A vibrational study of the activation sequence of C–H and C–C bonds of isobutene and 1-butene on Mo(110) and (4 × 4)-C/Mo(110) surfaces

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The thermal decomposition pathways of isobutene and 1-butene on both Mo(110) and (4 × 4)-C/Mo(110) surfaces have been studied using high-resolution electron energy loss spectroscopy (HREELS) in order to highlight the substantially different activities of these two surfaces towards the cleavage of C–H and C–C bonds. On clean Mo(110), the CH_2 group of isobutene decomposes upon heating to 150 K, producing either a σ/π-bonded isobutenylidene $[(CH_3)_2CCH]$ species or a 1,1-di-σ/π-bonded isobutenyl $[(CH_3)_2CC]$ species. Upon further heating, extensive C–H bond scission occurs to form hydrocarbon fragments which do not contain CH_3 or CH_2 groups, but appear to have largely intact carbon skeletons. By contrast, isobutene is molecularly adsorbed on the carbide-modified surface at 150 K. Further heating produces isobutylidyne $[(CH_3)_2HCC]$ by 300 K, which subsequently decomposes via C–C bond scission to generate surface methyl groups. The different activation sequence of the C–H and C–C bonds of isobutene on clean and carbide-modified Mo(110) surfaces is also qualitatively confirmed by comparative studies of 1-butene on the two surfaces.

Keywords: isobutene, 1-butene, Mo catalyst, reaction pathway, C–H bond activation, C–C bond activation, activation sequence

1. Introduction

One important area of research in heterogeneous catalysis concerns the ability to activate C–C and C–H bonds of hydrocarbon molecules selectively. A potentially interesting class of catalysts in this regard is the Group 6 carbides, since the surfaces of these carbide materials often show different activities towards the CC and CH bond cleavage as compared to those of the corresponding parent metals [1–3]. The goal of the studies in this letter is to study the selectivity of the Mo(110) and (4 × 4)-C/Mo(110) surfaces towards C–C and C–H bond activation. To do so, we have chosen to use isobutene as a probing molecule, because it is a simple, symmetrical molecule with only two types of CC and CH bonds. Furthermore, because the decomposition of isobutene has been studied on Ni(111) [4], Ru(0001) [5], and Pt(111) [6], the current work provides another comparison of the reactivities of carbide-modified early transition metal surfaces with those of late transition metals, particularly those of the Group 10 metals and the Pt-group metals [1–3].

This letter is organized as follows. To provide a point of reference for these studies, we will start by showing vibrational spectra of isobutene on an inert p(2 × 2)-O/Mo(110) surface. These vibrational spectra will be used to help identify the surface intermediates present on the clean and carbide-modified Mo(110) surfaces at 150 K following the adsorption of isobutene. Next, we will show vibrational spectra monitoring the thermal decomposition of isobutene on the clean and carbide-modified Mo(110) surfaces to demonstrate the different activation of C–H and C–C bonds on the two surfaces. We will also summarize the thermal decomposition pathways of isobutene on these two surfaces and compare with those of isobutene on Pt(111) and Ru(0001). Finally, we will discuss briefly comparative studies of the decomposition of 1-butene on Mo(110) and C/Mo(110) to demonstrate further the different reactivities of the two surfaces.

2. Experimental

The experiments reported in this paper were performed in an ultrahigh vacuum (UHV) chamber (base pressure 2×10^{-10} Torr) which has been described previously [7,8]. HREEL spectra were recorded in the on-specular and 20° off-specular directions using a spectrometer (LK-3000) which was operated such that the electrons had an energy of 6.0 eV and were incident on the surface at 60° from the normal. Typically, the elastic peak had a full width at half maximum (FWHM) of 30–35 cm^{-1} and an intensity of about 1×10^6 cps for a clean Mo(110) surface. Although the HREEL spectra were recorded with the sample temperature at 80 K, in the studies monitoring the thermal decomposition of isobutene, the surface was annealed for 30 s at each temperature of interest, prior to recording the corresponding HREEL spectrum.

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The isobutene, 1-butene (Matheson, research grade) and oxygen (Matheson, 99.99% purity) were used without further purification, although the purity was checked *in situ* regularly. All gases were admitted into the chamber via sapphire seal variable leak valves, and exposures were not corrected for differences in ion gauge sensitivity.

Clean Mo(110) surfaces and p(2 × 2)-O/Mo(110) surfaces were prepared by using procedures that have been previously described [2,7,9]. The (4 × 4)-C/Mo(110) surfaces were prepared by dosing/flashing cycles in which the Mo crystal was held at 600 K, exposed to 3 L of an alkene, typically ethylene or a C_4 1-alkene, and then flashed to 1250 K. This procedure was repeated until the peak-to-peak ratio of the C(KLL)/Mo(MNN 186 eV) Auger features was ∼0.20, which is sufficient to produce a p(4 × 4) LEED pattern [7].

The hydrocarbon overlayers in the current study were prepared by exposing Mo(110) or C/Mo(110) surfaces to 3 L of isobutene or 1-butene at 80 K. This exposure corresponds to approximately one half of a monolayer coverage, based on Auger electron spectroscopy (AES) and temperature-programmed desorption (TPD) studies (not shown). At this coverage, the chemisorbed isobutene and 1-butene molecules undergo complete decomposition on both Mo(110) and C/Mo(110) surfaces, and the only gas phase product observed is H_2 resulting from the decomposition of the C_4 molecules.

