

## In-Situ Soft X-ray Studies of Toluene Catalytic Oxidation on the Pt(111) Surface

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The catalytic oxidation of toluene on the Pt(111) surface has been characterized, in flowing oxygen pressures up to 0.01 Torr, using temperature-programmed fluorescence yield near-edge spectroscopy (TP-FYNES). During TP-FYNES oxidation experiments in flowing oxygen pressures, a dehydrogenated C<sub>7</sub>H<sub>7</sub>  $\eta^7$ -phenylmethylene intermediate is formed over the 190 to 300 K temperature range. Spectroscopic (FYNES) measurements clearly indicate that C–H bond activation occurs at the methyl group and the aromatic ring remains parallel to the surface. In contrast to the intermediates formed during benzene oxidation, no rearrangement of the aromatic ring occurs, signifying that the methyl group influences the structure of intermediates formed during toluene oxidation. This  $\eta^7$ -phenylmethylene intermediate dominates over the 300–370 K temperature range, but is oxidized rapidly above 370 K. Strongly adsorbed  $\eta^6$ -toluene and the stable  $\eta^7$ -phenylmethylene intermediate inhibit oxidation below 370 K by inhibiting oxygen adsorption. A slight increase in the rate of rapid oxidation above 370 K is observed with increasing oxygen pressures over the range of 0.0005 to 0.01 Torr. Temperature-programmed reaction spectroscopy (TPRS) indicates that the deep oxidation products on the Pt(111) surface are CO<sub>2</sub> and H<sub>2</sub>O. This combination of in-situ soft X-ray and UHV methods has provided a detailed mechanistic description of toluene catalytic oxidation on the Pt(111) surface.

## Introduction

Many industrial processes rely on transition metal catalysts to efficiently manufacture desired products and to remove unwanted pollutants.<sup>1</sup> For example, platinum is used in the automotive industry as a catalyst to remove carbon monoxide and unburned hydrocarbons from exhaust. Modern surface science has focused on exploring and understanding catalytic reactions to establish a molecular-level understanding of fundamental surface processes.<sup>2</sup> Using carefully selected combinations of surface science techniques to provide molecular-level information on the elementary reaction steps, mechanisms are characterized. Most of the work performed to date has been done under ultrahigh vacuum (UHV) conditions, since many surface-sensitive spectroscopies require the detection of electrons. However, techniques have been developed to characterize catalytic reactions at a molecular-level on model surfaces in elevated pressures.<sup>3–5</sup> Reactions are probed in-situ using single-crystal surfaces as model catalysts. These studies have shown that some catalytic reactions have different mechanisms under UHV conditions compared to elevated-pressure conditions. Thus, a more complete understanding of reaction mechanisms is gained from investigations done over a wide pressure range.

Deep oxidation of toluene has been characterized over a variety of catalyst surfaces. On noble metal catalysts a Langmuir–Hinshelwood mechanism is generally observed for the deep catalytic oxidation of nucleophilic organics.<sup>6</sup> The first step of the mechanism is the adsorption of molecular oxygen

and its rapid dissociation to form atomic oxygen. In the next step, an adsorbed organic molecule reacts with the surface oxygen. In contrast, the Mars-van Krevelen mechanism has been proposed as a model to describe toluene oxidation on a  $\gamma$ -alumina-supported platinum catalyst.<sup>7</sup> In this case, gas-phase toluene would react with the oxidized catalyst to give a reduced catalyst and the products. Gas-phase oxygen would then react with the reduced catalyst to regenerate an oxidized catalyst. These two mechanisms are similar and are differentiated primarily by the bonding energy of oxygen with platinum. For toluene, the activation energies obtained for both reduction and reoxidation of the catalyst surface are similar to those observed for benzene. Over Pt wires, the oxidation rate for toluene was found to be dependent on the oxygen partial pressure.<sup>8</sup> At low temperatures and large toluene-to-oxygen ratios the strong adsorption of toluene on the metal surface inhibited oxidation. The deep oxidation of toluene over Pt catalyst surfaces is a complex reaction that remains an active area of research. Since properties of catalytic materials have the potential to vary widely, characterizations based on single-crystal model catalyst surfaces provide a better molecular-level mechanistic description.

