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NEXAFS investigation of benzaldehyde reductive coupling to form stilbene on reduced surfaces of TiO_2(0 0 1)

Adrian B. Sherrill[a], Victor S. Lusvardi[c], Joseph Eng Jr.[d],
Jingguang G. Chen[a,b], Mark A. Barteau[a,*]

[a] Department of Chemical Engineering, Center for Catalytic Science and Technology, University of Delaware, Newark, DE 19716, USA
[b] Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, USA
[c] Dupont Research and Development, Wilmington, USA
[d] Lucent Technologies, Murray Hill, NJ, USA

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Abstract

Near-edge X-ray absorption fine structure (NEXAFS) was used to investigate the reaction of benzaldehyde on reduced surfaces of TiO_2(0 0 1) to form stilbene by reductive coupling of the carbonyl groups. Reductive coupling of carbonyls (commonly referred to as the “McMurry reaction”) has been extensively studied in both liquid slurries containing reduced metals and as a gas–solid reaction on reduced surfaces of titania. The reactive intermediate proposed for both slurry and surface chemistry is a metal pinacolate. Previous investigations of this chemistry on reduced TiO_2(0 0 1) have yielded circumstantial evidence supporting such an intermediate on the surface. However, spectroscopic evidence has proven difficult to obtain. In the current study, we employ NEXAFS to probe the chemical identity and orientation of reactive intermediates in the reductive coupling reaction further. By heating benzaldehyde-covered surfaces of TiO_2(0 0 1) to progressively higher temperatures and recording polarization-dependent NEXAFS spectra at the Ti L-edge and the O and C K-edges, one can track the progression of the reaction from benzaldehyde to the product, stilbene. These results support an adsorbate structure consistent with a pinacolate intermediate.

Keywords: NEXAFS; Reductive coupling; TiO_2(0 0 1); Benzaldehyde; Stilbene

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1. Introduction

Reduced surfaces of TiO_2(0 0 1) have been shown to be active for several types of carbon–carbon bond forming reactions under UHV conditions, including alkyne cyclotrimerization, aldol condensation, and reductive carbonyl coupling [1–8]. This activity presents the opportunity to study the mechanisms of these reactions using traditional laboratory techniques such as temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). In addition, we may extend the investigation by including synchrotron techniques, such as near-edge X-ray absorption fine structure (NEXAFS), to study adsorbate–surface interactions. As demonstrated in previous NEXAFS studies of adsorbates on metal and oxide surfaces, NEXAFS is a very useful tool in determining the chemical identity and the orientation of molecules on the surface [9–13]. In this paper, we present NEXAFS studies of the reductive cou-

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* Corresponding author. Present address: Department of Chemical Engineering, Center for Catalytic Science and Technology, University of Delaware, Newark, DE 19716, USA. Tel.: +1-302-831-8905; fax: +1-302-831-8201.
E-mail address: barteau@che.udel.edu (M.A. Barteau).

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pling reaction of benzaldehyde to form stilbene on the reduced surface of $TiO_2(0\,0\,1)$. This reaction has been extensively studied in the liquid phase (where it is more popularly known as the McMurry reaction) and has been proposed to proceed via a pinacolate intermediate. The pinacolate then eliminates oxygen to form the olefin product. This reaction involves a four-electron reduction of the adsorbate; liquid phase reactions call for stoichiometric slurries of low-valent titanium, usually derived from $TiCl_4$ [14–16]. The gas–solid reaction on metal oxide surfaces also requires low-valent cations; XPS studies in conjunction with TPD experiments demonstrate that the surface must be reduced for the reaction to occur, although no particular site has been identified with the reaction (an ensemble of reduced cations has been proposed as the active site) [5–8].

