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Reaction of Ethylene with Clean and Carbide-Modified Mo(110): Converting Surface Reactivities of Molybdenum to Pt-Group Metals

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Abstract: A comparative investigation of the surface reaction of ethylene with clean Mo(110) and carbide-modified Mo(110) has been carried out using high-resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD). As typically observed for early transition metals, the clean Mo(110) surface interacts very strongly with ethylene, as indicated by the decomposition of ethylene to produce C_2H_2 surface species at temperatures as low as 80 K. The surface acetylene species further decompose to atomic carbon and hydrogen at higher temperatures. The strong reactivity of the Mo(110) surface can be modified by the formation of carbide. The surface reactivity is modified in such a way that the reaction mechanism of ethylene on C/Mo(110) is very similar to those typically observed on Pt-group metal surfaces: At 80 K, ethylene molecules bond to the C/Mo(110) surface in the di-σ bonded configuration; a new surface reaction intermediate, which can be best described as ethylidyne species, is detected in the temperature range of 260−350 K. In addition, the interaction of ethylene with oxygen-modified Mo(110) is also compared to reveal the different modification effects of carbon and oxygen adatoms on the reactivities of Mo(110). The oxygen-modified Mo(110) surface is found to be inert toward the decomposition of ethylene, as indicated by the formation of weakly adsorbed π-bonded ethylene species at 80 K and by the reversible molecular desorption at higher temperatures.

I. Introduction

One of the most fundamental questions in chemistry is how to convert the reactivity of one group of elements to another. In general, transition metals on the left side of the Periodic Table are much more reactive than their counterparts on the right side. For example, early transition metals (Groups IVB-VIB) are known to be highly reactive toward the decomposition of unsaturated hydrocarbon molecules.[1−3] Such a high reactivity often leads to the cleavage of carbon−carbon bonds, which is not desired in many industrial reactions. On the other hand, the Group VIII metals, especially the Pt-group noble metals (Pt, Pd, Ir, Rh, Ru, Os), interact with unsaturated hydrocarbon molecules in a less reactive manner.[4,5] For example, these metals are excellent catalysts for hydrogenation reactions, during which a $-CH_2{=}CH_2-$ moiety is converted to $-CH_3\text{-}CH_3-$ with the carbon−carbon bond remaining intact. Because early transition metals are much less expensive than the Pt-group metals, it would be of significant importance if the reactivities of early transition metals could be converted to those of Pt-group metals. It has been demonstrated in catalysis literature[5] that the catalytic properties of early transition metals could be significantly modified by the formation of interstitial carbides, and that the modified reactivities often showed similarities to those of Pt-group metals. These conclusions were based primarily on catalytic reactor studies using amorphous powder carbide materials as catalysts.[5]

In order to understand the fundamental aspects of how the formation of interstitial carbides would convert the chemical properties of early transition metals to those of Pt-group metals, we have carried out a series of experiments to directly compare the reactivities of atomically clean Mo(110) and carbide-modified Mo(110) surfaces. The main objective of this paper is to provide spectroscopic evidence, by using ethylene as a probing molecule, to demonstrate that the surface reactivity of an early transition metal, such as molybdenum, can indeed be converted to those characteristic of Pt-group metals.

The advantage of using ethylene as a probing molecule is that the adsorption and decomposition of ethylene on transition metal surfaces have been investigated extensively in both experimental and theoretical studies. The interaction of ethylene with transition metals is usually described in terms of the Dewar-Chatt-Duncanson theory,[1] which involves primarily the donation-back-donation of π-electrons of ethylene and d-electrons of metals. In this mechanism, electrons in the highest filled π-orbital of ethylene are partially donated to an empty σ-orbital of the metal atom. Such a donation weakens the π-bond of ethylene and lowers the energy level of the lowest-lying antibonding π^*-orbital, which in turn allows a more efficient back-donation of electrons from the metal atom, further weakening the C=C bond. Recent calculations[1] have demonstrated a general trend in the bonding of ethylene across the second-row transition metal series. On the left side of the Periodic Table ethylene was found to form purely covalent bonds, resulting in a metallacyclopropane with a carbon−carbon single bond. On the right side of the Periodic Table the bonding was described as an optimize mixing between purely covalent bonding and donation-back-donation bonding. In the later case,

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(3) Bent, B. E. *Chem. Reviews*, **1996**, *96*, 1361; and references therein.

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the carbon−carbon bond distance is between that of a double and a single bond, indicating a weaker interaction of the C=C bond with the second-row group VIII metals. Accordingly, in experimental studies the reaction pathway of ethylene is often distinctly different from one group of metals to another.[2,3] For example, early transition metals are generally found to be highly reactive, leading to the formation of deep dehydrogenation products, C_2Hx ($x \leq 2$), with both carbon atoms bonding to the surface. These intermediates undergo further thermal decomposition to produce atomic carbon and hydrogen. The interaction of ethylene with the group VIII noble metals, in contrast, generally occurs via different mechanisms. It is now well established that the reaction of ethylene with group VIII noble metals, in particular the close-packed faces of Pt, Pd, Ir, Rh, and Ru, proceeds via an ethylidyne (CCH_3) intermediate, which has been discussed in detail in several recent review articles.[2,3] High- resolution electron energy loss spectroscopy (HREELS) is among the most widely used diagnostic techniques for identification of this surface reaction intermediate.[4]

II. Experimental Methods

The experiments were carried out in a three level stainless steel ultrahigh vacuum (UHV) chamber previously described elsewhere.[7] Briefly, the chamber is equipped with a double-pass cylindrical mirror electron energy analyzer (CMA) for Auger- and photoelectron spectroscopy measurements, a Mg/Al dual anode X-ray source for X-ray photoelectron spectroscopy, a random flux shielded quadrupole mass spectrometer (QMS) for temperature programmed desorption studies and low-energy electron diffraction (LEED) optics for surface structure determination. The bottom level of the chamber is equipped with an LK3000 double-pass high-resolution electron energy loss spectrometer (HREELS) for vibrational analysis. The HREELS spectra reported here were acquired with a primary beam energy of 6 eV. Angles of incidence and reflection were 60° with respect to the surface normal in the specular direction. Count rates in the elastic peak were typically 5×10^5 to 1×10^6 cps, and the spectral resolution was between 30−35 cm^{-1} fwhm (full-width at half maximum). For TPD experiments the Mo(110) sample was heated with a linear heating rate of 3 K/s.

The single crystal sample was a [110] oriented, 1.5 mm thick molybdenum disk (99.999%), 12 mm in diameter, and was purchased from Metal Crystals and Oxides, Ltd., Cambridge, England. The Mo(110) surface was cleaned using standard procedures, as described in detail previously.[7] After cleaning the Mo(110) surface displayed a sharp characteristic bcc(110) LEED pattern. Sample cleanliness was verified with Auger spectroscopy and HREELS. All gases were of research purity and were used without further purification. Exposures are estimated from uncorrected ion gauge readings, expressed in units of Langmuir (L), with $1\ L = 1.33 \times 10^{-6}$ mbar·s.

III. Results

3.1. Adsorption and Reaction of Ethylene on Clean Mo(110). 3.1.1. Low Temperature Adsorption. Figure 1 shows vibrational spectra, recorded in the on- and off-specular directions, after the clean Mo(110) surface was exposed to ethylene at a surface temperature of 80 K. At low exposures (up to ~1 L exposure, Figure 1a,b), vibrational features are observed at 250, 390, 740, 905, 1130 and ~2900 cm^{-1}. The two additional features at 1875 and ~2200 cm^{-1} are due to trace amounts of contaminant CO[7] and N_2,[8] respectively, which adsorb onto the surface during dosing and data acquisition (~40 min). From the vibrational intensities of these two features in the specular HREELS spectra and from the TPD peak areas of CO and N_2, we estimate the coverages for both of these contaminants to be less than 0.04 monolayers (ML).

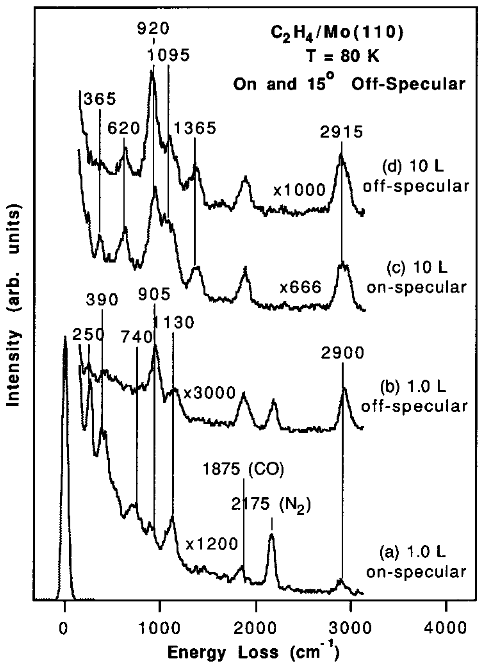

Figure 1. HREELS spectra recorded after exposing Mo(110) to 1 L and 10 L of C_2H_4 at 80 K. The spectra were recorded at on- and 15° off-specular directions.

