In-Situ Spectroscopic Monitoring of the Ambient Pressure Hydrogenation of C₂ to Ethane on Pt(111)

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RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

ABSTRACT

The hydrogenation of C₂ molecules formed on the Pt(111) surface through acetylene exposure at 750 K was monitored in situ with reflection absorption infrared spectroscopy (RAIRS) in the presence of up to 10 Torr of H₂. The coverage of post-reaction surface carbon was measured with Auger electron spectroscopy. The RAIR spectra show that C₂ is hydrogenated to an ethylidyne intermediate. The hydrogenation of ethylidyne was also monitored at 400 K for H₂(g) pressures of 1.0×10⁻² to 10 Torr. At H₂(g) pressures greater than 1.0 Torr, ethylidyne is completely hydrogenated. In an attempt to probe the nature of the C₂ adsorption sites, RAIR spectra of coadsorbed CO were obtained. It is found that while C₂ does not block CO adsorption, the spectra indicate that the surface carbon is free of hydrogen. In contrast, ethylidyne blocks CO adsorption sites. In the presence of coadsorbed CO, complete hydrogenation of ethylidyne occurs at 450 K versus 400 K in the absence of CO.

Keywords

C₂, dicarbon, carbon hydrogenation, carbidic carbon, graphitic carbon, in-situ RAIRS

1. Introduction

The reactivity of carbonaceous layers adsorbed on transition metal catalysts during catalytic reactions is important because it can alter the reaction kinetics and products. If the coverage of the carbon is high enough, the reaction will not proceed. This is called "coking" of the catalyst [1]. Since the carbon present on the surface can be either carbidic or graphitic depending on the reaction temperature, the reactivity of these species needs to be studied in detail. This study focuses on the reactivity towards ambient pressure H_2 of a carbidic layer mainly consisting of C_2 molecules created by the decomposition of C_2H_2 on Pt(111) at 750 K. Unlike a graphitic or graphene layer formed from ethylene or acetylene decomposition on the surface at temperatures greater than 800 K [2], C_2 can be hydrogenated and ultimately removed from the surface through formation of ethane.

The stability and hydrogenation of C_2 on Pt(111) has been studied previously by Deng et al. under ultra high vacuum (UHV) conditions using reflection absorption infrared spectroscopy (RAIRS), temperature programmed reaction spectroscopy (TPRS), and Auger electron spectroscopy [3]. They showed that the exposure of acetylene and ethylene to Pt(111) held at 750 K produced adsorbed C_2 molecules and C atoms, respectively. While the surface carbon was completely dehydrogenated at 750 K, this temperature was still low enough to prevent formation of a graphitic layer, which STM studies have shown begins at 800 K [2]. An exposure of C_2H_2 to Pt(111) at 750 K produced a carbon coverage of 0.34 ML as determined from the Auger spectra [3]. The crystal was then cooled to 88 K and H_2 was coadsorbed. After the crystal was annealed to 400 K, three species, methylidyne (CH), ethynyl (C_2H), and ethylidyne (CCH_3) were detected on the surface at coverages of 0.04, 0.05, and 0.11 ML, respectively. This showed that most of the surface carbon had been hydrogenated to C_2H_x species [3].

In contrast to the experimental results implying that C_2 is stable on Pt(111), Density Functional Theory (DFT) calculations have found that C atoms are more stable than C_2 molecules [4] and are the product of the decomposition of ethynyl on the Pt(111) surface [5, 6]. However, an earlier proposed method for estimating surface reaction energies concluded that dissociation of C_2 to C on Pt(111) should be endothermic [7]. Fischer-Tropsch catalysis involves production of hydrocarbons from carbon-carbon coupling reactions starting with CH_x ($x = 0, 1, 2$ or 3) formed from the decomposition of methane or CO on metal surfaces [8]. Coupling of C_1 species has been seen experimentally on metals such as Ru(0001) [9] and Pt(111) [10]. Smirnov, et al. showed that atomic carbon deposited on Pt(111) formed C_2 , which was then hydrogenated to ethylidyne [11]. Also, Deng et al., exposed Pt(111) to a mixture of $^{12}C_2H_2$ and $^{13}C_2H_2$ and showed with RAIRS that the C_2 molecules were not formed by a surface coupling reaction [3]. The stability and reactivity of these species were also confirmed in a recent scanning tunneling microscopy (STM) study [12].