The nature of the surface intermediate for this reaction remains unclear, as the pinacolate intermediate proposed has not been spectroscopically identified. Some evidence for the pinacolate intermediate in carbonyl coupling has been indirectly obtained in TPD experiments examining the reductive coupling of acetophenone on reduced $TiO_2(0\,0\,1)$ [6]. It was observed that, in addition to the expected olefin product (2,3-diphenyl-2-butene), small amounts of the corresponding pinacol (2,3-diphenyl-2,3-butanediol) also desorbed from the surface. It was proposed that a portion of the pinacolate intermediates formed were unable to deoxygenate when bound at sites that did not incorporate a sufficient number of reduced titanium centers [6]. XPS studies of the C(1s) photoemission region have shown the presence of surface alkoxide functions following adsorption of cyclic ketones (which is consistent with the formation of a surface pinacolate), but XPS was unable to resolve the characteristics of the adsorbate beyond this [5]. Similar studies for benzaldehyde adsorbed on reduced $TiO_2(0\,0\,1)$ were unable to resolve alkoxide-like carbon centers [7].

The tunability and the intensity of synchrotron light sources present us with a powerful tool to learn about the characteristics of adsorbates. Extensive work has been done with NEXAFS on metals and metal oxides, nitrides, and carbides [9,12]. In addition, NEXAFS has been used to study the orientation of conjugated adsorbates in such reactions as the cyclotrimerization of alkynes on metals and the dehydrocyclization of 1-hexene [10,11]. We have studied the population of cationic states on sputtered surfaces of $TiO_2(0\,0\,1)$ as a companion to earlier work done using XPS [13]. In this paper, we present NEXAFS spectra at several different temperatures for benzaldehyde adsorbed on reduced $TiO_2(0\,0\,1)$, in conjunction with TPD experiments with benzaldehyde. The NEXAFS spectra provide snapshots of the surface adsorbates during these TPD experiments. Furthermore, by studying the intensity of the near-edge features of the carbon and oxygen K-edges as a function of the orientation of the incident light, we may learn about the chemical identity and the orientation of relevant organic intermediates.

2. Experimental

TPD experiments were conducted in a Physical Electronics 550 vacuum system with a typical base pressure of 3.5×10^{-10} Torr. The vacuum system was equipped with a UTI 100C quadrupole mass spectrometer and a sputter gun for surface reduction. The single crystal surface was prepared by polishing a $10\,\mathrm{mm}\times5\,\mathrm{mm}\times1\,\mathrm{mm}$ $TiO_2(0\,0\,1)$ crystal with progressively finer diamond pastes to a final grit size of $0.25\,\mu\mathrm{m}$. Tantalum wires were then spot welded to a tantalum foil plate onto which the crystal was clipped. The crystal support was then spot welded to the mounting assembly of the sample probe. The temperature of the crystal was monitored by a thermocouple junction glued to the crystal edge with ceramic paste. The crystal temperature was controlled during TPD by resistive heating across the support wires using a 14 A power supply and a PID controller. The sample probe contained a hollow inner bore into which liquid nitrogen was poured, allowing the crystal to cool as low as 150 K. The probe was capable of linear translation and 360° of rotation about its axis. A typical TPD experiment consisted of sputter reduction of the crystal surface by 3 kV Ar^+ ions for 1 h, followed by annealing the crystal to progressively higher temperatures to reoxidize the surface to controlled extents. The crystal was then cooled to 160 K and exposed to 5.5×10^{-9} Torr of benzaldehyde for 30 s through a dosing needle directed at the crystal surface. During reactant adsorption and evacuation, the crystal was cooled further to 150 K, at which temperature the TPD experiment commenced. Twenty mass fragments were monitored simultaneously by the QMS, which was multiplexed with a PC. A temperature ramp of 1 K/s was used throughout the experiments.

The NEXAFS measurements were conducted on the U1 beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The two-stage UHV chamber is equipped with an ion sputtering gun, a quadrupole mass spectrometer, and an Auger electron spectrometer. All NEXAFS spectra were recorded with a partial electron yield detector with a retarding voltage of −200 eV. The resolution of the synchrotron monochromator was set at 0.4 eV near the carbon K-edge region. All NEXAFS spectra reported have been divided by the signals from a gold reference grid, which measures the incident beam intensity simultaneously with the NEXAFS spectra, and then by the corresponding ratio of the spectra of a clean surface taken at the same incidence angle [9].