The low frequency feature at 250 cm^{-1} is also present in the spectrum of the clean Mo(110) surface, indicating that it is related to the vibrational motion of the Mo(110) substrate. Previous surface phonon studies indicate that, for a metal substrate with a C_{2v} symmetry, at least one dipole-active surface phonon mode is expected in this frequency range.[9] We therefore assign this feature to the surface phonon mode of the Mo(110) substrate.

One important observation in Figure 1a,b is the absence of any vibrational feature in the frequency range of 1300−1450 cm^{-1}, which is the spectroscopic region for the relatively intense scissor modes of CH_2 groups. A comparison of the on- and off- specular HREELS spectra of the 1 L C_2H_4/Mo(110) surface also reveals that the relative intensities of the vibrational features change significantly. The intensities of the 250, 390, 740 and 1130 cm^{-1} features decrease substantially in the off-specular measurements (notice the different expansion factors), suggesting a dipolar excitation mechanism for these vibrational modes.[9]

The HREELS spectra displayed significant changes at exposures above 1 L, as demonstrated in Figure 1c,d. Vibrational features were detected at 365, 620, 920, 1095, 1365 and ~2915 cm^{-1}. The feature at 1875 cm^{-1} is again due to contaminant CO. The most significant spectroscopic difference between the low and high ethylene exposures is the onset of two new vibrational features at higher exposures at 620 and 1365 cm^{-1}, respectively. A comparison of Figure 1c,d indicates that the relative intensities of the vibrational features are nearly the same in the on- and off-specular measurements.

To assist the assignment of the vibrational features, spectra for corresponding low and high exposures were also recorded

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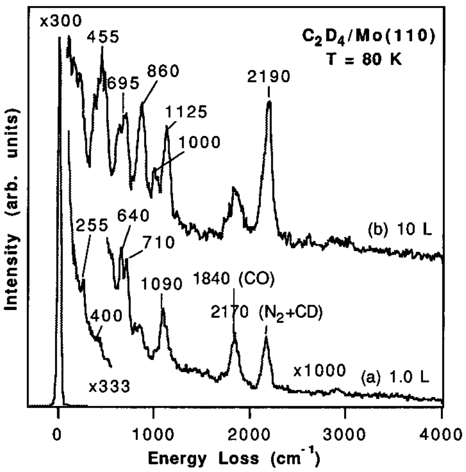

Figure 2. HREELS spectra recorded after exposing Mo(110) to 1 L and 10 L of C_2D_4 at 80 K.

after exposing the sample to the deuterated compound, C_2D_4. These spectra are shown in Figure 2. After an exposure of 1 L C_2D_4 (Figure 2a) at 80 K, vibrational features were observed at 255, 400, 640, 710, 1095 and 2170 cm^{-1}. Similar to that observed for C_2H_4, significant spectroscopic changes occurred at C_2D_4 exposures greater than 1 L. As shown in Figure 2b, vibrational features at 455, 695, 860, 1000, 1125 and 2190 cm^{-1} were detected after an exposure of 10 L C_2D_4.

3.1.2. Thermal Decomposition of Ethylene on Mo(110). Figure 3 shows the desorption of hydrogen after exposing Mo(110) to 1 L and 10 L of ethylene at 80 K. The only desorption product, resulting from the decomposition of adsorbed ethylene, is hydrogen at all ethylene exposures. At ethylene exposures up to 1 L, hydrogen desopriton is characterized by one peak centered at approximately 432 K. After exposing the surface to a saturation dose of 10 L at 80 K, a second hydrogen desorption feature is detected at approximately 301 K. In addition, at ethylene exposures ≥1 L, molecularly desorbed ethylene was also detected in the TPD measurements at approximately 150 K (spectra not shown). The amount of ethylene decomposition as a function of exposure is shown in the inset of Figure 3. The AES measurements were carried out after the ethylene-exposed surfaces were heated to 1200 K. At exposures up to 1 L, the amount of atomic carbon on the surface, as approximated by the AES peak-to-peak height ratio of the C(KLL)/Mo(MNN) features, increases almost linearly with ethylene exposure at 80 K. The AES ratio increases only slightly at higher exposures, from 0.12 at 1 L to 0.15 at 10 L. Based on the relative sensitivity factors for the C(KLL) and Mo(MNN) transitions,[10] these two AES ratios correspond to atomic C/Mo ratios of 0.24 and 0.30, respectively.

Figure 4 shows a comparison of hydrogen TPD spectra from C_2H_4/Mo(110) and H/Mo(110). These two surfaces were prepared by exposing Mo(110), at 80 K, to 10 L ethylene and hydrogen, respectively. This exposure results in saturation coverages for both molecules at 80 K. The TPD spectrum of hydrogen/Mo(110) is characterized by a desorption peak at 415 K, which has an asymmetric shoulder on the high temperature side. More details about the TPD and vibrational investigations of the dissociative adsorption of hydrogen on various surface sites of Mo(110) will be published elsewhere.[11] The most important difference in Figure 4 is the absence of the 301 K desorption peak from the hydrogen/Mo(110) surface. In fact, TPD measurements following the dissociation of hydrogen on Mo(110) never reveal any desorption features at $T < 350$ K at all hydrogen coverages.[11]

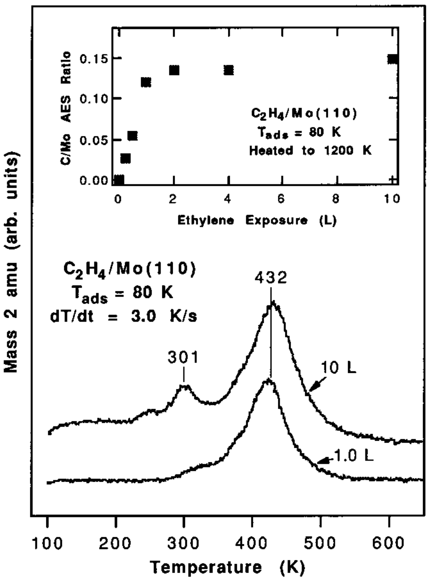

Figure 3. TPD spectra of hydrogen following the thermal decomposition of ethylene on Mo(110). The inset shows the AES peak-to-peak height ratios of C(KLL)/Mo(MNN) as a function of ethylene exposures at 80 K after subsequently heating to 1200 K.

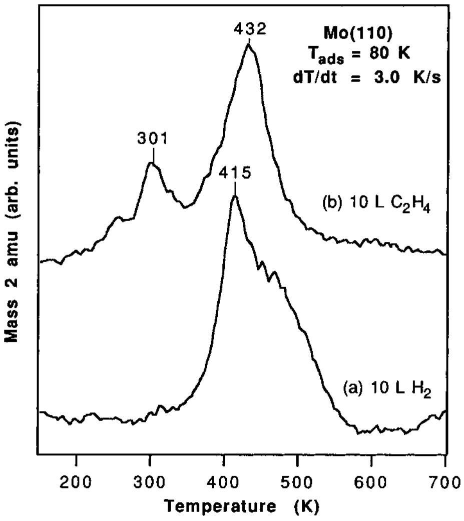

Figure 4. Comparison of TPD spectra of hydrogen from Mo(110) surfaces exposed to 10 L C_2H_4 and 10 L H_2 at 80 K.

In order to further investigate the origin of the hydrogen desorption feature at 301 K, we have carried out coadsorption experiments with C_2D_4 and C_2H_4. Figure 5 shows the TPD spectra following the desorption of D_2, HD and H_2. The clean Mo(110) surface was first exposed to 1 L C_2D_4 and subsequently to 9 L C_2H_4 at 80 K. The TPD spectra of all three hydrogen isotope molecules contain a low temperature desorption peak at 301 K and a high temperature peak at 417−441 K. However, the relative peak areas of these two TPD features are very different for the three molecules. The peak area ratios of the low and high temperature features change from ≤0.02 for D_2 to 0.25 for H_2.

