

# Substrate-Dependent Reaction Pathways of Ethylene on Clean and Carbide-Modified W(110) and W(111)

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The decomposition of ethylene was utilized as a probe reaction to determine the chemical properties of carbide-modified W(110) and W(111) using high-resolution electron energy loss spectroscopy (HREELS) and temperature-programmed desorption (TPD) measurements. Ethylene adsorbed via a di- $\sigma$  configuration on both clean and carbide-modified W(110). Most of the di- $\sigma$  bonded ethylene converted to ethylidyne species by 200 K. In contrast, ethylene decomposed to form vinylidene and acetylide intermediates without forming ethylidyne at 90 K and 200 K on clean and carbide-modified W(111). Thermal desorption results showed clean W(111) to be twice as active as W(110) toward the decomposition of ethylene. The presence of the carbide overlayer reduced the activity of the W(111) surface by  $\sim 50\%$ , whereas carbide-modification only reduced the activity of the W(110) surface by  $\sim 30\%$ . This study showed that the reaction pathways of ethylene on carbide-modified surfaces were strongly dependent on the structure of the metal substrate.

## 1. Introduction

It is well-known that early transition metals (Groups IVB–VIB) are very reactive toward the decomposition of unsaturated hydrocarbons.<sup>1–4</sup> It has also been demonstrated that the surface reactivity of early transition metals can often be converted to those of the Pt-group metals when modified by the formation of carbides.<sup>5,6</sup> Our research group has carried out a series of investigations probing the fundamental aspects of converting the chemical properties of early transition metals to be Pt-like.<sup>5,7–11</sup> Specifically, comparative studies of the reactivity of ethylene on carbide overlayers and on the corresponding parent metal surfaces have been reported on the close-packed Ti(0001),<sup>8</sup> V(110),<sup>11</sup> and Mo(110)<sup>10</sup> substrates. A significant finding in these studies is the detection of the ethylidyne (CCH<sub>3</sub>) intermediate on the carbide-modified surfaces. Since the formation of the ethylidyne species is observed exclusively on the Pt-group metal surfaces,<sup>2,12</sup> the identification of this intermediate on carbide-modified Ti(0001), V(110), and Mo(110) offers further support to the similarities between the two classes of materials.

While the formation of ethylidyne has been associated with Pt-group metals, it has also been shown that the production of this intermediate is structure-sensitive. In most cases, the formation of ethylidyne was reported on the closed-packed planes of Pt-group metals with 3-fold symmetry.<sup>11</sup> For example, the dissociation of ethylene resulted in the formation of ethylidyne on Pd(111),<sup>13,14</sup> whereas vinyl (CHCH<sub>2</sub>) species were detected instead of the ethylidyne intermediate on Pd(100).<sup>15</sup> Similarly, Hatzikos and Masel have reported the formation of ethylidyne on the (5  $\times$  20)Pt(100) surface.<sup>16</sup> In contrast, ethylene dehydrogenated to a mixture of vinylidene (CCH<sub>2</sub>) and acetylenic

species on the unconstructed (1  $\times$  1)Pt(100) surface. The authors attributed the differences in the ethylene decomposition pathway to variations in the adsorption site geometry. Because all available adsorption sites on the (5  $\times$  20)Pt(100) surface possess 3-fold symmetry, ethylene is expected to interact in a similar fashion as on Pt(111). In contrast, the (1  $\times$  1) Pt(100) surface does not have the 3-fold sites required for the ethylidyne intermediate.<sup>16</sup>

The goals of the current study are primarily 2-fold. The first is to use ethylene as a probe molecule to determine whether the ethylidyne intermediate can be produced on carbide-modified W(110). The second is to determine the effect of substrate structure by comparing the carbide layer on the closed-packed W(110) with the more open-structured W(111) surfaces. The remainder of this paper is organized as follows. After briefly describing the experimental procedures, we present thermal desorption and vibrational spectra which monitor the decomposition of ethylene on clean and carbide-modified W(111) and W(110). In the discussion section, the decomposition activity of each surface toward ethylene will be estimated on the basis of Auger and thermal desorption data. In addition, the intermediates formed from ethylene decomposition will be identified when possible. Last, we will compare the results obtained from C/W(111) and C/W(110) with those from other carbide-modified surfaces.<sup>8,10,11,17–19</sup>

## 2. Experimental Section

**2.1. Techniques.** The UHV chamber used in the current study has been described in detail previously.<sup>8–10</sup> Briefly, it was a three-level stainless steel chamber (base pressure of  $4 \times 10^{-10}$  Torr) equipped with Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and a random flux shielded quadrupole mass spectrometer for temperature-programmed desorption (TPD) in the top two levels. The LK3000 double-pass high-resolution electron energy loss spectrometer (HREELS) was located the bottom level. The HREEL spectra reported here were acquired with a primary beam energy of 6 eV. Angles

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of incidence and reflection were  $60^\circ$  with respect to the surface normal in the specular direction. Count rates in the elastic peak were typically in the range of  $4 \times 10^4$  to  $2 \times 10^5$  counts per second, and the spectral resolution was between 35 and  $60 \text{ cm}^{-1}$  fwhm (full width at half-maximum). For TPD and HREELS experiments, the W(111) and W(110) samples were heated with a linear heating rate of 3 K/s.

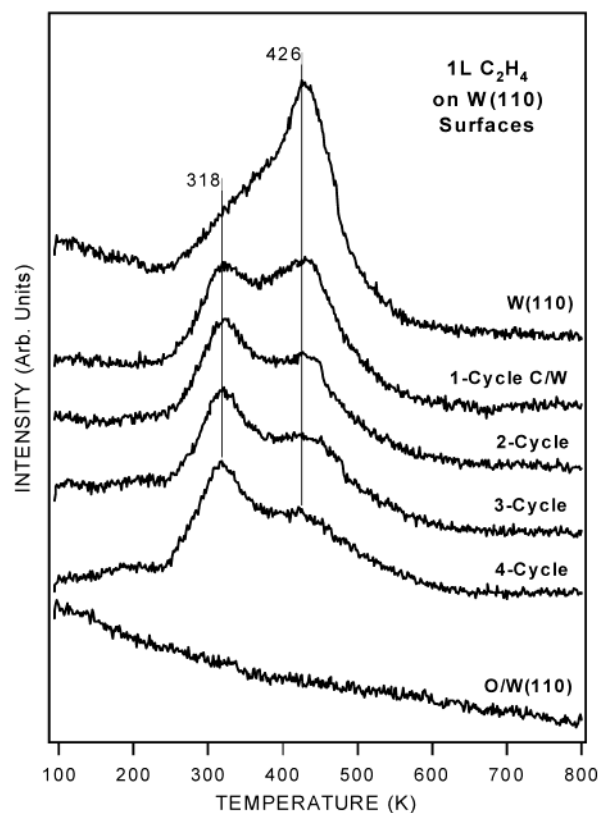
The single-crystal samples were [110] and [111] oriented, 1.5 mm thick, and 10 mm in diameter tungsten disk (99.999%), and were purchased from Metal Crystals and Oxides, Ltd., Cambridge, England. The crystals were spot-welded directly to two tantalum posts that served as electrical connections for resistive heating, as well as thermal contacts for cooling with liquid nitrogen. With this mounting scheme, the temperature of the crystals could be varied between 90 and 1200 K. Ethylene (99.99% purity) and oxygen (99.99% pure) were obtained from Matheson and were used without further purification. In all experiments, the gas exposures were made by backfilling the vacuum chamber with the crystal temperature held at 90 K and located in front of the leak valve. Exposures are reported in Langmuirs ( $1.0 \text{ Langmuir (L)} = 1 \times 10^{-6} \text{ Torr s}$ ) and are uncorrected for ion gauge sensitivity.

