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Propylene Oxidation Mechanisms and Intermediates Using in Situ Soft X-ray Fluorescence Methods on the Pt(111) Surface

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Abstract: The oxidation of propylene preadsorbed on the Pt(111) surface has been characterized in oxygen pressures up to 0.02 Torr using fluorescence yield near-edge spectroscopy (FYNES) and temperature-programmed fluorescence yield near-edge spectroscopy (TP-FYNES) above the carbon K edge. During oxidation of adsorbed propylene, a stable intermediate was observed and characterized using these soft X-ray methods. A general in situ method for determining the stoichiometry of carbon-containing reaction intermediate species has been developed and demonstrated for the first time. Total carbon concentration measured during temperature-programmed reaction studies clearly indicates a reaction intermediate is formed in the 300 K temperature range with a surface concentration of 0.55×10^{15} carbon atoms/cm^2. By comparing the intensity of the C−H σ^* resonance at the magic angle with the intensity in the carbon continuum, the stoichiometry of this intermediate can be determined unambiguously. Based on calibration with molecular propylene (C_3H_6) and propylidyne (C_3H_5), the intermediate has a C_3H_5 stoichiometry for oxygen pressures up to 0.02 Torr. A set of normal and glancing angle FYNES spectra above the carbon K edge was used to characterize the bonding and structure of this intermediate. Spectra of known coverages of adsorbed propylene and propylidyne served as standards. The spectra of di-σ propylene, propylidyne, and the intermediate were curve fit as a group with consistent energies and widths of all primary features. Based on this procedure, the intermediate is 1,1,2-tri-σ 1-methylvinyl. The stoichiometry and temperature stability range of the 1-methylvinyl intermediate formed in oxygen pressures up to 0.02 Torr is identical with the stoichiometry and stability of the same intermediate formed during oxidation of preadsorbed propylene by excess coadsorbed atomic oxygen.

Introduction

Catalytic oxidation of simple hydrocarbons is used extensively for the calorimetric sensing of hydrocarbons and for the removal of unburned hydrocarbon from exhaust streams. Despite the importance of deep hydrocarbon oxidation, the molecular mechanisms of deep oxidation processes on metal surfaces have not previously been explored in higher oxygen pressures and are just beginning to emerge in UHV.[1−6]

C_2 oxidation studies on Pt single crystals, foils, and thin films have been reported previously, including studies of the oxidation of ethylene and acetylene by coadsorbed atomic oxygen to form water and carbon dioxide.[5,7−13] The oxidation process on these materials proceeds via sequential oxydehydrogenation followed by oxidation of dehydrogenated surface species. Studies of C_3 oxidation mechanisms have recently been reported on Pt single crystals, foils, and thin films.[14,15] Recently we found that propylene oxidation by coadsorbed oxygen on the Pt(111) surface proceeds via a C_3H_5 intermediate with removal of the vinyl hydrogen based on TPRS studies in UHV.[14] Studies of propylene oxidation with coadsorbed oxygen on a Pt foil and 100 Å Pt films supported on sapphire also indicate that oxydehydrogenation preceded skeletal oxidation.[15] Similar sequential oxydehydrogenation results were obtained during studies of cyclopropane oxidation on the Pt(111) surface.[16] Using a combination of HREELS, TPD, and isotope studies, Madix et al. have recently conducted mechanistic studies of alkene oxidation with coadsorbed oxygen on the Pd(100) surface.[3,4] Sequential oxidation is also observed on the Pd surface where the vinyl hydrogen is removed in the first step followed by skeletal oxidation and removal of methyl hydrogens. They propose that the acidity of the vinyl hydrogen becomes larger than that of the methyl hydrogen because of adsorption induced changes in the vinyl C−H bond strength. A tri-σ propyl species with a stoichiometry of C_3H_5 was proposed as the intermediate for reaction of coadsorbed oxygen and propylene on the Pd surface. TPRS propylene oxidation studies on Rh(111) indicate that increased acidity of the vinyl C−H bond also is involved

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in deep oxidation.[6] A recent study of catalytic alkane deep oxidation on Ni, Pd, and Pt foils indicates that Pt is the most active surface for alkane oxidation, with the C−H bond strength of the alkane dictating reactivity trends.[1] These studies clearly indicate that surface properties and reactant properties both play major roles in controlling oxidation reactions.

The bonding and orientation of propylene to the Pt(111) surface has been studied using NEXAFS.[17] Spectra for ethylene and ethylidyne on the Pt(111) surface are also available in the literature.[18] Both propylene and ethylene bond to the Pt(111) surface in a di-σ configuration. The C−C bond is parallel to the surface in these adsorbed species as indicated by the relative intensities of the π^* and C═C σ^* resonances in normal and glancing incidence. For ethylidyne, the π^* resonance resulting from the carbon p orbitals which bond to the surface confirm the perpendicular orientation of the C−C bond to the surface. The large σ^* C−C resonance observed at glancing incidence is also consistent with the known perpendicular orientation of ethylidyne. The σ^* C−C peak location in ethylidyne at 295.3 eV indicates a shortened C−C bond.[18,19]

