

# Adsorbate conformation determines catalytic chemoselectivity: crotonaldehyde on the Pt(111) surface†

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Received (in Cambridge, UK) 13th January 2005, Accepted 16th February 2005

First published as an Advance Article on the web 24th February 2005

DOI: 10.1039/b500590f

**Molecular orientation, which depends on surface coverage, determines whether or not catalytic hydrogenation is chemoselective.**

The metal-catalysed heterogeneous chemoselective hydrogenation of  $\alpha$ ,  $\beta$ -unsaturated aldehydes to yield unsaturated alcohols is mechanistically interesting and experimentally challenging because the thermodynamics strongly favour hydrogenation of the C=C bond rather than the C=O bond. These reactions are also technically important as the products are important intermediates in the production of fine chemicals and pharmaceuticals. Achieving selective hydrogenation of only the C=O bond calls for the manipulation of kinetic effects in order to favour the desired reaction pathway. As a consequence, the heterogeneous chemoselective hydrogenation of unsaturated aldehydes, especially crotonaldehyde (CH<sub>3</sub>CH=CHCHO), has been extensively studied, both experimentally and theoretically, and a recent comprehensive review of the subject is available.<sup>1</sup> Hydrogenation may be carried out at both the gas–solid and gas–liquid interfaces and a variety of factors have been proposed to account for the range of behaviour observed, including molecular geometry and electronic structure and the structure and composition of the solid catalyst. However, because most work has concentrated on the measurement of catalytic rates and selectivities, with few direct observations on the relevant adsorbed species, well-founded and fundamental insight is largely lacking. de Jesus and Zaera<sup>2</sup> studied the adsorption of crotonaldehyde on Pt(111) by means of infrared spectroscopy under conditions of uncertain adsorbate coverage. They concluded that the C=O bond was parallel to the metal surface at “low coverage” and speculated that a degree of molecular re-orientation may have occurred at some higher coverage. However they were unable to provide a detailed analysis of the C=C bond orientation. Here, by quantitatively determining the molecular conformation of crotonaldehyde as a function of its coverage on a well defined platinum (111) surface, we find a strong re-orientation of the C=O bond at high adsorbate coverage, whereas the C=C geometry remains unperturbed. As we shall see, this is in good accord with experimental observations of the dependence of selectivity towards unsaturated alcohol formation on partial pressure (coverage) of the reactant.<sup>3–5</sup> It also verifies recent theoretical proposals<sup>6</sup> about the coverage dependence of the

adsorption geometry of the C=C–C=O framework in these molecules when adsorbed on the Pt(111) surface.

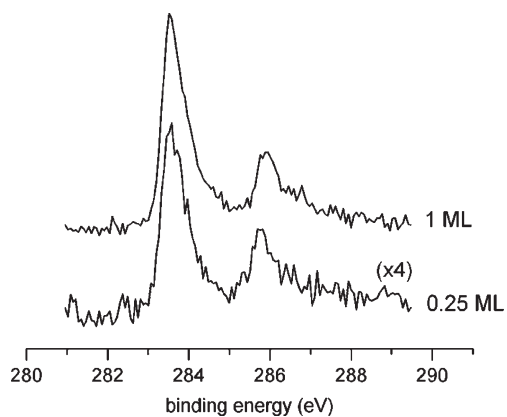
A combination of near edge X-ray absorption fine structure (NEXAFS) spectroscopy and high resolution XPS were used to examine the C=C and C=O bonds in adsorbed crotonaldehyde and their orientation with respect to the metal surface. Measurements were carried out on the SuperESCA beamline at the ELETTRA synchrotron radiation facility in Trieste, Italy, using well established procedures described in detail elsewhere<sup>7</sup> and the data were analysed according to standard methodology.<sup>8</sup> Control experiments using XPS showed that there were no detectable beam damage effects on the adsorbed layer during the acquisition of NEXAFS data.

