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Mechanism of acetylene oxidation on the Pt(111) surface using in situ fluorescence yield near-edge spectroscopy

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Abstract

In situ studies of acetylene oxidation on Pt(111) have been performed with both fluorescence yield near-edge spectroscopy (FYNES) and temperature-programmed FYNES (TP-FYNES) for temperatures up to 600 K and flowing oxygen pressures up to 0.009 Torr. Low-temperature spectroscopic (FYNES) results indicate that at 150 K acetylene adsorbs with the C–C backbone tilted slightly up from the Pt(111) surface, consistent with the formation of an η^2-μ_3-CCH_2 surface intermediate. When acetylene is preadsorbed on the Pt(111) surface, forming the η^2-μ_3-CCH_2 intermediate, oxidation occurs in a single step over the 330–420 K temperature range. In the presence of excess oxygen, little effect on the rate of oxidation is seen when the oxygen pressure is increased, as observed previously for oxidation of adsorbed propyne on the Pt(111) surface. Comparison between the intensity of the C–H σ^* resonance and the intensity in the carbon continuum clearly shows that the adsorbed hydrocarbon intermediate maintains a 1:1 C–H stoichiometry throughout oxidation, suggesting that oxydehydrogenation and skeletal oxidation occur simultaneously above 330 K. Identical reaction temperature profiles observed for (1) reaction of coadsorbed acetylene and atomic oxygen, and (2) reaction of acetylene and oxygen from the gas phase signify that in both cases a direct, bimolecular surface reaction mechanism occurs during oxidation. For the catalytic studies, a large temperature hysteresis, which is associated with inhibition of oxygen adsorption by acetylene, is observed during thermal cycling. Detailed isothermal kinetic studies performed in flowing oxygen pressures indicate that the apparent activation energy for oxidation is 20.3 ± 2.0 kcal/mol with a pre-exponential factor of $10^{10.3\pm1.0}\ s^{-1}$. Taken together, these results clearly indicate that surface properties and reactant properties both play major roles in controlling oxidation reactions over an extended range of reaction conditions.

Keywords: Near-edge X-ray absorption fine structure (NEXAFS); Oxidation; Surface chemical reaction; Platinum; Low index single crystal surfaces

1. Introduction

The catalytic oxidation of simple hydrocarbons such as acetylene is important for hydrocarbon combustion processes, the removal of unburned hydrocarbons from exhaust streams, and calorimetric hydrocarbon sensing. More specifically, platinum-based catalysts are used in the automotive industry to remove unburned carbon monoxide and hydrocarbons from emissions [1]. In this application, the ability to rapidly and completely oxidize carbon monoxide and hydrocarbons is crucial for maintaining optimum emission levels. High-performance catalysts have properties such as high activity, long-term stability, and selectivity, all of which could be enhanced through an understanding of surface reactions. As part of this approach, surface structures and active sites are identified through the use of simplified model systems, such as single crystal surfaces. Despite the importance of hydrocarbon oxidation, molecular mechanisms of catalytic oxidation processes on metal surfaces under ultrahigh vac-

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uum (UHV) conditions are just beginning to emerge [2–11] and have only recently been examined by our group in pressures of flowing oxygen [12–16].

The nature of acetylene bonding on the clean Pt(111) surface remains an active area of research [17–28]. At 90 K, acetylene bonds nearly parallel to the surface and is rehybridized through interaction with the metal orbitals [20]. Ultraviolet photoemission spectroscopy (UPS) and high-resolution electron energy loss spectroscopy (HREELS) studies suggest that below 140 K acetylene is roughly sp^2 hybridized with some additional π bonding that tilts the molecule away from the surface plane [21,24–26]. This tilted geometry for adsorbed acetylene has been supported in recent sum frequency generation (SFG) spectroscopy experiments [17]. Using SFG, the authors found evidence of an adsorbed vinylidene species (η^2-μ_3-CCH_2) on Pt(111) at 125 K. This vinylidene species has also been suggested by other researchers [19,21,28]. During acetylene temperature-programmed desorption (TPD) experiments, hydrogen desorbs in several peaks between 400 and 720 K, above which acetylene becomes fully dehydrogenated to carbon [19,28]. The dehydrogenation reaction has been suggested to progress primarily through this vinylidene, not an ethylidyne, intermediate. The decomposition reaction is limited by the breaking of the C–H bond with an activation energy of 20.6 ± 2.0 kcal/mol and a pre-exponential factor of $10^{8.8\pm1.2}\ s^{-1}$ [19].

Temperature-programmed reaction spectroscopy (TPRS) experiments (UHV conditions) and molecular beam studies (up to 10^{-4} Torr) have previously been used to investigate the reaction of acetylene and oxygen at temperatures up to 1000 K [28,29]. As suggested by the molecular beam study, the first step in the oxidation process was the activation of C–H bonds. Surface carbon then reacts with surface oxygen to form CO, which then either desorbs or oxidizes further to CO_2. Additionally, the author concluded that at high oxygen pressures ($\sim 10^{-4}$ Torr), the reaction rate is limited by the mobility of surface oxygen atoms [29]. In a TPRS study of coadsorbed atomic oxygen and acetylene, it was determined that acetylene oxidation proceeds through an intermediate with 1:1 C–H stoichiometry, suggesting that acetylene is oxidized totally as C_2H_2 [28]. The main oxidation products (and peak temperatures) were CO_2 (330 K) and H_2O (335 K). The activation energies reported for the main peaks were ~ 12.8 and 11.1 ± 1.6 kcal/mol for carbon dioxide and water, respectively. Other detected products and peak temperatures include H_2 (415 K, shoulder at 460 K), CO (535, 640, and 700 K), and O_2 (800 K, only at low acetylene coverages). There was residual carbonaceous residue on the Pt(111) surface after TPRS, and no partial oxidation products were detected [28].