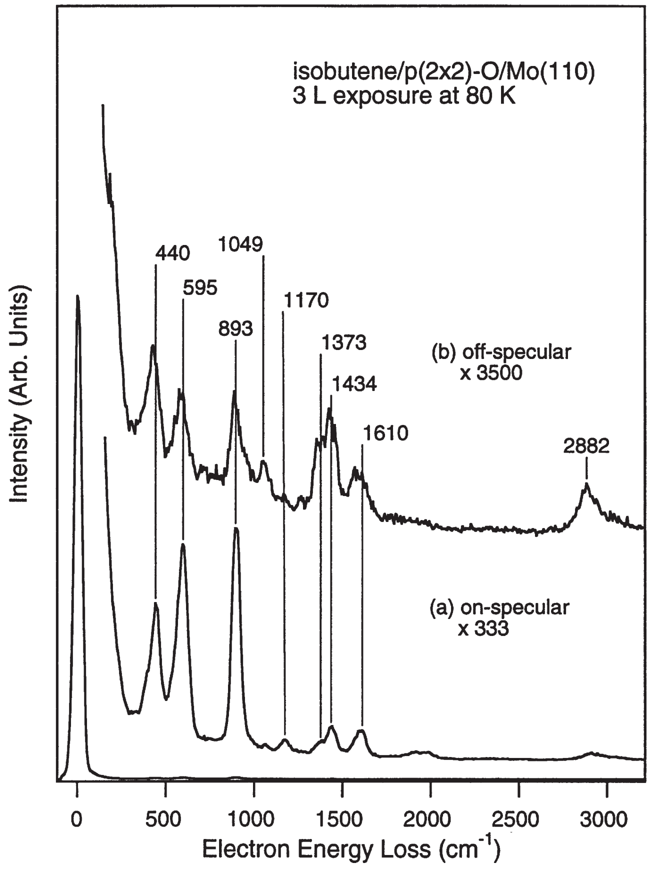

Figure 1. (a) On-specular spectrum of isobutene on the p(2×2)-O/Mo(110) surface taken at 80 K. (b) 20° off-specular spectrum of isobutene on the same surface as (a).

3. Results and discussion

3.1. Reaction pathways of isobutene on Mo(110) and C/Mo(110)

3.1.1. Identification of surface intermediates at 150 K

To assist in making vibrational assignments for isobutene on Mo(110) and C/Mo(110), we show in figure 1 the on- and off-specular HREEL spectra obtained after exposing a chemically inert p(2 × 2)-O/Mo(110) surface at 80 K to 3 L of isobutene. The vibrational frequencies in figure 1 agree well with previously reported vibrational assignments for multilayers of isobutene physisorbed on a Ni(111) sur-

Table 1
Vibrational mode assignments for isobutene adsorbed on p(2 × 2)-O/Mo(110) and p(4 × 4)-C/Mo(110).[a]

Mode description	Isobutene		
	physisorbed on Ni(111) [4]	on p(2 × 2)-O/Mo(110) at 80 K (this work)	on p(4 × 4)-C/Mo(110) at 150 K (this work)
ω(CCC)	225	–	392
δ(CCC)	445	440	480
ν(Mo–O)	–	595	–
ν_s(H_3C–C–CH_3)	815	–	710
ω(CH_2)	885	893	879
ν_a(H_3C–C–CH_3)	970	–	960
ρ(CH_3)	1055	1049	1035
ν(Mo–O) (overtone)	–	1170	–
δ_s(CH_3)	1380	1373	1353
δ_a(CH_3)	1450	1434	1434
ν(C=C)	1660	1610	1596
ν_s(CH_3)	2870	2882	2874
ν_a(CH_3)	∼2910	–	2943

[a] All frequencies are in wavenumbers.