The interactions of toluene with the Pt(111) surface have been characterized using several UHV surface science techniques.<sup>9–13</sup> Toluene is strongly adsorbed on the metal surface through  $\pi$ -bonding, and the aromatic ring is oriented parallel to the plane of the surface.<sup>9,11–12</sup> Less than 10% of a saturated coverage desorbs upon heating, as shown by thermal desorption experiments.<sup>10</sup> Isotope experiments clearly indicate that C–H bond activation first occurs with increasing temperature at the methyl group. Characterization of annealed coverages using NEXAFS and EELS has revealed that a  $\eta^7$ -phenylmethylene intermediate is formed over the 300 to 350 K temperature range by

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dehydrogenation at the methyl group.<sup>11,13</sup> This singly dehydrogenated intermediate  $\pi$ -bonds through the aromatic ring and  $\sigma$ -bonds through the methylene group to the platinum surface. In addition to these limited studies of toluene adsorption and reactivity on the Pt(111) surface, the deep oxidation of toluene has been characterized on Pd and Ru single-crystal surfaces.<sup>14–16</sup> On the  $(2 \times 2)\text{-O-Pd(111)}$  surface, toluene is oxidized to produce carbon dioxide, carbon monoxide, and water.<sup>16</sup> A fraction of toluene desorbs by 300 K, while the remainder is oxidized by coadsorbed oxygen. Initial water desorption begins at 250 K, and peaks at 320 K. Isotopic labeling experiments show that this initial water formation results from oxidation of the methyl hydrogens. Water, carbon dioxide, and carbon monoxide all desorb in peaks at 455 K, which indicates that oxydehydrogenation and skeletal oxidation are both occurring over the same temperature range. After all of the oxygen is consumed, hydrogen and adsorbed carbon are produced by dehydrogenation of the remaining toluene-derived hydrocarbon fragments.

To connect studies of deep oxidation on platinum catalysts with those on model surfaces under UHV conditions, we have applied a combination of soft X-ray absorption spectroscopies at the C–K-edge to characterize toluene catalytic oxidation on the Pt(111) surface. These methods have been used previously to characterize oxidation mechanisms for other light hydrocarbons on the Pt(111) surface.<sup>17–20</sup> In this work, fluorescence yield near-edge spectroscopy (FYNES) and temperature-programmed FYNES (TP-FYNES) have been used to characterize the deep oxidation of toluene in pressures up to 0.01 Torr of flowing oxygen. Below 190 K, toluene is strongly adsorbed on the Pt(111) surface in a  $\eta^6$ -configuration that results in the tilting of the C–H bonds away from the surface plane. With increasing temperature, a small fraction of toluene is desorbed molecularly, while the remainder forms a  $\text{C}_7\text{H}_7$  surface intermediate over the 190 to 300 K temperature range. This  $\eta^7$ -phenylmethylene surface intermediate is stable over the 300 to 370 K temperature range, but above 370 K the intermediate rapidly reacts with surface oxygen. Both temperature-programmed UHV and elevated-pressure oxidation experiments have supplied in depth information on the mechanisms and intermediates during toluene catalytic oxidation on the Pt(111) surface.

## Experimental Section

The soft X-ray experiments were performed on the surface science end station located on the U7A beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. These experiments and the experimental setup have been described in detail previously.<sup>20</sup> 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 window remains out for vacuum experiments and is inserted when experiments are conducted in pressures of flowing oxygen. The Pt(111) crystal was mounted on Ta wire supports at the end of a 6-ft liquid nitrogen cooled re-entrant manipulator insert. Temperature was measured with a Type K thermocouple spot-welded to the back of the crystal and was controlled with a RHK temperature controller. The crystal was cleaned in the lower chamber by initial  $\text{Ar}^+$  sputtering, followed by annealing briefly at 1000 K. During experimental runs, the sample was cleaned by heating the crystal at 600 K in 0.002 Torr of oxygen for 60 s, followed by a 10 s exposure to carbon monoxide. Reactive gases were admitted to the background through leak valves.

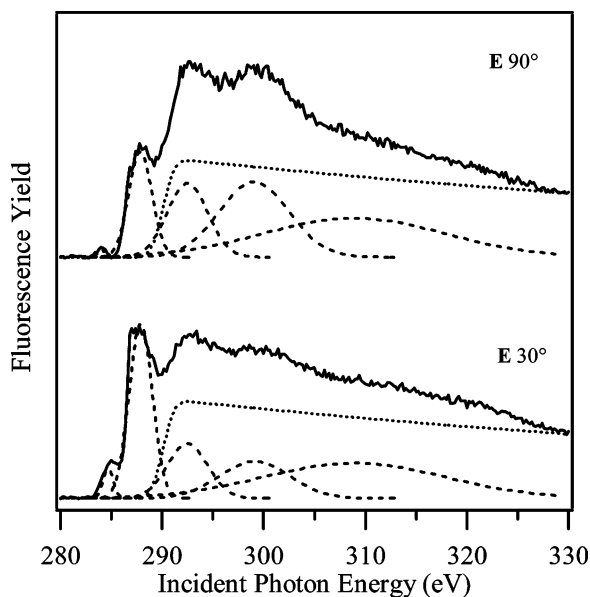
FYNES and TP-FYNES experiments were performed using a proportional counter optimized for fluorescence detection at the C–K-edge.<sup>21</sup> To limit the contribution from fluctuations in the ring current, all spectra have been normalized by the intensity measured at a Au grid upstream from the Al window valve. Fluorescence yield spectra were collected with  $150\ \mu\text{m}/150\ \mu\text{m}$  slits, giving an overall resolution of 0.4 eV. All spectra of adsorbed species have been divided by spectra of the clean surface taken on the same ring fill to ensure reproducibility. Spectra of adsorbed species were recorded at 100 K (toluene) and 250 K (oxidation intermediate), while spectra of the clean surface were recorded at 500 K to limit CO adsorption from the background. The temperature-programmed oxidation experiments were performed with  $450\ \mu\text{m}/450\ \mu\text{m}$  slits, which results in a resolution of 1.2 eV and an intensity of 10 000 counts/s for a saturated CO coverage with the window inserted. Data were averaged over a 4 s interval which results in a signal-to-noise ratio of about 4:1 for a saturated CO coverage. The heating rate was 0.5 K/s during these temperature-programmed experiments.