While the hydrogenation of C_2 on Pt(111) at ambient pressure has not been previously studied, the reaction of carbon atoms created through the decomposition of ethylene at 600 K with H_2 at atmospheric pressure was monitored in a ^{14}C radiotracer study [13]. While the initial reaction was fast, the process slowed down quickly and most of the carbon atoms were not hydrogenated to methane. Ethylidyne reacting under one atmosphere of H_2 was also monitored from 300 to 470 K and was found to be hydrogenated quickly at temperatures greater than 345 K [13]. The hydrogenation of ethylidyne is of great interest because it is a spectator species during ethylene and acetylene hydrogenation to ethane. Tillekartne, et al. concluded that ethylidyne will not be hydrogenated at 300 K in 100 Torr of H_2 because the needed surface sites are not available due to the high coverage of H atoms [14].

Carbon monoxide has been used as a probe of the properties of ethylidyne on Pt(111) in UHV and ambient pressure environments [15, 16]. Ethylidyne acts as an electron donor, causing a large red shift in the terminal site CO peak and creating a disordering effect in the adsorbed bridge site CO molecules [15]. In a recent study, the coadsorption of CO on Pt(111) was found to increase the ethylene hydrogenation temperature from 300 to 400 K, which is the temperature where CO desorbs making surface sites available for the reaction [16].

Since the previous experimental work showed that C_2H_2 decomposition on Pt(111) at 750 K produces mainly C_2 molecules, the focus here is on the hydrogenation of C_2 to ethane under ambient pressure H_2 . The rate limiting step is ethylidyne formation, which was confirmed by adsorbing ethylidyne on the surface and performing several experiments in which the pressure in the cell was varied from 1.0×10^{-2} to 10 Torr of H_2 at 400 K. When the H_2 pressure is greater than 1.0 Torr, the hydrogenation reaction proceeds quickly and ethylidyne is fully hydrogenated. Ambient pressure CO was also used to probe C_2 hydrogenation. The data show that C_2 does not block CO from adsorbing on the surface to any significant extent, but the CO blocks surface sites needed for the hydrogenation reaction. The CO spectra show that the C_2 species are completely dehydrogenated after exposure of C_2H_2 to Pt(111) at 750 K, a conclusion that cannot otherwise be reached with RAIRS alone. In ethylidyne hydrogenation experiments, coadsorbed CO was found to block hydrogen adsorption sites, which increases the hydrogenation temperature of ethylidyne from 400 to 450 K.

2. Experimental

The experiments were performed in an UHV chamber coupled to an ambient pressure cell. For the acquisition of RAIR spectra, a Bruker 70v FTIR with a manually rotatable polarizer (p-

polarized light for surface studies) and MCT detector were used. At the start of every experiment, the Pt(111) crystal was annealed to 1200 K for two minutes. As shown in each figure, a certain coverage of C₂ or CCH₃ was formed by exposing the Pt(111) surface to C₂H₂ or C₂H₄, respectively. The exposures are given in Langmuir (1×10^{-6} Torr s = 1 L). For experiments with ambient pressures of CO and H₂, the pressures were measured with a convectron gauge. This gauge limits the H₂ pressure to less than 10 Torr, as it becomes non-linear above about 1.0 Torr. In Figures 1 and 2, 512 scans were acquired while the crystal was held at 400 K. Each spectrum was acquired in approximately two minutes. For all other spectra in Figures 3, 4 and 5, 1024 scans were acquired. For Figure 3, the crystal was held at a constant temperature of 400 K while acquiring the spectra, while in Figures 4 and 5, spectra were acquired at 300 K after the crystal was annealed to the target temperature for 30 seconds. For Figures 4 and 5, when an ambient pressure of CO was added to the cell, gas phase CO peaks were also present in the spectra. These peaks were removed by rotating the polarizer, acquiring spectra with s-polarized light, and performing spectral subtraction ($\Delta R_p/R_p - \Delta R_s/R_s$) to reveal the peaks of CO adsorbed on the surface. This method of RAIRS, denoted as polarization-dependent RAIRS, and the chamber design were described previously [17, 18].

