bond cleavage. The methane yield is much larger than that found following both ethylene and propylene adsorption on oxygen-modified molybdenum. This effect is rationalized using the bonding model outlined above from the variation in the position of the π orbital through the homologous series ethylene, propylene, 2-butenes. © 1998 Elsevier Science B.V.

Keywords: Chemisorption, Low index single crystal surfaces, Molybdenum, Soft X-ray photoelectron spectroscopy, Temperature programmed spectroscopy, 2-Butenes

1. Introduction

Oxygen-modified molybdenum catalyzes olefin metathesis, where the activity varies with metal oxidation state and where molybdenum dioxide has been shown to display the largest activity [1–5]. Unfortunately, both ethylene and propylene merely adsorb molecularly and desorb intact from this surface [6, 7]. In contrast, however, the chemistry of both ethylene and propylene are profoundly influenced by the presence of oxygen overlayers

[6, 7]. Several reaction pathways are identified for both of these, including methane formation, self-hydrogenation and complete thermal decomposition to yield carbon and hydrogen. The detection of methane is particularly intriguing, since the proposed first step in olefin metathesis is the formation of a carbene active site [8–16]. This is proposed to further react with an alkene during olefin metathesis forming a metallocycle which thermally decomposes via the reverse of this pathway, yielding products. Alternatively, of course, carbenes can recombine to reform alkenes, a route which has been suggested previously as one which leads to carbide destruction [17]. This is also a

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metathetic pathway, since it results in the cleavage and reassembly of carbon–carbon double bonds, and this mechanism has been shown to operate at high catalyst temperatures (> 650 K) [5].

Several routes to carbene formation have been proposed for organometallic centers. One suggests that a labile methyl-group hydrogen can be rapidly removed, forming an allylic intermediate which can hydrogenate to yield a metallacycle. This then reacts to evolve an alkene and deposit a carbene onto the surface [18,19]. In the case of propylene adsorption, this pathway would lead to ethylene desorption and the formation of a carbene. Unfortunately, no ethylene desorption is detected in that case. An alternative pathway proposes hydrogenation of the alkene to form an alkyl species which then decomposes via α -hydride elimination [20]. In general, however, adsorbed alkyl groups thermally decompose on transition-metal surfaces by β -hydride elimination [21]. In order to investigate this chemistry further, we have examined the adsorption of 2-butenes on oxygen-covered Mo(100), where similar hydrogenation and decomposition reactions are found as for propylene. In this case, substantial amounts of methane are also formed. If carbene formation from 2-butenes is similarly preceded by methyl hydrogen abstraction, this will result in the formation of a metallocycle containing a methyl group at an α -position. This should thermally decompose to yield ethylene or propylene and to deposit a methyl carbene and a carbene, respectively. As shown below, these are not found.

A final possibility on an extended metal surface is that the carbon–carbon double bond is sufficiently weakened by adsorption onto oxygen-modified molybdenum that it can cleave directly. In this case, 2-butenes would lead directly to form methyl carbenes. Photoelectron spectroscopy suggests that this reaction in fact takes place. The main desorption product (apart from the molecular species, hydrogenation and decomposition products) is methane. It is shown elsewhere in support of this proposal that methyl carbenes deposited onto oxygen-covered Mo(100) by thermally decomposing 1,1-diiodoethane do indeed thermally decompose to yield methane [22].

2. Experimental

Two pieces of equipment were used for these experiments, which have been described in detail elsewhere [23,24]. Briefly, the first consists of an ion- and sublimation-pumped, bakeable ultrahigh vacuum chamber operating at a base pressure of $< 1 \times 10^{-10}$ Torr following bakeout. The Mo(100) sample can be heated to 2100 K and cooled to ~ 80 K via thermal contact to a liquid-nitrogen filled reservoir. Resistive heating was used to collect temperature-programmed desorption (TPD) data. These were collected using a computer-multiplexed quadrupole mass spectrometer which could record up to five masses sequentially using a heating rate of 10 K s^{-1} .

The chamber was also equipped with a four-grid retarding field analyzer (RFA) which was used to obtain LEED images of the sample and to collect Auger data. The sample was cleaned by heating in $\sim 2.5 \times 10^{-7}$ Torr of oxygen at 1200 K for 5 min to remove carbon and then rapidly heating in vacuo to 2100 K to remove oxygen. This resulted in the diffusion of further carbon to the surface, and this procedure was repeated until no impurities, particularly carbon, were noted on the surface after heating to 2100 K.

Ultraviolet photoelectron spectra were obtained at the Wisconsin Synchrotron Radiation Center using the Aladdin storage ring using the Mark V Grasshopper monochromator. The chamber was equipped with a quadrupole mass analyzer and a double-pass cylindrical mirror analyzer which was used to collect both Auger and photoelectron spectra. The analyzer was operated at a pass energy of 25 eV to collect photoelectron spectra, and this yielded an overall spectral resolution of 0.15 eV. Photoelectron spectra were excited using 60 eV radiation, which has been shown previously to yield the optimum C 2s to background intensity ratio on Mo(100) [25].

The 2-butene (Aldrich, WI; 99.9% purity) was transferred to a glass bottle and further purified by repeated bulb-to-bulb distillations and stored in glass until use. Deuterated 2-butene (MSD Isotopes, 99 at.% D) was used as received. The oxygen (AGA Gas, Inc. OH; 99%) was transferred

from the cylinder to a glass bulb and also redistilled.

Oxygen overlayers were prepared by saturating the Mo(100) surface (20 L O₂ exposure at 1050 K, 1 L = 1 × 10⁻⁶ Torr · s) and annealing to various temperatures to remove oxygen to obtain the requisite coverage [26–29]. MoO₂ films were grown using a literature protocol [30], where metallic molybdenum was oxidized using 3 × 10⁻⁵ Torr of oxygen for 120 s with the sample heated to 1050 K.