TP-FYNES experiments and preparation of surface species were conducted in the following manner. After the crystal was cleaned and cooled to 190 K, a saturated coverage of toluene was dosed. Once the surface carbon concentration reached the saturation level, the leak valve was closed and the crystal was cooled to 170 K. Next, oxygen was introduced, and the ion gauge was turned off. The ultimate pressure was achieved by a combination of throttling the gate valve in front of the turbo pump and controlling the leak valve while monitoring the pressure with a 1 Torr capacitance manometer. Throttling the turbo pump results in a system with 10% flow. CO TP-FYNES was used to confirm the performance of this system and reproduce published results. Repeated experiments indicate thermal transitions are reproducible to 2 K. Absolute carbon coverage for toluene was estimated by comparing the carbon continuum levels at 330 eV observed during these experiments and experiments with a saturated CO coverage. Since the absolute carbon concentration for a saturated CO coverage is known to be  $9.6 \times 10^{14}$  molecules/cm<sup>2</sup>, it is possible to estimate absolute surface carbon concentration for any carbon-containing, adsorbed species.<sup>22</sup>

The TPRS experiments were conducted on the Ann Arbor ultrahigh vacuum (UHV) chamber at the University of Michigan, which has been described in detail previously.<sup>23</sup> The crystal was cleaned by cycles of  $\text{Ar}^+$  sputtering and heating in background pressures of oxygen. Surface cleanliness was verified by Auger electron spectroscopy (AES) and oxygen temperature-programmed desorption (TPD). The experiments were performed using a UTI 100C mass spectrometer interfaced with a PC. A heating rate of 5 K/s was used for these experiments. Initially, the toluene was purified by freeze–pump–thawing several times and the purity was checked by mass spectrometry. After that, the toluene was freeze–pump–thawed at the start of each set of experiments. The reactive gases were directly dosed using stainless steel capillaries and variable leak valves. For oxygen exposures, the crystal was placed 5 mm away from the doser, while for toluene exposures the crystal was placed 25 mm away from the doser. All gas exposures for TPRS were performed with the crystal temperature below 100 K. Saturated atomic oxygen coverages were prepared by heating saturated coverages of molecular oxygen to 150 K.

## Results

The adsorption and bonding of toluene on the Pt(111) surface has been characterized using FYNES. Spectra shown in Figure

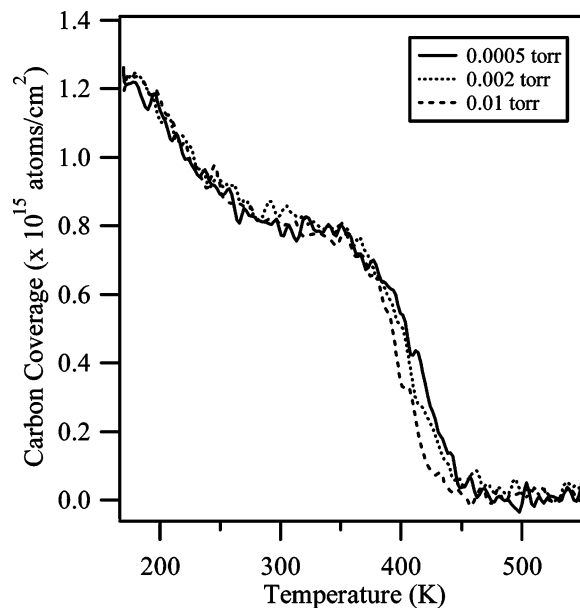


**Figure 1.** FYNES, recorded at normal ( $90^\circ$ ) and glancing ( $30^\circ$ ) incidences, of a saturated coverage of  $\eta^6$ -toluene adsorbed on the Pt(111) surface.