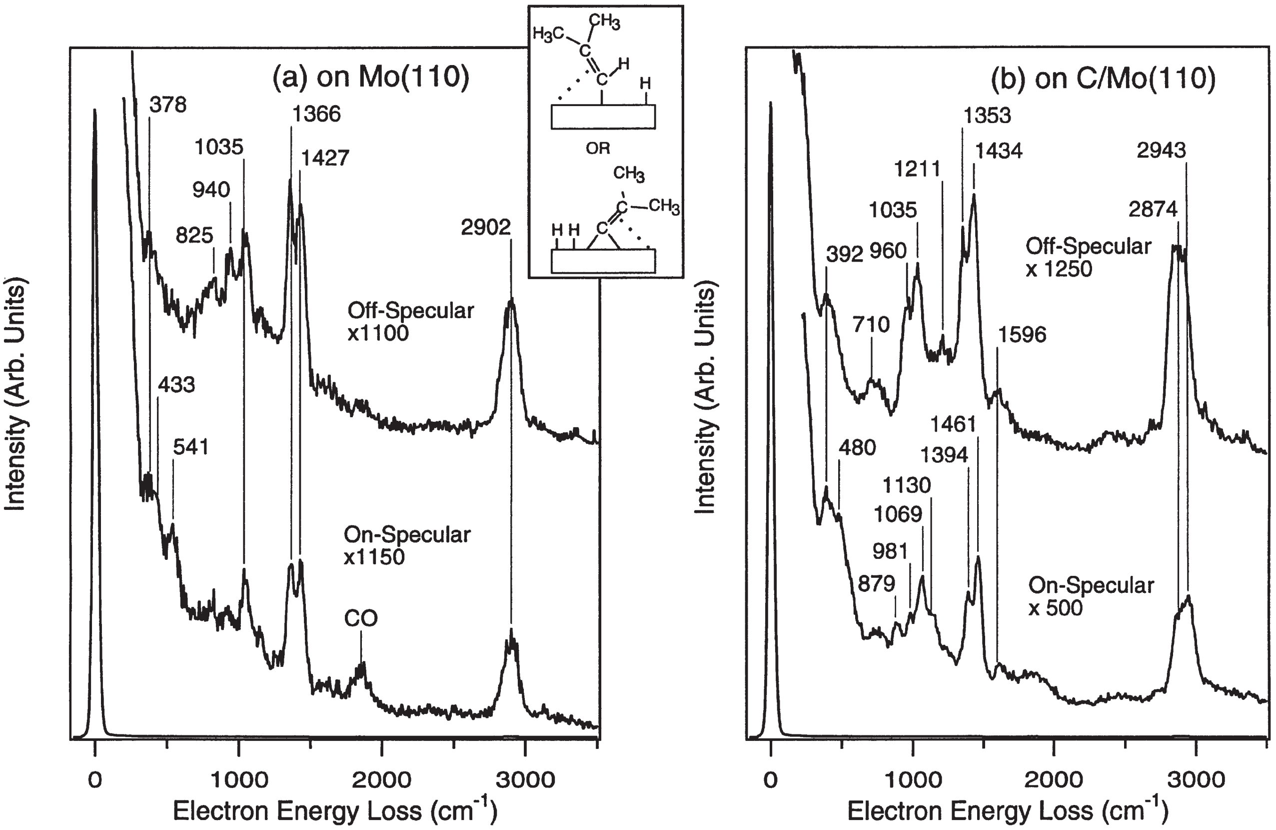

Figure 2. (a) On- and 20° off-specular spectra of isobutene on the clean Mo(110) surface after flashing to 150 K. The inset shows a drawing of two possible intermediates, σ/π-bonded isobutenylidene (top) and 1,1-di-σ/π-bonded isobutenyl (bottom), which would be consistent with the vibrational spectra. (b) On- and 20° off-specular spectra of isobutene on the (4×4)-C/Mo(110) surface after flashing to 150 K.

face [4], confirming that isobutene interacts only weakly with the $p(2 \times 2)$-O/Mo(110) surface. Although a complete vibrational assignment of the features in figure 1 is given in table 1, we focus here on the following two features: (1) the $\nu(C{=}C)$ feature at 1610 cm^{-1}, whose presence indicates that the interaction between the C=C bond and the O/Mo(110) surface is sufficiently weak so that the sp^2-hybridization is maintained, and (2) the $\omega(CH_2)$ feature at 893 cm^{-1}, which shows a strong angle-dependent variation in intensity, indicating, based on the surface dipole selection rule, that the isobutene molecules are adsorbed with the molecular planes nearly parallel to the surface. As will be evident in the discussion below, these two features together are diagnostic for weakly interacting, molecularly adsorbed isobutene. As such, their presence (or absence) can be used as a guide for identifying the surface intermediates formed during the decomposition of isobutene on the clean and carbide-modified Mo(110) surfaces.

In figure 2(a), we show the on- and off-specular spectra obtained after exposing a clean Mo(110) surface at 80 K to 3 L of isobutene, flashing to 150 K, and cooling again to 80 K. Importantly, though the $\omega(CCC)$ and $\nu_a(CH_3{-}C{-}CH_3)$ features at 378 and 940 cm^{-1}, respectively, clearly indicate that the C_4 skeleton is essentially intact, the differences between figure 2(a) and figure 1 clearly show that isobutene interacts more strongly with the clean Mo(110) surface than with the $p(2 \times 2)$-O/Mo(110) surface. This stronger interaction is illustrated, for example, by the absence of the $\nu(C{=}C)$ bond, which indicates that carbon atoms of the double bond have become sp^3-hybridized. Additionally, we note that there is no strong $\omega(CH_2)$ feature near 890 cm^{-1}, as observed in figure 1. In principle, such behavior could be caused either by a molecular adsorption geometry that is not parallel to the surface, or by the absence of the CH_2 groups due to decomposition. However, we can exclude the former possibility, since the rehybridization of the C=C bond must result in an essentially flat-lying geometry. Additional evidence for the decomposition of the CH_2 groups is provided indirectly by the broad loss feature to the low energy side of the 825 cm^{-1} feature (cf. figure 2(a), top spectrum). The broadness of this feature indicates that it is comprised of two or more peaks, and we note that, in other studies of hydrocarbon decomposition on Mo(110), it has been shown that surface hydrogen exhibits a broad ν(Mo–H) mode near 800 cm^{-1} [2,9,10]. Thus, based on the absence of a $\omega(CH_2)$ feature and the presence of a broad ν(Mo–H) feature near 800 cm^{-1}, we conclude that the CH_2 group of isobutene has decomposed on the Mo(110) surface by 150 K. This behavior is also consistent with studies of ethylene on Mo(110) which showed that facile dehydrogenation occurs even at 80 K [11]. A summary of the vibrational mode assignments for the features in figure 2(a) is given in table 2.