3. Results

Fig. 1 displays a series of difference photoelectron spectra collected using 60 eV photons after exposing an MoO₂ surface to 8 L of 2-butene. The spectrum of the MoO₂ surface prior to 2-butene adsorption is shown for comparison, and is indicated as “clean”. This exhibits sharp features up to about 2 eV binding energy (BE) due to emission

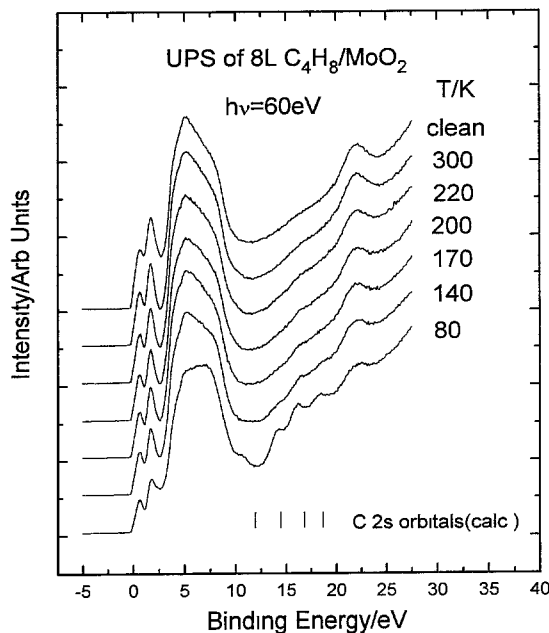


Fig. 1 Ultraviolet photoelectron spectra obtained following 2-butene adsorption (8 L) on an MoO₂ surface as a function of sample annealing temperature. The annealing temperatures are displayed adjacent to the corresponding spectrum. These spectra were excited using 60 eV photons.

from the substrate d-orbitals, and has a broad feature between 4 and 9 eV binding energy (BE) due to emission from the oxygen 2p levels and a peak at 22 eV BE due to emission from the O 2s level. Note that this leaves a window between ~9 and 21 eV where the levels due to C 2s-derived molecular orbitals are found. This reveals the presence of three intense features at 14 ± 0.2, 16.5 ± 0.2 and 18.5 ± 0.2 eV BE due to levels arising from the interactions of the 2s orbitals on the carbon atoms. The peak position calculated from Hückel theory using a prescription outlined by Potts et al. [31,32] are represented as vertical lines below these spectra. The calculated peak positions of the three highest binding-energy peaks of 2-butene agree extremely well with the experimental positions, except that the peak predicted to be at ~12 eV BE is not seen. Spectra for 2-butene shown below for thicker condensed layers (see, e.g., Fig. 3) demonstrate that the intensity of this peak is low. These features decrease rather uniformly in intensity as the MoO₂ sample is heated. This chemistry (or lack of it) is further illustrated by the data of Fig. 2, which displays temperature-programmed desorption spectra collected after exposing MoO₂ to 5 L of 2-butenes. These show a narrow feature at ~160 K and a broader peak centered at 300 K with intensity at 2, 27 and 41 amu. Careful comparison of the desorption peak areas with the fragmentation pattern of 2-butene indicates that both of these features are due to the desorption of 2-butene itself. The 160 K feature is assigned to the desorption of multilayers of butene since it grows with increasing exposure without saturating, and the peak at 300 K to the desorption of an overlayer. A simple Redhead analysis, assuming a pre-exponential factor of 1 × 10¹³ s⁻¹ and using the experimental heating rate of 10 K s⁻¹, yields a desorption activation energy of ~18 kcal mol⁻¹. Note that the relatively large width of this peak suggests a rather lower value of the pre-exponential desorption factor.

The corresponding series of photoelectron spectra for clean Mo(100) are displayed in Fig. 3. These are plotted as difference spectra, where the spectrum of clean Mo(100) is subtracted from those of the 2-butene-covered surfaces to accentuate adsorbate-induced features. Again, the calcu-

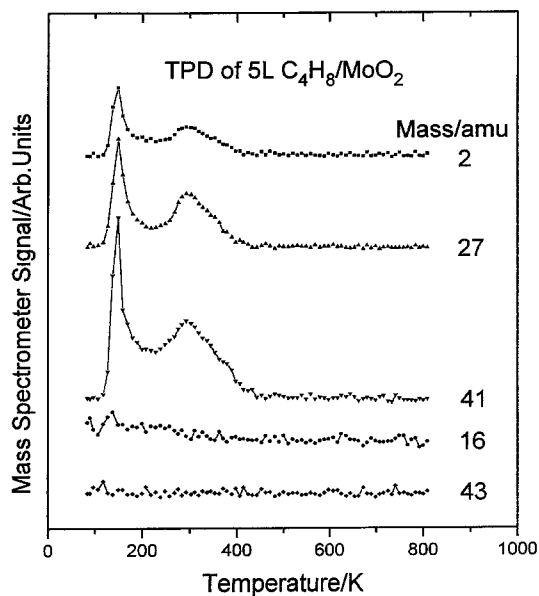


Fig 2 Temperature-programmed desorption spectra collected at several masses following exposure of MoO_2 to 5 L of 2-butene. The masses monitored are displayed adjacent to the corresponding spectrum.