**TABLE 1: FYNES Resonance Assignments for  $\eta^6$ -Toluene Adsorbed on the Pt(111) Surface**

energy (eV)	resonance
284.7	$\pi^*_{1,2}$
287.9	$C-H \sigma^* + \pi^*_3$
292.5	$\sigma^*_1$
299.1	$\sigma^*_2$
308.9	multiple scattering

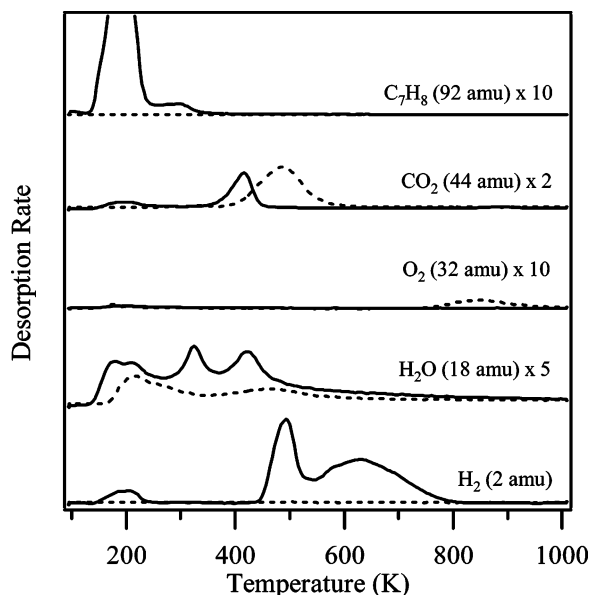
1 were collected at normal ( $90^\circ$ ) and glancing ( $30^\circ$ ) incidences of the electric field vector with respect to the surface normal. Both spectra were normalized to zero fluorescence yield below 280 eV and to a constant fluorescence yield at 330 eV. The spectra were curve fit after subtracting a step function (shown as a dashed curve) placed at a position of 290.1 eV and used to simulate the adsorption edge. Both spectra were curve fit using identical step functions, peak energies, and peak widths. Details of the curve fitting procedure are found in the literature.<sup>24</sup> Each spectrum consists of five resonances resulting from transitions from the C 1s orbital to unfilled valence orbitals. The first four peaks have been assigned to the following resonances:  $\pi^*_{1,2}$  (284.7 eV),  $C-H \sigma^* + \pi^*_3$  (287.9 eV),  $\sigma^*_1$  (292.5 eV),  $\sigma^*_2$  (299.1 eV). As with propylene and benzene, the peak at 308.9 eV has been assigned to a multiple scattering resonance.<sup>17,20</sup> Above 330 eV, the resonances are solely the result of transitions from the C 1s orbital to the carbon continuum. These resonance assignments have been summarized in Table 1 and are based on previous work involving benzene and toluene.<sup>11,20,25–26</sup> Tilt angles for chemical bonds in adsorbed species are calculated on the basis of the intensity ratio for resonances in spectra collected at two different angles of incidence.<sup>27</sup> The peak intensity of the  $\pi^*_{1,2}$  resonance in the spectrum for normal incidence is lower than the peak intensity in the spectrum for glancing incidence. Using the intensity ratio  $I_{90^\circ}/I_{30^\circ}$  and a polarization factor of 0.85, a tilt angle of  $0^\circ \pm 2^\circ$  relative to the surface normal has been calculated for the  $\pi^*_{1,2}$  orbital. The same calculation has been done for the  $C-H \sigma^*$  resonance. The peak intensity in the spectrum for normal incidence is higher than the peak intensity in the spectrum for glancing incidence. A tilt angle of  $45^\circ \pm 5^\circ$  relative to the surface normal has been calculated for this orbital.



**Figure 2.** TP-FYNES recorded at the carbon continuum (330 eV) for the oxidation of a saturated coverage of toluene as a function of increasing oxygen pressure.

The deep catalytic oxidation of toluene, in pressures of flowing oxygen ranging from 0.0005 to 0.01 Torr, has been characterized using TP-FYNES at 330 eV and at normal incidence. As discussed in the previous paragraph, at this energy the fluorescence yield is a direct measure of the amount of carbon adsorbed on the surface and the intensity is independent of orientation. As seen in Figure 2, the carbon coverage is monitored while heating a saturated coverage of toluene in a background pressure of flowing oxygen. These spectra were normalized first by setting the intensity above 450 K to zero carbon coverage, then by setting the intensity at 170 K equal to the carbon coverage for a saturated toluene coverage. A saturated coverage of toluene corresponds to  $1.23 \times 10^{15}$  C atoms/cm<sup>2</sup> (or  $1.76 \times 10^{14}$  molecules/cm<sup>2</sup>) based on direct comparison with the fluorescence yield for a saturated coverage of CO. The initial decrease in carbon coverage is gradual and occurs from 190 to 300 K. This decrease corresponds to the removal of  $4.0 \times 10^{14}$  C atoms/cm<sup>2</sup>, or 33% of the carbon coverage. From 300 to 370 K the intensity remains at a constant level. In the presence of oxygen, the carbon coverage rapidly decreases to zero over the temperature range 370 to 450 K. A slight increase in the rate of carbon removal above 370 K is observed with an increase in oxygen pressure.