In this work, we report on the oxidation of acetylene over an extended pressure range, with the use of in situ fluorescence yield near-edge spectroscopy (FYNES) techniques. The techniques have previously been applied to characterize mechanisms and intermediates during oxidation of other light hydrocarbons on the Pt(111) surface [12–16]. Spectroscopic results confirm acetylene is adsorbed at 150 K with the C–C backbone tilted away from the surface. This acetylene-derived intermediate oxidizes in one step beginning at 330 K and ending at 420 K. During oxidation, a 1:1 C–H stoichiometry is maintained, suggesting oxydehydrogenation and skeletal oxidation occur concurrently. Similar results were obtained for experiments involving preadsorbed acetylene reacting with flowing oxygen and flowing acetylene reacting with flowing oxygen. These findings have provided detailed insight into the mechanism of acetylene oxidation on platinum catalyst surfaces over an extended range of experimental conditions.

2. Experimental

All experiments were conducted on the U7A beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory with a fluorescence yield detector optimized for carbon fluorescence [30]. The U7A beamline is described in detail elsewhere [12]. The Pt(111) crystal was orientated within 0.5° of the low index plane and was mounted on Ta wire supports attached to the end of a 6-foot liquid nitrogen-cooled re-entrant manipulator insert. Temperature was measured with a Type K (chromel–alumel) thermocouple spot welded to the back of the crystal and was controlled with a RHK temperature controller. The crystal was initially cleaned by cycles of Ar^+ sputtering followed by annealing to 1000 K. Once sulfur was removed via Ar^+ bombardment, the crystal was cleaned by heating to 600 K in 0.002 Torr of flowing O_2 for 60 s, followed by a 20-s anneal at 1000 K. Reactive gases, acetylene-d_2 (Cambridge Isotopes 99%), propyne (Aldrich 98%), and oxygen (Matheson 99.999%l), were background dosed into the chamber with leak valves. Before dosing, propyne was purified by several freeze-pump-thaw cycles. Acetylene-d_2 was used after exchange processes in the gas doser were below 5%. Flow was maintained throughout reactivity experiments with a throttled turbo pump, and oxygen pressures were measured with a capacitance manometer.

Spectra (FYNES experiments) were taken with 150 μm/150 μm slits, yielding an overall energy resolution of 0.4 eV. The spectra of the adsorbed species were corrected by division with a clean spectrum taken during the same ring fill. In analyzing the FYNES data, we placed the carbon edge function at the energy of the XPS maximum of C 1s of acetylene on Pt(111) of 285.0 eV plus the work function of Pt(111) with an adsorbed layer of acetylene of 4.1 eV [31], yielding a placement of 289.1 eV. FYNES spectra were peak-fitted, after subtraction of the carbon step edge function, with the use of Gaussian functions. The functional form of the step edge, location of the step edge, determination of bond angles, and peak fitting in general are described in the literature [32,33].

All kinetic, or transient, experiments were performed with 450 μm/450 μm slits, yielding a 1.2-eV energy resolution and a fluorescence intensity at 330.0 eV in the carbon continuum of 10,000 counts/s for a saturated CO coverage. A 2000-Å, 20% transmittance Al window inserted immediately upstream of the reaction chamber was used for all in situ reactivity experiments. The window allows reaction chamber pressures up to 10 Torr while maintaining UHV conditions upstream of the reaction chamber. All temperature-programmed experiments used a heating rate of 0.5 K/s. Data were averaged over a 4-s interval, yielding a signal-to-noise ratio near 4:1 for a saturated CO coverage. The experimental configuration allows for 2–3 K temperature resolution during the temperature-programmed experiments. Repeated experiments indicate that thermal transitions are reproducible to 2 K. Most transient experiments were done at 330.0 eV (in the carbon continuum) and at normal incidence. At this energy, the signal is an unambiguous determination of the amount of carbon on the surface. Other energies may be monitored to measure the concentration of specific structural aspects of adsorbed molecules that have well-resolved resonances (i.e., C–H σ^* at 288.0 eV). Absolute carbon coverage was determined from a comparison of carbon continuum levels of the TP-FYNES of acetylene and a saturated coverage of CO. Because the absolute surface concentration for a saturated CO coverage is known (9.6×10^{14} CO molecules/cm^2) [34], absolute surface carbon concentrations were calculated and are used throughout this paper. CO fluorescence yields in the carbon continuum (330.0 eV) were monitored to guarantee reproducibility of intensities.

TP-FYNES experiments were conducted in the following manner. First, we cleaned the crystal by heating it to 600 K in oxygen, then flashed it to 1000 K. Once the clean crystal cooled to 150 K, an acetylene coverage was dosed via a leak valve while the surface carbon concentration was monitored at 330.0 eV. When the surface carbon coverage was saturated, the leak valve was closed and oxygen was introduced via a leak valve with the ion gauge off. Reaction pressures were achieved with a combination of pump throttling and leak valve control. Once the desired oxygen pressure was reached and stabilized, the crystal was resistively heated from 100 to 600 K at a rate of 0.5 K/s while fluorescence intensity was monitored.

Catalytic in situ X-ray absorption spectroscopy (CIXAS) experiments were performed in the following manner. While the crystal was cool, the 2000-Å Al window was put in place and the turbo pump was throttled. Acetylene was dosed into the chamber with a variable leak valve, and the pressure was monitored with an ion gauge. Once the desired pressure of the hydrocarbon reactant was maintained, oxygen was introduced into the chamber through another variable leak valve. The ion gauge was turned off, and once the desired oxygen pressure was maintained, the crystal was heated to 600 K, thus creating a clean platinum surface since oxygen was always present in excess. While the fluorescence yield was monitored at 330.0 eV, the crystal was first cooled to 150 K at 0.5 K/s, then heated to 600 K at 0.5 K/s.