HREELS results following the thermal decomposition of ethylene on the clean Mo(110) surface are shown in Figure 6. Figure 6a−c show the thermal behavior of the C_2H_4/Mo(110) surface, prepared by exposing Mo(110) to 1 L of ethylene at 80 K. The sample was heated for 30 s to the indicated temperatures, which were chosen on the basis of the TPD results.

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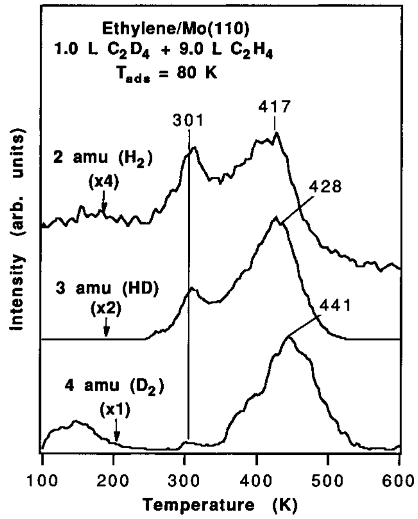

Figure 5. Comparison of TPD spectra of D_2, HD and H_2 following the thermal decomposition of ethylene on clean Mo(110). The adsorbed layer was prepared at 80 K by first dosing 1 L C_2D_4 followed by dosing 9 L C_2H_4.

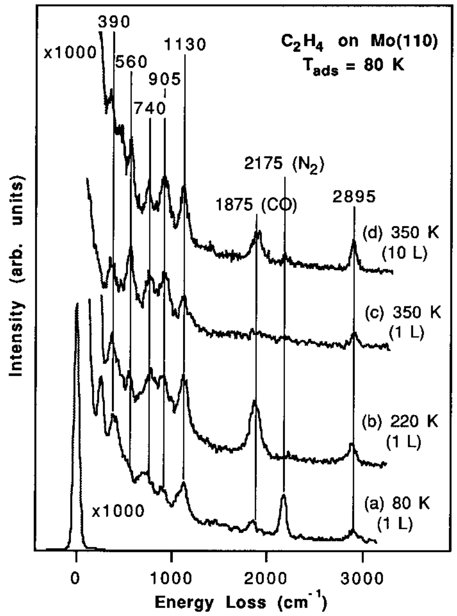

Figure 6. HREELS results following the thermal decomposition of 1 L C_2H_4 on Mo(110). A HREELS spectrum, obtained after heating a 10 L C_2H_4/Mo(110) surface to 350 K, is also compared. All HREELS spectra were recorded at 80 K.

As shown in Figure 6a−c, the number of vibrational features and their frequencies remain essentially the same at temperatures up to 350 K. Minor spectroscopic changes in this temperature range are due to the desorption and decomposition of CO and N_2 impurities.[7,8] The occurrence of a vibrational feature at 560 cm^{-1} in Figure 6c, related to the ν(Mo−O) mode, is a result of contaminant CO decomposition.[7] For comparison, Figure 6d shows the HREELS spectrum after heating a 10 L C_2H_4/Mo(110) surface to 350 K. This spectrum is very similar to Figure 6c, suggesting the formation of a similar surface intermediate at 350 K, independent of the initial ethylene exposures at 80 K. After further heating the C_2H_4/Mo(110) surfaces to 450 K, which is above the TPD desorption temperature of hydrogen, all hydrocarbon related vibrational features disappear in the HREELS spectra (not shown); the only intense feature is the ν(Mo−C) mode of the atomic carbon on Mo(110).

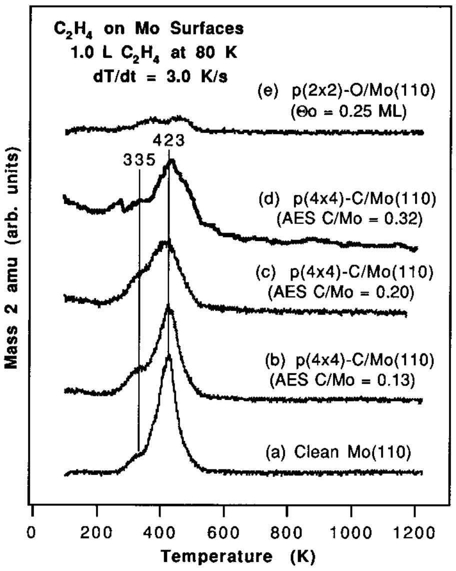

Figure 7. Comparison of TPD spectra of hydrogen following the decomposition of ethylene on clean and chemically modified surfaces. See text for the preparation of chemically modified Mo(110) surfaces.

3.2. Adsorption and Reaction of Ethylene on Chemically-Modified Mo(110). In this section, we will describe results for the reaction of ethylene with chemically modified Mo(110) surfaces. Our primary focus was on carbide-modified Mo(110) surfaces. The reaction of ethylene on oxygen-modified Mo(110) was used as a chemically inert model system to demonstrate the different modification effects by carbon and oxygen. The preparation of carbide-modified Mo(110) surfaces have been discussed in detail previously[7,12,13] In brief, carbide-modified surfaces were prepared by exposing Mo(110) to ethylene at 600 K followed by annealing to 1200 K. During annealing, carbon diffuses into the sample and fills interstitial lattice sites. The accumulation of carbon in this manner during repetitive dosing/annealing cycles can be followed by AES; C/Mo(110) surfaces with different AES C/Mo ratios can be obtained by controlling the number of dosing/annealing cycles.[13] The C/Mo(110) surfaces used in the current study, with an AES C(KLL)/Mo(MNN) ratio in the range of 0.13−0.32, are characterized by a p(4 × 4) LEED pattern. The exact structures of the p(4 × 4)-C/Mo(110) surfaces are not known at present.[12,13] Oxygen-modified surfaces were prepared by direct dissociation of molecular oxygen. All oxygen modified-surfaces used in this study were characterized by a p(2 × 2) LEED pattern, which corresponded to an oxygen coverage of $\theta_O = 0.25$ ML.[14]

Figure 7 compares thermal desorption spectra of hydrogen from the decomposition of ethylene on clean and chemically-modified Mo(110) surfaces. The bottom spectrum was obtained from the clean Mo(110) surface, followed by carbide-modified Mo(110) surfaces with different C/Mo ratios as determined by AES, and an oxygen-modified surface with 0.25 ML of atomic oxygen. All surfaces were exposed to 1 L of ethylene at 80 K. The desorption of hydrogen, resulting from the thermal decomposition of ethylene, is observed from the clean Mo(110) surface as well as C/Mo(110) surfaces. The hydrogen peak areas from all C/Mo(110) surfaces are $\geq$80% of that from clean Mo(110), indicating that the C/Mo(110) surfaces remain reactive toward the decomposition of ethylene. In contrast, the peak area of hydrogen from oxygen-modified Mo(110) is $<$ 7% of that from Mo(110), demonstrating that the decomposition of ethylene is inhibited by the presence of as little as 0.25 ML of chemisorbed oxygen on Mo(110).

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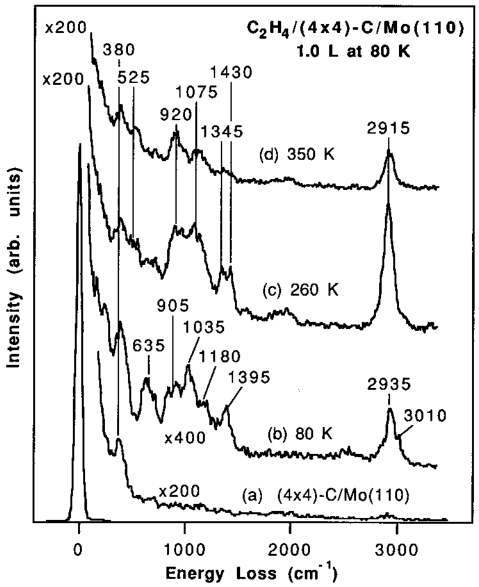

Figure 8. HREELS results following the thermal decomposition of 1 L C_2H_4 on C/Mo(110). All HREELS spectra were recorded at 80 K.