**2.2. Preparation of Clean and Modified W(111) and W(110) Surfaces.** Both clean W(111) and W(110) crystal surfaces were prepared by cycles of  $\text{Ne}^+$  bombardment at 500 K (sample current  $\sim 6 \mu\text{A}$ ) and flashing to 1200 K. These 10-minute cycles were generally repeated several times before annealing at 1200 K. To remove carbon contamination, excess  $\text{O}_2$  was used to titrate carbide layers at elevated temperatures. At 1000 K, oxygen reacted with carbon-covered W(111) or W(110), which then desorbed as CO at temperatures above 1150 K. The oxygen treatment was repeated several times to remove both surface and bulk carbon. Auger analysis showed that the C and O impurities were both less than 1% of a monolayer after the above cleaning procedure.

The preparation of carbide-modified W(111) and W(110) surfaces, using ethylene or other unsaturated hydrocarbon molecules as a carbon source, has been described previously.<sup>5,7–11</sup> In the remainder of this paper, the carbide surfaces will be referred to as C/W(111) and C/W(110). In this work, the carbide surfaces were prepared by exposing the clean surfaces to ethylene at 90 K and then flashing to 1200 K; generally these procedures were repeated between 3 and 5 cycles. Three cycles of ethylene exposure on W(110) resulted in a diffuse ( $1 \times 1$ )-C/W(110) LEED pattern with an Auger C(KLL 272 eV)/W(MNN 182 eV) peak ratio between 0.36 and 0.42, or equivalent to an atomic C/W ratio between 0.38 and 0.45.<sup>20</sup> On the other hand, three cycles of dosing and annealing on W(111) produced a  $(\sqrt{3} \times \sqrt{3}) \text{ R}30^\circ$ -C/W(111) LEED pattern with an Auger C(KLL 272 eV)/W(MNN 182 eV) peak ratio between 0.55 and 0.70, corresponding to an atomic C/W ratio between 0.58 and 0.74.<sup>9</sup>

### 3. Results

**3.1. Reaction of Ethylene on W(110) Surfaces.** *3.1.1. TPD Results.* Figure 1 shows the desorption spectra of hydrogen after exposing 1.0 L of ethylene at 90 K to the clean and carbide-modified W(110) surfaces. For comparison, the hydrogen desorption spectrum from an oxygen-modified surface, prepared by exposing W(110) to 30 L of  $\text{O}_2$  at 600 K, is also shown in Figure 1. On clean W(110), the desorption feature is characterized by a broad asymmetric peak centered at 426 K. After one cycle of carbide-modification, two distinct hydrogen desorption states are observed at 318 and 426 K. As the cycles of carbide-



**Figure 1.**  $\text{H}_2$  desorption spectra obtained following the thermal decomposition of 1.0 L of  $\text{C}_2\text{H}_4$  adsorbed on clean and modified W(110) surfaces at 90 K;  $dT/dt = 3 \text{ K/s}$ .

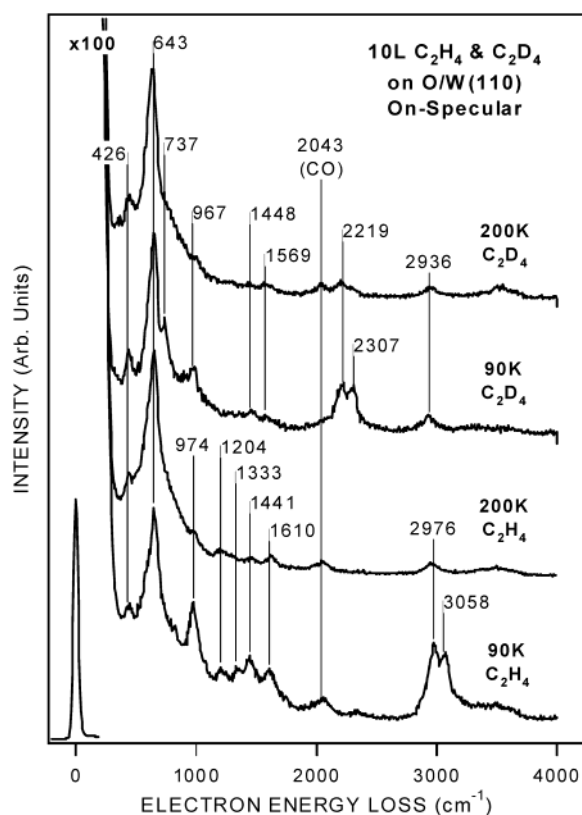
modification increase, the intensity of the 426 K peak continues to decrease while the 318 K peak increases slightly in intensity. As expected, the O/W(110) surface does not show any activity toward ethylene decomposition, as indicated by the absence of hydrogen desorption. AES measurements were carried out after the ethylene-exposed surfaces were heated to 600 K. By combining the C/W Auger peak ratios and hydrogen desorption peak areas, we are able to estimate and compare the decomposition activity of all surfaces; these calculations will be described in the Discussion.

**3.1.2. HREELS Results.** HREEL spectra for  $\text{C}_2\text{H}_4$  adsorbed on the W(110) surfaces are described in this section. We also present  $\text{C}_2\text{D}_4$  results to facilitate vibrational assignments. The exposures of ethylene were made with the crystal temperature at 90 K; the adsorbed layer was then heated to the indicated temperatures, and immediately cooled before the HREEL spectra were recorded. Finally, the height of the elastic peaks in all spectra has been normalized to unity, and the expansion factor for each individual spectrum represents the multiplication factor relative to the elastic peak.

