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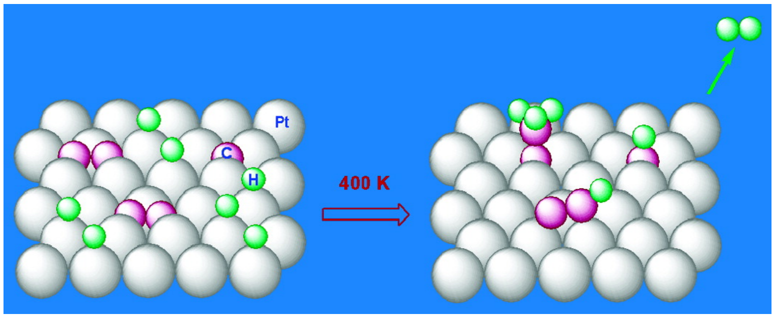

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Identification and Hydrogenation of C_2 on Pt(111)

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Abstract: Reflection absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD) were used to identify the molecular species formed upon the reaction of hydrogen with surface carbon that is deposited by exposing acetylene to a Pt(111) surface held at 750 K. At this temperature, the acetylene is completely dehydrogenated and all hydrogen is desorbed from the surface. Upon subsequent hydrogen exposure at 85 K followed by sequential annealing to higher temperatures, ethylidyne (CCH_3), ethynyl (CCH), and methylidyne (CH) are formed. The observation of these species indicates that carbon atoms and C_2 molecules exist as stable species on the surface over a wide range of temperatures. Through a combination of RAIRS intensities, hydrogen TPD peak areas, and Auger electron spectroscopy, quantitative estimates of the coverages of the various species were obtained. It was found that 79% of the acetylene-derived carbon was in the form of C_2 molecules, with the remainder in the form of carbon atoms. Essentially all of the acetylene-derived carbon could be hydrogenated. In contrast, 85% of an equivalent coverage of carbon deposited by ethylene exposure at 750 K was found to be inert toward hydrogenation.

Introduction

The characterization of the different forms of carbon that exist on transition-metal surfaces is of central importance to a variety of catalytic processes. In some cases carbon blocks active sites and poisons the catalyst, while in other processes carbon reacts on the surface to form the desired products. An example of the latter is the production of hydrocarbons from CO and H_2 by the Fischer–Tropsch process. A recent kinetic study of selectivity in cobalt-catalyzed Fischer–Tropsch synthesis of hydrocarbons explored the role of reactive carbon species, although as is typical in such studies there was no direct spectroscopic identification of the postulated intermediates.[1] The formation of C–H bonds on platinum surfaces is particularly relevant to hydrocarbon reforming. Few surface science techniques are able to distinguish between individual adsorbed carbon atoms and C_2 and higher C_n entitites, although it is known that the complete dehydrogenation of hydrocarbon molecules eventually leads to graphite monolayers.[2] It is not known, however, if the mobile carbon-containing species that aggregate into graphite consists of carbon alone or of both carbon and hydrogen. The identity and stability of surface species that contain only carbon is thus critically important. We recently used reflection absorption infrared spectroscopy (RAIRS) to show that the dissociative adsorption of ethylene on Pt(111) at 750 K produces C_1, which can then be hydrogenated to methylidyne, CH.[3] The results presented here demonstrate that C_1 and C_2 can be detected easily and distinguished through the RAIR spectra of their hydrogenation products.

There are several examples in the literature where the hydrogenation of surface carbon has been characterized with vibrational spectroscopy. High-resolution electron energy loss spectroscopy (HREELS) has been used to identify the CH_x species formed from the hydrogenation of C_1 on Ni(100) and Ru(0001).[4] Smirnov et al. have used HREELS to characterize the hydrogenation of carbon atoms deposited from the gas phase onto a Pt(111) surface held at 100 K.[5] At higher carbon coverages their method produces $C_{x,\mathrm{ads}}$ species, with $x \geq 2$, and they are able to detect with HREELS the formation of ethylidyne (CCH_3), which they attribute to the sequential hydrogenation of a stable C_2 species. The C_2 species that Smirnov et al.[5] observe necessarily is the result of C–C coupling, whereas using isotopically labeled adsorbates we show that the two carbon atoms of the C_2 adsorbate produced from acetylene dehydrogenation originate from the same acetylene molecule. Furthermore, our study appears to be the first to take advantage of the high sensitivity and high resolution of state-of-the-art RAIRS instruments to observe and distinguish several different hydrogenation products of surface carbon.