HREELS spectra following the thermal decomposition of ethylene on a carbide-modified Mo(110) surface are reproduced in Figure 8. The C/Mo(110) surface used in Figure 8 was characterized by a C/Mo AES ratio of ~0.20. Spectra obtained from C/Mo(110) surfaces with higher C/Mo AES ratios show similar sequence of spectroscopic evolutions as those depicted in Figure 8. Before exposure to ethylene the p(4 × 4)-C/Mo(110) surface exhibited a single C-Mo stretching vibration at ~380 cm^{-1} (Figure 8a). After exposure to 1 L ethylene at 80 K (Figure 8b), vibrational features were found at 635, 905, 1035, 1180, 1395 2935 and 3010 cm^{-1}. It is important to point out that this spectrum is qualitatively different from corresponding experiment on clean Mo(110) (Figure 1a). In addition, significant spectroscopic changes were observed after heating the surface to 260 K for 30 s. As shown in Figure 8c, a new set of vibrational features was found at 525, 920, 1075, 1345, 1430 and 2915 cm^{-1}. Further heating to 350 K (Figure 8d) did not strongly alter the spectra in terms of the number of vibrational features and their frequencies, although the intensities of these features decreased after the heating.

Figure 9 shows a comparison of on- and off-specular HREELS spectra of the thermal decomposition intermediate on the carbide-modified surface. The surface was prepared by exposing the C/Mo(110) surface to 5 L of ethylene at 80 K followed by heating to 300 K for 30 s. The on-specular spectrum (Figure 9a) is very similar to the 260 K spectrum in Figure 8 in terms of the number of vibrational features as well as their frequencies. Figure 9 shows that the relative intensities of all vibrational features alter only slightly in the on- and off-specular measurement.

To assist the vibrational assignments, HREELS spectra were also recorded following the thermal decomposition of C_2D_4 on the carbide-modified surface, as shown in Figure 10. After exposure to 1 L C_2D_4 at 80 K (Figure 10a), vibrational features were found at 405, 670, 870, 980, 1145, 2185 and 2255 cm^{-1}. Heating to 260 K (Figure 10b) again led to significant spectroscopic changes. The spectra displayed features at 560, 670, 870, 1015, 1105 and 2180 cm^{-1}. The relatively weak feature around 2920 cm^{-1} is due to adsorption and decomposition of a small fraction of non-deuterated ethylene molecules.

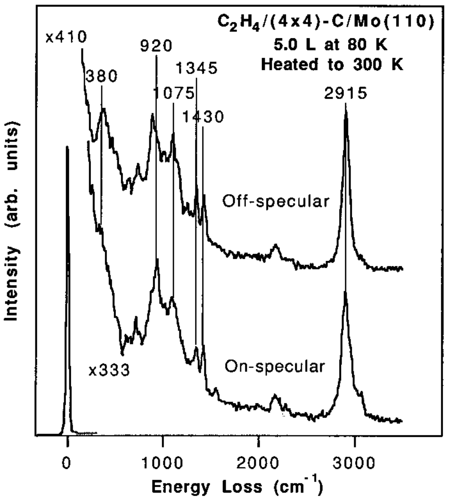

Figure 9. On- and off-specular HREELS spectra of the reaction intermediate on C/Mo(110). The adsorbed layer was prepared by dosing C/Mo(110) to 5 L C_2H_4 at 80 K followed by annealing to 300 K for 30 s.

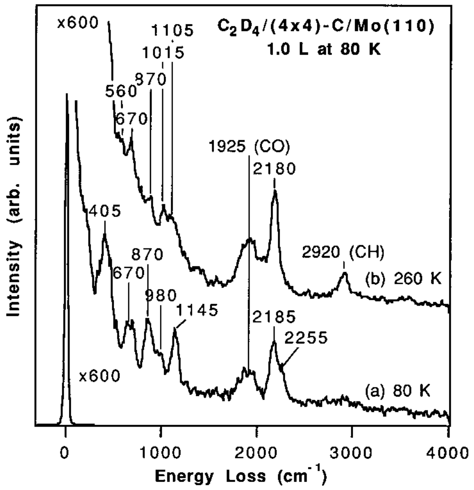

Figure 10. HREELS results following the thermal decomposition of 1 L C_2D_4 on C/Mo(110). All HREELS spectra were recorded at 80 K.

Finally, the thermal behavior of ethylene on an oxygen-modified surface was studied using HREELS. The O/Mo(110) surface was characterized by a p(2 × 2) LEED pattern with an oxygen coverage of 0.25 ML. Figure 11 shows a comparison of HREELS spectra recorded after exposing the surface to C_2H_4 (Figure 11a) and C_2D_4 (Figure 11b) at 80 K, and after heating the adsorbed layer to 220 K for 30 s (Figure 11c). The two low frequency features, at 390 and 595 cm^{-1}, are due to the deformation and stretching Mo−O motions of the O/Mo(110) substrate, respectively.[15] After exposing the O/Mo(110) to ethylene at 80 K, the HREELS spectrum shows one intense feature at 965 cm^{-1}, and other relatively weak features at 1170, 1335, 1420, 1595, 2975 and 3065 cm^{-1}. Similarly, the HREELS spectrum of the C_2D_4/O/Mo(110) surface shows one intense feature at 720 cm^{-1}, and other relatively weak features at 900, 980, 1130, 1270, 1500, 2240 and 2300 cm^{-1}. Vibrational features related to ethylene molecules almost completely disappeared after the adsorbed layer was heated to 220 K. This surface was again characterized by a p(2 × 2)-O LEED pattern and AES measurements revealed that the C(KLL)/Mo(MNN) ratio of this surface was less than 0.02. These observations suggest that, in agreement with the TPD results from the O/Mo(110) surface (Figure 7), the majority of adsorbed ethylene species desorbs from the O/Mo(110) surface without undergoing decomposition.

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Table 1. Vibrational Assignment of π-Bonded Ethylene Species

vibrational assignment	symmetry D_{2h}	symmetry C_{2v}	C_2H_4 (C_2D_4) (gas-phase)[20]	ω_H/ω_D	C_2H_4 (C_2D_4) (2 × 2)-O/Mo(110)	ω_H/ω_D
$\rho(CH_2)$ (CH_2-rocking) (ν_{10})	B_{2u}	B_2	826 (593)	1.39		
$\omega(CH_2)$ (CH_2-wagging) (ν_7)	B_{1u}	A_1	949 (720)	1.32	965 (720)	1.34
$\tau(CH_2)$ (CH_2-twisting) (ν_6)	B_{1g}	A_2	1222 (883)	1.38	1170 (900)	1.30
$\delta(CH_2)$ (CH_2-scissor) (ν_3)	A_g	A_1	1342 (981)	1.37	1335 (980)	1.36
$\delta(CH_2)$ (CH_2-scissor) (ν_{12})	B_{3u}	B_1	1444 (1078)	1.34	1420 (1130)	1.26
$\nu(CC)$ (ν_2)	A_g	A_1	1623 (1515)	1.07	1595 (1500)	1.06
$\nu_s(CH_2)$ (ν_{11})	B_{3u}	B_1	2989 (2200)	1.36	2975 (2240)	1.33
ν_a-CH_2 (ν_9)	B_{2u}	B_2	3106 (2345)	1.32	3065 (2300)	1.33

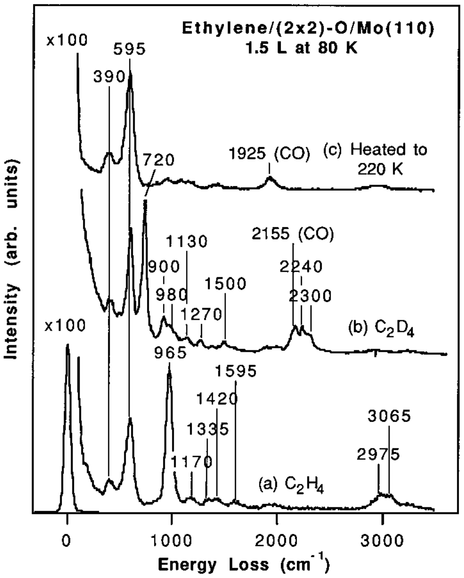

Figure 11. Comparison of HREELS spectra of C_2H_4 and C_2D_4 on O/Mo(110). A HREELS spectrum, obtained after heating the C_2H_4/O/Mo(110) surface to 220 K, is also compared.

IV. Discussion

4.1. Weak Interaction of Ethylene on O/Mo(110): Formation of π-Bonded Species. A simple qualitative comparison of the vibrational spectra indicates that the adsorption of ethylene and the subsequent reaction pathways are distinct for the three types of surfaces investigated in this study. Most straightforward is the interpretation of the results for ethylene interaction with the oxygen-modified Mo(110) surface. Ethylene molecules adsorb weakly at 80 K and desorb without significant amount of decomposition, as suggested by the hydrogen TPD spectrum (Figure 7e) and by the very low AES C/Mo ratio (≤ 0.02) following the TPD experiment.