HREELS measurements were first performed on the inert O/W(110) surface to identify vibrational features of molecularly adsorbed ethylene. Figure 2 compares the HREEL spectra recorded after exposing the O/W(110) surface to  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{D}_4$  at 90 K, and after heating the overlayer to 200 K. In the descriptions below, we will report the peak frequencies for  $\text{C}_2\text{H}_4$  first, followed by those for deuterated ethylene in parentheses. Two of the vibrational features on O/W(110), at 426 and  $643 \text{ cm}^{-1}$ , can be attributed to the deformation and stretching of the W–O motions, respectively.<sup>20,21</sup> After exposure to  $\text{C}_2\text{H}_4$  at 90 K, the HREEL spectrum on O/W(110) shows an intense peak at  $974 (737) \text{ cm}^{-1}$ , which is assigned to the  $\omega(\text{CH}_2)$  vibration. This strong feature is followed by the following weaker

**TABLE 1: Vibrational Assignments (cm<sup>-1</sup>) for  $\pi$ -Bonded Ethylene**

mode	C <sub>2</sub> H <sub>4</sub> (C <sub>2</sub> D <sub>4</sub> ) gas-phase <sup>a</sup>	$\omega_H/\omega_D$	C <sub>2</sub> H <sub>4</sub> (C <sub>2</sub> D <sub>4</sub> )/ O/Mo(110) <sup>b</sup>	$\omega_H/\omega_D$	C <sub>2</sub> H <sub>4</sub> (C <sub>2</sub> D <sub>4</sub> )/ O/W(110)	$\omega_H/\omega_D$	C <sub>2</sub> H <sub>4</sub> (C <sub>2</sub> D <sub>4</sub> )/ O/W(111)	$\omega_H/\omega_D$
$\rho(\text{CH}_2)$	826 (593)	1.39						
$\omega(\text{CH}_2)$	949 (720)	1.32	965 (720)	1.34	974 (737)	1.32	961 (737)	1.30
$\tau(\text{CH}_2)$	1222 (883)	1.38	1170 (900)	1.30	1204 (-)			
$\delta_s(\text{CH}_2)$	1342 (981)	1.37	1335 (980)	1.36	1333 (967)	1.38	1319 (981)	1.34
$\delta_{as}(\text{CH}_2)$	1444 (1078)	1.34	1420 (1130)	1.26	1441 (-)		1421 (1062)	1.34
$\nu(\text{CC})$	1623 (1515)	1.07	1595 (1500)	1.06	1610 (1569)	1.03	1596 (1495)	1.07
$\nu_s(\text{CH}_2)$	2989 (2200)	1.36	2975 (2240)	1.33	2976 (2219)	1.34	2976 (2239)	1.33
$\nu_a(\text{CH}_2)$	3106 (2345)	1.32	3065 (2300)	1.33	3058 (2307)	1.33	3064 (2320)	1.32

<sup>a</sup> Ref 30. <sup>b</sup> Ref 10.**Figure 2.** HREEL spectra recorded following 10 L exposure of ethylene (C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>D<sub>4</sub>) adsorption onto O/W(110) at 90 K.

modes:  $\tau(\text{CH}_2)$  at 1204,  $\delta(\text{CH}_2)$  at 1333 (967) and 1441,  $\nu(\text{C}=\text{C})$  at 1610 (1569),  $\nu_s(\text{CH}_2)$  at 2976 (2219), and  $\nu_a(\text{CH}_2)$  at 3058 (2307) cm<sup>-1</sup>. The presence of the 1610 (1569) and the sharp 974 (737) cm<sup>-1</sup> modes are characteristic of ethylene in the weakly  $\pi$ -bonded configuration.<sup>10,22</sup> The frequencies of ethylene on O/W(110) are assigned to their respective vibrational modes in Table 1. After the adsorbed layers are heated to 200 K, all of the features associated with ethylene disappear (aside from small readsorption peaks from the background), and only the two W–O vibrations remain.<sup>20</sup> These results are consistent with the TPD conclusion that O/W(110) is inert toward ethylene decomposition.

Figure 3 shows the vibrational spectra recorded after exposing 1.0 L of ethylene to clean W(110). At 90 K, the observed features are at 446, 697, 873, 994, 1082, 1177, 1427, and 2943 cm<sup>-1</sup>. Qualitatively, this spectrum is rather different from that of ethylene on O/W(110) at 90 K. The absence of a well defined  $\nu(\text{C}=\text{C})$  feature at  $\sim 1600$  cm<sup>-1</sup> indicates relatively strong interaction between ethylene and W(110). With the exception of the 994 cm<sup>-1</sup> mode, all of the vibrational features at 90 K can be assigned to those belonging to di- $\sigma$  bonded ethylene.

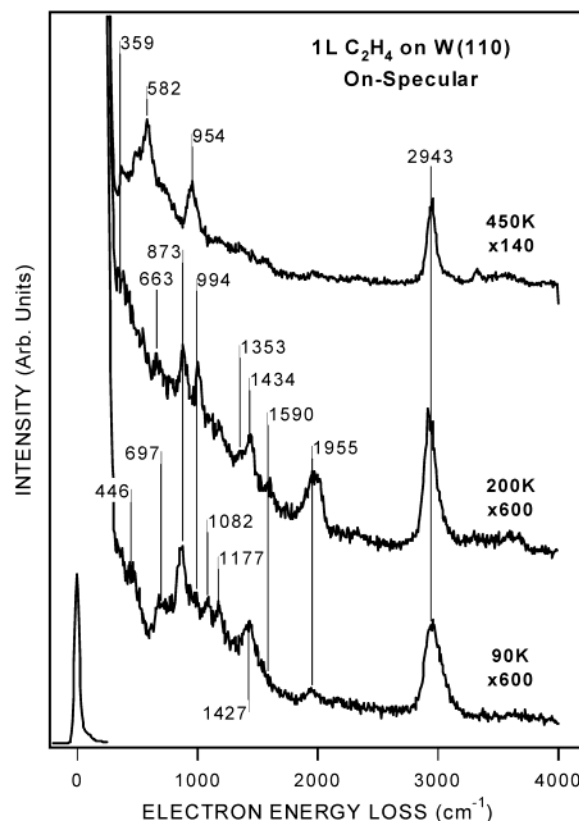
**Figure 3.** On- and off-specular HREEL spectra monitoring the thermal decomposition of 1.0 L of C<sub>2</sub>H<sub>4</sub> on W(110) following adsorption at 90 K.

Table 2 compares the vibrational assignments of di- $\sigma$  bonded ethylene on various surfaces. When heated to 200 K, two spectral changes are observed: (1) the 994 cm<sup>-1</sup> peak increases in intensity, and (2) a 1353 cm<sup>-1</sup> feature emerges. Overall, the vibrational spectrum at 200 K is very similar to those reported earlier for the ethylidyne (CCH<sub>3</sub>) intermediate.<sup>10</sup> Table 3 compares the vibrational assignments of ethylidyne on various surfaces. It is important to point out that ethylidyne is not the only intermediate present at this temperature. Specifically, the feature at 1590 cm<sup>-1</sup> cannot be assigned to any ethylidyne vibrational mode. The 1590 cm<sup>-1</sup> mode is most likely related to intermediates with unsaturated C=C bonds, such as the vinylidene (C=CH<sub>2</sub>) species. It is evident, however, from the relatively weak intensity of the 1590 cm<sup>-1</sup> feature that these intermediates are only the minority species. When heated to 450 K, the only observed vibrational modes are at 386, 582, 954, and 2943 cm<sup>-1</sup>. The two lower frequency modes can be assigned to the W–C vibrations, while the 954 and 2943 cm<sup>-1</sup> peaks are assigned to C<sub>x</sub>H<sub>y</sub> fragments, most likely methylidyne.<sup>15</sup>