Experimental Section

TP-FYNES and FYNES experiments were conducted on the U7A beamline at the National Synchrotron Light Source (NSLS) located at Brookhaven National Laboratory using a fluorescence yield detector optimized for carbon fluorescence.[20] The U7A beamline was recently converted into the toroidal-mirror spherical grating monochromator type similar to the spherical grating monochromator at U4B, described in detail elsewhere.[21] The major difference between the U7A setup and the U4B setup is a reduced acceptance in the horizontal fan from 15 to 10 mrad; however, since U7A only uses one mirror, the flux for the two beamlines is essentially the same.[22]

The U7A beamline surface science endstation is a bilevel experimental chamber dedicated to the investigation of complex surface intermediates important in catalysis.[23] The upper chamber (where these experiments were conducted) consists of two smaller chambers separated by a window valve equipped with a 2000 Å Al window, which is approximately 20% transparent at 330 eV. The chamber upstream of the window is the Io chamber, used to determine incident beam current. The chamber is turbo pumped with two sets of adjustable beam defining apertures used to reduce scattered light. Downstream of the apertures is a Au grid Io for determination of incident beam current. The chamber is equipped with a Au evaporator to reduce any contributions from contaminants on the Io grid. Downstream from the Au grid Io is the 2000 Å Al window. The window remains out for vacuum experiments and is inserted when experiments are conducted in pressures of reactants. Downstream of the Al window is another Au grid Io, followed by a clear path to the sample.

The Pt(111) crystal was mounted on Ta wire supports on the end of a 6 ft liquid nitrogen cooled re-entrant manipulator. Temperature was measured with a 0.01 mm chromel−alumel (type K) thermocouple spot welded to the back of the crystal and controlled with a RHK temperature controller. For all TP-FYNES experiments, a linear heating rate of 0.5 deg K/s was used. The crystal was cleaned by initial Ar^+ ion sputtering followed by annealing to 1000 K. During experimental runs, the sample was cleaned by annealing the crystal to 600 K in 0.002 Torr of oxygen for 1 min, followed by a 20 s anneal at 1000 K. Reactive gases were admitted to the background through leak valves. Flow was maintained throughout reactivity studies using a throttled turbo pump. Oxygen pressures were measured with a capacitance manometer.

Spectra at the U7A beamline were taken at 150 μm/150 μm slits, giving an overall resolution of 0.4 eV. All spectra of adsorbed species were divided by a clean spectrum, taken on the same ring fill, to ensure reproducibility. The kinetic experiments were performed with 450 μm/450 μm slits which results in a resolution of 1.2 eV and an intensity of 10000 cts/s for a CO monolayer with the window in. Data were averaged over a 4 s interval, which resulted in a signal-to-noise ratio of about 4/1 for a CO saturated monolayer. The heating rate was 0.5 deg K/s during temperature-programmed experiments. This combination of experimental considerations limits the temperature resolution for the temperature-programmed experiments to approximately 2−3 K. Repeated experiments indicate the experiments have thermal transitions that are reproducible to 2 K. CO TP-FYNES desorption spectra were used to confirm the performance of this system and reproduce published results. Absolute carbon coverage was determined by comparing the carbon continuum levels observed during TP-FYNES and experiments with a CO monolayer. Since the absolute carbon coverage for a CO monolayer in known to be 0.96×10^{15} molecules/cm^2, it is possible to determine absolute surface carbon concentration for any carbon containing adsorbed species.[24] CO monolayer fluorescence yield at 330 eV was checked regularly to ensure repeatability and consistency of experiments.

TP-FYNES experiments and preparation of surface species were conducted in the following manner. After the crystal was cleaned and cooled to 100 K, a monolayer of propylene was dosed. When the surface carbon concentration reached the saturation level, the leak valve was closed. Oxygen was introduced through a leak valve, the Ion Gauge was turned off, and the ultimate pressure was achieved by a combination of throttling the gate valve on the turbo pump and controlling the leak valve while monitoring the pressure with a 1 Torr capacitance manometer. Throttling the turbo pump resulted in a flowing system with 10% flow. During TP-FYNES experiments, the crystal was heated at 0.5 deg K/s to 600 K while monitoring carbon fluorescence averaged over a 4 s period. For intermediate preparation, the heating was stopped at the appropriate temperature, oxygen was removed (if present), the window was removed, the sample was cooled, and spectra were taken.

TPRS experiments were performed at the University of Michigan in an ultrahigh vacuum chamber equipped with turbomolecular, ion, and TSP pumps which combined to give a base pressure of 1×10^{-10} Torr.[14] The system was equipped with a quadrupole mass spectrometer for TPRS and Auger electron spectroscopy (AES) to verify surface cleanliness. Details of this experimental system and TPRS methods are available in the literature. All TPRS experiments were conducted with a 5 deg K/s heating rate.