3. Results and discussion

3.1. TPD

The TPD experiments we present here reproduce earlier more detailed work done by this group; therefore, we will focus only on the desorption spectra from the sputtered surface and the fully oxidized surface of $TiO_2(0\,0\,1)$ [7]. Fig. 1 illustrates the desorption spectra of the parent masses of the major products generated from the reduced surface: benzaldehyde ($m/e = 106$), benzene ($m/e = 78$), toluene ($m/e = 92$), and stilbene ($m/e = 180$). These spectra have been scaled by correction factors to account for differences in the sensitivity of the mass spectrometer. The benzaldehyde spectrum exhibits a low temperature feature at 180 K which is associated with molecular desorption. Fig. 2 shows the desorption of benzaldehyde dosed at varying exposures to the surface, illustrating the dependence of the 180 K desorption feature on the magnitude of the benzaldehyde exposure (the dosing pressures given represent the background pressure during dosing; direct dosing through the needle doser produces an effective pressure at the surface of between one and two orders of magnitude greater). In addition to benzaldehyde, stilbene (*cis* and *trans* isomers were not distinguished) and toluene desorbed at approximately 450 K in Fig. 1. The toluene feature is broad; earlier work indicated the presence of two features produced from the reduced surface. It is also important to note that the sputtered surface has been heavily reduced, and that the earlier work noted a correlation

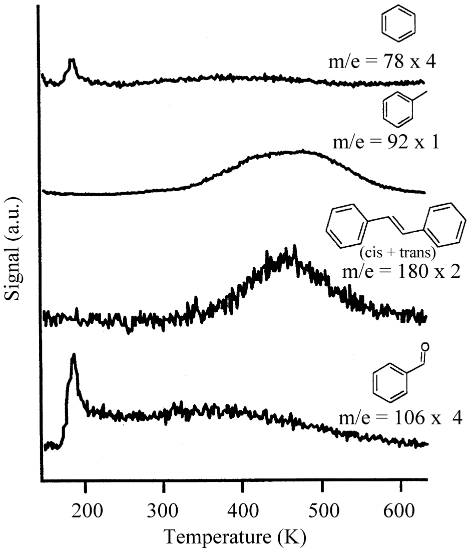

Fig. 1. TPD of benzaldehyde adsorbed onto sputtered $TiO_2(0\,0\,1)$ at 160 K: the desorption spectra of benzene ($m/e = 78$), toluene ($m/e = 92$), stilbene ($m/e = 180$) and benzaldehyde ($m/e = 106$) are illustrated.

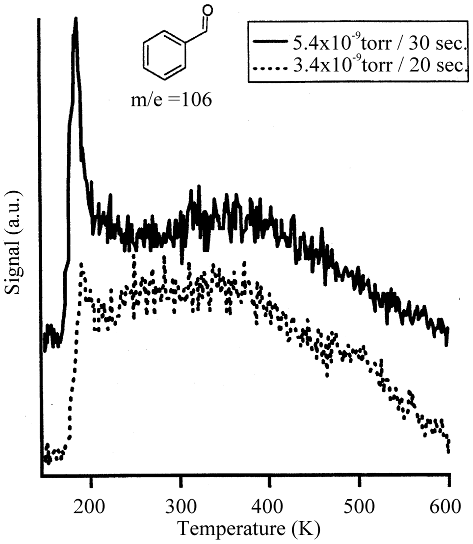

Fig. 2. TPD of two different exposure levels of benzaldehyde on sputtered $TiO_2(0\,0\,1)$ at 160 K.

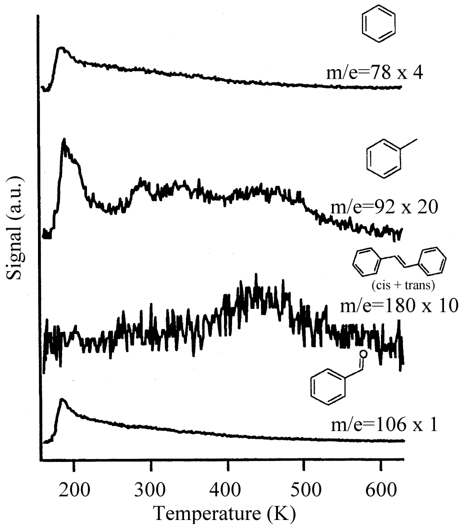

Fig. 3. TPD of benzaldehyde adsorbed onto oxidized TiO_2(0 0 1) at 160 K: the desorption spectra of benzene ($m/e = 78$), toluene ($m/e = 92$), stilbene ($m/e = 180$) and benzaldehyde ($m/e = 106$) are illustrated.

between the most heavily reduced sites and the enhanced production of toluene.