**TABLE 2: Vibrational Assignments ( $\text{cm}^{-1}$ ) for Di- $\sigma$  Bonded Ethylene on W(110) and C/W(110)**

mode	$\text{C}_2\text{H}_4(\text{C}_2\text{D}_4)/$ Pt(111) <sup>a</sup>	$\omega_{\text{H}}/\omega_{\text{D}}$	$\text{C}_2\text{H}_4(\text{C}_2\text{D}_4)/$ C/Mo(110) <sup>b</sup>	$\omega_{\text{H}}/\omega_{\text{D}}$	$\text{C}_2\text{H}_4/$ W(110)	$\text{C}_2\text{H}_4(\text{C}_2\text{D}_4)/$ C/W(110)	$\omega_{\text{H}}/\omega_{\text{D}}$
$\nu(\text{MC})$	470 (450)	1.04	380 (405)	0.94	446		
$\rho(\text{CH}_2)$	660 (-)		635 (-)		697	663 (-)	
$\tau(\text{CH}_2)$	790 (600)	1.32	905 (670)	1.35	873	873 (656)	1.33
$\omega(\text{CH}_2)$	980 (740)	1.32	1180 (870)	1.36	1177	1184 (906)	1.31
$\nu(\text{CC})$	1050 (900)	1.17	1035 (980)	1.06	1082	1055 (981)	1.08
$\text{CH}_2$ -scissor	1430 (1150)	1.24	1395 (1145)	1.22	1427	1427 (1143)	1.25
$\nu_s(\text{CH}_2)$	2920 (2150)	1.36	2935 (2185)	1.34	2943	2956 (2178)	1.36
$\nu_a(\text{CH}_2)$	3000 (2250)	1.34	3010 (2255)	1.35		3017 (2266)	1.33

<sup>a</sup> Ref 3. <sup>b</sup> Ref 10.**TABLE 3: Vibrational Assignments ( $\text{cm}^{-1}$ ) for Ethylidyne ( $\text{CCH}_3$ ) Species on W(110) and C/W(110)**

mode	$\text{C}_2\text{H}_4(\text{C}_2\text{D}_4)/$ Pt(111) at 415 K <sup>a</sup>	$\omega_{\text{H}}/\omega_{\text{D}}$	$\text{C}_2\text{H}_4(\text{C}_2\text{D}_4)/$ C/Mo(110) at 260 K <sup>b</sup>	$\omega_{\text{H}}/\omega_{\text{D}}$	$\text{C}_2\text{H}_4/$ W(110) at 200 K	$\text{C}_2\text{H}_4(\text{C}_2\text{D}_4)/$ C/W(110) at 200 K	$\omega_{\text{H}}/\omega_{\text{D}}$
$\nu_s(\text{MC})$	430 (410)	1.05	380 (-)		359	359 (379)	0.95
$\nu_{\text{as}}(\text{MC})$	600 (600)	1.00	525 (560)	0.94		663 (-)	
$\rho(\text{CH}_3)$	980 (790)	1.24	920 (670)	1.37	873	879 (717)	1.23
$\nu(\text{CC})$	1130 (1160)	0.98	1075 (1105)	0.97	994	994 (981)	1.01
$\delta_s(\text{CH}_3)$	1350 (990)	1.36	1345 (1015)	1.33	1353	1360 (-)	
$\delta_{\text{as}}(\text{CH}_3)$	1420 (1030)	1.38	1430 (-)		1434	1441 (1130)	1.28
$\nu_s(\text{CH}_2)$	2890 (2080)	1.39	2915 (2180)	1.34	2943	2929 (2178)	1.34
$\nu_{\text{as}}(\text{CH}_2)$	2950 (2220)	1.33					

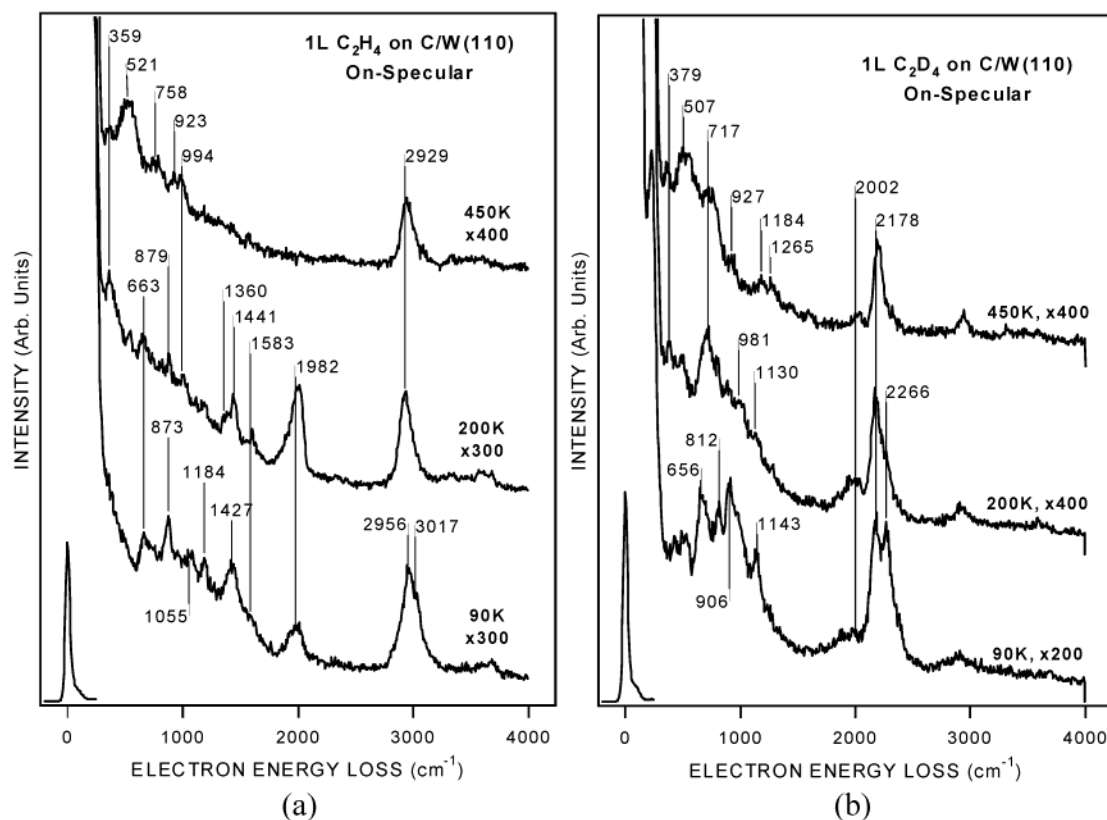
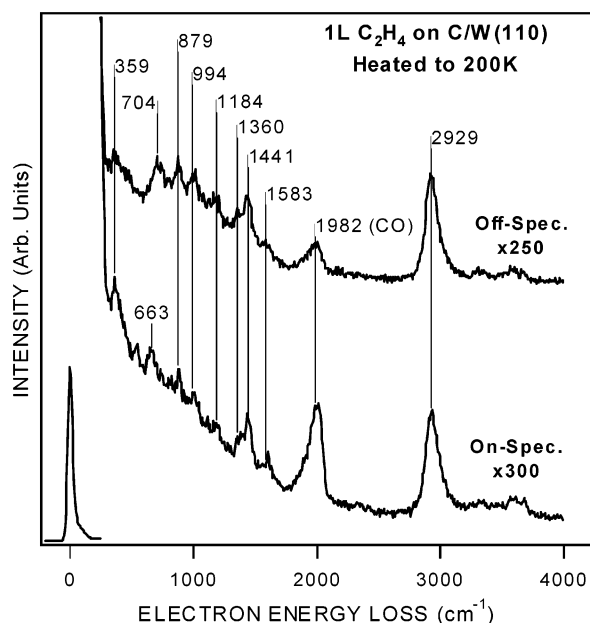
<sup>a</sup> Ref 3. <sup>b</sup> Ref 10.**Figure 4.** On-specular HREEL spectra monitoring the thermal decomposition of 1.0 L of (a)  $\text{C}_2\text{H}_4$  and (b)  $\text{C}_2\text{D}_4$  on C/W(110) following adsorption at 90 K.