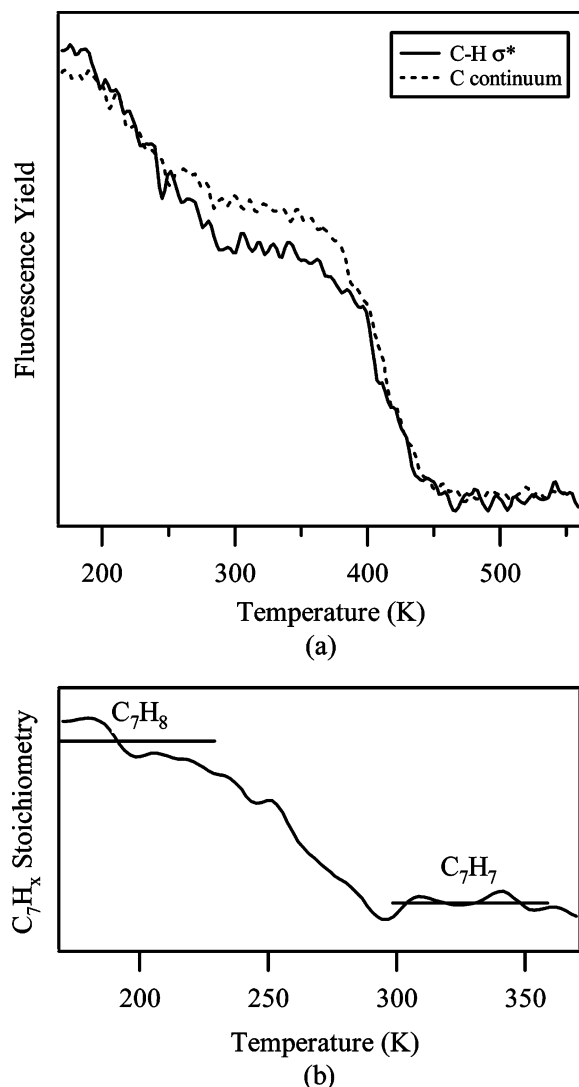
The products of the deep oxidation of toluene by coadsorbed atomic oxygen have been identified using TPRS. The transition from excess toluene to excess oxygen is shown in Figure 3. As shown in the mass 92 spectrum for excess toluene, the chemisorbed state is desorbed in a small peak at 300 K, but is finished desorbing by 330 K. The major products desorbed from the surface are carbon dioxide (mass 44 spectrum) and water (mass 18 spectrum). No significant concentrations of carbon monoxide were detected. The initial water desorption peak below 300 K results primarily from oxygen reacting with adsorbed background hydrogen and from adsorbed background water. The second water desorption peak is located at 320 K. The complete oxidation products, CO<sub>2</sub> and H<sub>2</sub>O, are desorbed between 350 and 500 K when toluene is in excess. For the condition of excess oxygen on the surface, carbon dioxide and water desorb from 400 to 600 K. For excess toluene, once the oxygen has been consumed by reaction, the remaining toluene



**Figure 3.** TPR spectra of toluene oxidation on the Pt(111) surface for the conditions of excess toluene (—) and excess oxygen (---).

is dehydrogenated to produce adsorbed carbon, and hydrogen, which is desorbed in two peaks, one at 500 K and one at 635 K, as seen in the mass 2 spectrum. No peaks are observed in either the mass 2 or the mass 92 spectrum when oxygen is in excess. Remaining atomic oxygen recombines and desorbs above 700 K for this toluene coverage. Soft X-ray experiments in flowing oxygen have been performed to determine the structure and stoichiometry of surface intermediates present during toluene deep oxidation on the Pt(111) surface.

The C–H stoichiometry during oxidation was established by temperature-programmed experiments conducted to measure the intensity of the C–H  $\sigma^*$  resonance (287.9 eV) at an angle of 55°. At this “magic” angle resonance intensities are independent of molecular orientation on the surface.<sup>28</sup> As shown by the curve fitting in Figure 1, this resonance falls below the absorption step, so there are no ambiguities related to overlap with the continuum. The intensity of the C continuum (330 eV) as a function of temperature was also determined using the same angle of incidence. For these experiments, saturated coverages of toluene were heated in 0.002 Torr of flowing oxygen. The results for this stoichiometry determination are presented in Figure 4. For both spectra in Figure 4a the intensity above 450 K has been normalized to zero. As clearly shown by the spectrum corresponding to the C–H  $\sigma^*$  resonance, a gradual drop in intensity occurs between 190 and 300 K. A similar drop in intensity is also observed in the spectrum corresponding to the C continuum. The drop in the intensity of the C–H  $\sigma^*$  resonance is larger than the drop for the C continuum. The molecular C–H stoichiometry is determined by taking the ratio of the C–H  $\sigma^*$  resonance to the surface carbon coverage (C continuum resonance). Figure 4b shows the C–H  $\sigma^*$  resonance spectrum divided by the C continuum spectrum. There is a constant level below 190 K, then a decrease in the ratio from 190 to 300 K. Above 300 K the intensity ratio remains constant until 370 K. The initial ratio in Figure 4b has been normalized to 8 C–H bonds, so this decrease corresponds to a drop in intensity from 8 to 7 C–H bonds, or a change in stoichiometry of  $C_7H_8$  to  $C_7H_7$ . A similar stoichiometry has been observed at higher temperature during thermal dehydrogenation of toluene on this same surface.<sup>13</sup> Quantitative changes in C–H stoichiometry during oxidation, using these in-situ soft X-ray methods,