TPD spectra from the annealed surface are shown in Fig. 3. The identities of the products are unchanged, although the surface is substantially less active for the production of toluene and stilbene. Most of the benzaldehyde desorbed unconverted. The preference for benzaldehyde desorption over reaction on oxidized surfaces of TiO_2(0 0 1) was demonstrated previously. The lack of activity of the oxidized surface towards the decomposition of benzaldehyde was further demonstrated by the precipitous decrease in adsorbate coverage as determined by C(1s) XPS [7]. The surface exhibited marginal activity for the production of stilbene, which desorbed in one peak centered at 450 K. Toluene desorption was also greatly diminished, although it did appear to desorb over a broad range of temperatures.

The primary conclusion from the TPD results is that significant changes in surface activity for both adsorption and reaction are coupled to the average oxidation state of the surface. In addition, the TPD results present us with the information necessary to select intermediate temperatures to isolate the salient adsorbate states along the reaction pathway for spectroscopic studies.

3.2. NEXAFS — benzaldehyde reaction on reduced TiO_2(0 0 1)

In the current study, we focus on the variation of the near-edge features that result from changes in the surface–adsorbate structures. For reference, we have presented NEXAFS spectra of the oxygen K-edge of bare TiO_2(0 0 1) reduced by ion bombardment and annealed to progressively higher temperatures in Fig. 4. As discussed in detail previously [13], the following changes occur as the annealing temperature of the crystal increases: (1) the $\Delta E(e_g - t_{2g})$ (at 532–535 eV) widens, and the intensity of the first feature relative to the second increases; (2) the σ^* feature at 546 eV shifts to a slightly higher energy and becomes more distinct from the feature at 541 eV; (3) the σ^* feature at 565 eV becomes more pronounced and shifts to higher energy (566 eV). All of these changes are due to the thermally induced conversion of reduced titanium oxides to the stoichiometric TiO_2(0 0 1) surface [13].

Fig. 5 shows the O K-edge spectra following the reaction of benzaldehyde on a reduced TiO_2(0 0 1) surface. The NEXAFS experiments were conducted by exposing an ion-bombarded single crystal of TiO_2(0 0 1) to 50 L exposure of benzaldehyde at 110 K. The crystal was then heated to progressively higher temperatures to create surfaces containing adsorbate structures peculiar to those temperatures.

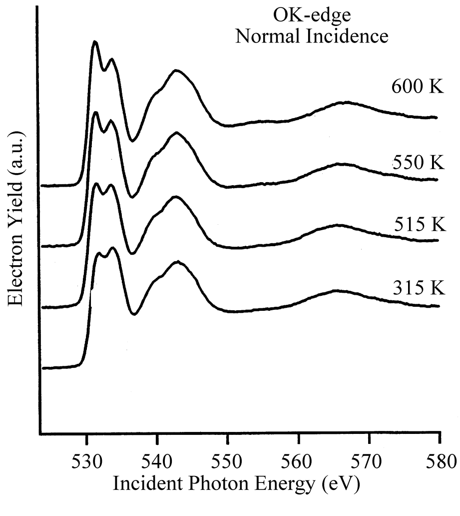

Fig. 4. Oxygen K-edge NEXAFS spectra of ion-bombarded TiO_2(0 0 1) annealed to progressively higher temperatures.