Figure 4a shows the vibrational spectra recorded after exposing 1.0 L of  $\text{C}_2\text{H}_4$  to C/W(110). To help assign the vibrational features, we have recorded the HREEL spectra obtained following the adsorption of  $\text{C}_2\text{D}_4$  on C/W(110), as shown in Figure 4b. As before, the frequencies for deuterated ethylene, when observed, will be listed in parentheses after those for  $\text{C}_2\text{H}_4$ . At 90 K, vibrational features for the  $\text{C}_2\text{H}_4/\text{C/W(110)}$  overlay are observed at 663, 873 (656), 1055 (981), 1184

(906), 1427 (1143), 1583, 2956 (2178), and 3017 (2266)  $\text{cm}^{-1}$ . Overall, the 90 K spectra on C/W(110) are nearly identical to those on clean W(110); however, the relatively weak peak at 1583  $\text{cm}^{-1}$  is more noticeable on C/W(110), indicating that the  $\text{C}=\text{C}$  bonds of at least a fraction of  $\text{C}_2\text{H}_4$  are still intact. When heated to 200 K, the spectra become somewhat difficult to assign, as features appear to overlap in the 800 to 1300  $\text{cm}^{-1}$  frequency range; however, one can still distinguish several





**Figure 5.** On- and off-specular HREEL spectra obtained following the adsorption of 1.0 L of C<sub>2</sub>H<sub>4</sub> on C/W(110) at 90 K and heated to 200 K.

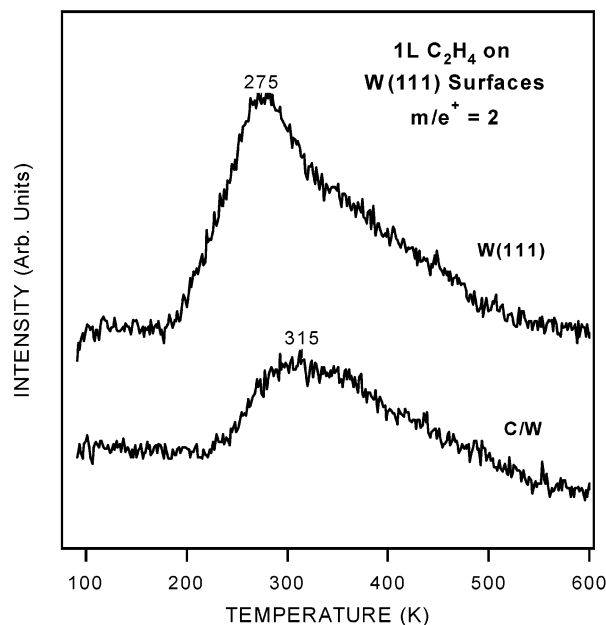
important characteristics. For example, the appearance of the 994 (981), 1360, and 1441 (1130) cm<sup>-1</sup> features is consistent with the formation of ethylidyne. As was the case on W(110), there are clearly other surface intermediates present. The detection of the relatively weak 1583 cm<sup>-1</sup> feature suggests the presence of C<sub>x</sub>H<sub>y</sub> fragments with C=C bonds intact, although it is important to point out that the  $\nu(\text{C}=\text{C})$  mode is not detected in the C<sub>2</sub>D<sub>4</sub> spectrum at 200 K. These observations again indicate that the 1583 cm<sup>-1</sup> peak is from a minority surface species. By 450 K, two modes attributable to  $\nu(\text{W}-\text{C})$  vibrations are detected at 359 (379) and 521 (507) cm<sup>-1</sup>. In addition, modes associated with C<sub>x</sub>H<sub>y</sub> are detected at 923, 994 (927), and 2929 (2178) cm<sup>-1</sup>.

Figure 5 focuses on the possible ethylidyne intermediate at 200 K by comparing the on- and off-specular HREEL spectra. A quick inspection shows the 359 cm<sup>-1</sup> ( $\nu_s(\text{W}-\text{C})$ ) mode to be weaker in the off-specular mode. The related  $\nu_{as}(\text{W}-\text{C})$  mode at 663 cm<sup>-1</sup> is also weak or nonexistent in the off-specular configuration. Additionally, the off-specular HREEL spectrum shows a peak at 704 cm<sup>-1</sup>, which is not observed in the on-specular mode. At present, we do not understand the origin of the angular dependence of the 663 and 704 cm<sup>-1</sup> features. Overall, the on- and off-specular HREEL spectra do not differ significantly for the remaining vibrational modes.

### 3.2. Reaction of Ethylene on W(111) Surfaces. 3.2.1. TPD

**Results.** Figure 6 shows the TPD results of hydrogen after exposing 1.0 L of ethylene at 90 K to the clean and carbide-modified surfaces of W(111). Hydrogen desorption is characterized by a broad, asymmetric peak centered at 275 K for W(111). The hydrogen peak intensity decreases significantly when the W(111) surface is modified by carbon. On C/W(111), the H<sub>2</sub> desorption peak is centered at ~315 K, which is slightly higher than that from clean W(111). The decomposition activity of the clean and modified W(111) surfaces will be quantified and compared with those from the W(110) surfaces in the Discussion.