lated peak positions [31, 32] are marked as vertical lines below these spectra. At low sample temperatures (up to 130 K), 2s-derived features are evident at 13.5 ± 0.2 , 15.5 ± 0.2 , 18.0 ± 0.2 and 20.0 ± 0.2 eV BE, and so exhibit essentially identical spacings as found for 2-butene on MoO_2 , but the absolute values are uniformly shifted by ~ 1.5 eV to higher binding energy on $\text{Mo}(100)$. The low binding-energy (13.5 eV) peak is now clearly evident. As the sample temperature is raised, there is a slight and uniform decrease in butene signal intensity. The constancy of the peak positions is emphasized by vertical lines in Fig. 3. Above ~ 190 K, these are replaced by spectra displaying features at 12.0 ± 0.2 and 17.5 ± 0.2 eV binding energy, and the positions of these features are also indicated by vertical lines in Fig. 3. These peaks are assigned to emission from the $\sigma^*(ss)$ and $\sigma(ss)$ orbitals of a C_2 hydrocarbon, respectively. This leads to a spacing $\Delta(\sigma^*(ss) - \sigma(ss)) = 5.5 \pm 0.4$ eV. As the sample is heated to higher temperatures, the 17.5 eV feature decreases in intensity so that a single feature remains at 12.5 eV

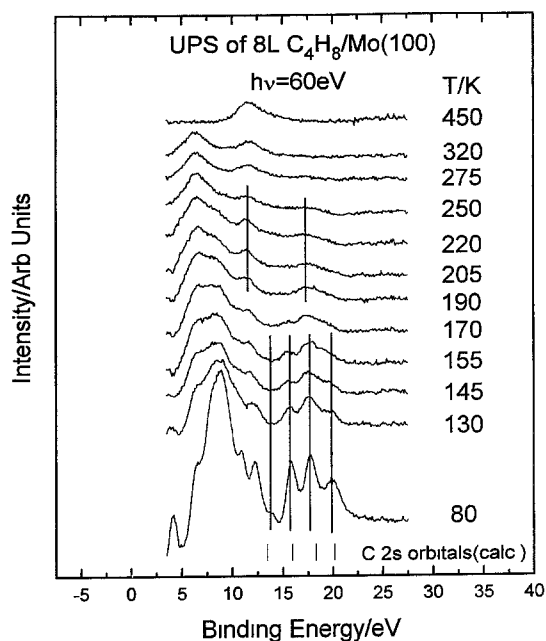


Fig. 3 Ultraviolet photoelectron difference spectra obtained following 2-butene adsorption (8 L) on a clean $\text{Mo}(100)$ surface as a function of sample annealing temperature. The annealing temperatures are displayed adjacent to the corresponding spectrum. These spectra were excited using 60 eV photons. Spectra were obtained by subtracting the spectrum of clean $\text{Mo}(100)$ from each of the spectra for adsorbate-covered $\text{Mo}(100)$.

binding energy. This spectral sequence suggests that 2-butene initially thermally decomposes at ~ 180 K to form an adsorbed C_2 hydrocarbon which further reacts to yield a C_1 hydrocarbon. Note that there is no drastic change in the positions of the 2s-derived peaks between 80 and 155 K. As emphasized above, the positions of these peaks agree well with those for gas-phase 2-butene, indicating that this adsorbs intact as 2-butene at 80 K and does not change into another surface C_4 species on heating to ~ 180 K, and that this directly thermally decomposes into an adsorbed C_2 hydrocarbon at this temperature.

The photoelectron difference spectra for 2-butenes adsorbed on a surface covered by 0.7 monolayers of oxygen are shown in Fig. 4. The spectrum of $\text{Mo}(100)$ covered with 0.7 monolayers of oxygen is shown for comparison (and designated "clean"). This displays features below ~ 3 eV BE

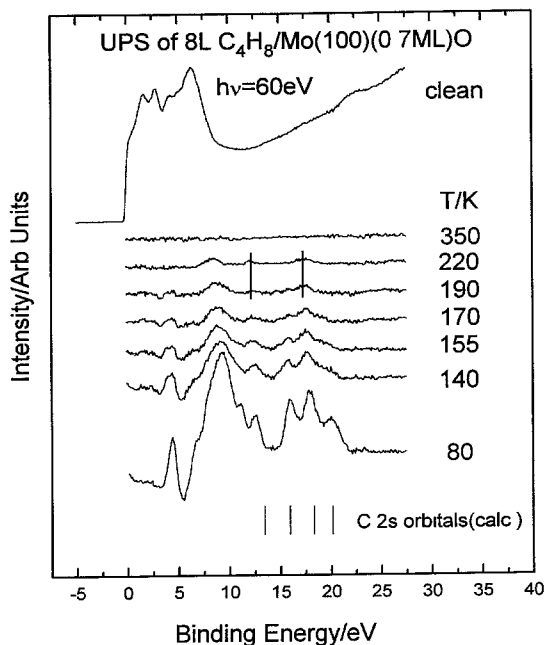


Fig. 4. Ultraviolet photoelectron difference spectra obtained following 2-butene adsorption (8 L) on a Mo(100) surface covered with 0.7 monolayers of oxygen as a function of sample annealing temperature. The annealing temperatures are displayed adjacent to the corresponding spectrum. These spectra were excited using 60 eV photons. Spectra were obtained by subtracting the spectrum of oxygen-covered Mo(100) from each of the spectra for adsorbate-covered Mo(100). The spectrum of 0.7 monolayers of O/Mo(100) is displayed at the top of this series.

due to emission from the molybdenum substrate, a feature at ~ 8 eV BE due to emission from the O 2p levels, and a weak feature at ~ 22 eV BE due to emission from the O 2s level. Intense features due to a condensed layer of 2-butene are evident at 80 K at 12.5 ± 0.2 , 16.0 ± 0.2 , 18.5 ± 0.2 and 20.5 ± 0.2 eV BE. Again, the spacing of these features is essentially identical to those calculated for 2-butene [31,32], but are ~ 0.5 eV higher in binding energy than the corresponding features on Mo(100). The multilayer desorbs on heating to 140 K (Fig. 6 and Fig. 7) leaving chemisorbed 2-butene on the surface, and also evident are peaks which are assigned to the formation of a C_2 compound on heating to ~ 190 K, although these are much less intense than those found on metallic molybdenum. The corresponding spectra for