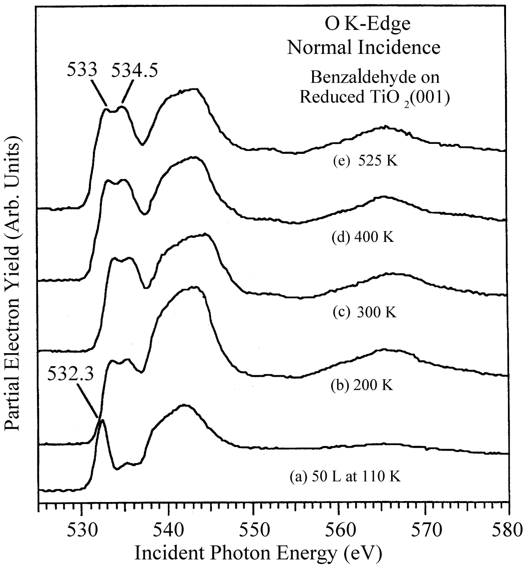

Fig. 5. Oxygen K-edge NEXAFS spectra of (a) multilayer benzaldehyde and (b–e) the reduced surface of $TiO_2(0\,0\,1)$ exposed to benzaldehyde and flashed to progressively higher temperatures. The incident light is normal to the surface.

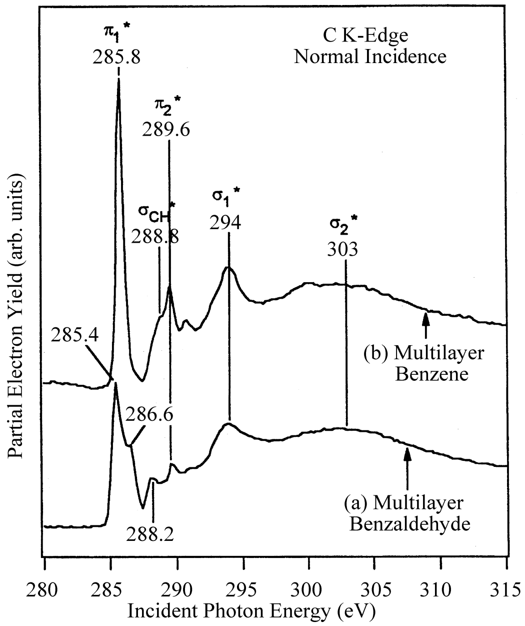

Fig. 6. Carbon K-edge NEXAFS spectra of (a) multilayer benzaldehyde and (b) multilayer benzene. The incident light is normal to the surface.

The crystal was then cooled and illuminated with synchrotron light for NEXAFS study. The spectrum (a) of Fig. 5 represents a multilayer of benzaldehyde adsorbed on the surface at 110 K. The multilayer is thick enough to effectively screen the transitions of the surface lattice oxygen, revealing only the transitions of the benzaldehyde adlayer. The π^* transition of the carbonyl shows up at 532.3 eV, and the σ^* transition appears at approximately 541.5 eV. In contrast, the spectrum from a surface exposed to benzaldehyde and heated to 200 K (after the molecular state of benzaldehyde has desorbed) represents the contributions from surface lattice oxygen atoms and the adsorbed coupling intermediate. The energy splitting between the t_{2g} and e_g edge features is about 1.0 eV. The σ feature is also more pronounced for the 200 K surface than for the multilayer. The 300 K surface displays similar positioning of the lattice oxygen π^* transitions, although the $\Delta E(e_g - t_{2g})$ widens slightly and the σ^* transition is diminished substantially in intensity. This suggests that oxygen atoms from the original adsorbate molecules have been donated to the surface of the metal oxide, and thus that stilbene is now adsorbed on the surface. The stilbene begins to desorb between 300 and 400 K, and the O K-edge feature is essentially indicative of a bare, reduced titania surface above this temperature range. Product desorption is nearly complete by 525 K, and the K-edge transition looks nearly identical to that of sputtered and partially reoxidized titania.

Fig. 6 illustrates the NEXAFS carbon K-edge of reduced titania surfaces exposed to 50 L of benzaldehyde. The C K-edge of multilayer benzene on a similarly prepared surface is presented for comparison. The transition at 285.8 eV is characteristic of the π^* anti-bonding orbitals of the aromatic carbon in benzene; the transition occurs at 285.4 eV for multilayer benzaldehyde. The benzaldehyde spectrum exhibits an additional π^* transition at 286.6 eV, which is characteristic of the carbonyl group. The transitions for σ^* anti-bonding orbitals for benzaldehyde are in good agreement with those for multilayers of benzene.