To identify the surface intermediate present on the clean Mo(110) at 150 K, we begin by noting that the absence of a ν(C=C) feature allows us to exclude possibilities such as π-bonded isobutenylidene [$(CH_3)_2CCH$] or isobutenyl [$(CH_3)_2CC$]. Furthermore, the surface intermediate is not isobutylidyne [$(CH_3)_2HCC$], because the features at ~825 and 940 cm^{-1}, attributable to ν_s(CH_3–C–CH_3) and ν_a(CH_3–C–CH_3) modes, respectively, are not characteristic of isobutylidyne [6]. Thus, the most likely remaining candidates are 1,1-di-σ/π-bonded isobutenyl or σ/π-bonded isobutenylidene, as shown in the inset of figure 2(a). Distinguishing between these two cases is difficult, since these two species probably are spectroscopically very similar.

Table 2
Vibrational mode assignments for the spectral features in figure 2(a).[a]

Mode description	On Mo(110) at 150 K	On Ni(111) [4] at 180 K
ω(CCC)	378	370
δ(CCC)		430
ν(M–C)	541	555
ν(Mo–H)	~800	–
ν_s(H_3C–C–CH_3)	825	845
ω(CH_2)	–	–
ν_a(H_3C–C–CH_3)	940	950
ρ(CH_3)	1035	1055
δ_s(CH_3)	1366	1380
δ_a(CH_3)	1427	1450
ν(C=C)	–	1595
ν_s(CH_3)	–	2870
ν_a(CH_3)	2902	2910

[a] The surface intermediate which gives rise to the spectrum in figure 2(a) could be either 1,1-di-σ/π-bonded isobutenyl or σ/π-bonded isobutylidene. All frequencies are in wavenumbers.

In figure 2(b), we show the on- and off-specular spectra obtained after a carbide-modified Mo(110) surface was exposed to 3 L of isobutene at 80 K, flashed to 150 K, and cooled again to 80 K. These spectra are consistent with molecularly adsorbed isobutene, as indicated by the ν(C=C) feature at 1596 cm^{-1}, which reveals that the carbon atoms in the double bond have not been rehybridized. Also consistent with the presence of a C=C bond is the ν(C–H) mode at 2943 cm^{-1}, which occurs in the frequency range expected for a terminal CH_2 group of an olefin. For the sake of the discussion below, we emphasize here that the features at 392, 480, 710, and 960 cm^{-1} confirm that the C_4 skeleton of isobutene is intact on the carbide-modified Mo(110) surface at 150 K. The vibrational assignments are summarized in table 1.

3.1.2. Thermal decomposition of isobutene on Mo(110) and (4 × 4)-C/Mo(110)

Upon heating to 300 K, isobutene dehydrogenates further on Mo(110) to generate new surface intermediates, as seen in figure 3(a). For example, the presence of a more prominent ν(Mo–H) feature at 804 cm^{-1} is consistent with