Kinetic parameters were obtained through a series of isothermal oxidation experiments. The sample was cleaned, cooled, and dosed with acetylene as in TP-FYNES experiments explained above. Fluorescence intensity in the carbon continuum (330.0 eV) was monitored, providing a quantitative measure of total concentration of carbon on the surface. Then the crystal was rapidly heated to the desired reaction temperature and stabilized (±0.5 K). The carbon concentration as a function of time was fit to the appropriate reaction order decay curve. By performing a series of kinetic experiments at selected oxygen pressures and temperatures, we determined the apparent activation energy, pre-exponential factor, and reaction orders.

3. Results

The fluorescence yield spectra for a saturated coverage of acetylene adsorbed on the Pt(111) surface at 150 K are shown in Fig. 1. The upper spectrum was taken at glancing incidence (30°), and the lower spectrum was taken at normal incidence (90°). The peak assignments were made based on comparisons with similar hydrocarbon NEXAFS spectra (i.e., those of propylene and propyne) and previously published NEXAFS spectra for adsorbed acetylene [12,13,32]. The peak at 284.0 eV corresponds to the π^* resonance of the C–C triple bond. The peak at 288.0 eV corresponds to the C–H σ^* resonance, and the peak at 297.0 eV is the C–C σ^* resonance. The 310.0-eV peak is a manifestation of spectra normalization, and the fit for this peak has been included to aid legibility. The intensity of the π^* resonance at 284.0 eV

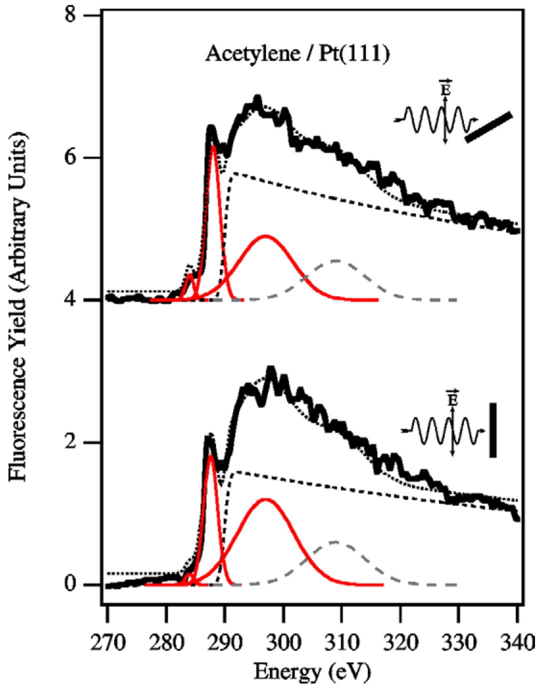

Fig. 1. FYNES spectra of adsorbed acetylene at normal (lower trace) and glancing (upper trace) incidences taken at 150 K.

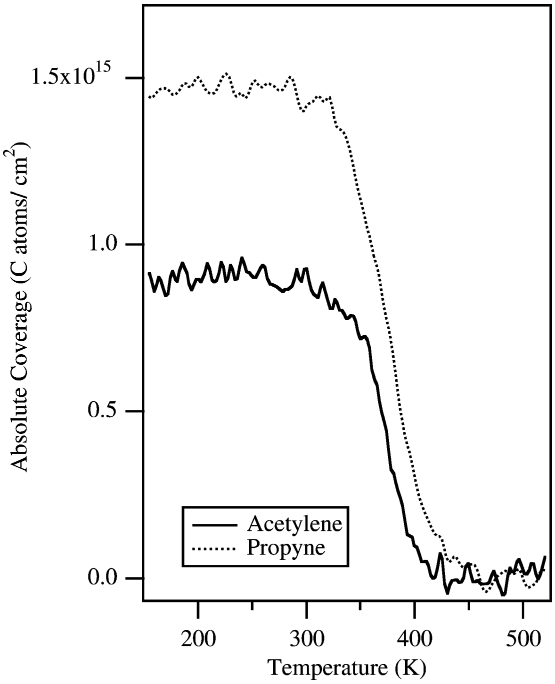

Fig. 2. TP-FYNES of saturated propyne and acetylene coverages in 0.002 Torr of oxygen taken at 330.0 eV. Oxidation occurs in one step for both species, beginning at 330 K until complete at 420 K.

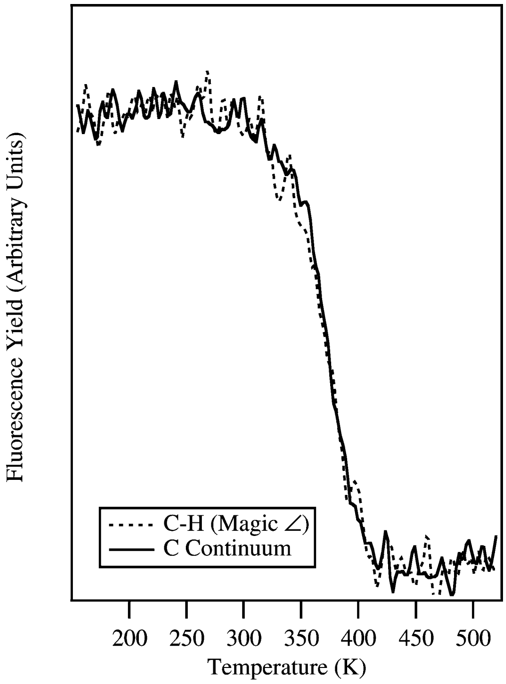

Fig. 3. TP-FYNES of saturated acetylene coverages in 0.002 Torr of oxygen at 288.0 eV (C–H σ^*) and 330.0 eV (carbon continuum) taken at the magic angle. Adsorbed acetylene maintains a 1:1 CH stoichiometry throughout the oxidation process. No oxydehydrogenated intermediates are detected.

is greatly reduced, and the position is shifted down in energy when compared with the peak in acetylene multilayer spectra (data not shown). For the multilayer spectra, the C–C π^* resonance appears at a higher energy of 285.4 eV. For the multilayer spectra, the C–C π^* resonance is the dominant peak, whereas for the monolayer spectra the π^* resonance intensity is decreased markedly.