Experimental Section

The experiments were performed in an ultrahigh vacuum (UHV) system with a base pressure under 1×10^{-10} Torr.[6] The platinum crystal was prepared and cleaned by standard methods.[7] The temperature-

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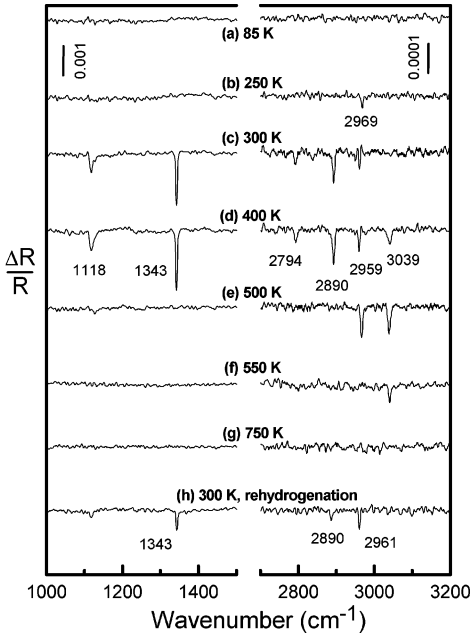

Figure 1. RAIR spectra of the reaction of surface carbon with hydrogen on Pt(111). (a) After a 0.5 L C_2H_2 exposure to the clean surface at 750 K. (b−g) After dosing with 40 L of H_2 at 85 K followed by consecutive annealing for 30 s at 250, 300, 400, 500, 550, and 750 K. (h) Following the 750 K anneal, the surface was cooled to 300 K and exposed to H_2 again. The IR spectra were recorded at 85 K after each anneal.

programmed desorption (TPD) experiments were conducted with a Balzers QMG112 quadrupole mass spectrometer. The heating rate in the TPD experiment is 2 K/s. The RAIRS experiments were conducted with a Bruker IFS-66v/S FTIR spectrometer. To obtain the optimum sensitivity, an InSb detector with a tungsten source was used in the 2200−4000 cm^{-1} range, and a mercury−cadmium−telluride (MCT) detector with a SiC source was used for the 800−2200 cm^{-1} range. Each IR spectrum was recorded with a resolution of 2 cm^{-1} and 1024 scans. The Auger electron spectra (AES) were obtained with a single-pass cylindrical mirror analyzer (PHI 10-155) using a 2 V ptp modulation. The clean Pt(111) crystal was exposed to acetylene, ethylene, and hydrogen by backfilling the chamber. The acetylene (99.6% purity) was purchased from BOC Gases and was subject to further purification by several freeze−pump−thaw cycles before use. Isotopically enriched acetylene ($^{13}C_2H_2$, 99%) was purchased from Sigma-Aldrich. Deuterium (99.5% purity) was purchased from Union Carbide, Inc., and ethylene (99.99%) and hydrogen (99.9999% purity) were purchased from Matheson Tri-Gas Inc.

Results

Figure 1 shows RAIRS results after exposing the surface held at 750 K to 0.5 L of C_2H_2 (L = Langmuir, 1 L = 1 × 10^{-6} Torr s) to produce surface carbon, followed by cooling to 85 K. The first spectrum, (a), is featureless demonstrating that exposure at 750 K leads to the complete dehydrogenation of acetylene, a fact confirmed by TPD measurements. However, after subsequent exposure to 40 L of H_2, and then annealing the surface to the indicated temperatures, several different species are detected. After annealing to 250 K, a C−H stretch mode at 2969 cm^{-1} appears, which we have previously assigned to the methylidyne (CH) species.[3] After the surface was further annealed to 300 K, additional peaks are observed at 1118, 1343, 2794, and 2890 cm^{-1}, which are readily assigned to the ν(CC), $\delta_s(CH_3)$, $2x\delta_{as}(CH_3)$, and $\nu_s(CH_3)$ modes, respectively, of ethylidyne. The peak that appears at 3039 cm^{-1} after the 400 K anneal is the C−H stretch of ethynyl (CCH). Annealing to 500 K results in the dissociation of ethylidyne, as indicated by the disappearance of the ethylidyne peaks, leaving only methylidyne (2959 cm^{-1}) and ethynyl (3039 cm^{-1}) on the surface, with only the latter still present after a 550 K anneal. After heating to 750 K, there is no evidence of any remaining C−H bonds. However, upon cooling to 300 K and exposing to an additional 40 L of H_2, the ethylidyne and methylidyne peaks reappear demonstrating that the reactive C_1 and C_2 species are still present. However, in this case no ethynyl is observed. Methylidyne, ethynyl, and ethylidyne are formed by the reaction of surface carbon atoms and C_2 molecules with adsorbed atomic hydrogen. Only atomic, rather than molecular, hydrogen is expected to be present on the surface as various studies indicate that H_2 adsorbs dissociatively on Pt(111), even at temperatures as low as 85 K.[8]