Fig. 7 presents spectra following the annealing of a multilayer of benzaldehyde on the reduced titania surface to different temperatures; the multilayer spectrum at 110 K has been reproduced here for comparison. After annealing to 200 K the NEXAFS spectrum shows a

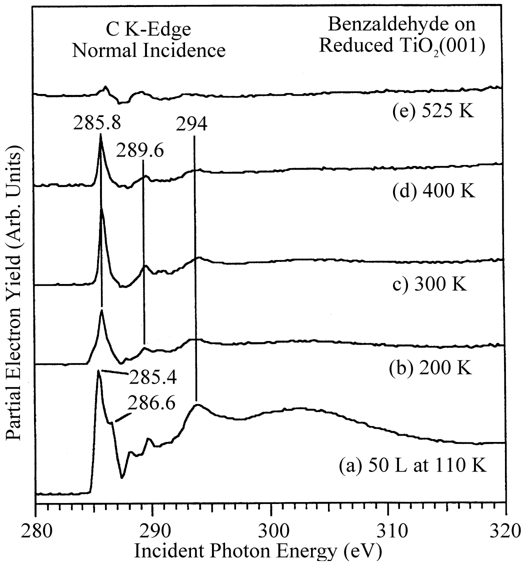

Fig. 7. Carbon K-edge NEXAFS of (a) multilayer benzaldehyde and (b–e) the reduced surface of $TiO_2(0\,0\,1)$ exposed to benzaldehyde and flashed to progressively higher temperatures. The incident light is normal to the surface.

π^* transition centered at 285.8 eV and a σ^* transition centered at 294 eV. These features are compatible with the multilayer spectrum, although the carbonyl transition is not as apparent in this spectrum. Also, the edge jump is substantially less for the 200 K spectrum, consistent with the desorption of multilayer benzaldehyde at 180 K (see TPD results in Fig. 2). By comparing Fig. 7b with Fig. 7a, it is obvious that the adsorbate layer at 200 K does not exhibit as pronounced a peak for the carbonyl at 286.6 eV as that of the multilayer spectrum, suggesting that either chemisorbed benzaldehyde or the pinacolate intermediate is the principal species on the surface at this temperature. After heating the surface to 300 K, the π^* transition sharpens and becomes more intense. The incident synchrotron light is normal to the surface for these spectra, so this behavior suggests that the π orbitals of the aromatic rings have become more parallel to the surface, since they interact more strongly with the wave vector of the incident beam. This would be expected of molecules of stilbene bound to the surface, for which the phenyl rings could rotate to minimize surface steric interactions. In TPD experiments, benzaldehyde has already begun to desorb by 400 K; that is echoed in the corresponding NEXAFS spectrum. The features retain the peak width and position shown from lower temperature spectra, but are less intense. The NEXAFS spectrum recorded after heating to 525 K reveals a near complete disappearance of C K-edge features.

Based on the oxygen K-edge spectra shown earlier, all of the oxygen atoms in benzaldehyde were donated to the surface at 300 K and above, indicating that the reductive coupling chemistry was completed below 300 K. Since molecular benzaldehyde desorbs from the surface at 180 K, the NEXAFS spectrum for an exposed surface subsequently flashed to 200 K may contain the transitions associated with the pinacolate intermediate, although it is not possible to resolve it from chemisorbed benzaldehyde.

3.3. NEXAFS — polarization-dependent measurements

One can also learn about the orientation of adsorbates using NEXAFS by illuminating the surface of the crystal with synchrotron light at different incident angles. As the π and σ orbitals interact differently with polarized light, it is possible to extract orientation information. Fig. 8a illustrates this for the carbon K-edge transition. The surface was exposed to benzaldehyde and then flashed to 250 K to remove the molecular state of benzaldehyde. The NEXAFS spectra were then recorded with the incident photon beam at normal (90°) or at glancing (30°) incidences. The NEXAFS spectra show no substantial difference in the intensity of the C K-edge features, indicating that either the phenyl rings are angled away from the surface, or that there is a random orientation of benzene rings on the surface and that one observes the averaged result of those dipole planes. On a flat single crystal surface with a symmetry higher than C_3, this behavior would be consistent with a tilt angle for the phenyl rings of 54° relative to the surface normal. However, the local orientation(s) of the sputtered surface are less clearly defined, and a distribution of phenyl group orientations is plausible. Were the surface covered in a random array of chemisorbed benzaldehyde, the oxygen K-edge would also appear to have no surface orientation dependence [9]. That is not the case, the polarization-dependent spectra showed that the carbonyl is tilted over on the surface as discussed below.