The HREELS spectra of ethylene on O/Mo(110) at 80 K (Figure 11) can be readily assigned to weakly adsorbed π-bonded molecular ethylene. Such a bonding configuration constitutes one extreme of the synergetic bond described by the Dewar-Chatt-Duncanson theory, namely the one which is dominated by the donation from the filled π-orbital of ethylene into a vacant metal orbital without any subsequent backdonation from the metal substrate. Ethylene bonding of this type is typical for the less reactive Group IB metals[16-18] and has also been observed on oxygen-modified early transition metal.[19] The assignment of the vibrational modes in Figure 11 to the π-bonded ethylene is given in Table 1. The similar vibrational frequencies between ethylene molecules in the gas-phase[20] and on O/Mo(110) again confirm a very weak interaction between ethylene and the oxygen-modified Mo(110) surface. In addition to the ethylene vibrational modes, two relatively weak features are also observed in the C_2D_4 spectrum at 1270 cm^{-1} and 2155 cm^{-1}, respectively. We are unable to assign the 1270 cm^{-1} feature because this frequency is not expected for any fundamental vibrational mode for C_2D_4; its frequency also differs from expected values of the overtone and/or combination modes of the more intense, low-frequency modes in Figure 11b. The 2155 cm^{-1} is most likely due to the adsorption of residue CO on the terminal sites, as has been previously observed on the O/Mo(110) surface.[21]

The observation of a very intense symmetric CH_2 wag mode, $\omega(CH_2)$, at 965 cm^{-1} (and the $\omega(CD_2)$ mode at 720 cm^{-1}) is another indication of the very weak interaction between ethylene and the O/Mo(110) substrate. The concept of correlating the adsorption strength to the intensity of the $\omega(CH_2)$ mode is first proposed by Ibach and Mills in the comparative studies of ethylene on Ag(110) and Pt(111).[9] For example, on the weakly adsorbed C_2H_4/Ag(110) surface, where C_2H_4 is π-bonded with its molecular plane parallel to the surface, the $\omega(CH_2)$ mode is by far the most intense feature.[9] A simple comparison with gas-phase C_2H_4 (D_{2h} symmetry) reveals that the $\omega(CH_2)$ mode is the only vibrational motion with a dipole moment perpendicular to the plane of molecules . Based on these observations, Ibach and Mills propose a general rule which states that for weakly chemisorbed molecules, the strongest dipole losses are those infrared active modes of the molecule in the gas phase which produce a perpendicular dipole moment when the molecule is adsorbed on the surface. They further state that the relative strength of dipole losses resulting from the breakdown of the symmetry is a measure of the adsorption strength. This is because a strong interaction of ethylene with the substrate would reduce the molecular symmetry from D_{2h} to symmetry groups of C_{2v} or lower, which would allow the detection of additional dipole-active modes with comparable intensities to that of the $\omega(CH_2)$ mode.[9,22] This observation will be demonstrated later for the strongly adsorbed di-σ ethylene on carbide-modified Mo(110).

The observed weak interaction of ethylene with oxygen-modified Mo(110) is likely due to an electronic modification of the Mo(110) substrate upon oxygen chemisorption, although we cannot exclude steric effects on the basis of our data. One possible explanation is that the electronegative oxygen atoms attract/localize the electron density of the substrate, reducing the degree of backdonation into the empty π^*-orbital of ethylene.

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Table 2. Vibrational Assignment of Chemisorbed Acetylene Species

vibrational assignment	C_2H_2 (C_2D_2) on Fe(110)[23]	ω_H/ω_D	C_2H_2 (C_2D_2) on Fe(111)[24]	ω_H/ω_D	C_2H_2 (C_2D_2) on Ru(001)[25]	ω_H/ω_D	1 L C_2H_4 (C_2D_4) on Mo(110) at 80 K (this work)	ω_H/ω_D
ν-CM	460 (420)	1.10	470 ( )		375 (350)	1.07	390 (400)	0.98
ρ_s-CH	700 (550)	1.27	660 ( )		520 ( )		740 ( )	
ρ_{as}-CH	870 (680)	1.28	( )		765 (585)	1.35	(640)	
δ_s-CH	1150 (935)	1.23	935 (710)	1.32	980 (715)	1.37	905 (710)	1.27
δ_{as}-CH	1415 (1140)	1.24	(905)				( )	
ν-CC	1240 (1235)	1.00	1145 (1130)	1.01	1135 (1085)	1.05	1130 (1090)	1.04
ν-CH	2940 (2210)	1.33	2850 (2130)	1.34	2940 (2210)	1.33	2900 (2170)	1.34

The formation of π-bonded ethylene species, as a result of oxygen-modification, appears to be true for all transition metal surfaces so far investigated.[2,22]

4.2. Strong Interaction of Ethylene on Mo(110): Formation of Acetylene at 80 K. The HREELS results indicate that the interaction of ethylene with clean Mo(110) is very strong. The vibrational features, obtained after exposing Mo(110) to up to 1 L of ethylene at 80 K (Figures 1a and 2a), are qualitatively different from those of gas phase values[20] and from those typically observed for chemisorbed ethylene molecules.[2,3] In particular, the HREELS spectra up to 1 L of C_2H_4 exposure do not contain any features in the frequency range of 1300−1450 cm^{-1} in either the on- or off-specular directions (Figure 1a,b). This is consistent with the complete absence of a CH_2 group. Upon comparison with available literature data we find our spectra to be most consistent with the vibrational data for chemisorbed acetylene species on metal surfaces.[22] Table 2 shows a comparison of the vibrational features in Figures 1a and 2a to those of chemisorbed acetylene on Fe(110),[23] Fe(111),[24] and Ru(001).[25] The relatively intense features in Figures 1a and 2a can be readily assigned to the characteristic C_2H_2 (C_2D_2) surface species: the ν(C−H) mode at 2900 (2710) cm^{-1}, the ν(C−C) mode at 1130 (1095) cm^{-1}, the symmetric in-plane δ_s(C−H) mode at 905 (710) cm^{-1}, the symmetric out-of-plane ρ_s(C−H) mode at 740 (535) cm^{-1}, the ν(Mo−C) mode at 390 (400) cm^{-1} and the surface phonon mode at 250 (255) cm^{-1}. The symmetric out-of-plane ρ_{as}(C−H) mode, which would be expected near 860−880 cm^{-1} for non-deuterated acetylene,[23] is resolved in the deuterated spectrum (Figure 2a) at 640 cm^{-1}. The detection of acetylene species indicates that the decomposition of ethylene occurs at temperatures as low as 80 K on clean Mo(110). The strong reactivity of Mo(110) toward ethylene is typical for early transition metals. For example, the low temperature decomposition of ethylene has been reported on other early transition metal surfaces, in particular on W(100) and W(110) surfaces.[22]

It should be pointed out that, for strongly chemisorbed hydrocarbon molecules, the normal modes in the frequency range of 800−1200 cm^{-1} are often composed of substantial amounts of both the CC stretch and CH (CD) bend internal coordinates.[20] The relative contributions vary for deuterated and non-deuterated hydrocarbons. As a result, the relative intensities of these vibrational features often differ substantially for the deuterated and non-deuterated compounds, as revealed by the comparison of the vibrational intensities in Figures 1a and 2a. It is also important to point out that the vibrational frequencies for the stretching motions of carbon−carbon and C−H bonds in Table 2 are significantly lower than their gas-phase values. This is related to the rehybridization of acetylene from sp (gas-phase) to sp^3 after adsorption on surfaces.[23−25]

In HREELS experiments vibrational modes can be excited either via the dipolar mechanism or the nondipolar mechanisms, such as the impact and resonance scattering processes.[9] The former mechanism obeys the surface dipole selection rule. It states that only those vibrations which belong to the totally symmetric representations, A, A_1 and A′, of the point groups describing the symmetry of the adsorbed complex will be excited by the dipole scattering mechanism. Experimentally, vibrational losses that are the result of dipole scattering appear in a scattering lobe that is sharply peaked in the specular direction. Comparisons of the on- and off-specular HREELS spectra therefore allow one to determine the dipolar or nondipolar nature for each individual vibrational mode, which in turn enable one to determine the symmetry of the adsorption complex. Upon adsorption on surfaces, the symmetry group of acetylene is reduced from $D_{\infty h}$ in the gas phase to several possible lower symmetry groups, such as C_{2v}, C_2, C_s (with symmetry plane either parallel or perpendicular to the carbon−carbon axis) and C_1 (no symmetry). The correlation tables for these symmetry groups have been provided previously.[23,24] As shown in Table 2, there are four C−H bending modes for adsorbed acetylene species. The number of dipole active C−H bending modes changes from one in C_{2v} to four in C_1 symmetry groups. Based on the number of dipole active C−H bending modes, several attempts have been made to derive the adsorption symmetry of chemisorbed acetylene on various surfaces.[22−26]