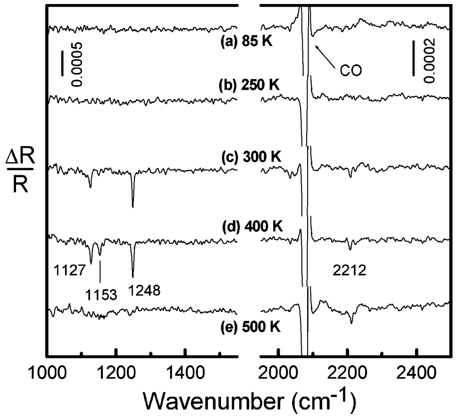

Figure 2. RAIR spectra of the reaction of surface carbon with deuterium. (a) After a 0.5 L C_2H_2 exposure at 750 K. (b−e) After dosing with 40 L of D_2 at 85 K followed by consecutive annealing for 30 s at 250, 300, 400, and 500 K. The IR spectra were recorded at 85 K after each anneal.

Figure 2 shows an experiment similar to that of Figure 1, but using D_2 instead of H_2 to hydrogenate the surface carbon. After the surface was annealed at 400 K, peaks at 1127, 1153, 1248, and 2212 cm^{-1} appear. The one at 2212 cm^{-1} is the C−D stretch of deuterated methylidyne (CD), whereas the other peaks are assigned to deuterated and partially deuterated ethylidyne. Thus, the ones at 1127 and 1248 cm^{-1} are ν(CC) and $\delta_s(CHD_2)$ of $CCHD_2$ and 1153 cm^{-1} is ν(CC) of CCD_3. These vibrational assignments are in agreement with previous studies.[9,10] Deuterated ethynyl (CCD) is not detected, presumably because the C−D stretch of this species is too weak to observe. The observation of H-containing species in Figure 2, even though the surface is exposed only to D_2, is due to adsorption of H_2 from the background. The strong peak at 2075 cm^{-1} is due to the adsorption of CO from the background. Although the CO peak is quite large, because of its intrinsically high intensity the CO coverage corresponding to this peak is only 0.02 monolayer (ML). This is based on the RAIRS intensity of the

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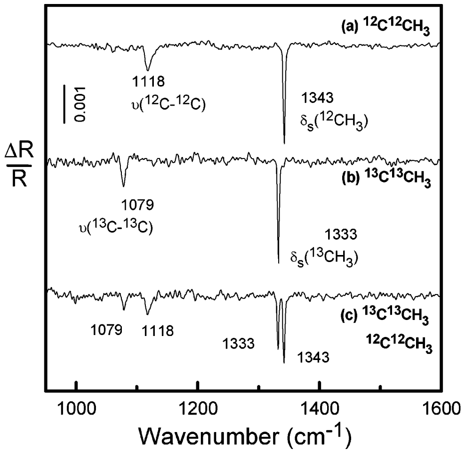

Figure 3. RAIR spectra of ethylidyne and ^{13}C-ethylidyne produced in the hydrogenation of surface carbon. The surface carbon was formed by exposure to the Pt(111) surface at 750 K to (a) 0.5 L of C_2H_2, (b) 0.5 L of $^{13}C_2H_2$, and (c) 0.5 L of a 1:1 gas-phase mixture of $^{12}C_2H_2$ and $^{13}C_2H_2$. Ethylidyne forms after the surface was dosed with 40 L H_2 at 85 K followed by annealing to 400 K for 30 s. The spectra were recorded at 85 K.

on-top CO at a coverage of 0.17 ML.[11] Such a low coverage of CO is unlikely to affect any of the surface chemistry reported here.