Results and Discussion

The oxidation of propylene with both coadsorbed excess oxygen and excess propylene is shown in the left and right panels of Figure 1, respectively. These results were discussed previously[14] and are included for comparison with the in situ results discussed here. In excess oxygen complete propylene-d_6 combustion is observed as indicated in the left panel of Figure 1 (5 deg K/s heating rate). For excess oxygen, the only desorbing species are O_2, D_2O, and CO_2, confirming complete combustion. Propylene-d_6 was used to reduce sensitivity to background water contamination. In excess propylene, molecular propylene desorption and incomplete oxidation are observed along with the complete oxidation as indicated in the right panel of Figure 1. Note that propylene desorbs molecularly in a peak that begins near 230 K and extends up to 285 K.

Experiments conducted at U7A utilized a 0.5 deg K/s heating rate, therefore we can estimate the expected desorption temperature shifts between the TPD experiments and the TP-FYNES

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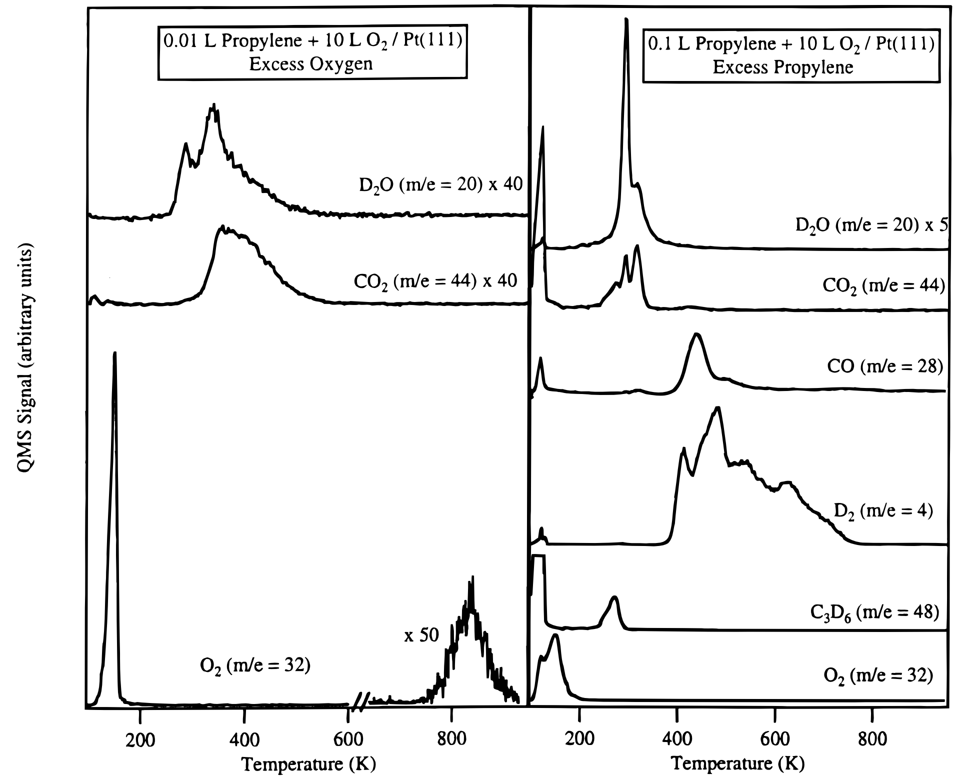

Figure 1. TPRS of coadsorbed propylene-d_6 and oxygen in conditions of excess oxygen and excess propylene-d_6, showing formation of C_3D_5 intermediate (left panel) and desorption of propylene-d_6 at 270 K (right panel).

experiments using a 1st order Redhead method to facilitate direct comparison with the next figure.[25] For the start of propylene desorption the shift is estimated to be 16 K. The propylene desorption peak starting at 230 K for a heating rate of 5 deg K/s would decrease to 214 K for a heating rate of 0.5 deg K/s.

With excess oxygen (left panel of Figure 1) the oxygen desorption trace contains two peaks attributed to desorption of molecular oxygen below 200 K and atomic oxygen recombination and desorption above 800 K. The desorption of excess oxygen confirms that excess oxygen is present through the reaction temperature range on the surface. Water is the only desorbing species containing hydrogen. The D_2O desorption trace has two features at 285 and 340 K. Based on careful peak fitting and integrating, the first peak at 285 K represents the loss of one deuterium from the propylene reactant.[14] CO_2 desorption coincides with the second water desorption trace beginning at 320 K and continues to 470 K. Propylene deep oxidation on the Pt(111) surface begins with oxydehydrogenation at 285 K before skeletal oxidation proceeds at 320 K and above.