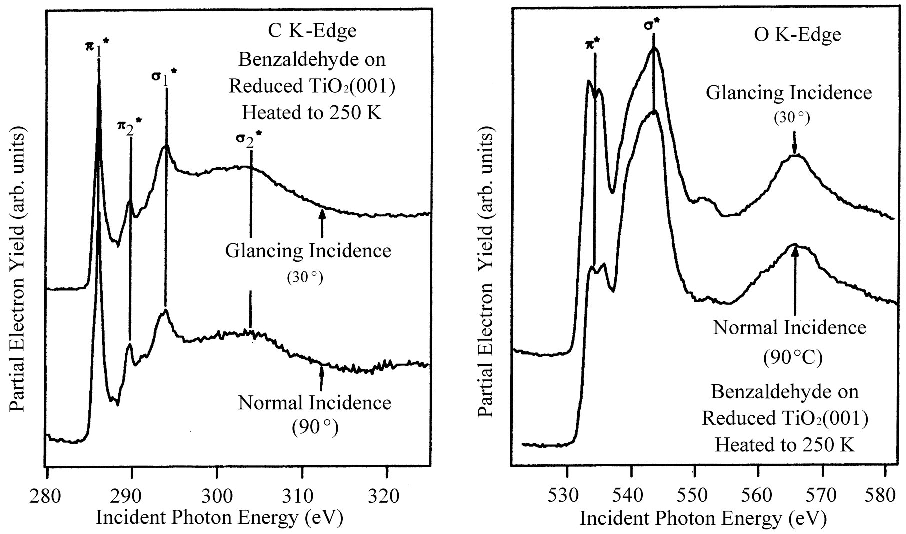

Fig. 8. NEXAFS of benzaldehyde exposed to the reduced surface of $TiO_2(0\,0\,1)$ and subsequently flashed to 250 K with the illuminating light at 90° incidence and 30° incidence to the surface. (a) Carbon K-edge; (b) oxygen K-edge.

Fig. 8b illustrates the oxygen K-edge spectra recorded at normal and glancing incidences. The ion-bombarded surface was cooled and exposed to benzaldehyde and then heated to 250 K to desorb molecular benzaldehyde from the surface. Light incident along the surface normal produced a relatively weak π^* transition at 533 eV. A carbonyl perpendicular to the surface would be expected to have strong π^* orbital coupling with the wave vector of the photon beam at normal incidence; this is not the case here. In contrast, the glancing incidence spectrum (30° to the surface plane) couples much more strongly with the π orbitals of the carbonyl, suggesting that the carbonyl bond is tilted at least 45° away from the nominal surface normal. Because the O K-edge region is complicated by contributions from the $TiO_2(0\,0\,1)$ substrate, at present we cannot provide more quantitative information about the tilting angle of the carbonyl groups. It is not clear why the carbonyl is tilted in this manner, although such a steep tilt could perhaps result from the coupling intermediate. The oxygen atoms, not yet donated to the surface lattice at this point, could occupy dangling bonds above the titanium atoms. If the intermediate is a pinacolate bound to neighboring surface cations, as usually depicted for reductive coupling in liquid–solid slurries, then considerable reorientation must accompany the rehybridization of the original carbonyl carbons from sp^2 to sp^3. Only the carbon–carbon bond formed in synthesis of the pinacolate from two aldehyde molecules would be expected to be oriented parallel to the surface plane; the orientation of all other bonds in this intermediate are expected to be skewed.