2-butene adsorbed on a Mo(100) surface covered by 1.2 monolayers of oxygen are shown in Fig. 5. 2-Butene adsorbed at low temperatures yields 2s-derived features at 13.5 ± 0.2 , 15.5 ± 0.2 , 18.0 ± 0.2 and 20.0 ± 0.2 eV BE, again shifted by ~ 0.5 eV from the data in Fig. 4 for $\theta_O = 0.7$ monolayers. The intensity of these peaks decreases on heating the sample, so that the difference spectrum is essentially featureless on heating to ~ 350 K. Again, the intensity of these peaks is much less than found on metallic Mo(100).

The deuterium (4 amu) desorption spectra collected following adsorption of C_4D_8 on various oxygen-covered Mo(100) surfaces are displayed in Fig. 6. This molecule was used to avoid contamination from hydrogen adsorbing from the background. This, however, turned out to be negligible

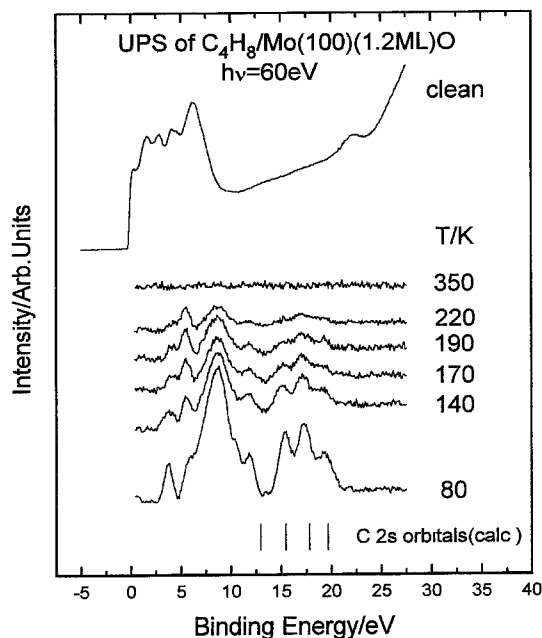


Fig. 5. Ultraviolet photoelectron difference spectra obtained following 2-butene adsorption (8 L) on a Mo(100) surface covered with 1.2 monolayers of oxygen as a function of sample annealing temperature. The annealing temperatures are displayed adjacent to the corresponding spectrum. These spectra were excited using 60 eV photons. Spectra were obtained by subtracting the spectrum of oxygen-covered Mo(100) from each of the spectra for adsorbate-covered Mo(100). The spectrum of 1.2 monolayers of O/Mo(100) is displayed at the top of this series.

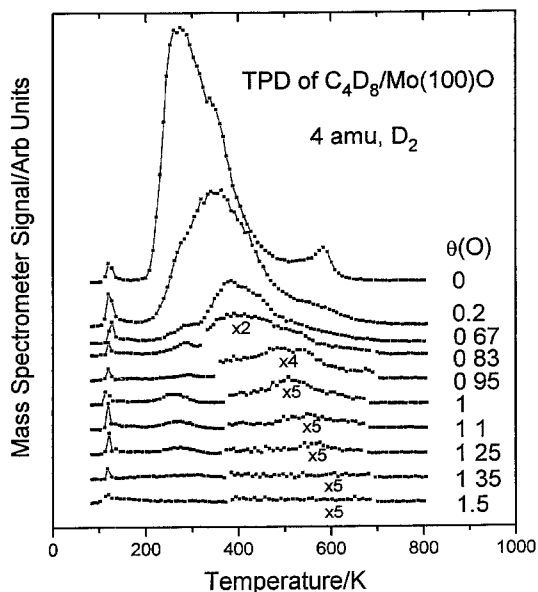


Fig 6 Deuterium (4 amu) temperature-programmed desorption spectra collected after saturating various oxygen-covered surfaces of Mo(100) with d_8 -2-butene. The oxygen coverages are displayed adjacent to the corresponding spectrum.

under the experimental conditions used here ($P < 1 \times 10^{-10}$ Torr). The spectrum for clean Mo(100) exhibits a broad feature centered at ~ 280 K. This peak shifts to higher temperatures as the oxygen coverage increases, and also decreases substantially in intensity with increasing coverage so that, when the oxygen coverage is about unity, the hydrogen yield is almost zero.

The corresponding molecular desorption spectra are displayed in Fig. 7, which monitors the signal at 46 amu, which is the most intense fragment in the pattern characteristic of 2-butene. Careful measurements of the other masses desorbing at these temperatures confirms that the features in Fig. 7 are due to deuterated 2-butene desorption. The spectra exhibit a peak centered at ~ 120 K due to the desorption of 2-butene multilayers, which accounts for the decrease in signal intensity observed in the photoemission spectra (Figs. 3–5) on warming the sample to 140 K. The molecular overlayer desorbs in states between 300 and 400 K, depending on oxygen coverage. For oxygen coverages between 0 and 0.95, the molecular desorption peak position increases with increasing oxygen