TP-FYNES oxidation experiments with acetylene (solid line) and propyne (dotted line) in 0.002 Torr of flowing oxygen were shown for comparison in Fig. 2. Both traces are taken at 330.0 eV, in the carbon continuum, so that the intensity represents a direct measure of the total amount of carbon on the surface. With the exception of the initial carbon coverage, the acetylene oxidation spectrum (solid line) is very similar to the propyne oxidation spectrum (dotted line). The saturation level for the propyne coverage is 1.45×10^{15} C atoms/cm^2, whereas the saturation level for the acetylene coverage is 9.1×10^{14} C atoms/cm^2. As observed in the figure, there is no molecular desorption of acetylene or propyne before oxidation begins around 330 K. For both acetylene and propyne, oxidation occurs in one step, beginning at 330 K, and proceeds until all carbon is oxidized at 420 K, suggesting simultaneous oxydehydrogenation and skeletal oxidation, as described in detail in a previous paper [13]. The decrease in carbon concentration is caused by skeletal oxidation, based on previous oxidation studies of propylene and propyne [12,13].

Fig. 3 displays TP-FYNES of saturated acetylene coverages in 0.002 Torr of flowing oxygen taken at two resonances: 330.0 eV, the carbon continuum (solid line), and 288.0 eV, the C–H σ^* resonance (dotted line). Both experiments were conducted at the magic angle, 53.5°, to eliminate any orientation dependence of the intensity [32]. Through a comparison of the intensities of the 330.0-eV trace and the 288.0-eV trace at the magic angle, the C–H stoichiometry may be determined throughout the oxidation process [12]. The fluorescence intensity ratio was calibrated with the use of adsorbates with known C–H ratios. The initial C–H ratio is known to be 1:1 in this case. As illustrated in Fig. 3, the spectra are essentially identical. Therefore, the stoichiometry remains constant at a 1:1 ratio throughout oxidation, clearly indicating that oxydehydrogenation and skeletal oxidation occur simultaneously. The data in Fig. 3, however, do not allow for differentiation between a C_2H_2 species and a CH species.

Fig. 4 compares a TP-FYNES experiment for a saturated coverage of acetylene heated in 0.002 Torr of oxygen (dashed trace) with a TP-FYNES experiment where preadsorbed atomic oxygen (0.25 ML) and acetylene were heated in 0.002 Torr of flowing oxygen (solid trace). Both TP-FYNES spectra were taken at 330.0 eV at normal incidence. Preadsorbed O inhibits acetylene adsorption, as indicated by the decrease in initial acetylene coverage to 7.5×10^{14} C atoms/cm^2 compared with 9.1×10^{14} C atoms/cm^2 for the saturated acetylene coverage (dashed trace). The onset temperature of oxidation for coadsorbed atomic oxygen and acetylene is 350 K, whereas oxidation begins at 330 K for the saturated acetylene coverage. The two oxidation processes are identical above 350 K. For both experiments the carbon concentration decreases dramatically above 350 K until all of the carbon is removed around 420 K.

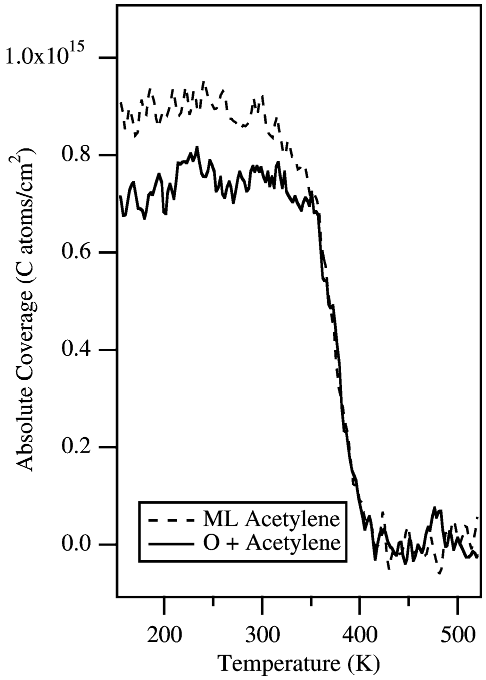

Fig. 4. TP-FYNES experiments of coadsorbed acetylene and atomic oxygen (solid trace) and a saturated acetylene coverage (dashed trace) in 0.002 Torr of oxygen suggest adsorbed atomic oxygen is a main oxidizing species in both cases. Intensities were measured at 330.0 eV.

TP-FYNES experiments for a saturated coverage of acetylene heated in selected oxygen pressures ranging from 0.0005 to 0.009 Torr are shown in Fig. 5. All three experiments began with the same surface carbon concentration of 9.1×10^{15} C atoms/cm^2. The carbon concentration remains unchanged for all three traces up to about 330 K. The onset temperature of oxidation is decreased slightly from 355 to 330 K as the ambient oxygen pressure is increased from 0.0005 to 0.009 Torr. For all three oxygen pressures oxidation continues until the surface is clean above 400 K.

Experiments with both reactants in the gas phase were performed to study the surface under catalytic conditions. Fig. 6 displays a typical CIXAS experiment with both acetylene (1×10^{-7} Torr) and oxygen (0.008 Torr) in the gas phase. The experiment began with a hot (600 K), clean crystal that was cooled at 0.5 K/s to 150 K (dotted trace) in the presence of the gases. The crystal remains clean up to $\sim$ 380 K, where the carbon content on the surface gradually begins to increase. Below 380 K, there is a sharp increase in carbon concentration until the surface reaches saturation by 180 K. The CIXAS saturation level of 7.5×10^{14} C atoms/cm^2 is less than that for a saturated coverage of acetylene (9.1×10^{14} C atoms/cm^2), but is identical to the carbon level obtained when acetylene is coadsorbed with 0.25 ML of oxygen (Fig. 4). Next, the sample was heated from 150 to 600 K, again at 0.5 K/s (solid trace). During heating, the sample remains saturated up to 350 K, where oxidation begins and the carbon level decreases. A clean surface is obtained by 470 K. The difference in coverage for a given temperature is indicative of a hysteresis effect. The heating and cooling segments differ by approximately 80 K under these conditions. Fig. 7 shows the heating segment of a CIXAS experiment in 0.002 Torr of oxygen and 1×10^{-7} Torr of acetylene (dotted line) and a TP-FYNES spectrum of coadsorbed acetylene and atomic oxygen (solid line) also performed in