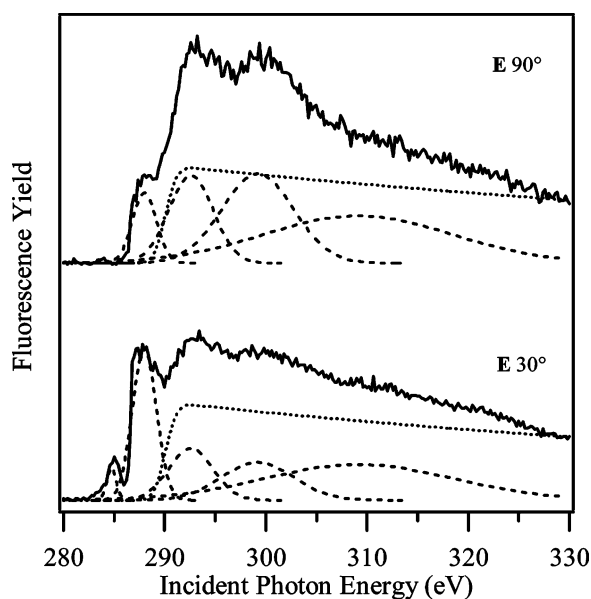


**Figure 4.** (a) TP-FYNES recorded at the C–H  $\sigma^*$  (287.9 eV) and carbon continuum (330 eV) energies during the oxidation of a saturated coverage of toluene in 0.002 Torr flowing oxygen. (b) Ratio of the C–H  $\sigma^*$  (287.9 eV) spectrum to the carbon continuum (330 eV) spectrum.

have been previously reported for propylene and benzene.<sup>17,20</sup> In good agreement with experimental errors for propylene and benzene, the error in the toluene C–H stoichiometry appears to be  $\pm 0.1$  C–H bonds, based on the experimental signal-to-noise in the data reported in this work.

The adsorption and bonding of the dehydrogenated oxidation intermediate has been characterized using FYNES. The intermediate was prepared by heating a saturated coverage of toluene in 0.002 Torr of flowing oxygen to 300 K, then cooling to 250 K. The spectra shown in Figure 5 were collected at 250 K and at normal (90°) and glancing (30°) incidences of the electric field vector with respect to the surface normal. Each spectrum was normalized and curve fit using the procedures described for the toluene spectra. The peaks present in the spectra have been assigned to the following resonances:  $\pi^*_{1,2}$  (284.7 eV), C–H  $\sigma^* + \pi^*_3$  (288.0 eV),  $\sigma^*_1$  (292.6 eV),  $\sigma^*_2$  (299.2 eV), and multiple scattering (309.1 eV). These resonance assignments have been summarized in Table 2 and are based on the assignments for toluene. Tilt angles for this oxidation intermediate have been calculated on the basis of the same methods used for toluene. A tilt angle of  $0^\circ \pm 2^\circ$  relative to the surface normal has been calculated for the  $\pi^*_{1,2}$  orbital, while a tilt angle of





**Figure 5.** FYNES, recorded at normal (90°) and glancing (30°) incidences, of  $\eta^7$ -phenylmethylene adsorbed on the Pt(111) surface.

**TABLE 2: FYNES Resonance Assignments for  $\eta^7$ -Phenylmethylene Adsorbed on the Pt(111) Surface**

energy (eV)	resonance
284.7	$\pi^*_{1,2}$
288.0	C–H $\sigma^* + \pi^*_3$
292.6	$\sigma^*_1$
299.2	$\sigma^*_2$
309.1	multiple scattering

$40^\circ \pm 5^\circ$  relative to the surface normal has been calculated for the C–H  $\sigma^*$  orbital. These structural determinations will be combined with the temperature-programmed oxidation experiments to develop a complete mechanistic description of toluene catalytic oxidation on the Pt(111) surface.