**3.2.2. HREELS Results.** HREEL spectra for C<sub>2</sub>H<sub>4</sub> adsorbed on the W(111) surfaces are described below. Both C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>D<sub>4</sub> results were recorded to facilitate the assignment of vibrational modes. Table 1 lists the vibrational frequencies of



**Figure 6.** H<sub>2</sub> desorption spectra obtained following the thermal decomposition of 1.0 L of C<sub>2</sub>H<sub>4</sub> adsorbed on clean and carbide-modified W(111) surfaces at 90 K; dT/dt = 3 K/s.

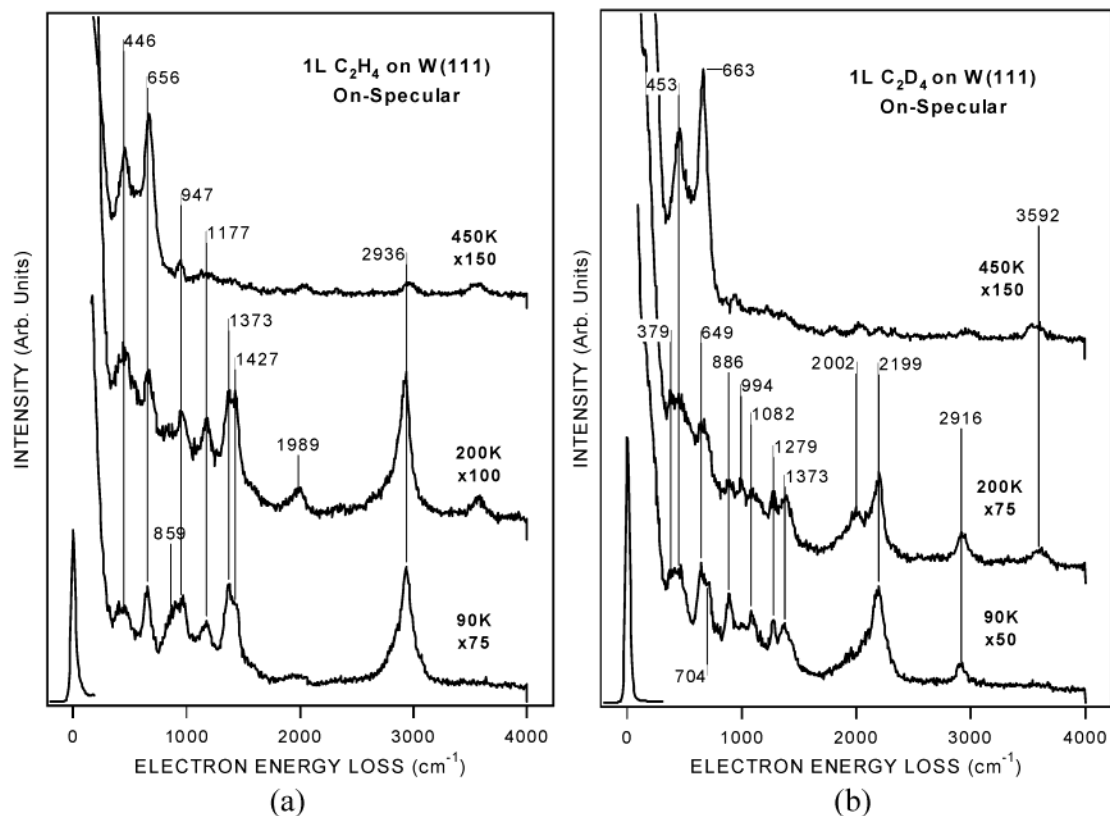
adsorbed ethylene on O/W(111) (spectra not shown). As was the case on O/W(110), the vibrational frequencies are very close to that of gas-phase ethylene, which indicates that ethylene is only weakly  $\pi$ -bonded to the O/W(111) surface.

Figures 7a and 7b show the HREEL spectra following the thermal decomposition of 1.0 L of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>D<sub>4</sub> on clean W(111). At 90 K, vibrational features for the C<sub>2</sub>H<sub>4</sub>/W(111) and C<sub>2</sub>D<sub>4</sub>/W(111) (in parentheses) overlayers are observed at 446, 656, 859 (649), 954 (704), 1177 (886), 1373 (1279), 1427 (1082), 2936 (2199) cm<sup>-1</sup>. By comparing these frequencies with other investigations of C<sub>2</sub> molecules on transition metal surfaces, we tentatively assign the 90 K spectra in Figures 7a and 7b to a mixture of vinylidene (C=CH<sub>2</sub>) and acetylide (C-CH) species.<sup>23,33,34</sup> Tables 4 and 5 provide a summary for these vibrational assignments. Only small changes in relative intensities are observed when the overlayer is heated to 200 K. By 450 K, the spectrum resembles that of a carbide-modified W(111) surface.<sup>9</sup>

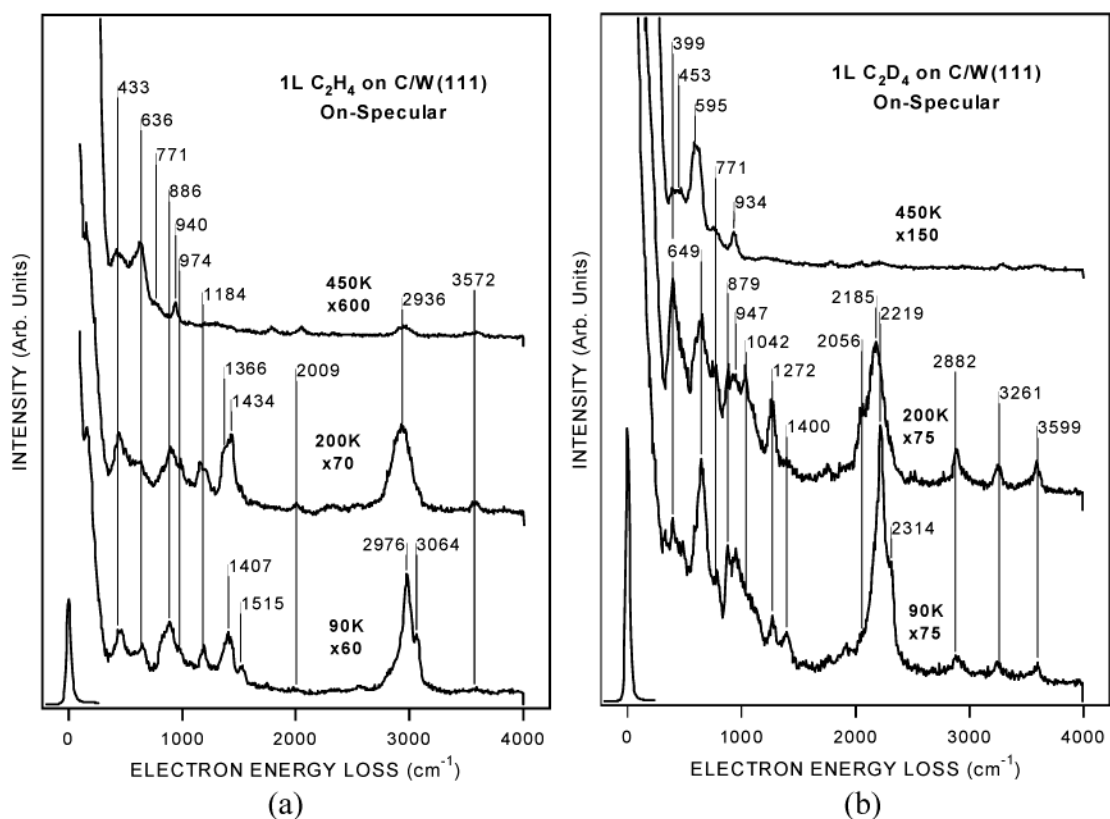
Figures 8a and 8b show the vibrational spectra recorded after exposing 1.0 L of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>D<sub>4</sub> to C/W(111). At 90 K, vibrational features for the C<sub>2</sub>H<sub>4</sub>/C/W(111) overlayer are observed at 433, 636, 886 (649), 974 (771), 1184 (879), 1407 (1042), 1515 (1400), 2976 (2219), and 3064 (2314) cm<sup>-1</sup>. When comparing the 90 K spectra obtained for C<sub>2</sub>H<sub>4</sub> on W(111) and C/W(111), one notices two distinct differences: (1) the presence of a well-resolved  $\nu(\text{C}=\text{C})$  mode at 1515 cm<sup>-1</sup>, and (2) the absence of a mode near 1350 cm<sup>-1</sup> on the C/W(111) surface. It is apparent from the presence of the 1515 cm<sup>-1</sup> mode that the carbide-modified surface is not nearly as active toward the decomposition of ethylene at 90 K, and that some ethylene are  $\pi$ -bonded to the surface. When the overlayer is heated to 200 K, the spectra appear to be nearly identical to those on W(111), which are similarly assigned to a mixture of vinylidene and acetylide intermediates. By 450 K, the HREEL spectrum is comparable to that of a C/W(111) surface.<sup>9</sup>