The observation of ethylidyne and ethynyl upon hydrogenation clearly shows the presence of the C_2 species on the surface. These C_2 molecules can originate either from C_2 fragments of the acetylene that was initially exposed to the surface at 750 K, or they can be due to a C−C coupling reaction between carbon atoms, as was observed in the work of Smirnov et al.[5] However, the latter possibility can be excluded definitively by the spectra of ethylidyne shown in Figure 3 that were obtained after the hydrogenation of surface carbon formed by exposure of the Pt(111) surface at 750 K to 0.5 L of (a) $^{12}C_2H_2$, (b) $^{13}C_2H_2$, and (c) a 1:1 gas phase mixture of $^{12}C_2H_2$ and $^{13}C_2H_2$. The measured full widths at half-maximum (FWHM) of the ν(CC) and $\delta_s(CH_3)$ peaks are 8 and 2.5 cm^{-1}, respectively, which makes the isotopic shifts easily detectable for both modes. If coupling of carbon atoms were responsible for the formation of the C_2 species that gives rise to ethylidyne upon hydrogenation, then peaks due to the mixed $^{12}C^{13}CH_3$ and $^{13}C^{12}CH_3$ ethylidyne species would have been observed. Instead, the spectrum of the mixture is simply a superposition of the spectra of the $^{12}C^{12}CH_3$ and $^{13}C^{13}CH_3$ species.

Ethylene provides a possible alternative precursor for generating surface C_2 molecules, yet the RAIRS data in Figure 4 demonstrate that it gives a distinctly different result than obtained with acetylene. These spectra were obtained in an analogous fashion to the spectra in Figure 1. The Pt(111) surface at 750 K was exposed to 1.0 L of ethylene and then cooled to 85 K where spectrum a was obtained. No peaks are observed in spectrum a, demonstrating that the ethylene was completely dehydrogenated. After exposing to 40 L of H_2 and annealing to higher temperatures only one peak appears, the methylidyne C−H stretch at 2969 cm^{-1}. The methylidyne dissociates by 550 K, as is characteristic of this species. The surface was heated to 750 K, which as expected yields no peaks. However, subsequent hydrogen exposure again yields a methylidyne peak showing that reactive C_1 species are still present on the surface.

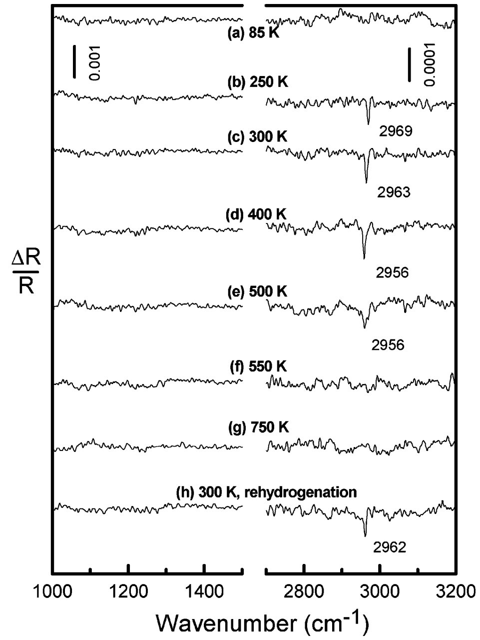

Figure 4. RAIR spectra of the reaction of surface carbon with hydrogen on Pt(111). (a) After a 1.0 L C_2H_4 exposure to the clean surface at 750 K. (b−g) After dosing with 40 L H_2 at 85 K followed by consecutive annealing for 30 s at 250, 300, 400, 500, 550, and 750 K. (h) Following the 750 K anneal, the surface was cooled to 300 K and exposed to H_2 again. The IR spectra were recorded at 85 K after each anneal.

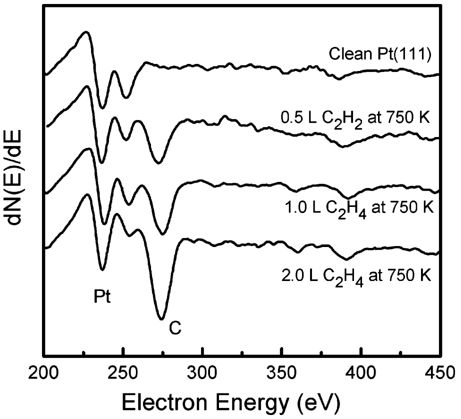

Figure 5. Auger spectra of surface carbon on Pt(111). The carbon layer was prepared by 0.5 L C_2H_2 and 1.0 and 2.0 L C_2H_4 exposures at a surface temperature of 750 K. The spectra were recorded at 300 K.