After the crystal was raised into the main chamber (UHV) following the gas exposures, it was annealed to 1100 K to remove adsorbed species from the surface. The crystal was allowed to cool to room temperature and Auger spectra were then acquired with an LK Technologies RVL2000 Auger-LEED system, which utilizes one electron gun for both techniques and has a mini-CMA for Auger studies. After the Auger spectra were acquired, the crystal was cleaned by oxygen exposure at an elevated temperature. Atomic adsorption grade (99.6%) C₂H₂ was purchased from Airgas. It was purified by the freeze-pump-thaw method and checked for purity

with mass spectrometry, as described previously [17]. Ethylene (99.99%) and carbon monoxide (99.99%) were purchased from Matheson Tri-Gas, while the ultra-high purity hydrogen (99.999%) was purchased from Praxair. All gases were verified to be pure with mass spectrometry.

3. Results

3.1. Hydrogenation of C₂ at 400 K and ambient pressure H₂

Figure 1(a) shows RAIR spectra following the exposure of H₂ to a C₂ covered Pt(111) surface. Before the spectra were acquired, C₂ was formed on the surface by exposure of 0.6 L of C₂H₂ to the crystal held at 750 K. The carbon coverage was approximately 0.30 ML as determined from the Auger spectra shown in Figure 1(b). This coverage was calculated to an estimated accuracy of $\pm 15\%$ from the ratio of the 273 to 237 eV peaks multiplied by 0.62 as described in previous work [19]. In order to verify the accuracy of this estimate, 10 L of C₂H₄ was exposed to a clean Pt(111) surface at 300 K, which formed 0.25 ML of ethylidyne (CCH₃) [20]. The crystal was then annealed to 1100 K. This should have produced a carbon coverage of 0.50 ML. As shown in Figure S1 in the supplemental information, a coverage of 0.57 ML was calculated from the Auger spectra. The 14% higher than expected carbon coverage could be due to CO or other carbon-containing species present on the surface. Figure 1(a) shows a spectrum acquired at 300 K followed by a spectrum after adding 1.0×10^{-2} Torr of H₂. The next spectrum was recorded after annealing to 400 K, a temperature where ethylidyne is stable and where hydrogen should mostly be desorbed making empty sites available. With the crystal at 400 K, 10 Torr of H₂ was then added and spectra were acquired versus time over a period of one hour. The first spectrum shows ethylidyne peaks at 1115 and 1344 cm⁻¹, due to the $\nu(\text{CC})$ and $\delta_s(\text{CH}_3)$ modes, respectively.

After the first three spectra at 400 K, no peaks are visible. The results in Figure 1 show that C_2 was hydrogenated to ethynidyne, which was then removed from the surface, presumably by hydrogenation to ethane. After the crystal was raised into the UHV chamber, it was annealed to 1100 K and cooled to 300 K. An Auger spectrum was then acquired to determine carbon coverage. As shown in Figure 1(b), after H_2 exposures of 20 and 60 minutes, the carbon coverages decreased to 0.17 and 0.09 ML, respectively. The Auger spectra confirmed that carbon was removed from the surface by hydrogenation.