The Pt(111) surface was cleaned by cycles of heating in oxygen ( $\sim 1 \times 10^{-7}$  mbar, 773 K) and Ar<sup>+</sup> bombardment at 323 K followed by annealing in vacuum at 1173 K. During the succeeding experiments, the integrity of the surface was checked periodically by LEED and XPS. Reagent grade crotonaldehyde (Sigma Aldrich) was purified by means of freeze–pump–thaw cycles and the vapour was dosed onto the Pt(111) surface *via* a collimator tube. The XP spectra are referenced to the Pt 4f<sub>7/2</sub> line at 70.9 eV and quoted crotonaldehyde coverages were determined by XPS. The monolayer point (=1 ML) was calibrated by fast XPS measurements during continuous uptake of crotonaldehyde at 77 K: onset of second layer formation was readily identified by a 0.1 eV upshift in the C 1s binding energy and relevant details are provided in the supplementary information.† The accuracy of our coverage calibration ensures that none of the data presented here are compromised by the onset of multilayer growth.

Fig. 1 shows C 1s XP spectra acquired at 77 K for 1 ML and 0.25 ML coverages of crotonaldehyde. In both cases, two peaks appear with an intensity ratio of 3:1 corresponding to the CH<sub>3</sub>CH=CH moiety<sup>9</sup> (283.6 eV) and the carbonyl carbon<sup>9</sup> (285.9 eV). These results, along with the observation of the C=C and C=O resonances in the NEXAFS spectra (see below) confirm that, at both coverages, the molecule adsorbs intact.

Carbon K-edge coverage NEXAFS data were acquired for 0.25 ML and 1 ML coverages at five angles of photon incidence ( $\theta$ ) ranging from grazing to normal incidence. Fig. 2 shows representative results for the case of *high* crotonaldehyde coverage (1 ML). The two  $\pi^*$  resonances of interest labelled A (285.0 eV) and B (287.1 eV) are associated with the C=C and C=O components of the molecule, respectively<sup>9</sup> (the sharp peak adjacent to resonance B is due to another C=C  $\pi^*$  resonance, see supplementary information for a complete assignment of the NEXAFS transitions†). Simple inspection of the data shows that

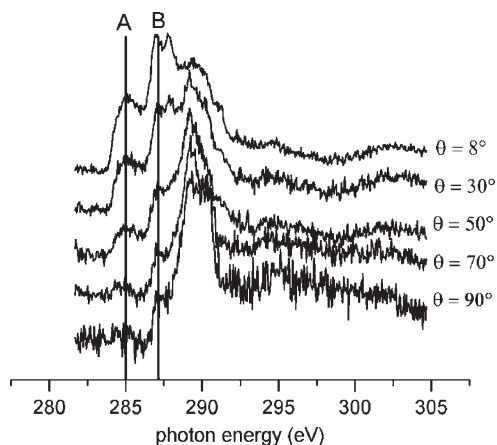
† Electronic supplementary information (ESI) available: NEXAFS transition assignment and XPS crotonaldehyde uptake. See <http://www.rsc.org/suppdata/cc/b5/b500590f>  
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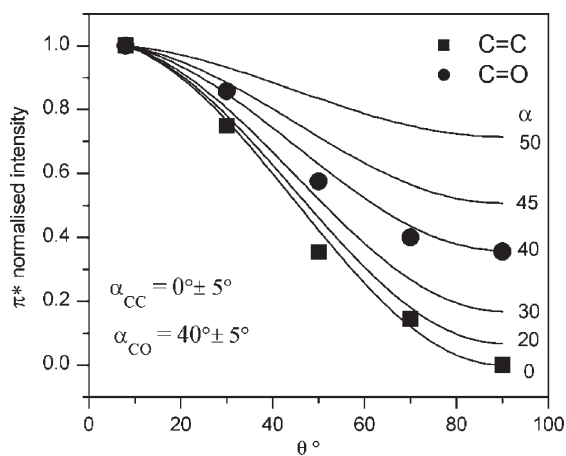
**Fig. 1** C 1s region XP spectra at 77 K for 1 ML and 0.25 ML coverages of crotonaldehyde.