In situ studies of oxidation of preadsorbed propylene monolayers in three pressures of oxygen ranging from 0.0005 to 0.02 Torr are shown in Figure 2. During these reaction experiments the concentration of carbon-containing species was measured by monitoring the fluorescence intensity at 330 eV in the carbon continuum. This measurement provides a quantitative measure of total concentration of carbon on the surface. Calibration of this signal was based on the well-known saturated CO monolayer concentration as indicated in the Experimental Section. Propylene was preadsorbed on the clean Pt(111) surface at 100 K, oxygen was introduced, and the sample was heated at 0.5 deg K/s while the carbon continuum fluorescence was monitored. A saturated propylene monolayer results in a carbon coverage of 0.90 × 10^{15} carbon atoms/cm^2 or 0.30 × 10^{15} propylene molecules/cm^2. The carbon concentration remains constant until 215 K where a sharp drop in the surface carbon concentration is observed independent of oxygen pressure. This initial drop is caused by the desorption of molecular propylene as seen in propylene desorption in the right panel of Figure 1. The temperature of desorption agrees with the estimated propylene desorption temperature of 214 K at 0.5 deg K/s and is independent of oxygen pressure as expected. Desorption of propylene is complete by 250 K at a 0.5 deg K/s heating rate.

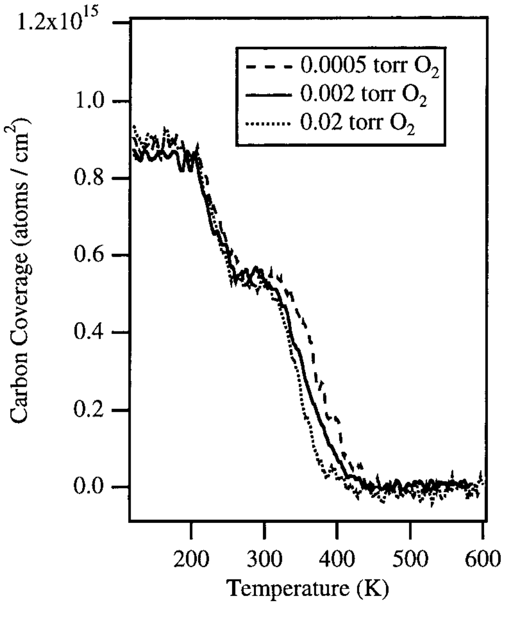

Figure 2. TP-FYNES of propylene in three O_2 pressures at 330 eV. After propylene desorption at 220 K, a stable carbon concentration is observed in the 275−320 K range, followed by a decrease at 350 K caused by skeletal oxidation.

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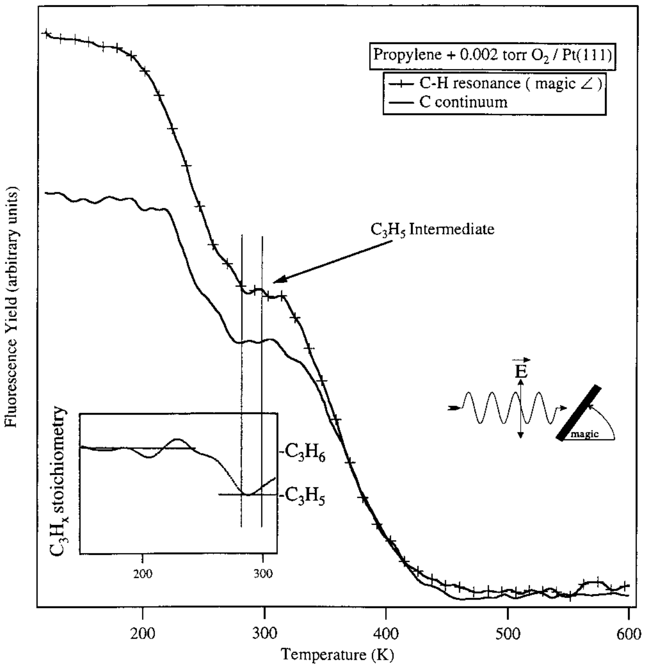

Figure 3. TP-FYNES of propylene in 0.002 Torr of oxygen taken at the C−H σ* resonance and carbon continuum, indicating the formation of a stable C_3H_5 intermediate at 285 K (inset).

The dominance of propylene desorption in this transition is further supported by stoichiometric determinations discussed later in this paper. With further increases in temperature, the surface carbon concentration remains constant at 0.55 × 10^{15} carbon atoms/cm^2 for nearly 50 deg. With temperature increases above 300 K the surface carbon concentration decreases until all the carbon has been removed. The initiation temperature for the second drop depends on oxygen pressure with larger oxygen pressures resulting in more rapid carbon removal. For an oxygen pressure of 0.0005 Torr, the rapid decrease begins near 325 K and is complete by 450 K (Figure 2, right trace). For a higher oxygen pressure of 0.02 Torr the carbon decrease begins near 305 and ends near 400 K (Figure 2, left trace). This second decrease in carbon concentration occurs in the temperature range associated with skeletal oxidation.