## Discussion

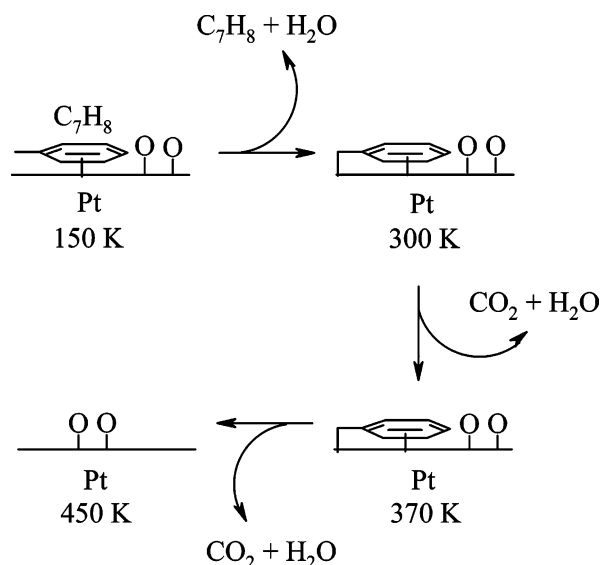
The catalytic oxidation of toluene on the Pt(111) surface has been characterized in flowing oxygen pressures ranging from 0.0005 to 0.01 Torr using in-situ soft X-ray methods. FYNES indicates that toluene rehybridizes upon adsorption on the Pt(111) surface, with the C–H bonds at angles of  $45^\circ \pm 5^\circ$ . Spectroscopic and temperature-programmed stoichiometric experiments clearly show that the deep oxidation of toluene proceeds through a singly dehydrogenated surface intermediate formed below 300 K. In the presence of flowing oxygen this intermediate is oxidized rapidly with increasing temperature above 370 K. A mechanism has been developed on the basis of the combination of elevated-pressure and UHV experiments.

The structure of toluene adsorbed on the Pt(111) surface has been characterized using FYNES. Changes within the molecular structure of toluene are observed on the basis of the fluorescence yield spectra shown in Figure 1. The tilt angle of the  $\pi^*_{1,2}$  orbital with respect to the surface normal is calculated to be  $0^\circ \pm 2^\circ$ . Previous EELS results have suggested that the chemisorption of benzene and toluene on the Pt(111) surface should be similar.<sup>12</sup> Unlike with benzene, though, the  $\pi$ -system of toluene is not strongly perturbed, as indicated by the calculation for the  $\pi^*_{1,2}$  orbital.<sup>20</sup> However, the C–H bond angle from the surface is estimated by this work to be  $45^\circ \pm 5^\circ$ , on the basis of the intensity ratio for the C–H  $\sigma^*$  resonance. In other work, we estimated the C–H bond angle for benzene adsorbed on Pt(111) to be  $44^\circ \pm 5^\circ$ , clearly indicating strong interaction

with the surface.<sup>20</sup> NEXAFS experiments and calculations have suggested that a tilt angle of up to  $40^\circ$  for the C–H bond was possible due to molecular rehybridization.<sup>29</sup> It has been proposed that the formation of metal–carbon bonds through surface interactions cause changes in the NEXAFS spectra of the adsorbed benzene.<sup>30</sup> This strong interaction between toluene and the Pt(111) surface clearly affects the molecular structure, which in turn affects the surface reactivity.

The adsorption and bonding of benzene and toluene on the surface appear to be similar on the basis of these FYNES results. Both benzene and toluene are strongly adsorbed on the Pt(111) surface. Yet, during oxidation, benzene forms a series of four intermediates,<sup>20</sup> while toluene forms only two intermediates. Substituent effects have been shown to influence the chemistry of aromatic molecules on the Ni(111) surface.<sup>31</sup> The inductive effect of the methyl group stabilizes the aromatic ring, which causes the structure to remain intact during oxidation. As a result, the dominant dehydrogenated intermediate formed during toluene oxidation is  $\pi$ - and  $\sigma$ -bonded to the surface. Temperature-programmed isotope experiments, NEXAFS, and EELS have shown that the formation of this intermediate results from the removal of one methyl hydrogen.<sup>11–13</sup> In addition, isotopic labeling experiments clearly suggest that carbon–hydrogen bond activation occurs first at the methyl group during toluene oxidation on the Pd(111) surface.<sup>16</sup> The adsorption geometries available for  $\eta^7$ -phenylmethylene are constrained, while benzene and benzene-derived intermediates adopt a number of different geometries during oxidation. For benzene adsorbed on bridge sites, the rearrangement of the aromatic ring decreases the energy for C–H bond activation.<sup>20</sup> As a result, benzene forms a tri- $\sigma$ -cyclohexadiene intermediate, which is subsequently oxygenated to form a  $\eta^5$ -cyclohexadienone intermediate. TP-FYNES experiments (data not shown) performed at the  $\pi^*_{1,2}$  resonance energy for toluene indicate no significant change in the structure of the aromatic ring during oxidation. Differences between intermediates formed for benzene and toluene are mainly caused by electronic and structural effects influencing the interaction of the aromatic ring with the platinum surface. The  $\eta^7$ -phenylmethylene intermediate is clearly more reactive than the  $\eta^5$ -cyclohexadienone intermediate, which may be the result of acid–base reactions during oxidation.