The comparison of the on- and off-specular HREELS spectra in Figure 1 reveals that the intensities of the ν(Mo−C) mode at 390 cm^{-1}, the ρ_s(C−H) mode at 740 cm^{-1} and the ν(C−C) mode at 1130 cm^{-1} decrease substantially in the off-specular measurement (notice the different expansion factors in Figure 1a,b), indicating they are excited primarily by the dipolar mechanism.[9] In contrast, the intensities of the δ_s(C−H) mode at 905 cm^{-1} and the ν(C−H) mode at 2900 cm^{-1} remain nearly constant in the on- and off-specular measurements, suggesting that these two modes are excited by the nondipolar mechanism.[9] These observations are similar to those reported for chemisorbed acetylene on Ru(001) by Parmeter et al.,[25] who demonstrated a nondipolar excitation mechanism for the δ_s(C−H) and ν(C−H) modes. Previous off-specular angular dependence studies of acetylene on Fe(110)[23] and Ni(111)[26] also indicated that the vibrational intensities of these two features are primarily contributed by the nondipolar scattering mechanism. Because of the different excitation mechanisms for the in-plane ρ_s(C−H) mode at 740 cm^{-1} and the out-of-plane δ_s(C−H) mode at 905 cm^{-1} in Figure 1, it is tempting to derive the symmetry of the acetylene species on the Mo(110) surface. However, as pointed out by Parmeter et al. for acetylene on Ru(001),[25] without detailed knowledge of the surface binding site of acetylene, assignment of these modes to "in-plane" and "out-of-plane" is not possible. At present, we would only like to point out that, because not all four C−H bending modes are

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detected in Figure 1, the symmetry group of the acetylene species on Mo(110) is C_s or higher.

The subsequent thermal decomposition of the acetylene species, at ethylene exposures up to 1 L, is straightforward, as indicated by the TPD spectrum in Figure 3 and the HREELS data in Figure 6a−6c. The HREELS spectra show the characteristic vibrational features of acetylene up to 350 K, at which temperature the desorption of hydrogen starts to become significant in the TPD spectrum. HREELS spectrum recorded after heating the adsorbed layer to 375 K for 30 s (not shown) revealed an overall decrease in the vibrational intensities of acetylene without producing any new vibrational features. These observations indicate that the acetylene species, once produced by the reaction of ethylene with Mo(110) at 80 K, remains to be the only stable intermediate until its eventual thermal decomposition to produce atomic carbon and atomic hydrogen, with the latter recombining to desorb as hydrogen gas. It is interesting to note that the desorption of hydrogen and the decomposition of acetylene species fall into a similar temperature range. One possible explanation is that hydrogen desorption is necessary to free up additional surface sites to allow the further decomposition of acetylene species.

At ethylene exposures >1 L at 80 K, the HREELS spectra reveal the presence of additional surface species, as shown in Figures 1c,d and 2b. After exposing the surface to 10 L ethylene, additional vibrational features are observed at 620 and 1365 cm^{-1} for C_2H_4, and at 455, 860 and 1000 cm^{-1} for C_2D_4. The vibrational frequencies of the pre-existing acetylene species are also shifted by up to ±35 cm^{-1}; the relative intensities of these features, in the on-specular HREELS spectra, are also significantly modified. By comparing with literature data,[4,22] the new vibrational features can be related to chemisorbed ethylene molecules. They can be assigned as the CH_2 (CD_2) rock mode at 620 (455) cm^{-1} and the CH_2 (CD_2) scissor mode at 1365 (1000) cm^{-1}. The 860 cm^{-1} feature in Figure 2b can be assigned as the CD_2 wag mode of C_2D_4; the corresponding CH_2 wag mode of C_2H_4 is not resolved in Figure 1c from the 1090 cm^{-1} feature. As will be discussed later for the interaction of ethylene with carbide-modified Mo(110), additional vibrational features of chemisorbed ethylene would appear in a similar spectroscopic range as that of the pre-existing acetylene, which might account for the frequency shifts in the acetylene vibrational features in Figures 1c and 2b.

Figures 1c and 1d show very similar on- and off-specular spectra for the 10 L surface, i.e., the surface with a mixture of acetylene and ethylene. This would suggest that the local symmetries for both acetylene and ethylene are C_1 (no symmetry). Since the acetylene/Mo(110) (prepared at ≤1L ethylene) overlayer demonstrates an angular dependence that is expected for a symmetry group of C_s or higher, one can argue that the adsorption of additional ethylene at higher exposures destroys the local symmetry of acetylene. More structure sensitive tools will be required to provide a more detailed description of this overlayer.

The TPD data shown in Figures 3−5 suggest that some of the molecularly adsorbed ethylene molecules, produced after 10 L exposure at 80 K, undergo further decomposition at higher temperatures. As shown in the TPD spectra in Figure 3, an additional hydrogen desorption peak is observed for the 10 L surface at 301 K. A comparison of the total hydrogen peak areas in Figure 3 shows an increase of approximately 25% when the ethylene exposure increases from 1 L to 10 L. This is in good agreement with the AES measurements (inset of Figure 3), which suggest that the C/Mo atomic ratios, after the TPD experiments, increase from 0.24 to 0.30. The HREELS spectrum, obtained after heating the 10 L surface to 350 K (Figure 6d), indicates that acetylene is the only surface species after heating to 350 K. In addition, the intensities of the acetylene features are slightly higher than heating the 1 L surface to 350 K (Figure 6c), qualitatively supporting the TPD and AES observations of an increase in the amount of decomposition as the ethylene exposure increases from 1 L to 10 L.

The additional hydrogen desorption peak, at 301 K, occurs at a much lower temperature than that for chemisorbed atomic hydrogen from Mo(110) (Figure 4). This observation suggests that this desorption peak is likely related to the recombination of hydrogen atoms that are not thermally accommodated with the Mo(110) surface. One possible mechanism is that a hydrogen atom, once produced by the decomposition of the C−H bond of ethylene, recombines with another hydrogen atom without adsorbing on the surface first. The origin of the other hydrogen atom could be either a pre-adsorbed hydrogen atom due to the decomposition of ethylene to acetylene at exposures ≤1 L or a hydrogen atom of an adjacent ethylene or acetylene molecule. Similar thermally unaccommodated reactions have been reported previously. For example, Sun and Weinberg have reported reactions involving unaccommodated atoms in the decomposition of formate on Ru(001).[27]

The TPD data following the coadsorption of C_2D_4 and C_2H_4 (Figure 5) also support the desorption mechanism involving an unaccommodated hydrogen atom. As shown in Figure 5, the low temperature desorption peak is nearly absent in the TPD spectrum of D_2. This is expected since all C_2D_4 molecules (at 1 L) decompose to produce chemisorbed C_2D_2 and D atoms at 80 K, and the chemisorbed D atoms recombine to desorb as D_2 only at higher temperatures. On the other hand, the TPD spectrum of H_2 shows a relatively strong low temperature peak at approximately 301 K. This is again expected because of the decomposition of molecularly adsorbed C_2H_4, which is present on the surface after the additional dose of 9 L C_2H_4. The presence of the low temperature peak in the TPD spectrum of HD further supports the assumption that the unaccommodated H atom recombines with either a pre-adsorbed D atom or with a D atom of a nearby C_2D_2 molecule. More detailed coadsorption experiments are needed to differentiate between these two possible mechanisms.

The TPD spectra in Figure 5 further confirms that the compositions of the adsorbed species are different from 1 L and 10 L exposures. The ratios of the low and high temperature peaks change from ≤0.02 for D_2 to 0.25 for H_2. This trend is reversed when the dosing sequence is reversed, i.e., by adsorbing 1 L of C_2H_4 followed by 9 L of C_2D_4 (spectra not shown). If a single chemical species, such as either ethylene or acetylene, is produced at both low and high ethylene exposures, one would expect to obtain very similar peak ratios of the low and high temperature desorption features for both H_2 and D_2, independent of the dosing sequence. Finally, the difference in the desorption temperatures of D_2 in Figure 5 (441 K) and H_2 in Figure 3 (427 K) can be readily explained by the kinetic isotope effect in either the cleavage of the C−H and C-D bonds of the surface species or the recombination of hydrogen and deuterium atoms.