In addition to measuring carbon concentration, fluorescence yield can be used to measure the concentration of specific structural aspects of adsorbed molecules which have well-resolved resonances. For dipole transitions in a fixed reference frame, the intensity of molecular resonances is independent of orientation of the molecule at the "magic angle" of 55°.[26] The intensity of the C−H σ* resonance at the magic angle was determined during a series of TP-FYNES experiments so that the stoichiometry of adsorbed species could be determined for a range of temperatures and oxygen pressures. The intensity of the C−H σ* at 287.8 eV and 55° together with the carbon continuum intensity at 330 eV is shown in Figure 3 for 1 ML of preadsorbed propylene which is undergoing oxidation in 0.002 Torr of O_2. The TP-FYNES of the C−H σ* resonance was taken at the magic angle so that the C−H σ* concentration could be determined accurately and calibrated by referring to the adsorbed propylene reactant. As shown later in Figures 4−6, the C−H σ*resonance is quite intense for these hydrogen-rich C_3 surface species and appears at 287.8 eV for all three species. In addition, the C−H σ* is well separated from other resonances and is well below the carbon edge so its intensity is a good measure of the number of C−H bonds. Both the C−H σ* and carbon continuum TP-FYNES remain constant from 100 to near 220 K, both signals decrease from 220 to 260 K, both remain constant from 285 to 310 K, and a second decrease is observed from 310 to 430 K. However, quantitative comparison clearly shows that the initial decrease for the C−H σ* resonance intensity is larger than the decrease in the carbon continuum intensity. Determination of C−H stoichiometry is made by dividing the two resonances. With the initial stoichiometry known at 150 K (C_3H_6), this division will indicate any changes in that stoichiometry. Inset in Figure 3 is the ratio of the intensities of the two resonances, calibrated against the C−H stoichiometry for propylene (C_3H_6) the reactant. The C−H stoichiometry remains C_3H_6 until 260 K, where a decrease in the relative intensity of the C−H σ* is observed. After the decrease ends at 285 K, a stable C_3H_5 stoichiometry is observed. The drop in H stoichiometry corresponds with water formation (compare Figure 1).

Table 1. FYNES Peak Positions (eV)

	π*	C−H σ*	C=C σ*		
propylene					
glancing	284.0	287.8	291.4	296.6	310
normal	283.8	288.0	291.8	296.0	307
propylene/Ag(110)[29]	285.0	288.4	293.0	299	
propylidyne					
glancing	284.0	287.8	291.0	294.8	309
normal	284.2	287.8	290.8	294.8	313
intermediate					
glancing	283.8	287.8	291	295.8	313
normal	284.0	287.8	291	296.4	311

FYNES. The fitted FYNES spectra of propylene, propylidyne, and the oxidation intermediate are shown in Figures 4−6. The analyses of the propylene and propylidyne spectra are included in this paper to assist in the identification of the oxidation intermediate. The spectra of these three related species were taken on the same ring fill, reducing effects from changes in background scattered light, with fluorescence yield normalized to ring current using the gold grid Io as described in the Experimental Section. Spectra were taken at two incident angles, 90° (normal) to the surface and 30° (glancing) to the surface for each of the species. All spectra are divided by a clean spectrum taken during the same fill, thus removing the detector function from the spectra and minimizing the effect of scattered light in the spectra. The spectra were normalized to the carbon continuum and were fitted as a group, using common peak fitting parameters including placement and width. The carbon edge function was placed at the energy of the XPS maximum of C1s of propylene on Pt(111) of 285.0 eV plus the work function of Pt(111) with an adsorbed layer of propylene of 4.4 eV,[27] yielding a placement of 289.4 eV. Spectra were fitted after subtraction of the carbon step edge using a combination of Gaussian and asymmetric Gaussian functions. The functional form of the step edge, location of the step edge, determination of resonance angle, and FYNES peak fitting in general is described in considerable detail by Outka and Stohr in refs 26 and 28. The location of all the peaks is reported in Table 1.

Propylene. Spectra of a monolayer propylene on the Pt(111) surface taken at normal and glancing incidence are shown in Figure 4. This saturated monolayer contains 0.90 × 10^{15} carbon atoms/cm^2. The assignments of the resonances are based on literature assignments, propylene on Ag(110),[26] ethylene on Pt(111),[18] and propylene on Pt(111).[17] The resonances observed

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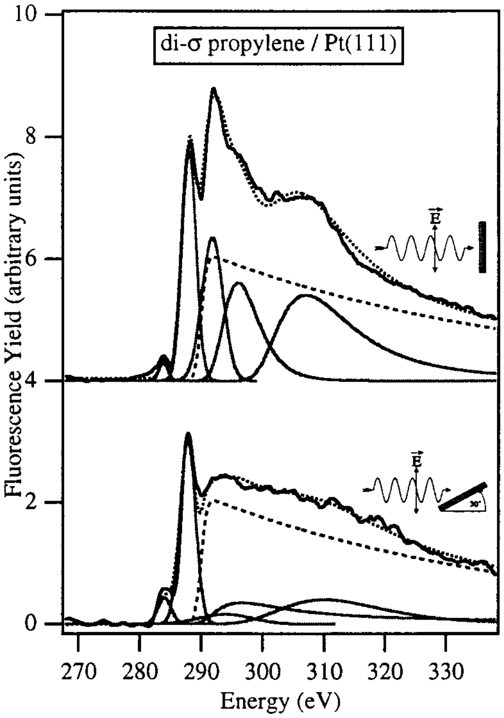

Figure 4. Normal and glancing spectra of propylene indicating a di-σ adsorption nearly parallel to the surface. Spectra of 1 ML of propylene were taken at 100 K.