The experiment shown in Figure 2 is identical to that of Figure 1, but with a higher C_2 coverage. As shown in Figure 2(b), after a 1.0 L exposure of C_2H_2 at 750 K, the carbon coverage was approximately 0.52 ML. The first spectrum in Figure 2(a) shows that no ethynidyne was formed after adding 1.0×10^{-2} Torr of H_2 at 300 K. After heating to 400 K and increasing the H_2 pressure to 10 Torr, the second from the top spectrum was acquired. Subsequent spectra were then obtained at two minute intervals at 400 K. Immediately after the increase in H_2 pressure, the ethynidyne peaks at 1118 and 1343 cm^{-1} appeared. Comparison of Figures 1 and 2 shows that a 70% higher carbon coverage leads to a 60% higher ethynidyne coverage and the ethynidyne remained on the surface for 18 minutes, which differs from the spectra in Figure 1, where the peaks were only present for six minutes. After the crystal was exposed to H_2 for 60 minutes, it was raised into the main chamber and an Auger spectrum was acquired, which indicated that approximately 0.28 ML of carbon remained on the surface.

To more clearly establish the nature of hydrogenation of the ethynidyne formed from hydrogenation of C_2 , the hydrogenation of ethynidyne formed directly from ethylene was also studied. Figures 3(a), (b), and (c) show the $\nu(CC)$ and $\delta_s(CH_3)$, and $\nu_s(CH_3)$ modes at 1117, 1339, and 2882 cm^{-1} , respectively, of 0.22 ML of ethynidyne formed by a 10 L exposure of C_2H_4

to the surface at 400 K. The cell was then pressurized with 1.0 Torr of H₂ and consecutive spectra were acquired. The peaks related to ethylidyne completely disappeared after 28 minutes. Figure 3(d) shows a plot of the peak area of the $\delta_s(\text{CH}_3)$ bending mode versus time using H₂ pressures from 1.0×10^{-2} to 10 Torr. The top set of data points shows that approximately 10% of the ethylidyne decomposed at 400 K after 28 minutes under UHV conditions (no H₂ added). Four separate experiments were then performed, varying the hydrogen pressure from 1.0×10^{-2} to 10 Torr of H₂. There is a large change in the hydrogenation rate and in the final ethylidyne coverage. An exponential function was fitted to each of the data sets, and the best fits were obtained for 1.0 and 10 Torr of H₂. This indicates that the reaction is first order in ethylidyne coverage. An accurate determination of the order with respect to hydrogen pressure could not be obtained because of non-linearity of the pressure gauge readings in this range. As the kinetics of ethylidyne hydrogenation has already been thoroughly described in previous publications, we have not performed a complete analysis of the limited data acquired here.

3.2. Probing the C₂-Covered Surface with Adsorbed CO

The nature of the interaction of adsorbates with metal surfaces can often be determined through RAIRS experiments of coadsorbed CO. In particular, if C₂ were to block CO adsorption, then the C₂ coverage could be titrated during hydrogenation by monitoring the CO coverage with RAIRS. A Pt(111) surface with a carbon coverage of 0.52 ML was prepared as for Figure 2(b). Figure 4(a) and (b) show peaks at 1852 and 1873 cm⁻¹ for CO on bridge sites and at 2097 cm⁻¹ for CO on terminal sites in an ambient of 1.0×10^{-2} Torr of CO above the clean surface at 300 K (blue spectrum), which should correspond to 0.6 ML of CO based on previous STM work [21]. This can be compared with the green spectrum for 1.0×10^{-2} Torr of CO above the carbon-covered surface, which yields approximately 0.5 ML of adsorbed CO, based on the reduction in

integrated RAIRS peak areas and the assumption that the areas are proportional to coverage. However, this assumption is often not valid at high CO coverages, where screening effects lead to a reduction in intensity [22]. Therefore the reduction in intensity on the carbon covered surface may be lower than 0.5 ML. The red spectrum was obtained after adding 1.0 Torr of H₂ and annealing the crystal to 500 K, which in the absence of CO would have removed C₂. The absence of any significant difference between the red and green spectra indicates that the presence of coadsorbed CO poisons the C₂ hydrogenation reaction. As an aside, we note that for the clean surface, the two bridge-site CO peaks are slightly lower in intensity in the presence of 1.0×10⁻² Torr of CO than for CO adsorbed on Pt(111) in UHV. This is attributed to an overlayer compression effect associated with the higher coverage achieved under an ambient pressure of CO. This is confirmed with the spectra in the supplementary information obtained after the cell was evacuated to 10⁻⁷, 10⁻⁸, and 10⁻⁹ Torr where the peak at 1873 cm⁻¹ disappeared leaving only peaks at 1851 and 2097 cm⁻¹. Similar results were seen in a previous RAIRS study [23].