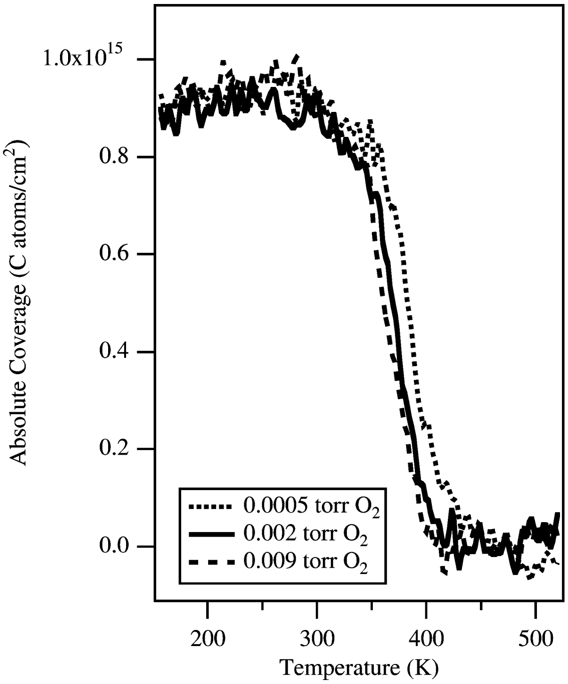

Fig. 5. TP-FYNES of saturated acetylene coverages in pressures up to 0.009 Torr. Onset temperature for oxidation is decreased with increasing oxygen pressure. Intensities were measured at 330.0 eV.

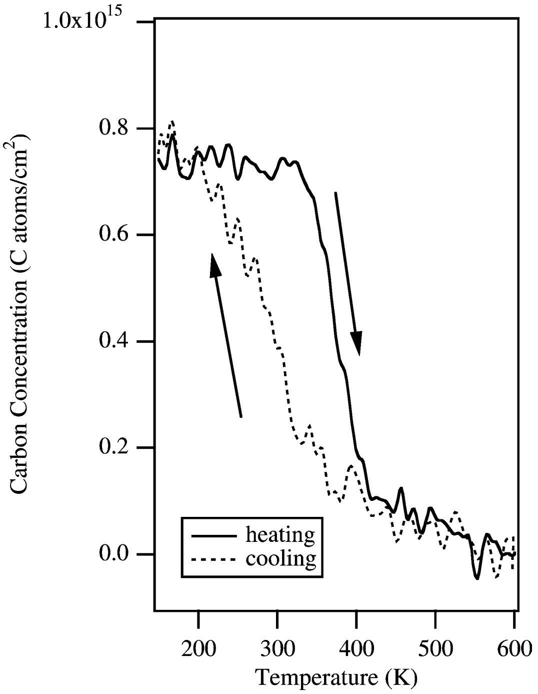

Fig. 6. CIXAS experiment with both acetylene (1×10^{-7} Torr) and oxygen (0.008 Torr) in the gas phase. The hysteresis loop illustrates the competition between oxidation and adsorption. Intensities are measured at 330.0 eV.

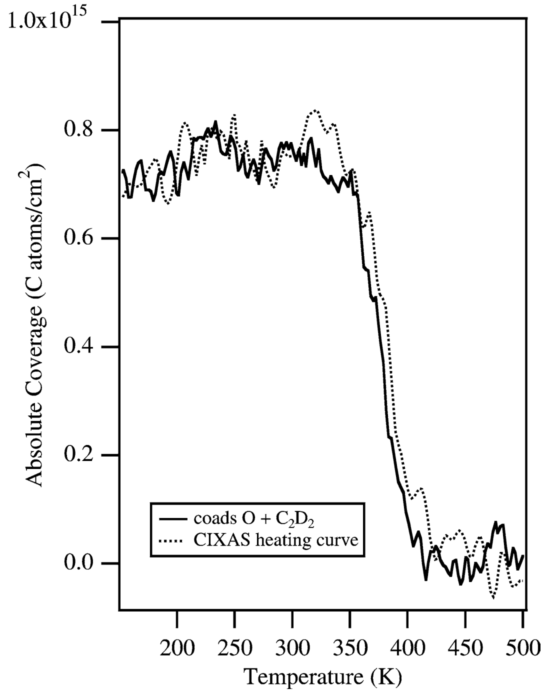

Fig. 7. The heating segment of a CIXAS experiment with 1 × 10^{-7} Torr of acetylene and a TP-FYNES experiment of coadsorbed atomic oxygen and acetylene. Both experiments were performed in 0.002 Torr of oxygen and intensities were measured at 330.0 eV.

0.002 Torr of oxygen, first illustrated in Fig. 4. The carbon saturation concentrations for these two curves are exactly the same, 7.5 × 10^{15} C atoms/cm^2. The spectra for the oxidation of the surface species for these two experiments mirror each other exactly, within the 2–3 K accuracy of the temperature measurement. In both traces, oxidation begins around 350 K and proceeds rapidly until the surface is clean above 420 K.