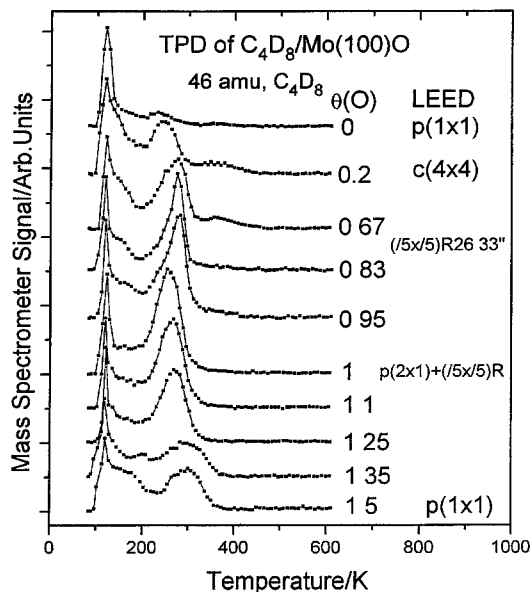


Fig 7 2-Butene (46 amu) temperature-programmed desorption spectra collected after saturating various oxygen-covered surfaces of Mo(100) with propylene. The oxygen coverages are displayed adjacent to the corresponding spectrum.

coverage, so that for clean Mo(100), the peak is centered at ~ 220 K and increases to 280 K with the addition of 0.67 monolayers of oxygen. This peak position remains constant up to 0.95 monolayers of oxygen. Note that in this regime, the surface exhibits a $(\sqrt{5} \times \sqrt{5})$ LEED pattern which has been assigned to a surface reconstruction. The peak shifts to ~ 250 K when 1 monolayer of oxygen is added to the surface and the peak temperature increases essentially linearly with increasing oxygen coverage, so that it is centered at ~ 300 K when the oxygen coverage is 1.5 monolayers.

The corresponding methane desorption spectra are displayed as a function of oxygen coverage in Fig. 8 after saturating with 2-butene. In contrast to the behavior found with both propylene and ethylene on oxygen-modified Mo(100), the methane yield following adsorption on clean Mo(100) is the largest, desorbing as an intense peak centered at 260 K. A small feature is also evident at ~ 390 K. As the oxygen coverage increases, the 260 K peak temperature increases and the yield from this state decreases, so that essentially no

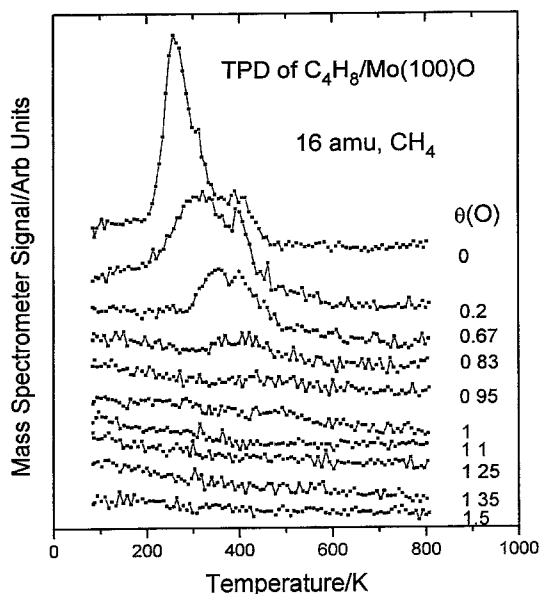


Fig. 8 Methane (16 amu) temperature-programmed desorption spectra collected after saturating various oxygen-covered surfaces of Mo(100) with 2-butene. The oxygen coverages are displayed adjacent to the corresponding spectrum.

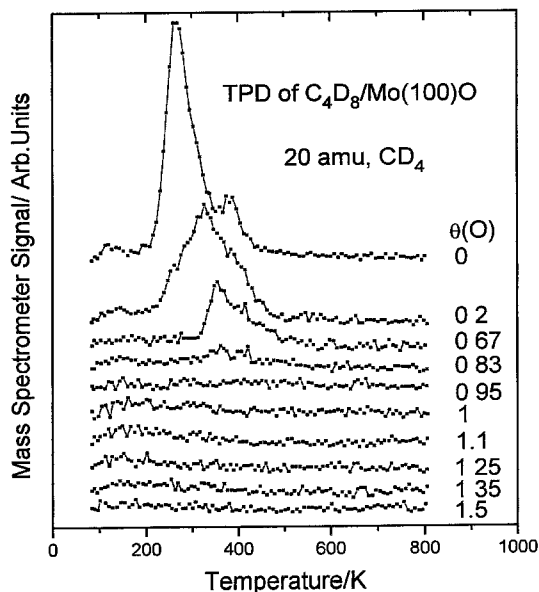


Fig. 9 Methane (CD_4 , 20 amu) temperature-programmed desorption spectra collected after saturating various oxygen-covered surfaces of Mo(100) with d_8 -2-butene. The oxygen coverages are displayed adjacent to the corresponding spectrum.

methane desorbs from a surface covered with one monolayer of oxygen. Since small amounts of surface hydrogen can substantially affect the methane yield on molybdenum, the experiment was repeated using d_8 -2-butene, and the results are displayed in Fig. 9. The spectra are essentially identical to those plotted in Fig. 8, except that the peaks are slightly better defined. Note that both sets of experiments were carried out using the same sample and temperature-measuring apparatus. The peak temperature increases to 325 K in the presence of 0.2 monolayers (ML) of oxygen and 350 K when the oxygen coverage is 0.67 ML. There is also a very slight change in the methane desorption peak temperature for CD_4 and CH_4 , where the former desorbs at ~ 267 K and the latter at ~ 260 K, suggesting the H (D) is involved in the rate-limiting step.