3.4. NEXAFS — reoxidation of TiO_2 by oxygen abstraction

Earlier work in this group utilized NEXAFS to study the reduction and oxidation mechanisms involved in preparing these surfaces. Among the results of that study, it was shown that it is possible to correlate the surface O/Ti ratio by the expression

$$\frac{\mathrm{O}}{\mathrm{Ti}} = 2\left(\frac{\text{O edge jump}}{\text{Ti edge jump}}\right)$$

when O/Ti is normalized to 2.0 for the unsputtered surface. This correlation was found to be in good agreement with earlier XPS work [13]. Fig. 9 presents the Ti L-edge and O K-edge spectra before and after benzaldehyde TPD. The changes in the ratio of the edge jumps for each are used to determine the O/Ti ratio before and after the TPD experiments. Before benzaldehyde has been adsorbed to the surface, the O/Ti ratio is about 1.33; following the reaction of benzaldehyde

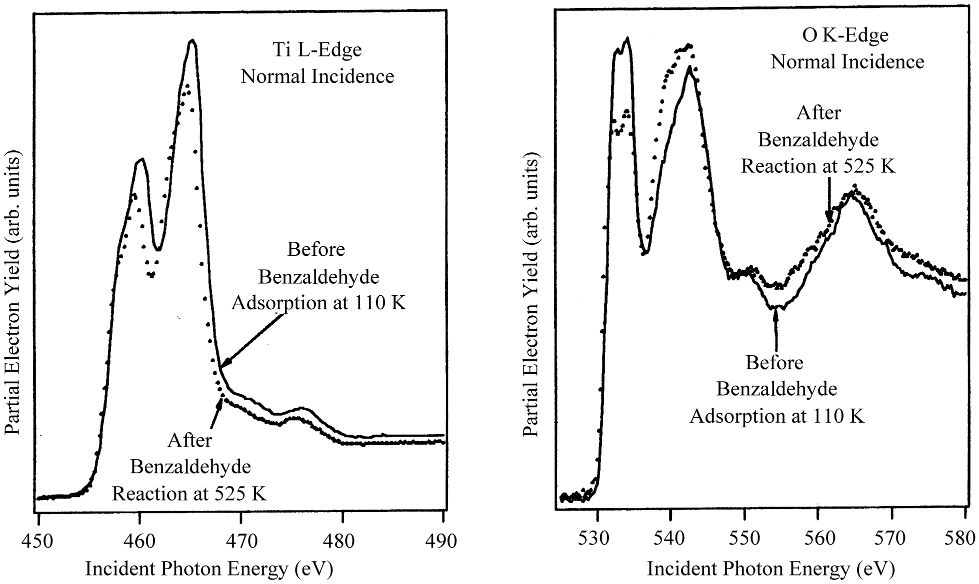

Fig. 9. NEXAFS of the reduced surface of $TiO_2(0\,0\,1)$ at 110 K prior to benzaldehyde exposure and after the desorption of the coupling product (stilbene) from the surface. The incident light is normal to the surface. (a) Titanium L-edge; (b) oxygen K-edge.

on the surface, the O/Ti ratio is about 1.4. The change in the O/Ti ratio is comparable to that calculated by Idriss et al. [7] from analysis of Ti(2p) XPS data before and after benzaldehyde reaction on the reduced surface. As is readily apparent from Fig. 9, the edge jump in the O K-edge region increases after completion of the coupling reaction, conclusively indicating that oxygen has been donated to the surface.

4. Conclusions

Although the analysis of some of the NEXAFS features is complicated by contributions from the oxide surface, the ability of this technique to probe surface–adsorbate interactions along the reaction pathway reveals information about reductive coupling on the $TiO_2(0\,0\,1)$ surface that was inaccessible to earlier studies. Examining the O K-edge as a function of annealing temperature indicates that all of the oxygen originally contained by the carbonyl groups is donated to the surface by 300 K, and thus reductive coupling is complete by 300 K. Polarization-dependent study of the C K-edge reveals that the phenyl rings are oriented at 54° to the surface. As stilbene is produced, the phenyl groups become more parallel to the surface to minimize steric interaction. The intermediate suggested by these results collectively is consistent with the pinacolate intermediate previously proposed, an intermediate in the process of rehybridization about a carbon center, converting from a chemisorbed carbonyl into an adsorbed olefin surface species.

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