Isothermal experiments were performed to elucidate kinetic parameters for acetylene oxidation. Oxidation of a saturated coverage of acetylene by 0.002 Torr of flowing oxygen at three reaction temperatures is shown in Fig. 8. For these isothermal experiments, a saturated coverage of acetylene was rapidly heated in the presence of oxygen to the desired reaction temperature and maintained at that temperature (±0.5 K), as indicated by $t = 0$ s. For all temperatures the oxidation reaction stopped by $t = 300$ s. After the reaction stopped, the temperature was increased to 600 K to obtain clean reference levels. The amount of acetylene oxidized increased with increasing reaction temperature. At 350 K, 45% of the acetylene coverage reacted, whereas at 360 K, 70% of the acetylene coverage reacted. Even at high oxidation temperatures and prolonged oxygen exposure times the reaction does not go to completion in this temperature and oxygen pressure range. The carbon concentration decay lines were fit to first-order exponential curves (upper panel). From these exponential fits at high coverages, rate constant values were obtained and used to construct an Arrhenius plot (lower panel). From this plot an apparent activation energy of 20.3 ± 2.0 kcal/mol was obtained with a pre-exponential factor of $10^{10.3\pm1.0}$ s^{-1}.

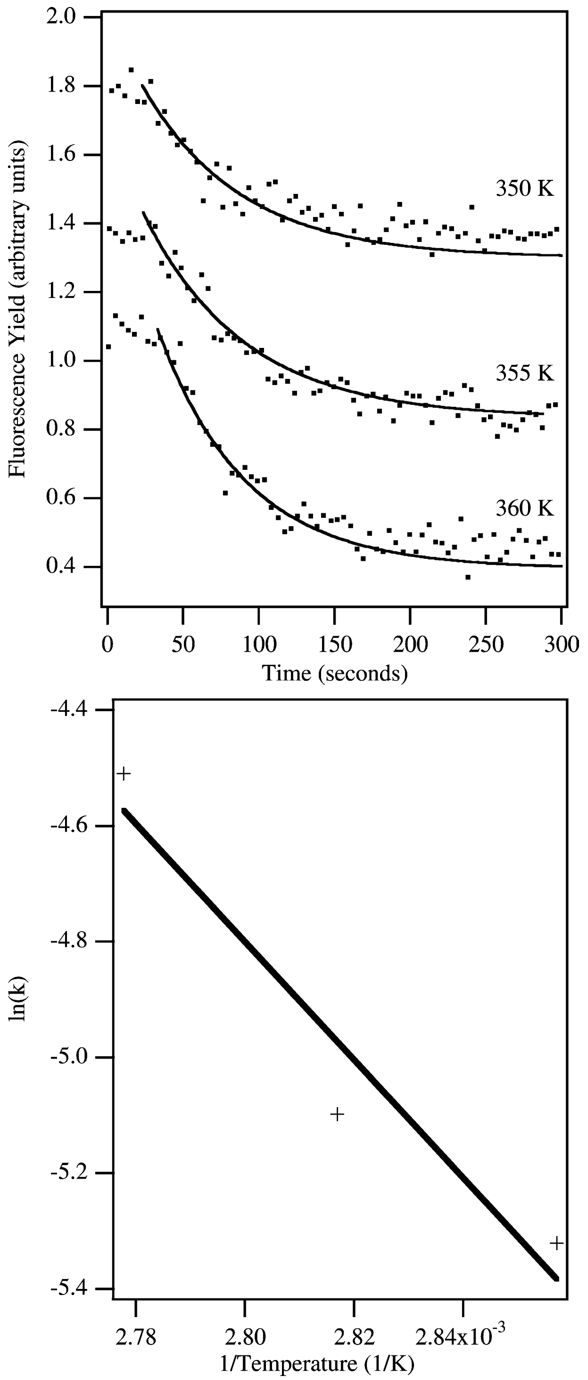

Fig. 8. Isothermal oxidation experiments for saturated acetylene coverages at three temperatures in 0.002 Torr of oxygen (upper panel). Intensities are measured at 330.0 eV. Arrhenius plot (lower panel) yielding an apparent activation energy of 20.3 ± 2.0 kcal/mol at high acetylene coverages.

4. Discussion

With a variety of in situ soft X-ray fluorescence yield techniques, insight has been gained regarding the molecu-

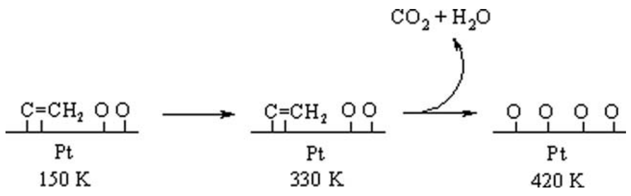

Fig. 9. Mechanism for acetylene oxidation on the Pt(111) surface in pressures of flowing oxygen.

lar mechanism of acetylene oxidation on the Pt(111) surface over an extended temperature and pressure range. FYNES experiments reveal that acetylene is strongly adsorbed on the metal surface. Temperature-programmed studies under a variety of initial conditions produce a clear picture of the stoichiometry of major molecular species involved in the oxidation mechanism. Isothermal oxidation experiments have given additional insight into the reaction kinetics and energetics.

The nature of acetylene bonding to Pt(111) at 150 K has been probed with FYNES (Fig. 1). In the first step of the mechanism, which is presented in Fig. 9, acetylene adsorbs on the Pt(111) surface at 150 K and subsequently rearranges such that the C–C backbone is tilted away from the surface. Comparisons to known standards indicate acetylene bonds to the surface with a 1:1 C–H stoichiometry. Upon adsorption, however, the π^* resonance is greatly diminished when compared with multilayer spectra under similar conditions, indicating π donation to the platinum metal. This decrease suggests a strong bonding interaction between the unsaturated π bonds and the platinum surface, as observed previously for the di-σ-bonded configurations of propylene and ethylene on Pt(111) [12,35]. The C–C resonances present at 284.0 and 288.0 eV indicate that the C–C bond remains intact upon adsorption on Pt(111). The angular dependence of the π system suggests acetylene is bonded with the C–C backbone tilted slightly up from the surface plane. However, exact determination of the C–C bond angle is difficult because of the limited signal-to-noise ratio. Orientation calculations, outlined by Stöhr [32] who used the peak areas of the 284.0 eV π^* transition, yield a tilt angle of approximately 30°. The C–C σ^* peak also suggests that the carbon backbone of acetylene is adsorbed at an angle slightly up from the Pt surface plane. Analysis of the 288.0 eV C–C σ^* peak yields similar results (tilt angle $\sim 30°$). This configuration is consistent with SFG results in which an η^2-μ_3-CCH_2 species is suggested for acetylene adsorbed to Pt(111) at 125 K [17]. This vinylidene species is shown to adsorb with the C–C backbone at an angle up from the surface plane. This configuration of acetylene on Pt(111) at low pressures would agree with the near $sp^{2.5}$ hybridization proposed by several researchers [20,21,24–26]. These results are also consistent with similar studies of propyne on Pt(111), where the C–C backbone was found to adsorb at a small angle to the surface [13].