Adsorbed 2-butene also self-hydrogenates, and the resulting spectra are displayed in Fig. 10 as a function of oxygen coverage, where the butane (58 amu) peak is centered at ~ 220 K and varies only slightly but does increase with increasing oxygen coverage. The butane yield also varies with

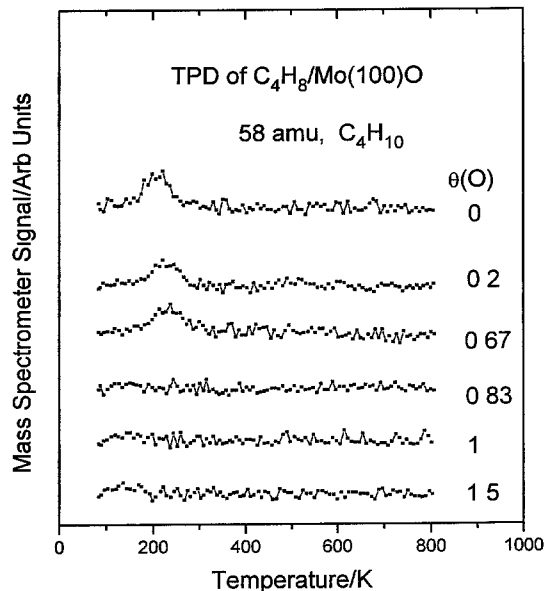


Fig. 10 Butane (58 amu) temperature-programmed desorption spectra collected after saturating various oxygen-covered surfaces of Mo(100) with 2-butene. The oxygen coverages are displayed adjacent to the corresponding spectrum.

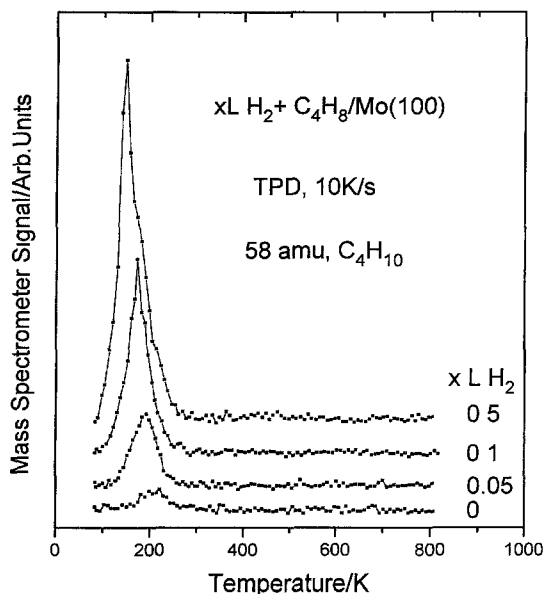


Fig 11 Butane (58 amu) temperature-programmed desorption spectra obtained following various exposures of a Mo(100) surface to hydrogen and then saturating the surface with 2-butene. Hydrogen exposures are displayed adjacent to the corresponding spectrum

oxygen coverage, so that an oxygen-saturated surface is essentially inactive for butene self-hydrogenation. However, as shown by the data of Fig. 11, the butane yield increases extremely rapidly with the addition of only very small amounts of hydrogen, so that a 0.05 L exposure of hydrogen leads to an almost five-fold increase in butane yield. The yield continues to increase with the addition of further hydrogen, and is accompanied by a decrease in peak temperature.

Finally, no other reaction products, in particular other alkenes such as ethylene or propylene, were detected. Neither were any products detected from reaction between hydrogen or carbon with the oxygen overlayer.

4. Discussion

Molybdenum oxide, in spite of being catalytically active under high external pressures of alkene at relatively high temperatures, is completely chemically inert under ultrahigh vacuum conditions, so

that 2-butene simply desorbs molecularly (Fig. 2) with an activation energy of ~ 18 kcal mol⁻¹. Therefore, on this surface, desorption is overwhelmingly the kinetically most favored reaction route.

In contrast, oxygen-overlayer modified Mo(100) is chemically much more reactive. The chemistry of 2-butenes on oxygen-covered Mo(100) is broadly similar to that found for other alkenes (e.g. ethylene [6] and propylene [7]). This includes molecular desorption, hydrogenation (to form butane), complete dehydrogenation to yield carbon and to desorb hydrogen, and the reactive formation of methane, ultimately via the hydrogenation of surface CH_x species.

The molecular desorption spectra are displayed in Fig. 7 and show that the desorption activation energy increases as a function of oxygen coverage between $\theta_{\text{O}}=0$ and $\theta_{\text{O}}=0.95$, and again from $\theta_{\text{O}}=1.0$ to $\theta_{\text{O}}=1.5$. This trend has been noted previously for ethylene [6] and propylene [7] adsorbed on oxygen-covered Mo(100). Assuming that the desorption activation energy correlates with the heat of adsorption, this indicates that the adsorption of 2-butene is via the donation of electron density to the d-orbitals of the substrate rather than via back-donation into vacant π^* antibonding levels. This effect has been noted previously [33,34]. Clearly, according to the Dewar–Chatt–Duncanson model [35,36], both bonding modes will operate simultaneously but, in the case of 2-butene (and propylene and ethylene) adsorption, π -electron donation dominates. The abrupt decrease in desorption activation energy as the oxygen coverage changes from 0.95 to 1.0 monolayers must be associated with a change of adsorption site. It is not clear what this is, except that at this point all of the four-fold hollow sites are occupied [27,28].