## 4. Discussion

**4.1. Decomposition Activity.** On the clean and carbide-modified W(111) and W(110) surfaces, gas-phase hydrogen and



**Figure 7.** On-specular HREEL spectra monitoring the thermal decomposition of 1.0 L of (a)  $C_2H_4$  and (b)  $C_2D_4$  on W(111) following adsorption at 90 K.



**Figure 8.** On-specular HREEL spectra monitoring the thermal decomposition of 1.0 L of (a)  $C_2H_4$  and (b)  $C_2D_4$  on C/W(111) following adsorption at 90 K.

surface carbon are the only products after the TPD measurements. To estimate the decomposition activity of ethylene on the clean and modified W surfaces, we combine the AES results,

recorded after TPD measurements to 600 K, with the hydrogen desorption peak areas. After the TPD measurement of 1.0 L of  $C_2H_4$  on clean W(111), AES results reveal an atomic C/W ratio

**TABLE 4: Vibrational Assignments (cm<sup>-1</sup>) for Vinylidene (C=CH<sub>2</sub>) Species**

vibrational assignment	C <sub>2</sub> H <sub>2</sub> on W(211) <sup>a</sup>	CCH <sub>3</sub> /Ru(001) <sup>b</sup>	C <sub>2</sub> H <sub>4</sub> (C <sub>2</sub> D <sub>4</sub> ) on W(111)	$\omega_H/\omega_D$	C <sub>2</sub> H <sub>4</sub> (C <sub>2</sub> D <sub>4</sub> ) on C/W(111)	$\omega_H/\omega_D$
$\tau(\text{CH}_2)$						
$\omega(\text{CH}_2)$	975	895	947 (704)	1.35	974 (771)	1.26
$\rho(\text{CH}_2)$		965				
$\delta(\text{CH})$	1448	1435	1427 (1082)	1.32	1407 (1042)	1.35
$\nu(\text{C}=\text{C})$	1596		- - (1373)		1515 (1400)	1.08
$\nu_s(\text{CH}_2)$	2922	2985	2936 (2199)	1.34	2976 (2219)	1.34
$\nu_{as}(\text{CH}_2)$		3050				

<sup>a</sup> Ref 23. <sup>b</sup> Ref 33.**TABLE 5: Vibrational Assignments (cm<sup>-1</sup>) of Acetylide (C–CH) Species**

vibrational assignment	C <sub>2</sub> H <sub>2</sub> on W(211) <sup>a</sup>	C <sub>2</sub> H <sub>4</sub> on Ni(110) <sup>b</sup>	C <sub>2</sub> H <sub>4</sub> (C <sub>2</sub> D <sub>4</sub> ) on W(111)	$\omega_H/\omega_D$	C <sub>2</sub> H <sub>4</sub> (C <sub>2</sub> D <sub>4</sub> ) on C/W(111)	$\omega_H/\omega_D$
$\nu_s(\text{M}-\text{C})$		380	446 (453)	0.98	433 (399)	1.09
$\nu_a(\text{M}-\text{C})$		465	656 (- -)		636 (- -)	
$\delta(\text{CH})$	1150		1177 (886)	1.33	1170 (879)	1.33
$\delta(\text{CH})$	800	790	859 (649)	1.32	886 (649)	1.37
$\nu(\text{CC})$	1360	1290	1373 (1279)	1.07	1366 (1272)	1.07
$\nu(\text{CH})$	~3000	2990			3064 (2314)	1.32

<sup>a</sup> Ref 23. <sup>b</sup> Ref 34.**TABLE 6: Activity of Clean and Carbide-Modified W(110) and W(111) toward Decomposition of Ethylene**

surfaces	activity (ethylene molecules/metal atom)
W(110)	0.144
W(111)	0.292
C/W(110)	0.104
C/W(111)	0.145

of ~0.58. Since each ethylene molecule decomposes to two surface carbons, the C/W ratio of ~0.58 corresponds to a decomposition activity of 0.29 ethylene molecules per W atom on the clean W(111) surface. Next, by comparing the H<sub>2</sub> TPD peak area from 1.0 L of ethylene on C/W(111) to that on W(111), we obtain a peak area ratio of 0.50; this leads to a decomposition activity of ~0.145 ethylene molecules per W atom on the C/W(111) surface.

Using the identical analysis method, we also estimated the decomposition activities of ethylene on W(110) and 4-cycle C/W(110). After TPD experiments to 600 K, we obtained an atomic C/W ratio of ~0.29 on W(110), corresponding to the decomposition activity of ~0.145 ethylene molecules per W atom. When comparing the H<sub>2</sub> TPD peak area of 1.0 L of ethylene on C/W(110) to that on W(110), we obtained a ratio of ~0.72. The activity of ethylene decomposition on C/W(110) is therefore estimated to be 0.10 molecules per W atom. Table 6 summarizes the ethylene decomposition activities on the clean and carbide-modified W(110) and W(111) surfaces. It is interesting to note that the activity of W(111) toward ethylene is much higher than that of W(110), which is most likely due to the corrugated nature of the W(111) surface. It is also important to note that while the hydrogen desorption temperatures of clean W(110) and W(111) differ by ~150 degrees, carbide-modification brings the desorption temperatures to ~315 K on both C/W(110) and C/W(111).