To control for the possibility that the different nature of the carbon produced from ethylene and acetylene might be due to differences in carbon coverage, AES spectra were obtained as shown in Figure 5. The carbon peak at 273 eV that results from an exposure of 0.5 L of acetylene is of the same height as that produced by a 1.0 L ethylene exposure, whereas a 2.0 L ethylene exposure yields about twice the surface carbon. Thus the RAIRS results in Figures 3 and 4 correspond to approximately the same overall carbon coverage. The AES results can be used to establish the absolute carbon coverage on the surface based on the intensity ratio, I_{273}/I_{237}, of the carbon peak at 273 eV to the Pt peak at 237 eV. By use of ^{14}C to provide an absolute measure of carbon coverage, Davis et al.,[12] determined that for sub-monolayers the carbon coverage is given by $0.62(I_{273}/I_{237})$ with an uncertainty of ±15%. On this basis, the absolute carbon

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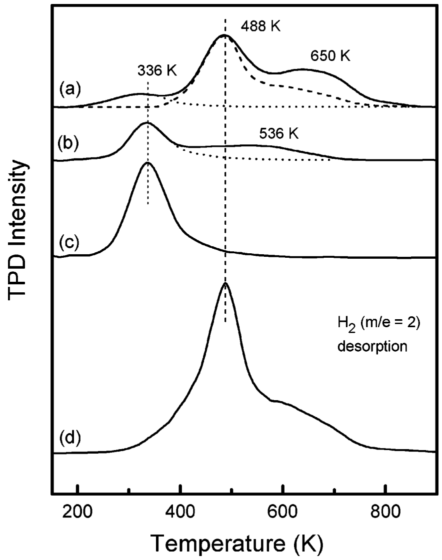

Figure 6. H_2 TPD results from Pt(111) after (a) exposure of 0.5 L C_2H_2 at 750 K and 40 L H_2 at 85 K followed by annealing to 300 K for 30 s, (b) exposure of 1.0 L C_2H_4 at 750 K and 40 L H_2 at 85 K followed by annealing to 300 K for 30 s, (c) exposure to 40 L H_2 at 85 K followed by annealing to 300 K for 30 s, and (d) exposure of 5.0 L C_2H_4 at 350 K.

coverages corresponding to the Auger spectra in Figure 5 are 0.34, 0.39, and 0.74 for the 0.5 L C_2H_2 and 1.0 and 2.0 L C_2H_4 exposures, respectively. As a test of the accuracy of these values, a carbon coverage of 0.44 ± 0.07 was obtained for a carbon layer produced from a saturation coverage of ethylidyne. The ethylidyne-derived carbon layer was obtained by a 5.0 L C_2H_4 exposure at 350 K followed by heating to 1200 K to completely dehydrogenate the ethylidyne to form a graphitic carbon layer. A saturation exposure of ethylene at 350 K is known to give an ethylidyne coverage of 0.25 ML (a carbon coverage of 0.50 ML).[13]

In addition to estimating the carbon coverage by Auger, values for the coverages of the hydrogenated species can be obtained from both RAIRS and TPD data based on known values of the saturation coverages of ethylidyne and hydrogen. A comparison of the ethylidyne RAIRS peak intensities for an ethylidyne coverage of 0.25 ML with the intensity observed in Figure 1 indicates an ethylidyne coverage of 0.11 ML. An independent value for the coverage of ethylidyne produced from carbon hydrogenation can be obtained from the TPD results of Figure 6. This figure shows hydrogen desorption from the hydrogenated carbon layers produced by acetylene and ethylene exposures at 750 K compared with a saturation coverage of hydrogen on the clean surface and with hydrogen desorption associated with the decomposition of 0.25 ML of ethylidyne. Qualitatively, these results confirm the observations made with RAIRS that the carbon layer produced from ethylene (b) differs significantly from the layer derived from acetylene (a). Figure 6a shows hydrogen desorption peaks at 336 and 488 K and a broader peak around 650 K. The first peak represents the recombinative desorption of hydrogen adsorbed on the metal surface. This is confirmed by comparing the hydrogen desorption from the carbon-free Pt(111) surface, Figure 6c, which was produced by dosing the clean surface with 40 L H_2 at 85 K followed by briefly annealing to 300 K. The second peak at 488 K in Figure 6a is clearly the desorption of hydrogen from the dehydrogenation of ethylidyne, as indicted by comparison with the hydrogen desorption from the saturation layer of ethylidyne in Figure 6d. The final stage of hydrogen desorption with a peak temperature of 650 K in Figure 6a is due to the dehydrogenation of methylidyne and ethynyl, as is the high temperature shoulder in Figure 6d. We see in Figure 6a that the amount of this high-temperature hydrogen desorption relative to the 488 K peak is larger compared with the pure ethylidyne decomposition case of Figure 6d. This reflects the fact that the direct hydrogenation of surface carbon produces methylidyne and ethynyl in amounts greater than those that are formed simply from the decomposition of the ethylidyne that is also produced.