Although CO is not useful for titrating the C₂ reaction, it can be used effectively to titrate the hydrogenation of ethylidyne and to study the influence of other species adsorbed on Pt(111) during the reaction. This is shown in Figures 5(a) and (b). In both figures, 5 L of C₂H₄ was exposed to the surface at 300 K, which created a saturated ethylidyne layer as indicated by the peaks at 1120, 1339, and 2882 cm⁻¹. For Figure 5(a), the surface was then exposed to 5 L of CO and peaks appeared at 1800 and 2024 cm⁻¹, due to bridge and terminal site CO. The CO pressure was raised to 1.0×10⁻² Torr, which increased the CO coverage and caused a splitting of the bridge site CO peak at 1800 cm⁻¹ into peaks at 1742 and 1807 cm⁻¹ and a blue shift of the terminal site CO to 2037 cm⁻¹. The increase in CO pressure also caused blue shifts in the three ethylidyne peaks: 1120 to 1126 cm⁻¹, 1342 to 1352 cm⁻¹, and 2882 to 2894 cm⁻¹. After heating to

500 K, the ethylidyne peaks largely disappeared yet the CO peaks were not restored to their values on the clean surface. Evacuation of the cell had little effect. After heating an ethylidyne covered surface to 500 K, previous work has shown that hydrogen-containing species such as CH and CCH remain on the surface and the results of Figure 5(a) imply that such species have a large effect of the amount and frequencies of coadsorbed CO.

Figure 5(b) shows the analogous results to those of Figure 5(a) but in the presence of 1.0 Torr of H_2 . Note that the intensity scales are different in Figures 5(a) and 5(b) and that the ethylidyne and CO peaks have similar intensities and frequencies in the two sets of spectra before annealing to 400 K. However, after annealing to 450 K, a large increase in CO peak intensities and frequencies is seen in Figure 5(b), which continues upon annealing to 500 K, with only a modest change in the bridge site CO peaks upon evacuation of the cell. The fact that the final CO spectrum in Figure 5(b) is essentially the same as for clean Pt(111), demonstrates that the ethylidyne has largely been removed by hydrogenation leaving the surface free of the C_xH_y species that were present on the surface after ethylidyne decomposition in the case of Figure 5(a). Note that a just barely detectable ethylidyne peak is still present at 1352 cm^{-1} in both Figures 5(a) and (b) even after the 500 K anneal, indicating that coadsorbed CO prevents complete hydrogenation or complete decomposition at 500 K.

4. Discussion

As shown in Figures 1 and 2, C_2 is hydrogenated to ethane through an ethylidyne intermediate when the Pt(111) crystal is exposed to ambient pressure H_2 . Since the quantity of gas phase ethane is too low to detect with RAIRS, unlike in our previous study of acetylene hydrogenation, Auger spectroscopy was used to show that hydrogenation removes carbon from the surface. The

higher C_2 coverage in Figure 2 compared to Figure 1 leads to a higher ethylidyne coverage upon hydrogenation. The higher ethylidyne coverage may also be partly due to a lower rate of ethylidyne removal by hydrogenation to ethane because fewer sites are available for the hydrogenation reaction. Because the rate at which C_2 is hydrogenated to ethylidyne at 400 K is comparable to the rate at which ethylidyne is hydrogenated to ethane under an ambient pressure of H_2 , the ethylidyne coverage remains lower than obtained by Deng et al. [3], by coadsorbing hydrogen and C_2 at low temperature and annealing in UHV to higher temperatures. Under the latter conditions there is only enough hydrogen to hydrogenate C_2 , but not enough to hydrogenate ethylidyne. In the UHV study of Deng et al. [3], 79% of the adsorbed carbon was found to be in the form of C_2 , with the remaining in the form of C atoms. It is therefore likely that the carbon left on the surface even after the 60 minute exposure to H_2 was in the form of carbon atoms. A previous study showed that atomic carbon on Pt(111) could not be hydrogenated even at atmospheric pressure and 600 K [19]. If we assume that only the C_2 species are hydrogenated, leaving the majority of the remaining carbon in the form of C atoms, the carbon coverage in the form of C_2 species remaining on the surface from the experiment shown in Figure 1 will be 0.11 and 0.03 ML after 20 and 60 minutes, respectively. These results show that the C_2 species are almost completely hydrogenated after the one hour exposure. In contrast, for the higher initial carbon coverage used in Figure 2, the carbon coverage assigned to C_2 species would be 0.17 ML after one hour of exposure to an ambient of 10 Torr of H_2 .