The data of Figs. 10 and 11 indicate that 2-butenes can react with adsorbed hydrogen to form an alkane. In common with other hydrocarbons on molybdenum and oxygen-covered molybdenum, the hydrogenation product yield is a strong function of hydrogen coverage, so that very low exposures of hydrogen drastically enhance the degree of hydrogenation. Thus, a 0.05 Langmuir hydrogen exposure, giving a relative

coverage of $\sim 7\%$ of a monolayer, increases the butane yield by a factor of five. A similar effect has been seen at high pressures, where the rate of hydrogenation of adsorbed hydrocarbons on molybdenum are a very non-linear functions of hydrogen pressure [37]. Note that this is in contrast to the effect found on palladium, for example, where the yield of ethylene formed by acetylene hydrogenation varies linearly with hydrogen coverage [38]. One possible explanation for this effect is that, when an alkene bonds to the surface via π donation to the surface, it will be slightly positively charged, whereas bonding on palladium is predominantly via back-donation into vacant π^* orbitals, which leads to a slightly negatively charged adsorbate. Hydrogen, since its 1s orbital lies well below the metal's Fermi level, is negatively charged. This suggests that, in the case of a reaction between hydrogen and an alkene on molybdenum, the interaction is attractive so that the "local" hydrogen coverage near the adsorbed alkene is larger than the average coverage. Measurements of work-function changes as a function of alkene coverage will help to clarify some of these issues. Finally, the hydrogenation activation energy increases slightly with increasing oxygen coverage (Fig. 10), in accord with the bonding scheme outlined above.

Also as noted above, a portion of the adsorbed 2-butene thermally decomposes to yield hydrogen and deposit carbon. The kinetics of this process are reflected in the hydrogen desorption spectra shown in Fig. 6. Here, the total thermal desorption yield decreases with increasing oxygen coverage, and the total hydrogen desorption yield is shown plotted in Fig. 12 as a function of oxygen coverage. Note that this hydrogen reacts with 2-butene or adsorbed C_1 species to form butane (Fig. 10) and methane (Figs. 8 and 9), respectively, and presumably accounts for the yield of these products decreasing to zero for $\theta_O \approx 1.0$. The approximately linear decrease in hydrogen yield as a function of oxygen coverage (Fig. 12) is essentially identical to the behavior found for ethylene and propylene [6,7]. Since it has been shown that oxygen occupies the four-fold hollow sites on Mo(100) [28], it is suggested that the total thermal decomposition of alkenes takes place on these sites.

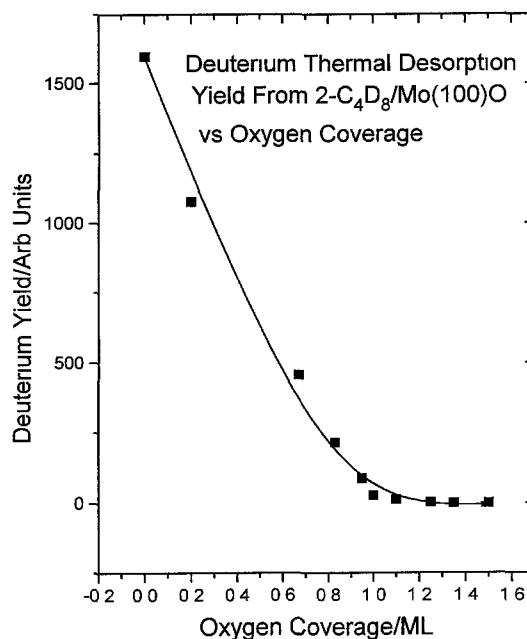


Fig. 12 Plot of the total hydrogen thermal desorption yield from 2-butene adsorbed onto oxygen-covered Mo(100) as a function of oxygen coverage

A substantial amount of methane is formed on the surface where, in this case, the clean Mo(100) surface yields the largest amount of methane and the yield decreases with increasing oxygen coverage. Note that no other products are found to desorb (in particular ethylene or propylene). The use of isotopically labelled compounds allows these to be searched for carefully (e.g. so that carbon monoxide can be distinguished from ethylene), and confirms their complete absence in temperature-programmed desorption. This suggests that the surface C_1 species are not formed via an intervening allylic species which reacts to make a metallocycle [18,19], since this should then decompose to form ethylene and propylene, neither of which are detected. In addition, the photoelectron spectra, which are the clearest for clean Mo(100) (Fig. 3), which is also the surface which forms the largest amount of methane, show that the four peaks due to the 2s-derived molecular orbitals of 2-butene merely decrease in intensity prior to forming adsorbed C_2 hydrocarbons. The different structure of any intervening allylic or metallocyclic species

would give rise to different 2s-derived orbital spacings. This result therefore suggests that the adsorbed C_4 species reacts directly to form C_2 groups. Note that the two peaks evident between ~ 190 and 250 K assigned to the presence of C_2 groups evolves into a single peak after heating to ~ 275 K, indicating the formation of C_1 species, in accord with the methane detected in temperature-programmed desorption (Figs 8 and 9). The $\sigma-\sigma^*$ peak spacing for the C_2 hydrocarbon formed on Mo(100) from 2-butene decomposition (Fig. 3) is 5.5 ± 0.4 eV. The corresponding spacings for ethylene and acetylene adsorbed on Mo(100) at low temperature are 5.1 ± 0.2 and 5.6 ± 0.2 , respectively. Direct comparison between these values is difficult, since the 2s ionization energy for the α -carbon of a methyl carbene will be chemically shifted due to binding to molybdenum. Nevertheless, the spacing found in this case is within the range of a double or triple carbon-carbon bond.

In order to further examine this chemistry, we have carried out preliminary experiments to co-adsorb hydrogen and $CH_2I-CH=CH_2$ on oxygen-covered Mo(100). This can potentially react to form an allylic species by removal of iodine, and further addition of surface hydrogen at the β position would yield the metallocycle. This chemistry should be evidenced by ethylene and methane desorption. However, the only products detected are propylene and propane, suggesting that hydrogenation at the α position is significantly more probable than at the β position [39].