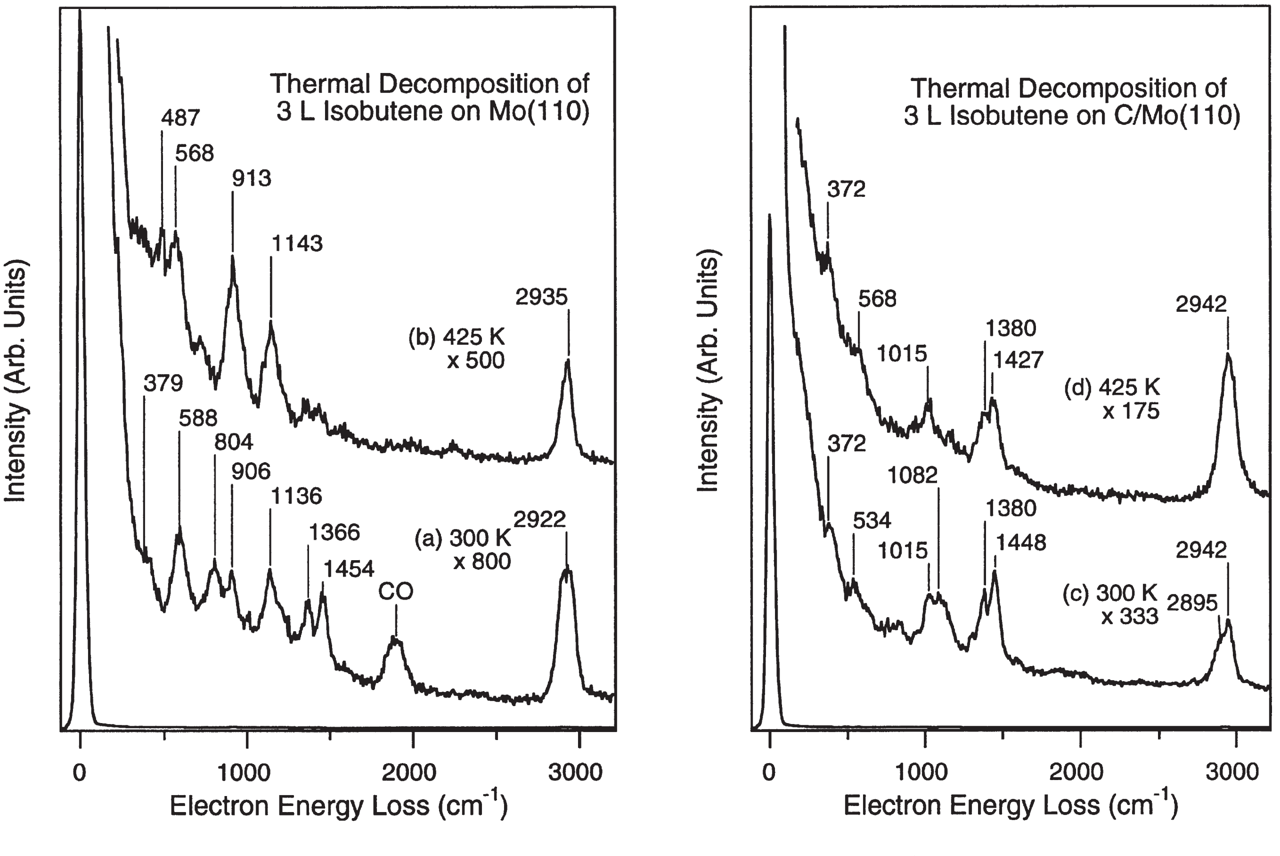

Figure 3. HREEL spectra monitoring the thermal decomposition of isobutene on clean and carbide-modified Mo(110). All spectra were recorded in the on-specular direction.

additional C–H bond scission. This conclusion is also supported by the appearance of a new feature at 906 cm^{-1}, which is in a frequency range typical for δ(C–H) vibrations, as determined by comparisons with vibrational studies of methylidyne (CH) on various single crystal transition metal surfaces [12–16]. Also consistent with further dehydrogenation is the sharp attenuation of the $\rho(CH_3)$ mode at 1035 cm^{-1}, suggesting that some surface methyl groups have decomposed. The features at 379 and 1136 cm^{-1} result from ω(CCC) and ν(C–C) motions, respectively. The presence of these two features indicates that the C_4 carbon skeleton has not completely decomposed. Finally, the feature at 588 cm^{-1} is assigned to a ν(Mo–C) stretch [7].

After heating to 425 K (figure 3(b)), the hydrocarbon fragments remaining on the Mo(110) surface are further dehydrogenated. Evidence for this behavior is given by the significant decrease in the intensities of the CH_2 deformation features between 1200 and 1500 cm^{-1} and by the concomitant increase in the relative intensity of the δ(C–H) mode at 913 cm^{-1} [12–16]. On the basis of these arguments, the feature at 2935 cm^{-1} must result mainly from the ν(C–H) vibrations of an extensively dehydrogenated hydrocarbon species. This conclusion is also supported by our temperature-programmed desorption studies (not shown), which reveal that the H_2 desorption feature occurs at ~400 K following a 3 L dose of isobutene on Mo(110) at 80 K. The remaining features at 487, 568 and 1143 cm^{-1} result from vibrational modes involving carbon bonds. The feature at 487 cm^{-1} can be assigned to a δ(CCC) mode, based on a comparison with a previous study of isobutene decomposition on Ni(111) [4], while the feature at 568 cm^{-1} can be assigned to a metal–carbon stretching vibration, based on our studies of hydrocarbon chemistry on Mo(110) [2,7,9,10]. The feature at 1143 cm^{-1} is assigned to a ν(C–C) mode. Again, the presence of the δ(CCC) and ν(C–C) modes suggests that the C_4 carbon skeleton has not completely decomposed even after heating to 425 K.

Unlike the case for the Mo(110) surface, the spectrum of the intermediates on a carbide-modified Mo(110) surface at 300 K (figure 3(c)) is not consistent with extensive dehydrogenation of isobutene, but rather the formation of isobutylidyne. By comparing with previously published data for isobutylidyne on Pt(111) [6], the main features in figure 3(c) can be straightforwardly assigned as follows: 2942 cm^{-1} $\nu_a(CH_3)$; 2895 cm^{-1} $\nu_s(CH_3)$; 1448 cm^{-1} $\delta_a(CH_3)$; 1380 cm^{-1} $\delta_s(CH_3)$; and 1082 and 1015 cm^{-1}, coupled ν(C–C) and $\rho(CH_3)$ vibrations. The feature at 534 cm^{-1} is assigned to ν(Mo–C) vibrations characteristic of the (4 × 4)-C/Mo(110) surface [7], while the 372 cm^{-1} feature probably results from a $\nu(Mo–CH_3)$ vibration originating from the decomposition of a fraction of isobutylidyne, as discussed below.

Upon heating to 425 K, we obtained a spectrum which is somewhat similar to the one obtained at 300 K (cf. figure 3 (c) and (d)). However, one key difference is that the broad, unresolved coupled ν(C–C) and $\rho(CH_3)$ loss features between 1000 and 1100 cm^{-1} in figure 3(c), characteristic of isobutylidyne, have been replaced by a single sharp feature at 1015 cm^{-1} in figure 3(d). Such behavior reflects the further decomposition of the isobutylidyne intermediate by 425 K. Based on comparisons with vibrational data reported in the literature [6,17,18], we conclude that the spectrum shown in figure 3(d) is most consistent with the presence of adsorbed methyl groups. On this basis, we assign the vibrational features as follows: 2942 cm^{-1} $\nu(CH_3)$; 1427 cm^{-1} $\delta_a(CH_3)$; 1380 cm^{-1} $\delta_s(CH_3)$; 1015 cm^{-1} $\rho(CH_3)$; and 372 cm^{-1} $\nu(Mo–CH_3)$. The remaining feature at 568 cm^{-1} is assigned to ν(Mo–C) vibrations, based on prior studies of hydrocarbon decomposition on the Mo(110) surface [2,9,10]. Finally, note that the conversion of isobutylidyne to adsorbed methyl groups is not quantitative. Our temperature-programmed desorption studies (not shown) reveal a moderately intense H_2 desorption feature at ~400 K from the C/Mo(110) surface following a 3 L dose of isobutene at 80 K. Based on this result, it is likely that only a fraction of the methyl groups of the isobutylidyne intermediate is converted to surface methyl, while the rest decomposes.