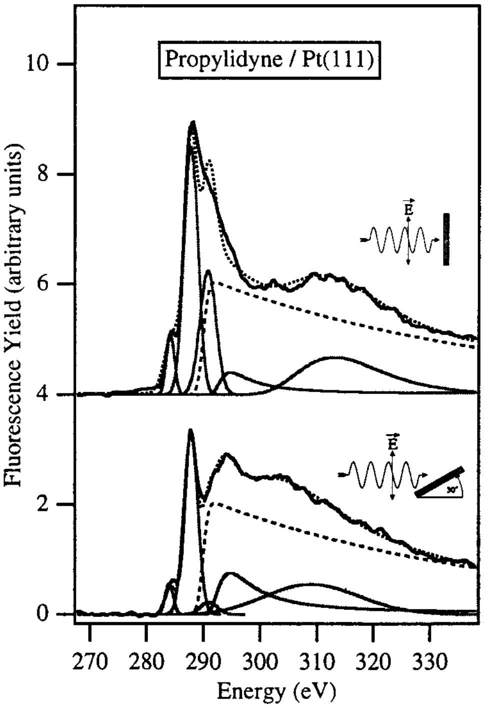

Figure 5. Normal and glancing spectra of propylidyne. 1 ML of propylene was heated to 330 K in a vacuum and cooled to 150 K.

in Figure 4 have been assigned as the following: 284 eV is C═C π *; 288.0 eV is C−H σ*; 293.8 eV is C−C σ*; and 296.0 eV is C═C σ*. The resonance above 310 eV was not assigned but is thought to be a multiple scattering peak and has been observed in NEXAFS spectra for several adsorbed species including propylene on Ag(110).[29] Recent experiments confirm that this resonance is not Pt−C bonding, due to its existence in multilayer spectra of propyne on Pt(111).[30] The published geometry for adsorbed propylene on Pt(111) is a di-σ configuration adsorbed parallel to the surface as determined by EELS[31] and previous NEXAFS studies.[17] No uncertainty was given for the orientation of propylene in the previous NEXAFS study. In this study (Figure 4), the presence of a very small C═C π* in the normal incidence spectrum and a stronger C═C π* resonance in the glancing incidence spectrum indicates propylene is adsorbed nearly parallel to the surface. Calculations based on the degree of polarization of the incident light indicate the C═C π* resonance is oriented 10° from the surface normal and therefore propylene is adsorbed at a 10° angle to the surface. A strong C═C σ* resonance in the normal spectrum and a very weak to nonexistent resonance in the glancing spectrum also indicates propylene adsorbs nearly parallel to the surface (exact calculations cannot be done due to the uncertainty in the step function). Analysis of the normal and glancing incidence propylene spectra confirms previously reported results, with propylene adsorbed nearly parallel to the surface in a di-σ configuration.

The C−H σ* resonance can also be used to help determine adsorbate orientation due to its large intensity and location below the carbon edge. Below the carbon edge the uncertainty in edge height and width is removed as variables in the peak fit and integration. Analysis of the C−H σ* resonance supports a di-σ, near parallel configuration for adsorbed propylene. Assuming parallel adsorption in a di-σ configuration, the olefinic hydrogens are oriented 30° from the surface plane. Projection of the free rotating methyl group (also 30° from the surface plane) indicates the average position of the C−H bond in the methyl group is 36° from the surface normal. Assuming equal contributions from all C−H bonds in the adsorbed propylene, the average C−H bond is 33° from the surface normal. Analysis of the C−H σ* resonances gives an average of 30° from the surface normal. The agreement between these numbers lends strong support to a nearly parallel adsorbed configuration. Although the calculation involves the averaging over 6 hydrogens, the actual calculation is fairly accurate, for the C−H σ * resonance occurs before the step edge and therefore is independent of the fit of the atomic edge jump.

The FYNES spectrum of propylene on Pt(111) is very similar to the published spectrum with a few minor differences. Our spectrum indicates a small π* resonance in normal incidence, whereas the published spectrum does not. This small resonance gave the orientation of the C1−C2 bond on Pt(111) to be 10° to the surface, instead of parallel to the surface. This difference may be a result of limited signal-to-noise ratio in the previous published spectra. Our spectra also include the addition of two new peaks, the C−C σ* resonance at 291.4 eV and the 310 eV multiple scattering resonance. Both new resonances appear to be present in the published propylene spectra; however, they are difficult to identify due to the signal-to-noise ratio.

Propylidyne. The orientation and bonding of propylidyne has also been verified on the Pt(111) surface, with the C1−C2 bond perpendicular to the surface.[32] The concentration of the propylidyne monolayer is 0.55 × 10^{15} carbon atoms/cm^2. The resonances in the spectra (Figure 5) have been assigned based on the previous propylene assignments and the NEXAFS assignments of ethylidyne on Pt(111).[18] The resonances are

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assigned as follows: As with ethylidyne, the 284 eV resonance involves the C1 p-orbitals triple bonded to the surface; like propylene, 287.8 eV is C−H σ*; the two peaks at 290.8 and 294.0 eV are the two C−C σ* resonances, the lower energy resonance (most apparent in the normal spectra) being the C2−C3 σ* resonance and the higher energy resonance (most apparent in the glancing spectra) being the C1−C2 σ* resonance. Again, the 310 eV peak is multiple scattering resonance described for propylene above. The orientation of propylidyne on the surface was analyzed using glancing and normal spectra.