For the hydrogenation of the ethylene-derived surface carbon, Figure 6b shows a peak at 336 K and extended higher-temperature desorption with a peak at around 536 K. As in Figure 6a, the first peak represents the recombinative desorption of hydrogen from the metal surface. However, in contrast to Figure 6a, the higher temperature desorption is due solely to the decomposition of methylidyne, the only hydrogenation product of the ethylene-derived surface carbon. This is consistent with the RAIRS data in Figure 4, which reveals that methylidyne decomposes at surface temperatures above 500 K.

The dotted lines in parts a and b of Figure 6 represent the recombinative hydrogen desorption TPD profile taken from Figure 6c but scaled to fit the 336 K peaks. Similarly, the dashed line in Figure 6a represents the hydrogen desorption due to the dehydrogenation of ethylidyne taken from Figure 6d but scaled to fit the 488 K peak. Thus, the fact that the area under the dashed line in Figure 6a is only 53% of the area of the hydrogen TPD curve in Figure 6d for 0.25 ML of ethylidyne implies an ethylidyne coverage due to C_2 hydrogenation of 0.13 ML. This is in good agreement with the coverage of 0.11 ML determined from RAIRS intensities.

Absolute coverages can also be derived from the hydrogen TPD peak areas based on the known absolute hydrogen saturation coverage on the clean surface. An early study[14] shows that, at 150 K, the saturation coverage of atomic hydrogen on clean Pt(111) is $1.2\ (\pm\ 0.4) \times 10^{15}\ \mathrm{cm}^{-2}$ (0.8 ML). The peak area of the dashed curve in part a corresponding to ethylidyne decomposition is 0.39% of the TPD area for a saturation coverage of hydrogen implying an ethylidyne coverage of 0.11 ML, consistent with the estimates given above. Hydrogen that does not originate from ethylidyne decomposition or from recombinative desorption from the metal is obtained by subtracting the areas under the dotted and dashed curves from the total area under the solid curve in Figure 6a. This corresponds to a hydrogen coverage of 0.09 ML and hence a combined methylidyne and ethynyl coverage of 0.09 ML. For the dehydrogenation of the ethylene-derived carbon, the broad peak at 536 K in Figure 6b is equivalent to an H coverage of 0.06 ML. This is also presumably the methylidyne coverage, since this is the only species detected with RAIRS.

Although the H_2 TPD peak areas only provide a combined coverage of ethynyl and methylidyne of 0.09 ML, the use of RAIRS intensities permits the separate coverage of each species to be determined. The ratio of the IR peak intensity for the C−H stretch of methylidyne in Figure 1d to that in Figure 4d is about 2/3. The methylidyne observed in Figure 1d corresponds to the

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Table 1. Absolute Coverages (ML[a]) of Carbon and Hydrogenated Carbon Species

	carbon coverage	CH	CCH	CCH_3
C_2H_2-derived[b]	0.34 ± 0.05	0.04 ± 0.02	0.05 ± 0.02	0.11 ± 0.02
C_2H_4-derived[c]	0.39 ± 0.06	0.06 ± 0.02		

[a] 1 ML = 1.5 × 10^{15} cm^{-2}. [b] Carbon deposited by exposing surface at 750 K to 0.5 L of C_2H_2(g). [c] Carbon deposited by exposing surface at 750 K to 1.0 L of C_2H_4(g).