As shown in Figure 3, ethylidyne is readily hydrogenated at 400 K because the needed surface sites are available. A previous study indicated that on top sites are occupied by H atoms at 300 K and under 10^{-1} Torr of H_2 [24]. As ethylidyne occupies the fcc three-fold hollow sites, it does not block H atom adsorption sites and the reaction is unimpeded. As noted earlier, we could not

determine the actual reaction order with respect to hydrogen pressure. However, the reaction rate clearly rises rapidly with hydrogen pressure. To produce C_2H_6 from CCH_3 , three hydrogen atoms must be added and this presumably occurs in a stepwise fashion to produce ethylidene ($CHCH_3$) and ethyl (CH_2CH_3) intermediates on the surface. These two species will not be seen in the spectra as they are readily hydrogenated at much lower temperatures than 400 K [25, 26], implying that they would react as soon as they formed.

Carbon monoxide cannot be used to titrate the C_2 coverage during the hydrogenation reaction because CO blocks H_2 adsorption and dissociation. An ambient pressure of CO produces an overlayer compression effect on the C_2 -covered surface similar to what is seen at high CO coverage on the clean Pt(111) surface. As evident from comparison of the CO spectra in Figures 4 and 5, much less CO can adsorb on the ethylidyne-covered surface, making hydrogen sites available. This is a plausible explanation of why ethylidyne but not C_2 can be hydrogenated in the presence of coadsorbed CO. The fact that the CO spectrum in Figure 5(a) in the presence of the ethylidyne-decomposition products, which still contain hydrogen but do not give rise to observable RAIRS peaks under these conditions, is so different from the spectrum of CO on the surface prepared through C_2H_2 exposure at 750 K, implies that the latter surface is covered with carbon only. For ethylidyne hydrogenation, CO can be used to titrate the ethylidyne coverage as it is removed from the surface. A comparison of Figures 4 and 5 shows that in the presence of coadsorbed ethylidyne, the terminal site CO peak shifts from 2097 to 2037 cm^{-1} and the disordered bridge site peaks shift from 1852 and 1873 to 1741 and 1807 cm^{-1} , respectively. This agrees with previous work on the coadsorption of CO with ethylidyne [15]. Finally, the temperature of ethylidyne hydrogenation is increased by 50 K to 450 K, corresponding to the onset of CO desorption, which frees sites needed for the hydrogenation reaction to proceed. This

agrees with the work by Chen, et al. which studied the inhibition of ethylene hydrogenation by CO [16].

5. Conclusions

The decomposition of acetylene at 750 K produces C₂ molecules on Pt(111) that are hydrogenated to ethane at 400 K in the presence of 1.0×10^{-2} to 10 Torr of H₂ through an ethylidyne intermediate. Rapid hydrogenation of a saturation coverage of ethylidyne in 10 Torr of H₂ indicates that the formation of ethylidyne is the rate limiting step in the hydrogenation of C₂ to ethane. On the C₂-covered surface, CO saturates to a coverage similar to that of the clean surface and is high enough to block hydrogen from adsorbing and reacting with C₂. Therefore CO cannot be used to titrate the C₂ coverage during hydrogenation. However, in the case of an ethylidyne-covered surface, the saturation CO coverage is low enough to permit ethylidyne hydrogenation to proceed. When CO was coadsorbed with the products of ethylidyne decomposition, the CO spectra revealed the presence of hydrogen-containing species, even though those species could not be directly detected with RAIRS. The CO spectra thus implied that the carbon layer produced from the decomposition of C₂H₂ at 750 K produces a surface that is free of all hydrogen-containing carbon species.