3.1.3. Comparison of reaction pathways of isobutene

Figure 4 shows a schematic diagram summarizing the decomposition pathways of isobutene on the Mo(110) and (4 × 4)-C/Mo(110) surfaces. This diagram highlights the significantly different chemistries which occur on these two surfaces, particularly in the activation sequence of the C–H and C–C bonds on the two surfaces. Isobutene interacts strongly with clean Mo(110), as seen by the occurrence of C–H bond scission at temperatures as low as 150 K, as well as by the rehybridization of the C=C bond. At higher temperatures, the methyl groups begin to decompose, leading to the production of hydrocarbon intermediates containing no CH_2 or CH_3 groups by 425 K. In contrast, on the carbide-modified Mo(110) surface, isobutene is molecularly adsorbed at 150 K, but reacts to form isobutylidyne by 300 K. Subsequent heating to 425 K produces methyl groups and carbon on the surface.

The origin of the different decomposition mechanisms of isobutene on these two surfaces is currently not well-understood and likely results from several different effects. For example, one critical parameter is the degree of interaction between the C=C bond and the surface, which governs the adsorption geometry. For isobutene on Mo(110), the strong interaction between the carbon atoms in the double bond and the surface implies that the molecular plane of isobutene and its subsequent decomposition intermediates are most likely tilted towards the reactive Mo(110) surface. Consequently, because the methyl groups would be in close proximity to the surface as the temperature is increased, it is perhaps not surprising that the methyl groups would react and decompose. On the other hand, the interaction of the C=C bond with the carbide-modified Mo(110) surface is substantially weaker, as evidenced by the ability of the molecule to tilt away from the surface to form isobutyli-

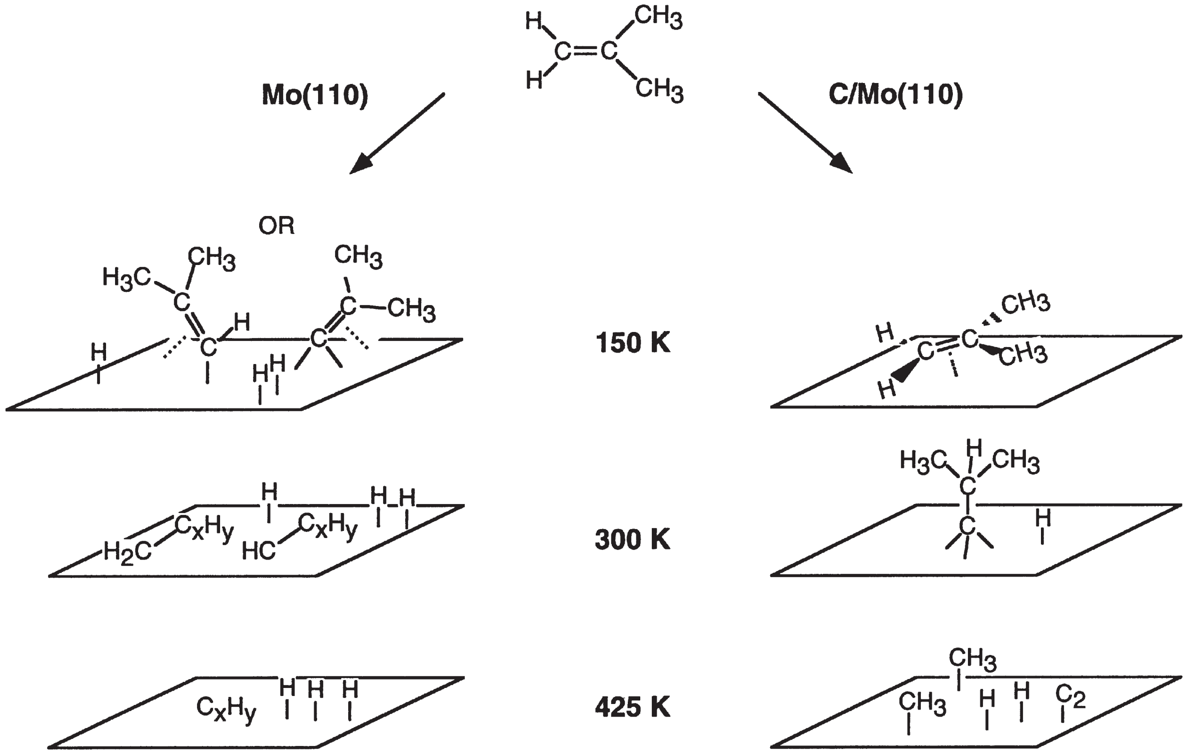

Figure 4. A schematic diagram summarizing the decomposition mechanisms of isobutene on the clean and carbide-modified Mo(110) surfaces.

dyne at 300 K. Thus, one could argue that the methyl groups in isobutylidyne would show less tendency to decompose because they are pointing away from the surface.