Using the p-orbital resonance at 284 eV, the orientation of the orbital is estimated to be nearly parallel to the surface (10°). Similar to ethylidyne, the C1−C2 σ* resonance at 294.8 is much larger at glancing incidence than at normal incidence. The analysis of these two resonances indicates a C1−C2 bond nearly perpendicular to the surface, similar to ethylidyne. The C−H σ * resonance intensity has been used to confirm possible orientation. With a perpendicular C1−C2 bond, the two hydrogens and methyl group on C2 bond 19.5° from the surface plane. Projection of the average orientation of the methyl group yields an average of 39° from the surface plane for the average C−H bond. Averaging with the other two hydrogens gives an overall C−H orientation of 31° from the surface normal for propylidyne oriented normal to the surface. Analysis of the C−H σ* resonance data shown in Figure 5 gives an average orientation of 28° from the surface normal for the C−H bonds. This good agreement lends support to a near perpendicular orientation of the C1−C2 bond. Using other resonances to determine orientation is difficult for propylidyne due to possible overlap and the effect of step height on the overall area of resonances. The orientational information in the propylidyne spectra supports the current understanding of propylidyne orientation on the Pt(111) surface.

The FYNES spectrum of propylidyne compares nicely to the published spectrum of ethylidyne, with the major spectral differences attributed to propylidyne's additional methyl group. Similarities can been seen in the resonances associated with C−Pt bonding at 284 eV and the C1−C2 σ* resonance at 294.0 eV. The additional methyl group can be seen in the larger C−H σ* resonance in both normal and glancing incidence and the highly angular dependent C−C σ* resonance at 291.0 eV as compared to the published ethylidyne spectrum.

Propylene Oxidation Intermediate. The propylene derived intermediate was prepared by heating a saturated layer of propylene containing 0.90 × 10^{15} carbon atoms/cm^2 in the presence of 0.002 Torr of oxygen to 275 K. This resulted in the formation of an intermediate containing 0.55 × 10^{15} carbon atoms/cm^2. The oxygen was removed and the spectrum were taken at 275 K. The spectrum of the propylene oxidation intermediate is similar in many ways to the spectrum of adsorbed propylene. The normal and glancing spectra (Figure 6) contain five resonances that have been assigned based upon the assignments for propylene and propylidyne: 284 eV is the carbon p-orbital bonded to the surface as in propylidyne, or the π* resonance seen in propylene; 289.8 eV is C−Hσ*; 290.8 eV is C−Cσ*; 295.8 is another C−Cσ*; and 310 eV is the multiple scattering resonance. These spectroscopic similarities are the result of similarities in the basic molecular framework of these C_3 species.

The intensity differences discussed below clearly indicate that the bonding with the surface is different for these three species. The stoichiometry of the intermediate was determined to be C_3H_5 by TP-FYNES as shown in Figure 3 and discussed above. Even though the stoichiometries of the intermediate and propylidyne are the same, comparison of the spectra clearly indicates that the oxidation intermediate is not propylidyne. The next three paragraphs discuss the specifics of the π* and σ* resonances.

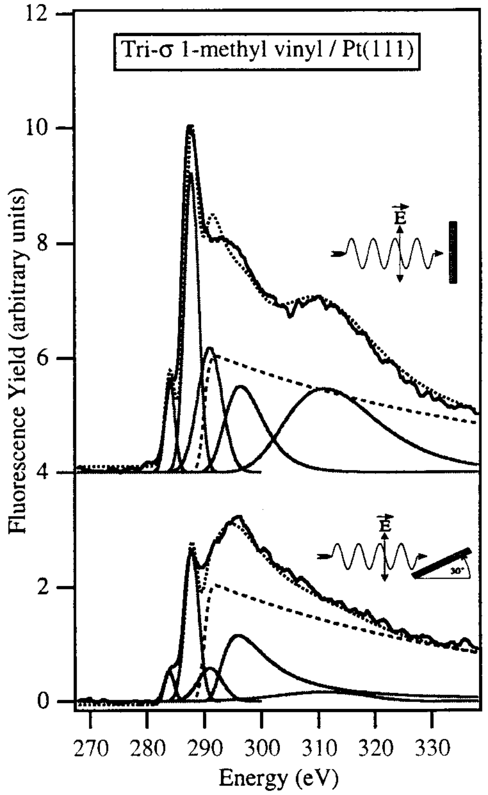

Figure 6. Normal and glancing spectra of the oxidation intermediate, 1-methylvinyl. 1 ML of propylene was heated in 0.002 Torr of oxygen to 275 K.