4.3. Decomposition of Ethylene on C/Mo(110): Formation of Ethylidyne Species. The reaction mechanisms of ethylene on C/Mo(110) are distinctly different from either Mo(110) or O/Mo(110). As revealed by the hydrogen TPD spectra in Figure 7, the C/Mo(110) surface remains reactive toward the decomposition of ethylene. The hydrogen desorption peak at 423 K broadens and a low temperature peak at 335 K becomes more pronounced on C/Mo(110) surfaces with higher C/Mo

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Table 3. Vibrational Assignment of di-σ Bonded Ethylene Species

vibrational assignment	C_2H_4 (C_2D_4) on Pt(111)[4a]	ω_H/ω_D	C_2H_4 (C_2D_4) on Ru(001)[4b]	ω_H/ω_D	C_2H_4 (C_2D_4) on (4 × 4)-C/Mo(110) (this work)	ω_H/ω_D
ν_s-MC	470 (450)	1.04	460 (420)	1.10	380 (405)	0.94
CH_2-rock	660 ( )		775 ( )		635 ( )	
CH_2-twist (s)	790 (600)	1.32	900 (700)	1.29	905 (670)	1.35
CH_2-wag (s)	980 (740)	1.32	1145 (900)	1.27	1180 (870)	1.36
ν-CC	1050 (900)	1.17	1040 ( )		1035 (980)	1.06
CH_2-scissor (s)	1430 (1150)	1.24	1450 (1210)	1.20	1395 (1145)	1.22
ν_s-CH_2	2920 (2150)	1.36	2940 (2210)	1.33	2935 (2185)	1.34
ν_{as}-CH_2	3000 (2250)	1.34	3050 (2295)	1.33	3010 (2255)	1.35

Table 4. Vibrational Assignment of Ethylidyne Surface Intermediates

vibrational assignment	C_2H_4 (C_2D_4) on Pt(111) $\xrightarrow{\Delta}$ 415 K[4a]	ω_H/ω_D	C_2H_4 (C_2D_4) on Ru(001) $\xrightarrow{\Delta}$ 280 K[4b]	ω_H/ω_D	$(CH_3C)Co_3(CO)_9$ ($(CD_3C)Co_3(CO)_9$) (IR; Cal.)[21]	ω_H/ω_D	C_2H_4 (C_2D_4) on (4 × 4)-C/Mo(110) $\xrightarrow{\Delta}$ 260−300 K (this work)	ω_H/ω_D
ν_s-MC	430 (410)	1.05	480 (480)	1.00	401 (393)	1.02	380 ( )	
ν_{as}-MC	600 (600)	1.00	( )		555 (536)	1.04	525 (560)	0.94
ρ-CH_3	980 (790)	1.24	1000 (800)	1.25	1004 (828)	1.21	920 (670)	1.37
δ_s-CH_3	1350 (990)	1.36	1370 (1000)	1.37	1356 (993)	1.37	1345 (1015)	1.33
δ_{as}-CH_3	1420 (1030)	1.38	1450 ( )		1420 (1031)	1.38	1430 ( )	
ν-CC	1130 (1160)	0.98	1140 (1150)	0.99	1163 (1182)	0.98	1075 (1105)	0.97
ν_s-CH_3	2890 (2080)	1.39	2945 (2190)	1.34	2888 ( )		2915 (2180)	1.34
ν_{as}-CH_3	2950 (2220)	1.33	3045 (2280)	1.34	2930 (2192)	1.34	( )	

ratios. The overall areas of the hydrogen desorption peaks from carbide-modified surfaces remain to be ≥80% of that from the clean Mo(110) surface, suggesting a similar decomposition probability of ethylene on clean and carbide-modified surfaces.

However, the HREELS spectra, obtained after exposing C/Mo(110) to 1 L of C_2H_4 or C_2D_4 at 80 K (Figures 8b and 10a), are clearly different from the corresponding spectra of ethylene on either clean (Figures 1 and 2) or oxygen-modified (Figure 11) surfaces. Unlike the dissociative adsorption on the clean Mo(110) surface, ethylene adsorbs on the C/Mo(110) surface molecularly intact. Furthermore, unlike the weakly adsorbed π-bonded species on O/Mo(110), the vibrational frequencies and relative intensities of ethylene species on C/Mo(110) are substantially different from those of gas phase ethylene molecules. By comparing to literature data,[2−4,22] the vibrational features in Figures 8b and 10a can be assigned to strongly adsorbed, di-σ bonded C_2H_4 or C_2D_4, respectively. A vibrational assignment of the observed HREELS features is given in Table 3, where it is compared with those of di-σ bonded ethylene molecules adsorbed on Pt(111)[4a] and Ru(001).[4b] As shown in Table 3, the vibrational features at 3010 (2255) and 2935 (2185) cm^{-1} can be readily assigned to the asymmetric and symmetric CH_2 (CD_2) stretching modes, respectively. These frequencies are lower than the corresponding values for gas phase C_2H_4 (C_2D_4), which are observed at 3106 (2345) and 2989 (2200) cm^{-1}, respectively.[20] The observation of lower CH_2 stretching frequencies for the di-σ bonded ethylene has been reported on various metal surfaces[2,22] and has been attributed to the rehybridization of carbon from sp^2 in the gas phase to sp^3 in the strongly bonded di-σ configuration on metal surfaces.

As compared in Table 3, other vibrational features of ethylene on C/Mo(110) also appear in the characteristic vibrational frequency range of the di-σ bonded ethylene species. The vibrational feature at 1395 (1145) can be assigned to the scissor mode of the CH_2 (CD_2) groups. The isotopic ratio (ω_H/ω_D) of this pair of features, 1.22, is much smaller than the expected value of 1.41. A low (ω_H/ω_D) ratio seems to be rather common for the di-σ bonded ethylene species on most transition metal surfaces.[28] For example, the (ω_H/ω_D) ratios of the CH_2 scissor modes have been reported to be 1.24 on Pt(111),[4a] 1.20 on Ru(001),[4b] 1.15 on Ni(110)[28a] and 1.19 on Ni(111).[28b] For strongly adsorbed ethylene, the normal modes in the frequency range of 800−1200 cm^{-1} are often composed of substantial amounts of the CC stretch, CH_2 wag and CH_2 twist internal coordinates.[9,20] As a result, the vibrational assignment in this frequency range is often somewhat ambiguous. The vibrational frequencies of the CC stretch, CH_2 wag and CH_2 twist normal modes also vary significantly from one substrate to another,[4,22,28] as shown in Table 3 by the large variation of the vibrational frequencies of these three modes on the surfaces of Pt(111), Ru(001) and C/Mo(110).

A new surface intermediate is detected after heating the ethylene exposed C/Mo(110) surface to the temperature range of 260−300 K (Figures 8c and 10b). An inspection of the frequencies and relative intensities of the vibrational features clearly reveals that the intermediate is neither di-σ bonded ethylene nor acetylene. By comparing with literature data, the vibrational features in Figures 8c and 10b can be best described as being due to an ethylidyne species, CCH_3 (CCD_3).[4,22] Table 4 shows a comparison of the vibrational assignment of ethylidyne species on Pt(111),[4a] Ru(001)[4b] and on C/Mo(110). Vibrational frequencies of a well characterized molecular cluster compound, $(CH_3C)Co_3(CO)_9$, are also compared in Table 4.[29] The formation of ethylidyne species on C/Mo(110) is suggested by the observation of the ν(C−C) mode at 1075 (1105) cm^{-1} and the characteristic group frequencies related to the CH_3 group, which are the intense $\nu_s(CH_3)$ feature at 2915 (2180) cm^{-1}, the $\delta_{as}(CH_3)$ and $\delta_s(CH_3)$ modes at 1430 and 1345 (1015) cm^{-1}, respectively, and the $\rho(CH_3)$ mode at 920 (670) cm^{-1}.