direct hydrogenation of surface carbon, whereas in Figure 1e, there is additional methylidyne produced from the dehydrogenation of ethylidyne. Because we only want to quantify the methylidyne that is produced from the direct hydrogenation of the acetylene-derived carbon, the methylidyne RAIRS peak in Figure 1d, rather than in Figure 1e is used. This therefore implies that, of the 0.09 ML of hydrogen obtained by subtracting out the dashed and dotted curves in Figure 6a, 0.04 ML is due to methlylidyne and 0.05 ML is due to ethynyl. The acetylene-derived carbon coverages corresponding to ethylidyne, ethynyl, and methylidyne are 0.22, 0.10, and 0.04 ML, respectively. The total carbon coverage associated with these species is thus 0.36 ML, compared with the total carbon coverage of 0.34 ± 0.05 ML determined by AES. This implies that essentially all of the surface carbon produced by a 0.5 L acetylene exposure at 750 K is in a form that can subsequently undergo hydrogenation. This is in marked contrast to the ethylene-derived carbon, where only 15% of the surface carbon can be hydrogenated to CH. The coverages of the various species are summarized in Table 1.

Discussion

There are several previous studies that are highly relevant to the findings reported here. Although our focus is on the C_2 species produced from acetylene decomposition, other studies have focused more broadly on the nature of carbon layers on metal surfaces and their reactivity. Surface carbon is generally divided into two types: carbidic and graphitic, with the latter generally unreactive. Hutson et al. have reviewed the characteristics of the two forms as determined with various electron spectroscopies.[15] The carbidic layers that they considered were made either from CO or C_2H_4 decomposition, and they mainly discussed layers on nickel surfaces. Although as they and others note,[16] AES line shapes can be used to distinguish different forms of surface carbon, our spectrometer does not provide sufficient resolution to do so. Nevertheless, Hutson et al.[15] make some general statements about the temperature range at which carbidic carbon transforms into graphite, which imply that by 750 K, all carbon should be in a graphitic form. Land et al.,[17] used STM to study the thermal evolution of ethylene to graphitic monolayers on Pt(111) and generally found that a temperature of 800 K marked the formation of graphite with lower temperatures giving larger carbon clusters. Perhaps the prior work most relevant to our studies is that of Smirnov et al., who were specifically interested in the reactivity of the surface carbon toward hydrogen.[5] They deposited carbon atoms directly from the gas phase onto a Pt(111) surface held at 100 K, and then studied the reactivity of the carbon layer as a function of annealing temperature with HREELS. They found that temperatures greater than 800 K resulted in the formation of unreactive graphite but that hydrogen was still contained in the hydrogenated layer up to 700 K, as determined by TPD. Their results are similar to ours in that no CH bonds were detectable with HREELS above 550 K. Although Smirnov et al.[5] studied the reactivity as a function of carbon coverage, only their lowest coverages correspond to the coverage that we used. Their conclusion that only CH is produced from a surface covered exclusively with C atoms is consistent with our findings. At higher carbon coverages, C−C bond formation occurs, and they identified the C_2 species through its hydrogenation to ethylidyne. While there have been other reports[18] of C−C coupling reactions on Pt(111), Smirnov et al.,[5] provide a clear case of coupling between carbon atoms rather than by way of a CH_x species. This is why it was important to consider C−C coupling as a possible origin of the C_2 that we detect.

We chose a 0.5 L acetylene exposure at 750 K for several reasons. First, 750 K is a temperature that is high enough to ensure that all of the hydrogen is removed giving a pure carbon layer. Second, based on previous studies it should be low enough to avoid complete formation of unreactive graphite. Third, we found that a 0.5 L exposure gives sub-monolayer coverages thus ensuring that there is sufficient bare metal surface available for the dissociative adsorption of hydrogen. The surprising observation here is that, for the same carbon coverage and the same exposure conditions, acetylene-derived carbon differs from ethylene-derived carbon, with the C_2 species being detected in the former case but not in the latter. Prior to the observation of graphitic carbon with STM for annealing temperatures of 800 K or above, Land et al., observed that carbon was in the form of clusters.[17] In their experiment, they annealed a saturation layer of ethylene to increasingly higher temperatures and observed carbon-containing clusters above 500 K with a bimodal distribution of heights. Clusters consisting of 10 atoms had heights of one atomic layer while two layer high clusters contained 20 carbons. Obviously, STM provides no information on the hydrogen content of the clusters nor do the STM results preclude the possibility that there are isolated carbon atoms or CH species on the surface following ethylidyne decomposition. Our observation that most of the ethylene-derived carbon is unreactive toward hydrogen, with the only active form being carbon atoms that form methylidyne, is consistent with both a large fraction of the carbon being in the form of either graphite or carbon clusters. Although Land et al.[17] do not classify their clusters as graphitic or carbidic, the work of Hutson et al.[15] makes it clear that there is a range of temperatures where a form intermediate between carbidic and graphitic prevails. Since RAIRS only provides information on the carbon that is reactive, it provides essentially no new information on the ethylene-derived carbon, most of which is unreactive.