However, while rationalizing the decomposition mechanisms based on geometrical arguments is intuitively appealing, we emphasize that there are other effects governing the reaction pathways which are also important but not well-understood. For example, although isobutylidyne forms on (4 × 4)-C/Mo(110), Pt(111) [6], and Ru(0001) [5], the subsequent decomposition mechanisms are quite different. Isobutylidyne decomposes on Pt(111) by 420 K to produce a substantially dehydrogenated C_4H_4 intermediate [6], rather than the surface methyl groups as observed on C/Mo(110). On Ru(0001), it has been reported that isobutylidyne decomposes to produce ethylidyne [5]. Thus other parameters, such as the surface electronic structure or site-blocking effects, are likely to be important and should be studied in order to achieve a more complete understanding of the differences in the activation sequences of the C–H and C–C bonds.

3.2. Reaction pathways of 1-butene on Mo(110) and (4 × 4)-C/Mo(110)

To emphasize the different activation sequence for C–H and C–C bonds on Mo(110) and C/Mo(110), we also performed vibrational studies of 1-butene on these two surfaces. Because the C=C double bond is situated at the terminal position for both 1-butene and isobutene, one would expect the decomposition pathways of 1-butene on Mo(110) and C/Mo(110) to be similar to those of isobutene on the same surfaces.

Figure 5 compares HREEL spectra of 1-butene on clean and carbide-modified Mo(110), taken at 300 and 425 K. The vibrational spectra of 1-butene are much more complex than those of isobutene due to the presence of internal CH_2 and CH groups in the former molecule. We do not attempt at this time to provide a complete assignment of the vibrational features in figure 5. Nevertheless, the spectra in figure 5 clearly indicate that the decomposition pathways of 1-butene on Mo(110) are different from those on C/Mo(110). For example, although the 1-butene spectra taken at 300 K both show features between 1200 and 1500 cm^{-1}, characteristic of CH_2 or CH_3 deformation modes (cf. figure 5 (a) and (c)), there are some major differences between the two spectra. For example, a relatively intense ν(Mo–H) mode at 785 cm^{-1} is present in figure 5(a), indicative of significant dehydrogenation of the 1-butene overlayer on Mo(110), just as in the case for isobutene on this surface at 300 K (figure 3(a)). Additionally, figure 5(a) contains a pronounced feature at 1123 cm^{-1}, not present in figure 5(c), which at least suggests that the hydrocarbon intermediates on these surfaces at 300 K are different. Although we have not identified these intermediates definitively through isotopic labeling studies, it is plausible that 1-butene converts to butylidyne on C/Mo at 300 K, just as ethylene converts to ethylidyne [11] and isobutene converts to isobutylidyne (figure 3(c)) on this surface in this temperature range. Also consistent with the formation of butylidyne on C/Mo at 300 K is the good correspondence between the spectral features in figure 5(c) with those of butylidyne