Acknowledgment

We gratefully acknowledge financial support from the National Science Foundation (CHE-1464816).

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Figure 1. Figure 1(a) shows spectra acquired after the Pt(111) crystal held at 750 K was exposed to 0.6 L C_2H_2 , and allowed to cool to 300 K. 1.0×10^{-2} Torr of H_2 was then added at 300 K. After the crystal was annealed to 400 K, another spectrum was acquired. After 10.0 Torr of H_2 was added, consecutive spectra were acquired (512 scans/spectrum). Figure 1(b) shows Auger spectra all acquired at 300 K of a clean Pt(111) surface, after the crystal was exposed to 0.6 L of C_2H_2 at 750 K, and after the crystal was exposed to 10 Torr of H_2 for 20 and 60 minutes, respectively, raised into the UHV chamber, and annealed to 1100 K.

Figure 2. Figure 2(a) shows spectra acquired after the Pt(111) crystal held at 750 K was exposed to 1.0 L of C_2H_2 and allowed to cool to 300 K. 1.0×10^{-2} Torr of H_2 was then added at 300 K. After the crystal was annealed to 400 K, another spectrum was acquired. After 10 Torr of H_2 was added, consecutive spectra were acquired (512 scans/spectrum). Figure 2(b) shows Auger spectra all acquired at 300 K of a clean Pt(111) surface, after the crystal was exposed to 1.0 L of C_2H_2 at 750 K, and after the crystal was exposed to 10 Torr of H_2 for 60 minutes, raised into the UHV chamber, and annealed to 1100 K.

Figure 3. Figures 3(a), (b), and (c) show the $\nu(\text{CC})$, $\delta_s(\text{CH}_3)$, and $\nu_s(\text{CH}_3)$ modes after the crystal was exposed to 10 L of C_2H_4 at 400 K. 1.0 Torr of H_2 was then added and consecutive spectra were acquired (1024 scans/spectrum, approximately four minutes per spectrum). Figure 3(d) shows the $\delta_s(\text{CH}_3)$ peak area after forming CCH_3 and adding the indicated pressures of H_2 . The curves are exponential fits to the data. Time $t = 0$ corresponds to when the scanning of the ethylidyne spectrum was finished but prior to the addition of H_2 to the cell. The initial $\delta_s(\text{CH}_3)$ peak area in (d) is indicated by the solid black circle. The peak area was the same for each H_2 pressure used.

Figure 4. Figures 4(a) and (b) show the $\nu(\text{CO})$ peaks assigned to the bridge and terminal site CO, respectively. The green spectrum shows the CO peaks after 1.0×10^{-2} Torr of CO was added to the cell at 300 K with the Pt(111) surface covered with 0.52 ML of carbon. The red spectrum was obtained after adding 1.0 Torr of H₂ and annealing to 500 K. For comparison, the blue spectrum shows results for the clean Pt(111) surface that was exposed to 1.0×10^{-2} Torr CO. (For interpretation of references to color in this figure, the reader is referred to the web version of this article.)

Figure 5. In Figure 5(a), 5 L of C_2H_4 was exposed to a clean Pt(111) surface at 300 K. In Figure 5(a), 5 L of CO was then exposed to the ethylidyne covered surface. 1.0×10^{-2} Torr of CO was then added. The crystal was then annealed to 500 K. In Figure 5(b), after the 5 L C_2H_4 exposure, 1.0×10^{-2} Torr CO, and 1.0 Torr of H_2 were added, and the crystal was annealed to 400, 450 and 500 K. In both Figures, the cell was then evacuated to a pressure of approximately 10^{-9} Torr.