Though both carbide-modified surfaces exhibited similar hydrogen desorption temperature and ethylene decomposition activity, HREELS results indicated differences in the reaction pathway of ethylene on C/W(110) and C/W(111). Specifically, on C/W(110), ethylene adsorbed in a di- $\sigma$  configuration upon adsorption at 90 K, most of which converted to ethylidyne by

200 K and further decomposed to C<sub>x</sub>H<sub>y</sub> fragments by 450 K. In contrast, ethylene adsorbed on C/W(111) to form a mixture of acetylide and vinylidene intermediates, which remained stable until above 200 K. At 450 K, all C–H and C–C bond scissions were complete. Our group has previously reported comparative studies of C/W(111) and C/W(110) using NO,<sup>24</sup> cyclohexene,<sup>9,27</sup> and methanol<sup>25,26</sup> as probe molecules. For example, we found that that C/W(110) was less reactive than C/W(111) toward NO. The C/W(110) surface was also less selective than C/W(111) toward the production of gas-phase N<sub>2</sub> from NO.<sup>24</sup> In addition, on C/W(111) approximately 67% of the adsorbed cyclohexene selectively dehydrogenated to benzene,<sup>9</sup> whereas less than 20% of the cyclohexene reacted to produce gas-phase benzene on C/W(110).<sup>27</sup> Finally, although both C/W(111) and C/W(110) possessed similar surface activity toward the dissociation of methanol, the two carbide-modified surfaces showed different product distributions following methanol decomposition.<sup>25,26</sup> These results suggested that the chemical properties of the carbide overlayer depended strongly on the substrate structure. The current results further confirmed the different activity between C/W(111) and C/W(110).

Another useful comparison can be made between the carbide-modified surfaces and their respective clean metal surfaces. Judging from the HREELS measurements, it appeared that the surface intermediates from the dissociation of ethylene are similar between W(110) and C/W(110), as well as between W(111) and C/W(111). These comparisons suggested that the initial fraction of adsorbed ethylene must have readily decomposed on the highly active W(110) and W(111) surfaces to produce surfaces resembling C/W(110) and C/W(111). As a result, the subsequently adsorbed ethylene essentially interacted with carbide-modified surfaces. This hypothesis was consistent with the TPD results that the amount of ethylene undergoing decomposition was significantly reduced on the carbide-modified surfaces relative to the respective clean surfaces.

**4.2. Formation of the Ethylidyne Species on Carbide-Modified W(110), Mo(110), V(110), and Ti(0001).** As described earlier, ethylene interacted with the C/W(110) surface via a di- $\sigma$  bond configuration at 90 K. By 200 K, evidence of ethylidyne formation was indicated by the characteristic doublet feature at 1360 and 1441 cm<sup>-1</sup>, and a very strong  $\nu(\text{CH}_3)$  mode at 2956 cm<sup>-1</sup>. The vibrational assignments were further supported by the studies of deuterated ethylene. It is important to point out that ethylidyne was not the only intermediate detected on the C/W(110) surface at 200 K, as suggested by the presence the relatively weak mode at 1583 cm<sup>-1</sup>.

Though peak assignments showed the presence of ethylidyne on C/W(110), the relative intensities of Figures 4 and 5 were somewhat different from literature data of ethylidyne on Pt-group metals.<sup>30</sup> For example, Steininger and co-workers reported that on Pt(111), the dipole active  $\nu(\text{Pt}-\text{C})$ ,  $\nu(\text{C}-\text{C})$ , and  $\delta_s(\text{CH}_3)$  modes are at least five times more intense than the other features,<sup>3</sup> since the C–C bond was observed to be perpendicular to the surface. In addition, the presence of the ethylidyne on Pt-group metals is typically characterized by a strong CH<sub>3</sub> deformation mode at 1360 cm<sup>-1</sup> and relatively weak C–H stretching mode. With such an adsorption geometry, one would expect the relative intensities of ethylidyne vibrational modes on Pt(111) to change substantially in the off-specular HREELS measurements.<sup>3</sup> In contrast, the spectra in Figure 5 did not exhibit significant differences between the on- and off-specular spectra. The observation that all of the vibrational modes were dipole-active may be explained by the lack of periodicity of the C/W(110) surface on the atomic scale, an assertion supported

by our inability to obtain a clear and unambiguous LEED pattern. An earlier scanning tunneling microscopy (STM) study on the C/W(110) surface indicated that this surface was reconstructed on the atomic scale, resulting in a vertical buckling of up to 0.5 Å with a horizontal periodicity of 3–4 Å.<sup>31</sup>

The conversion of di- $\sigma$  bonded ethylene to ethylidyne has been previously reported for carbide-modified Ti(0001),<sup>8</sup> V(110),<sup>11</sup> and Mo(110).<sup>10</sup> On C/Mo(110), the ethylidyne intermediate was observed to be stable between 260 K and 350 K. Ethylidyne was observed on C/Ti(0001) after heating to 300 K.<sup>8</sup> The low-temperature conversion of adsorbed ethylene to ethylidyne was observed on C/V(110) after heating to 150 K.<sup>11</sup> In these studies, it was interesting to note that the relative intensities of the ethylidyne vibrational modes all differed from surface to surface. As was the case for C/W(110), studies on C/Mo(110) and C/Ti(0001) also revealed the lack of significant differences between the on- and off-specular modes for ethylidyne.

Thus far, ethylidyne species have been observed on carbide-modified Ti(0001),<sup>8</sup> V(110),<sup>11</sup> Mo(110),<sup>10</sup> and W(110), all of which are closed-pack surfaces. On the other hand, the C/W(111) surface did not exhibit the reaction pathway to form ethylidyne. It is likely that highly active metal sites were still exposed for reaction with ethylene even after carbide-modification. As a result, HREELS results showed the presence of deep dehydrogenated products such as acetylide, but not ethylidyne.

## 5. Conclusions

The TPD and HREELS results clearly showed that the reaction pathways of ethylene on C/W(110) and C/W(111) were dependent on the substrate structure. On clean and carbide-modified W(110), ethylene was converted from a di- $\sigma$  configuration to the ethylidyne intermediate when heated from 90 K to 200 K. The observation of ethylidyne on C/W(110) was consistent with previous studies on other carbide-modified, closed-packed surfaces such as Ti(0001), V(110), and Mo(110). On the other hand, ethylene formed a mixture of vinylidene and acetylide species upon adsorption on clean and carbide-modified W(111). On both W(110) and W(111) substrates, the presence of carbidic carbon did not significantly alter the reaction pathways of ethylene in relation to the respective clean surfaces. TPD results, however, did show significant changes in the decomposition activity and hydrogen desorption temperature after the W(111) and W(110) surfaces were modified by carbon.

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