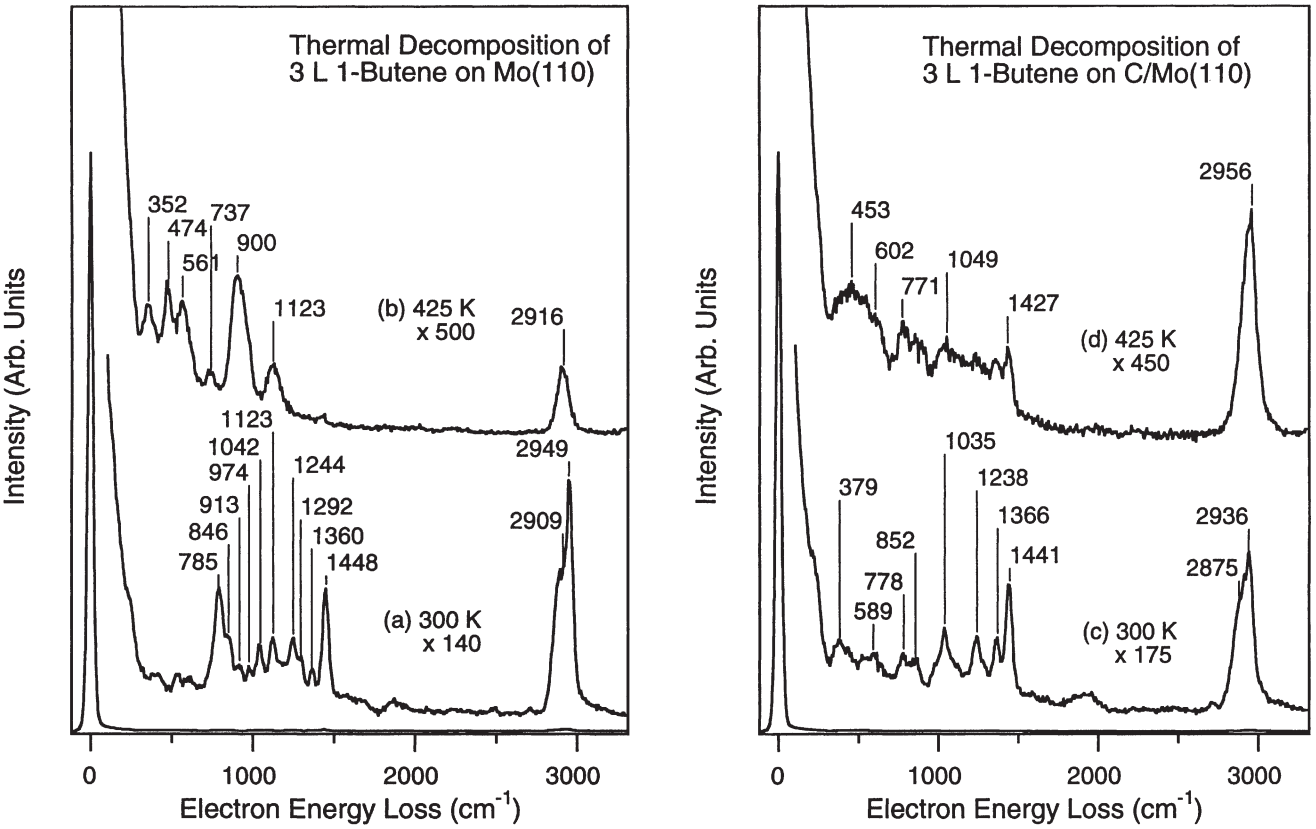

Figure 5. HREEL spectra monitoring the thermal decomposition of 1-butene on Mo(110) and C/Mo(110). All spectra were recorded at 80 K in the on-specular direction.

on Ru(0001) [5] and on Pt(111) [6], especially for the region above 700 cm^{-1}. However, we emphasize again that more studies are necessary for a definitive assignment of the different hydrocarbon intermediates on Mo(110) and C/Mo(110) at 300 K.

The HREEL spectra of 1-butene taken after flashing to 425 K (figure 5 (b) and (d)) show that the activation sequence of the C–H and C–C bonds on Mo(110) and C/Mo(110) is qualitatively similar to that of isobutene. For example, the spectrum shown in figure 5(b) is rather similar to that obtained after heating isobutene to the same temperature (figure 3(b)), indicating that 1-butene decomposes to form an extensively dehydrogenated intermediate on clean Mo(110) by 425 K as well. Again, this conclusion is supported by our temperature-programmed desorption studies, which show that H_2, resulting from the decomposition of 3 L of 1-butene, desorbs at ~400 K. The spectral features in figure 5(b) can be assigned as follows: 474 cm^{-1} δ(CCC); 561 cm^{-1} ν(Mo–C); 900 cm^{-1} δ(C–H); 1123 cm^{-1} ν(C–C); and 2916 cm^{-1} ν(C–H). The presence of the δ(CCC) and ν(C–C) modes, as well as the absence of any deformation modes of CH_2 and CH_3 in the 1200–1500 cm^{-1} region, indicate that the decomposition of 1-butene on Mo(110) occurs primarily by the cleavage of the C–H bonds, with the C–C skeleton remaining largely intact. On the other hand, CH_2 or CH_3 groups are more stable on the carbide-modified Mo(110) surface at 425 K, as indicated by the presence of CH_2 or CH_3 deformation modes between 1200 and 1500 cm^{-1} and the CH_2 or CH_3 rocking modes between 750 and 1100 cm^{-1} [6] in figure 5(d). The corresponding off-specular measurements (spectra not shown) also confirm the absence of CH_2 or CH_3 groups on clean Mo(110), and their presence on the C/Mo(110) surface. However, we point out that our temperature-programmed desorption experiments shown an H_2 desorption feature at ~400 K following a 3 L dose of 1-butene on C/Mo(110) at 80 K, suggesting that a fraction of the 1-butene could become extensively dehydrogenated or decompose completely.

Finally, it is instructive to compare the decomposition mechanism of butylidyne observed in our studies with those of butylidyne on late transition metal surfaces [6,17,19–21]. Temperature-programmed desorption results have shown that heating a 1-butene layer on Pt(111) to 400 K produces a surface C : H composition of C_4H_2 [6]. Interestingly, the corresponding HREEL spectra suggest that there are no CH_2 or CH_3 groups remaining on the Pt(111) surface, in contrast to the 425 K spectra of 1-butene on the C/Mo(110) surface [6]. Also, it has been proposed that the C_4 skeleton of 1-butene remains intact [6]. On Ru(0001) surfaces, it appears that the chemistry is quite different: butylidyne decomposes by 300 K to produce ethylidyne [5], suggesting that C–C bond scission can occur. Such differences in decomposition pathways again point to the possibility that many different factors can control decomposition pathways of hydrocarbons on transition metal surfaces.

4. Conclusions

We have compared the thermal decomposition pathways of isobutene on the Mo(110) and (4 × 4)-C/Mo(110) surfaces. For the clean Mo(110) surface, dehydrogenation is the primary reaction, occurring between 150 and 425 K to produce an extensively dehydrogenated surface species which appears to have a largely intact carbon skeleton. By contrast, simple dehydrogenation is suppressed on the (4 × 4)-C/Mo(110) surface. Instead, isobutene converts to isobutylidyne at 300 K and then subsequently decomposes via C–C bond scission to form surface methyl groups that are thermally stable on C/Mo(110) up to 425 K. Such a difference in the sequence of C–H and C–C bond cleavage is also qualitatively confirmed by the different decomposition pathways of 1-butene on Mo(110) and C/Mo(110) surfaces.

The relative stability of CC versus CH bonds on Mo(110) and C/Mo(110) reported here provide some fundamental insights into the different hydrogenolysis activities of molybdenum and molybdenum carbide [22]. Because hydrogenolysis reactions occur via the selective cleavage of C–C bonds, an effective catalyst should promote facile C–C bond cleavage while maintaining CH_n ($n \geqslant 2$) moieties. The results presented in this letter therefore suggest that the carbide-modified Mo(110) surface is better suited for hydrogenolysis reactions, which is consistent with previous reports showing that molybdenum carbides exhibit superior hydrogenolysis activity compared to molybdenum [22].

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