The absolute carbon concentration for a saturated coverage of acetylene as determined in this study is 9.1×10^{14} C atoms/cm^2 (Fig. 2). Since there are 1.52×10^{15} atoms/cm^2 for Pt(111), this would correspond to a coverage of ~ 0.60 C atoms/Pt atom or ~ 0.30 molecules/Pt atom. The acetylene carbon levels were obtained by direct comparison of fluorescence yield measurements of a saturated CO coverage and saturated acetylene coverage. Since the absolute saturated coverage of CO on Pt(111) is well known (9.6×10^{15} C atoms/cm^2) [34], this method of direct comparison of carbon concentrations is highly reproducible and accurate. This method has been used to determine highly reproducible carbon concentration levels for adsorbed propylene, propyne, benzene, toluene, and ethylene [12–15,35]. The coverage value of 0.30 molecule/Pt atom agrees with the (2×2) structure and 0.25 molecule/Pt atom coverage proposed by other researchers [18,22]. Based on quantitative XPS measurements, the absolute acetylene coverage on the Pt(111) surface at room temperature has been suggested to be 0.53 ± 0.07 molecule/Pt atom, where the authors interpret the (2×2) super structure as a (2×1) superstructure in three domains [27]. This value was obtained by a comparison of C 1s XPS peaks of adsorbed CO and acetylene and relating it to the clean Pt 4f peak. The method outlined in this work compares carbon levels directly and is supported by previous work; thus, a saturation coverage of ~ 0.30 molecule/Pt atom is indicated.

In pressures of oxygen, oxydehydrogenation and skeletal oxidation occur simultaneously for acetylene oxidation on the Pt(111) surface (Fig. 4). This step of the mechanism shown in Fig. 9 is supported by TPRS studies of coadsorbed atomic oxygen and acetylene under UHV conditions [28]. In previous TPRS work, CO_2 and H_2O peaks formed simultaneously with peak maximums around 330 K. There were no H_2 or H_2O peaks below 330 K, indicating that oxydehydrogenation did not occur before skeletal oxidation. The ambient oxygen pressure does not alter this basic mechanism, as observed in Fig. 5. The onset temperature of oxidation decreased slightly from 355 to 330 K as the ambient oxygen pressure was increased from 0.0005 to 0.009 Torr. Similar results were found for propyne oxidation on Pt(111) [13]. Propyne was found to oxidize in one step beginning at 330 K and ending at 420 K over a broad pressure range (UHV to 0.009 Torr of oxygen). This similarity suggests that the C–C π donation to the Pt(111) surface found in propyne and acetylene increases the C–H bond strength, thus limiting oxydehydrogenation. In contrast, oxydehydrogenation precedes skeletal oxidation in propylene, benzene, and toluene oxidation on Pt(111) [12,14,15]. Propylene forms a stable dehydrogenated intermediate (1-methylvinyl) at 210 K, and skeletal oxidation does not occur until 330 K [12]. Initial fluorescence-yield studies of ethylene oxidation on Pt(111) indicate an oxidation mechanism resembling propylene oxidation as opposed to acetylene oxidation [35]. Taken together, the above results clearly indicate that the C–H bond is more reactive in alkenes than in alkynes.

Throughout the oxidation mechanism, a constant 1:1 C–H stoichiometry is maintained, as illustrated in Fig. 3.

Similar results have been found for the TPRS experiments of coadsorbed atomic oxygen and acetylene on Pt(111) [28]. This finding could be explained by one of the two following mechanisms: (1) adsorbed acetylene is oxidized in two steps with a CH intermediate or (2) the adsorbed η^2-μ_3-CCH_2 intermediate remains intact on the surface and is oxidized completely by surrounding oxygen. To compare, oxidation experiments of propyne show a constant C_3H_4 stoichiometry throughout the oxidation process, indicating that propyne remains intact throughout the oxidation process [13]. Propyne and acetylene have similar structures and bond strengths, suggesting they will follow a similar oxidation mechanism. All evidence indicates the C–C bond remains intact until 330 K, and the adsorbed η^2-μ_3-CCH_2 intermediate is the primary hydrocarbon species involved in the oxidation mechanism without any other stable intermediates formed.

Acetylene oxidation experiments with coadsorbed atomic oxygen (Fig. 4) provide additional insight regarding the oxidation mechanism. Skeletal oxidation of acetylene occurs at the same temperature for (1) the reaction of a saturated acetylene coverage in flowing oxygen and (2) the reaction of smaller acetylene coverages (caused by preadsorbed atomic oxygen) in flowing oxygen. This comparison shows that the main oxidizing species involved are the η^2-μ_3-CCH_2 intermediate and atomic oxygen in both cases. These data support a similar oxidation mechanism, even during steady-state catalytic oxidation of acetylene. In Fig. 7, the heating portion of the steady-state catalytic oxidation experiment (flowing acetylene and oxygen pressures) and heating experiments with preadsorbed acetylene and preadsorbed atomic oxygen have identical carbon intensities and temperature profiles over the entire temperature range. These results indicate that coadsorbed atomic oxygen and the adsorbed η^2-μ_3-CCH_2 intermediate are the main species involved in the oxidation mechanism, even under steady-state conditions.