An alternative pathway involving initial partial hydrogenation to form an adsorbed alkyl species, which would then lead to a carbene by α -hydride elimination [20], would also cause changes in the peak positions of the 2s-derived levels for the adsorbed 2-butene which, as noted above, does not take place. Clearly, since 2-butene hydrogenates to butane (Fig. 10 and Fig. 11), an adsorbed alkyl intermediate, the first step in this reaction pathway, must form. However, in general, adsorbed alkenes have been found to decompose via β -hydride elimination on transition-metal surfaces [40]. Again, preliminary results obtained by adsorbing C_2H_5I on oxygen-covered Mo(100)

reveal that this either reacts to form ethylene by β -hydride elimination, or further hydrogenates to form ethane [41]. In the case of an adsorbed alkyl species, α -hydride elimination would lead to a methyl carbene. Once again, preliminary experiments on the adsorption of CH_3-CHI_2 show that this thermally decomposes to yield methane on Mo(100) for lower oxygen coverages. Higher oxygen coverage leads to ethylene desorption at ~ 400 K [22].

It is therefore suggested that the adsorbed alkenes react to form carbenes via a direct cleavage of the carbon-carbon double bond, which is weakened by adsorption on to the molybdenum surface. As noted above, alkenes appear to adsorb on this surface predominantly by donation of their π electrons to the substrate rather than via electron back-donation into empty π^* orbitals. Corroborative evidence for a dissociative pathway to carbene formation is provided by the data of Fig. 13, which plots the methane yield as a function of oxygen coverage. In all cases, the methane yield decreases to zero for oxygen coverages greater

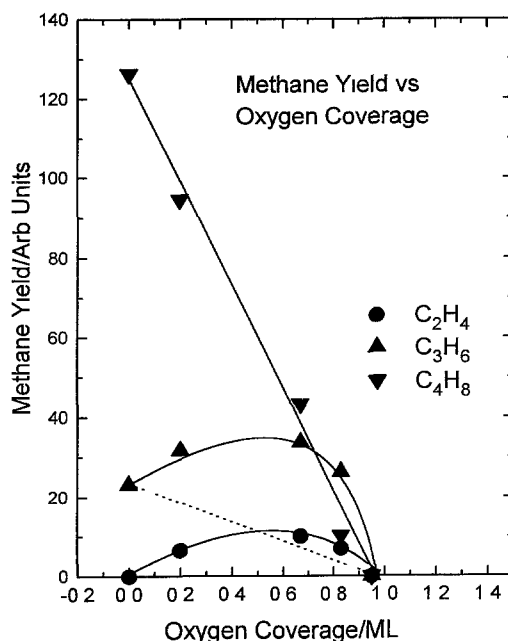


Fig. 13 Plot of the methane yield following the adsorption of an homologous series of alkenes (ethylene, propylene and 2-butene) on various oxygen-covered Mo(100) surfaces

than unity. The methane yield from ethylene is zero for clean Mo(100) and increases with increasing oxygen coverage to reach a maximum at ~ 0.6 monolayers of oxygen and decreases once again for higher oxygen coverages. The trend for methane formed from 2-butene is completely different and the yield decreases linearly with increasing oxygen coverage and is the largest for clean Mo(100). If it is assumed that carbenes form by direct dissociation of the double bond, the methane yield from propylene, which should form methyldiene and ethylidene, should be a linear combination of both trends. Note that the absolute yields will depend on the carbon–carbon bond dissociation probability, and the data of Fig. 13 suggest that this probability decreases in the order 2-butene > propylene > ethylene. However, the methane yield for propylene is indeed a linear combination of the trends for both ethylene and 2-butene. Some methane is formed from propylene on clean Mo(100). However, rather than decreasing with increasing oxygen coverage as found for 2-butene, the yield increases with increasing oxygen yield, reaches a peak with the addition of ~ 0.6 monolayer of oxygen and decreases to zero when 1 ML of oxygen has been added. This effect is illustrated by showing a linear decrease in methane yield as the dotted line in Fig. 13.

Finally, it is clear that the total methane yield varies in the order 2-butene > propylene > ethylene. It was proposed above that bonding of the alkene to the surface is via the donation of π -electrons to the molybdenum substrate. Since this results in the removal of electrons from a bonding orbital, this will weaken the C=C double bond, presumably leading to a corresponding increase in dissociation probability. The position of the π orbital in alkenes is substantially affected by the presence of a methyl group, so that the binding energy of the π orbitals in ethylene is 10.5 eV, 9.7 eV in propylene and 9.1 eV in 2-butene [42]. These shifts are fairly substantial and indicate that the π orbital should be rather closer to the Fermi level in 2-butene than in ethylene. This indicates that the extent of electron donation from the π orbitals to the substrate should be larger for 2-butene than for ethylene, leading to a larger decrease in bond order and therefore an increased bond dissociation prob-

ability in the order found experimentally. Additional evidence for this trend is that the desorption activation energy for the molecular species varies in the order $C_4H_8 > C_3H_6 > C_2H_4$ [6,7].

5. Conclusions

2-Butene reacts on oxygen-covered Mo(100) either by completely thermally decomposing to form carbon and hydrogen, or by hydrogenating to yield butane, or by thermally decomposing to form methane. The first reaction appears to take place on the four-fold hollow sites, and hydrogenation products are formed by reaction with surface atomic hydrogen. Methane appears to be formed via the production of methyl carbenes formed directly on this surface by dissociation of the carbon–carbon bond. This chemistry is broadly similar to that found for both ethylene and propylene on oxygen-covered Mo(100).

Acknowledgements

We gratefully acknowledge support of this work by the US Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under Grant No. DE-FG02-92ER14289. This work is based on research conducted at the Synchrotron Radiation Center, University of Wisconsin–Madison, which is supported by the NSF under Award No. DMR-95-31009.

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