The fact that most of the acetylene-derived carbon in our experiment is in the form of C_2, where both carbon atoms are derived from the same acetylene molecule, indicates that this form of carbon is both remarkably stable with respect to

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dissociation and unreactive toward agglomeration into larger carbon clusters. However, these C_2 molecules readily react with hydrogen indicating highly selective chemical properties. Furthermore, as our results on the repeatability of the C_2 hydrogenation−dehydrogenation reactions show, there is significant loss in reactive C_2 after annealing the hydrogenated acetylene-derived carbon layer to 750 K. This is not surprising since we are essentially annealing an ethylidyne layer, which is known to produce unreactive graphite by 800 K. The fact that the hydrogen-free C_2 layer shows less tendency than an ethylidyne layer to form graphitic carbon is likely due to a greater mobility of the hydrogenated species. It has been demonstrated that ethylidyne has a high mobility,[19] and this may be a general feature of hydrogenated carbon species as opposed to bare carbon clusters. Finally, the most obvious explanation for the different behavior of ethylene and acetylene upon dosing at 750 K is that the stronger CC triple bond in the latter inhibits C−C bond cleavage during the dehydrogenation reaction, whereas both C−H and C−H bond cleavage occur together for ethylene. It would be an interesting study to perform detailed theoretical calculations for the activation energies for the relevant steps in the decomposition of the two molecules.

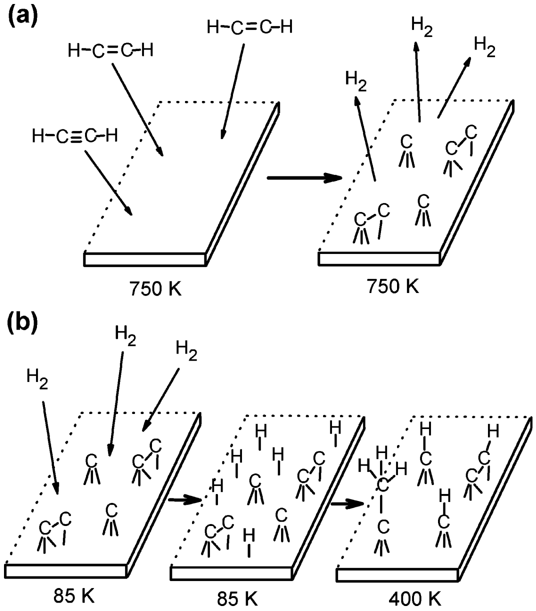

Figure 7. Reaction schemes indicating the species formed upon exposing the surface to acetylene at 750 K (a) and after cooling to low temperature, exposing to hydrogen, and annealing to 400 K (b).

Summary

Upon exposure to a Pt(111) surface held at 750 K, acetylene undergoes complete dehydrogenation to produce surface carbon that is primarily in the form of C_2 molecules with smaller amounts of adsorbed carbon atoms. The C atoms can be hydrogenated to the CH species, while C_2 is hydrogenated to a mixture of ethylidyne (CCH_3) and ethynyl (CCH). Isotopic labeling experiments conclusively demonstrate that both carbon atoms of a C_2 molecule originate from the same acetylene molecule. Subsequent annealing of the hydrogenated carbon layer to 750 K leads to complete dehydrogenation, but carbon atoms and C_2 molecules are still present, although at lower coverage, as indicated by the reappearance of the CH and CCH_3 species upon additional hydrogen exposure. An overall reaction scheme summarizing these findings is given in Figure 7. In contrast, an equivalent coverage of carbon produced by ethylene exposure undergoes significantly less hydrogenation and yields only a low coverage of the methylidyne (CH) species, with most of the carbon in an unreactive form. The unreactive carbon is presumably in the form of graphite, as it is well known that graphite monolayers form on Pt(111) from ethylene decomposition. The different nature of the carbon layers produced from ethylene and acetylene exposures suggests that the higher CC bond order in acetylene leads to significantly different kinetics in the steps between the intact molecule and the carbon layer.

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