Although all vibrational features in Figures 8c and 10b can be assigned to the ethylidyne species, the relative intensities of our spectra are somewhat different from the literature data.[22] For example, ethylidyne species were found to be on the 3-fold sites of Pt(111) with the C−C bond perpendicular to the surface, resulting in a C_{3v} symmetry for the adsorbate complex.[4a] As a result, the on-specular HREELS spectrum is characterized by

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the dipole active ν(Pt−C), ν(C−C) and $\delta_s(CH_3)$ modes; these features are at least five times more intense than the other vibrational features.[4a] Furthermore, as expected for the perpendicularly adsorbed species, the relative intensities of ethylidyne on Pt(111) change substantially in the off-specular HREELS measurements[4a] However, as shown in Figure 9, the ethylidyne species on C/Mo(110) show very minor differences between the on- and off-specular measurements. Except that the ν(Mo−C) mode is better resolved in the off-specular spectrum, the relative intensities of the ethylidyne features remain nearly the same in the on- and off-specular measurements. By comparing Figure 9 with Table 4, it is clear that all vibrational features of the ethylidyne species on C/Mo(110) are observed in the on-specular HREELS. This observation suggests that all these vibrational modes are dipole-active, which can only be achieved when the symmetry group of the surface complex is C_1 (no symmetry). There are several ways to explain the C_1 symmetry of the ethylidyne surface species. One is that the ethylidyne species are adsorbed in a random and non-perpendicular adsorption geometry with respect to the C/Mo(110) substrate. Another possibility is that the C/Mo(110) surface itself is not flat on the length of atomic scale. Considering the fact that the p(4 × 4) LEED pattern exists over a large range of C/Mo stoichiometries (AES ratios of C(KLL)/Mo(MNN) from 0.13 to 0.32 in the current study), it is rather difficult to describe the C/Mo(110) surface by a simple and non-reconstructed overlayer structure with a 4 × 4 surface periodicity. A recent scanning tunneling microscopy (STM) study of C/W(110) surfaces indicates that the carbide-modified W(110) surface is reconstructed on the atomic scale, resulting in a vertical buckling of up to 0.5 Å with a horizontal periodicity of 3 - 4 Å.[30] If similar atomic scale reconstruction also occurs on the C/Mo(110) surface, it might account for the lack of symmetry for the ethylidyne surface complex on this surface. Again, studies with more precise structural tools, such as the atomic resolution STM[30] or tensor LEED[31] techniques, would provide a more definitive description of the adsorbate and substrate structures of ethylidyne on C/Mo(110).

4.4. Similar Surface Reaction Mechanisms of C/Mo(110) and Pt-Group Metals. The results shown above clearly indicate that the surface chemistry of Mo(110) can be significantly modified by the formation of carbide. The very strong interaction between ethylene and Mo(110), characteristic for early transition metals, can be significantly “tamed” by the formation of carbide. Furthermore, unlike the oxygen-modified Mo(110) surface that becomes inert toward the decomposition of ethylene, the carbide-modified Mo(110) surface remains active toward the decomposition of ethylene, although the decomposition temperature and reaction intermediates are qualitatively different from the clean Mo(110) surface. More importantly, the modified reaction pathway on C/Mo(110) is very similar to those typically observed for the decomposition of ethylene on close-packed faces of Pt-group metals.[3,22] As observed on C/Mo(110) in this study, the reaction mechanisms of ethylene on Pt-group metals surfaces are characterized by the formation of strongly adsorbed di-σ species at 80 K and by the production of ethylidyne species as the decomposition intermediate at higher temperatures.

In addition, the thermal stability of the ethylidyne species on C/Mo(110) is also similar to those on Pt-group metals. On C/Mo(110), the ethylidyne species are found to be stable in the temperature range of 260−300 K; the decomposition becomes significant at 350 K, as indicated by the evolution of hydrogen in the TPD measurements (Figure 7) and by the decrease of vibrational intensities in the HREELS data (Figure 8d). In comparison, ethylidyne is thermally stable in the temperature range of approximately 340−415 K on Pt(111),[4a] 280−360 K on Ru(001)[4b] and 180−300 K on Ir(111).[4e]

The formation of ethylidyne species on Pt-group metal surfaces, and the lack of this intermediate in the decomposition of ethylene on early transition metal surfaces, demonstrate an important difference in the formation and/or decomposition of metal−carbon bonds on the two types of surfaces. On Pt-group metal surfaces, the production of ethylidyne indicates that one of the metal−carbon bonds, produced at low temperatures by the formation of di-σ ethylene, can be broken at higher temperatures with the carbon−carbon bond still intact. For example, a recent vibrational study following the thermal decomposition of ethylene on Pt(111) demonstrates a gradual transformation of di-σ ethylene ($Pt{-}CH_2\text{-}CH_2\text{-}Pt$) to ethylidene ($Pt_2\text{-}CH\text{-}CH_3$) and to ethylidyne ($Pt_3\text{-}C{-}CH_3$).[32] In contrast, on early transition metal surfaces the metal−carbon bonds remain intact once they are produced. The subsequent thermal decomposition of the adsorbate/substrate complex occurs at the carbon−carbon bonds instead of the metal−carbon bonds, as observed on clean Mo(110). Such a difference in the sequence of bond-cleavage could be one of the primary reasons why Pt-group metals are superior catalysts than early transition metals for dehydrogenation/hydrogenation reactions, which require that the catalyst facilitates the C−H bond cleavage/formation without breaking the carbon−carbon bonds. The observation of ethylidyne species on the C/Mo(110) surface indicates that the bond-cleavage sequence of the carbon−carbon and metal−carbon bonds of the adsorbate/substrate complex resembles those on Pt-group metals. This observation could explain the very similar catalytic activities of molybdenum carbides and Pt-group metals for the dehydrogenation and hydrogenation of hydrocarbon molecules.[5]

The most important conclusion from the current study is that the surface reactivity of Mo(110) can be converted to that of Pt-group metals. This observation implies that the C/Mo(110) surface can be used as a reliable model system to understand the fundamental aspects of how the formation of interstitial carbides would convert the chemical properties of early transition metals to those of Pt-group metals. One obvious advantage of using carbide-modified surfaces as model systems is that they allow one to utilize powerful surface science spectroscopies,[6] which would be otherwise impossible for powder materials. For example, we have recently applied the combination of Near-Edge X-ray Absorption Fine-Structure (NEXAFS), X-ray Photoelectron Spectroscopy (XPS), LEED and TPD to investigate the relationship between the location of carbon and the reactivity of the carbide-modified Mo(110) model surfaces.[13] These results indicate that the Pt-like properties can only be achieved when carbon atoms are occupying the interstitial sites instead of the surface sites. In addition, carbide-modified Mo(110) surfaces can also be used as a model system for future surface science measurements of the density of states (DOS) near the Fermi level, which has been postulated by band structure calculations to be the main reason for the similar catalytic properties of early transition metal carbides and Pt-group metals.[33]

V. Conclusions

From the results and discussion given above, we summarize the following important observations for the reaction of ethylene with clean and chemically modified Mo(110) surfaces:

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[30] Bode, M.; Pascal, R.; Wiesendanger, R. *Surf. Sci.* **1995**, *344*, 185.

[31] Jentz, D.; Rizzi, S.; Barbieri, A.; Kelly, D. G.; Van Hove, M. A.; Somorjai, G. A. *Surf. Sci.* **1995**, *329*, 14.

[32] Cremer, P.; Stanners, C.; Niemantsverdriet, J. W.; Shen, Y. R.; Somorjai, G. *Surf. Sci.* **1995**, 328, 111.

(1) The clean Mo(110) surface interacts very strongly with ethylene, as indicated by the decomposition of ethylene to acetylene at temperatures as low as 80 K. The acetylene species decompose to produce atomic carbon and gas phase hydrogen at $T > 350$ K. No other thermal decomposition intermediates are observed on the clean Mo(110) surface.

(2) The strong reactivity of Mo(110) can be inhibited by chemisorbed oxygen with a coverage as low as 0.25 ML. Ethylene molecules only weakly interacting with the O/Mo(110) surface to produce π-bonded ethylene species at 80 K, which desorb molecularly at $T < 150$ K without decomposition.

(3) The surface reactivity of C/Mo(110) is qualitatively different from either clean or oxygen-modified Mo(110) surfaces. While the carbide-modified Mo(110) remains reactive toward the decomposition of ethylene, the decomposition occurs via a different reaction pathway. Ethylene adsorbs on C/Mo(110) in the strongly bonded di-σ configuration at 80 K; ethylidyne species are produced as reaction intermediates in the temperature range of 260−300 K. This reaction pathway is characteristic for the decomposition of ethylene on closed-packed Pt-group metals. These results indicate that the Mo(110) surface can be modified by carbon in such a way that it converts the reactivity of Mo to that of Pt-group metals. This observation is in excellent agreement with catalysis data that molybdenum carbides often show catalytic reactivities that are unique for Pt-group metals, especially for dehydrogenation and hydrogenation reactions.[5]

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(33) See, for example, Eberhart, M. E.; MacLaren, J. M. in Ref. 5b, p 107.