A mechanism for the catalytic oxidation of a saturated coverage of toluene on the Pt(111) surface has been developed and is shown in Figure 6. Coverage estimates based on a saturated coverage of CO show that a saturated coverage of toluene consists of  $1.76 \times 10^{14}$  molecules/cm<sup>2</sup>, which agrees with previous experimental results.<sup>12</sup> During the initial step of the mechanism from 190 to 300 K, strongly adsorbed  $\eta^6$ -toluene forms a dehydrogenated  $\eta^7$ -phenylmethylene intermediate. The formation of this intermediate is most clearly seen in Figure 4. The water desorption peak at 320 K in the mass 18 spectrum for excess toluene in Figure 3 also supports this conclusion. The initial rate of carbon removal, as observed in Figure 2, corresponds to desorption of toluene on the basis of comparisons with TPRS. For the condition of excess toluene on the surface, as seen in the mass 92 spectrum in Figure 3, toluene desorption is complete by 330 K. For the TP-FYNES experiments, toluene weakly adsorbed on the surface should be completely desorbed by 300 K. (A decrease in heating rate from 5 K/s to 0.5 K/s results in a temperature decrease of 30 K, assuming first-order desorption.<sup>32</sup>) As seen in Figure 3, above 350 K toluene is oxidized to form CO<sub>2</sub> and H<sub>2</sub>O. Reaction-limited peaks for both products are observed from 350 to 500 K, which clearly indicates that oxydehydrogenation and skeletal oxidation are



**Figure 6.** Mechanism for toluene catalytic oxidation on the Pt(111) surface in pressures of flowing oxygen.

both occurring over this temperature range. During TP-FYNES, surface reaction to form carbon dioxide and water appears to occur from 350 K until 370 K, when the surface reaction becomes rapid.

Oxidation of toluene on the Pt(111) surface proceeds through a bimolecular surface reaction. Previous catalytic experiments have shown that strong toluene adsorption on platinum surfaces inhibits oxidation.<sup>8</sup> In the experiments reported here, inhibition of oxygen adsorption by toluene is also clearly seen. The strong adsorption of toluene inhibits the adsorption of oxygen, and as a result, oxidation is inhibited below 370 K. The desorption rate for toluene does not depend on the oxygen pressure. Yet the oxidation rate does, although oxidation above 370 K is fast. Toluene strongly adsorbed on the surface undergoes oxydehydrogenation to form a dehydrogenated surface intermediate, which is stable over the 300 to 370 K temperature range. Over this temperature range, the principal surface species is a  $\eta^7$ -phenylmethylene intermediate. On the basis of TP-FYNES and TPRS results reported here, inhibition will become an important factor over the 300 to 370 K temperature range, depending on reaction conditions. The dominant rate-limiting steps are clearly carbon–hydrogen and carbon–carbon bond activation.

## Conclusions

The reaction mechanism and intermediates for toluene catalytic oxidation on the Pt(111) surface have been characterized using a combination of in-situ soft X-ray and UHV methods. As shown by temperature-programmed kinetic and spectroscopic measurements, the reaction proceeds through a stable  $\eta^7$ -phenylmethylene surface intermediate. Below 190 K,  $\eta^6$ -toluene is adsorbed on the Pt(111) surface with the C–H bonds at angles of  $45^\circ \pm 5^\circ$ . In the first step of the mechanism, from 190 to 300 K, oxydehydrogenation of adsorbed toluene forms a surface intermediate with  $C_7H_7$  stoichiometry. FYNES of this intermediate clearly indicates the aromatic ring remains parallel to the surface plane with the C–H bonds at angles of  $50^\circ \pm 5^\circ$  from the surface plane. In contrast to benzene oxidation on the Pt(111) surface, no change in the structure of the ring is observed for toluene during oxidation, indicating the methyl group influences the reactivity of aromatic ring during catalytic oxidation. As determined by TPRS, weakly adsorbed toluene is desorbed from the surface over this same temperature range.

During TP-FYNES, toluene oxidation is inhibited below 370 K by the strong adsorption of  $\eta^6$ -toluene and  $\eta^7$ -phenylmethylene, which prevents oxygen adsorption. The dehydrogenated intermediate is the dominant surface species over the 300 to 370 K temperature range. This reactive intermediate is rapidly oxidized with increasing temperature above 370 K. Carbon dioxide and water have been identified as the gas-phase products of deep oxidation on the Pt(111) surface using TPRS. This detailed mechanistic picture of toluene catalytic oxidation on the Pt(111) surface illustrates the capabilities of these coupled UHV surface science experiments and in-situ soft X-ray methods. Current efforts are underway to characterize toluene catalytic oxidation on more complex model surfaces, which include Pt thin films and nanoparticulate catalysts. Additional experiments will be aimed at understanding the influence of acid–base reactions and substituent effects during catalytic oxidation in pressures of flowing oxygen.

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