The resonance at 284 eV could be the result of π orbitals in the di-σ bonding of propylene, or the π orbitals of a multiply bound carbon. The angular dependence of the resonance intensity indicates the orbital is nearly parallel to the surface, whereas the π* from adsorbed propylene was nearly perpendicular to the surface plane. The orientation of the resonance at 284 eV suggests that the intermediate contains a carbon with multiple bonds to the surface.

The C−H σ* resonance at 289.8 eV has a large dependence upon incidence angle. Analysis indicates the average C−H σ* resonance is 20° from the surface plane, much closer to the surface plane than either propylene or propylidyne. The rotation of the methyl group away from the surface, due to loss of the vinyl hydrogen, would reorientate the three methyl hydrogens closer to the surface plane and account for this feature.

The C−C σ* resonance near 296 eV contains orientational information as well. The C−C σ* resonance at glancing is much larger than that for propylene, indicating that on dehydrogenation the average C−C bond moves toward the surface normal. In combination with the change in the average C−H orientation, the reorientation of the C−C bonds appears to be caused primarily by rotation of the methyl group away from the surface plane on dehydrogenation.

These results indicate that adsorbed 1-methylvinyl is the dominant intermediate for propylene oxidation on the Pt(111) surface over a wide range of pressures. For coadsorbed oxygen, a similar intermediate was proposed for propylene oxidation on Pt(111)[14] and Pd(100).[4] The 1-methylvinyl intermediate formed on the Pt(111) surface is formed by oxidative removal

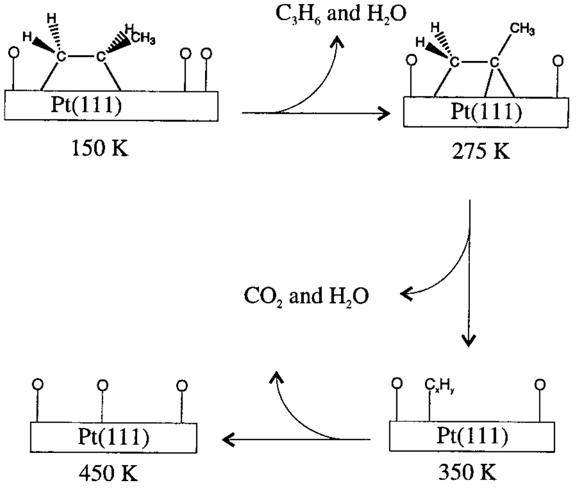

Figure 7. Cartoon representing oxidation pathway of propylene in excess oxygen.

of the vinyl hydrogen from adsorbed propylene, replaced with a surface bond. The C1 in this species has one surface bond, and the C2 has two surface bonds rotating the methyl group toward the surface normal. Since the C1−C2 bond is expected to remain essentially parallel to the surface, the two hydrogens on C1 remain at 30° to the surface normal (as for propylene). The average projection of the free rotating and upturned methyl hydrogens is 19° (from 36° in propylene). Therefore the average hydrogen in the proposed intermediate would be expected to have a bond angle of 23° to the surface plane, with the FYNES data indicating the average C−H bond angle to be 20°. This agreement between the proposed structure and the C−H experimental data provides clear support for the proposed bonding of 1-methylvinyl.

In summary, the combination of the stoichiometric and spectroscopic techniques clearly indicates a 1-methylvinyl intermediate formed over a wide range of pressure during oxidation of propylene. This is an interesting species where C2 is doubly bound to the surface causing a reorientation of the methyl group. Multiple bonding of C2 to the surface and the upturned methyl group is indicated by the π^*, C−H σ^*, and C−C σ^* resonances.

Mechanism. The combination of TP-FYNES, FYNES, and TPRS led us to the mechanism shown in Figure 7. Coadsorbed propylene and atomic oxygen are on the surface at 150 K. Upon heating to 275 K, both propylene and water desorb, resulting in formation of the 1-methylvinyl intermediate coadsorbed with atomic oxygen. By 350 K skeletal oxidation has begun, with dehydrogenated (hydrogen poor) hydrocarbon components remaining on the surface, to be fully oxidized away by 450 K. The mechanism shown in Figure 7 is stable for a very wide range of conditions. From UHV with coadsorbed oxygen to 0.02 Torr of oxygen, the oxidation of propylene proceeds through the 1-methylvinyl intermediate after the removal of the vinyl hydrogen.

Conclusions

The oxidation of propylene on the Pt(111) surface was studied and characterized over a wide range of oxygen pressures, from coadsorbed oxygen in UHV to 0.02 Torr of oxygen in the gas phase. A stable oxidation intermediate was observed for propylene oxidation and characterized using both TP-FYNES and FYNES. Comparison of the C−H σ^* resonance at magic angle and C continuum determined the stoichiometry of the C_3H_5 intermediate. Comparison of the FYNES spectra of propylene, propylidyne, and the intermediate indicated that the intermediate is an adsorbed 1-methylvinyl species adsorbed nearly parallel to the surface. In both UHV and 0.02 Torr of oxygen, oxydehydrogenation of adsorbed propylene occurs prior to skeletal oxidation creating this intermediate. Further oxidation of the intermediate temperatures above 320 K depends on oxygen pressure and coverage.

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