CIXAS experiments were performed with pressures of both oxygen and acetylene flowing over the platinum surface. Fig. 6 illustrates the hysteresis effect observed for acetylene oxidation. Similar behavior has been observed for several catalytic systems that involve inhibition by adsorbed species [36]. In this CIXAS experiment, the hysteresis is associated with the competition between oxidation and reactant adsorption. To illustrate, first the cooling cycle is discussed. Above 500 K, the platinum surface is free of any adsorbed hydrocarbon species (see Fig. 6). In this case, the atomic oxygen on the surface reacts rapidly and removes any hydrocarbons on the surface. As the temperature decreases, the oxidation rates decrease exponentially and the acetylene arrival rate remains constant. Below 380 K, carbon begins to build up on the surface (see Fig. 6). Adsorption of acetylene begins to dominate the competition between adsorption and oxidation in this temperature range. Below 220 K, the surface is saturated with the adsorbed acetylene-derived intermediate and adsorbed atomic oxygen. As the sample is heated, the surface remains saturated with this intermediate until surface reaction between the adsorbed acetylene and atomic oxygen starts at 350 K. Above 350 K, the oxidation rate increases exponentially and the acetylene arrival rate is constant. Above 420 K, the surface is dominated by adsorbed atomic oxygen and the oxidation rate is rapid relative to the acetylene arrival rate. The surface remains in this active state with further increases in temperature. These same hysteresis affects have also recently been observed in temperature-programmed experiments with flowing pressures of propyne and oxygen [37].

The isothermal experiments shown in Fig. 8 have yielded a 20.3 ± 2.0 kcal/mol apparent activation energy for the oxidation of high acetylene coverages. This value compares favorably with isothermal experiments of propyne oxidation on Pt(111), where an activation energy of 17 kcal/mol was obtained [13]. In a coadsorbed atomic oxygen and acetylene TPRS study, an activation energy of 12.8 kcal/mol was obtained [28]. First-order Redhead analysis of the 330 K CO_2 peak observed in the TPRS work yields a 24.3 ± 2.4 kcal/mol activation energy when a 10^{13} s^{-1} prefactor is assumed [38]. The Redhead method and the measured $10^{10.3\pm1.0}$ s^{-1} prefactor yield an activation energy of 20.2 ± 2.0 kcal/mol for these data. Thus, the activation energies obtained from these studies agree favorably with published results.

The isothermal experiments for saturated coverages of adsorbed acetylene in large excesses of oxygen shown in Fig. 8 indicate that the reaction does not go to completion. Although the present experiments probe this reaction in substantial detail, we do not have a definitive explanation of this intriguing result. Similar incomplete reactions were observed for propyne oxidation on the Pt(111) surface under comparable conditions [13]. We do not see any intrinsic heterogeneity in the surface acetylene, and temperature-programmed desorption studies show no intrinsic heterogeneity in the Pt(111) surface. Taken together, these results suggest the incomplete reaction may be associated with induced heterogeneities in reactant coverages that may be associated with adsorbate–adsorbate interactions. Several experiments suggest this phenomenon exists only over a limited temperature and pressure range. Preliminary experiments suggest the reaction does go to completion at higher temperatures and higher oxygen pressures.

In a temperature-programmed desorption (TDS) study of adsorbed acetylene, the activation energy for the initial removal of hydrogen from acetylene was 20.6 ± 2.0 kcal/mol with a pre-exponential factor of $10^{8.8\pm1.2}$ s^{-1} [19]. A comparison of the activation energy obtained in this study, 20.3 ± 2.0 kcal/mol, with the value obtained in the TDS study suggests the oxidation of the acetylene-derived intermediate is most likely initiated by C–H bond activation. This conclusion is supported by a molecular beam study of acetylene oxidation, where research suggests that the initial step in oxidation is the removal of hydrogen atoms from adsorbed acetylene [29]. In all, activation energy results are consistent with experiments on similar hydrocarbons on Pt(111) where the reactions are initiated by C–H bond breaking [13].

However, these experiments clearly show that no measurable concentration of an oxydehydrogenated intermediate builds up on the surface. Therefore, initial C–H bond breaking must be followed by rapid skeletal oxidation.

5. Conclusions

The oxidation of acetylene on the Pt(111) surface was studied over a wide range of temperatures in flowing oxygen pressures up to 0.009 Torr. Based on fluorescence yield spectra, at 150 K acetylene bonds to the Pt surface tilted slightly up from the surface plane via the π system, forming the adsorbed η^2-μ_3-CCH_2 intermediate. In situ experiments clearly show that the acetylene-derived surface intermediate maintains a 1:1 C–H stoichiometry throughout the oxidation process. Therefore, oxydehydrogenation and skeletal oxidation occur simultaneously over the wide range of conditions studied. Based on these results and comparisons with previous studies of propyne oxidation and several literature studies, the C–C bond remains intact during oxidation. For preadsorbed acetylene oxidized by 0.002 Torr of oxygen, an initial activation energy of 20.3 ± 2.0 kcal/mol was determined with isothermal oxidation experiments. All experiments indicate atomic oxygen and the η^2-μ_3-CCH_2 intermediate are the primary species involved in the oxidation mechanism. In experiments with flowing pressures of acetylene and oxygen, a hysteresis loop is present and is caused by the competition between adsorption rates and oxidation rates. The heating cycle of these catalytic experiments yields results similar to those of oxidation experiments with coadsorbed atomic oxygen and acetylene. Taken together, these results suggest that coadsorbed atomic oxygen and the acetylene-derived intermediate are the dominant surface species, even under steady-state catalytic conditions over extended pressure and temperature ranges. Further work on other model catalyst surfaces, such as stepped Pt surfaces and nanostructured Pt thin films, is currently under way. Results from these experiments will be used to bridge the “materials gap” to provide a more complete mechanistic picture of hydrocarbon deep oxidation on platinum catalyst surfaces.

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