the intensity of resonance A decreases rapidly with increasing angle of incidence, vanishing altogether at normal incidence. The angular dependence of B is clearly less pronounced, and there is appreciable residual intensity at normal incidence. Therefore we can immediately draw the qualitative conclusion that the C=C bond lies essentially parallel to the Pt surface whereas the C=O bond is tilted. Quantitative evaluation of the tilt angles ( $\alpha$ ) with respect to the metal surface may be achieved by calculating the  $\pi^*$  resonance intensity variation as a function of photon incidence angle, according to the standard method described by Stohr,<sup>10</sup> and comparing the results with experiment. The results of this procedure are illustrated in Fig. 3, from which it is apparent that at 1 ML coverage the C=C bond lies parallel to the surface ( $\alpha = 0^\circ$ ) whereas the C=O bond is strongly tilted.

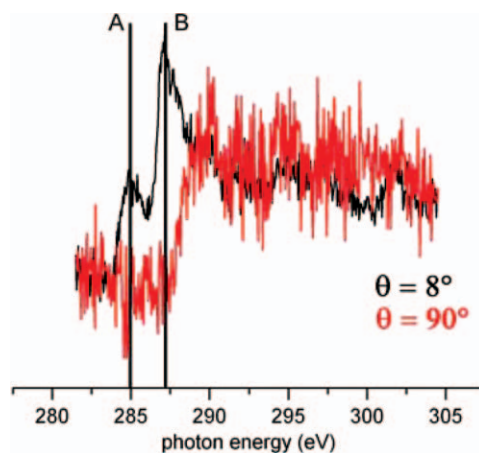
Fig. 4 shows grazing and normal incidence NEXAFS spectra for the case of low crotonaldehyde coverage (0.25 ML). It is immediately evident that the adsorption geometry is very different from the high coverage case: now, resonances A and B *both* vanish at normal incidence ( $\theta = 90^\circ$ ). This shows that at low coverages the C=C and C=O bonds are *both* parallel to the metal surface. Such coverage-dependent changes in adsorption geometry are not unusual and generally ascribed to the effects of intermolecular interactions within the adsorbed layer.<sup>11</sup> Interestingly, in the present case they also appear to affect catalytic behaviour.



**Fig. 2** C K-edge NEXAFS spectra for 1 ML of crotonaldehyde adsorbed at 77 K.



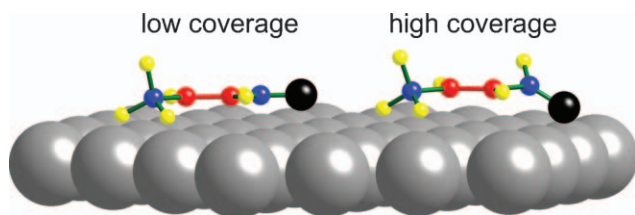
**Fig. 3** The  $\pi^*$  resonance intensities normalised to the intensity at  $8^\circ$  for both C=C bond and the C=O bond for 1 ML coverage.



**Fig. 4** C K-edge NEXAFS spectra for 0.25 ML of crotonaldehyde adsorbed at 77 K.

We may now discuss the implications of our findings for the catalytic hydrogenation of both crotonaldehyde<sup>3,4</sup> and 3-methyl crotonaldehyde<sup>5</sup> where it is found that increasing reactant partial pressure (*i.e.* increasing reactant coverage) results in an increase in selectivity towards formation of the (desired) unsaturated alcohol product. Our NEXAFS results clearly show that the orientation of the C=C bond with respect to the metal surface is invariant with reactant coverage, whereas the C=O bond undergoes a pronounced re-orientation as coverage increases, becoming strongly tilted (either “up” or “down”) with respect to the surface ( $\alpha = 40^\circ$ ). We infer that the tilt must be “down” because (i) experiment shows that at high coverage C=O hydrogenation is favoured as opposed to inhibited (the latter would be consistent with upward tilt); (ii) DFT calculations<sup>6</sup> indicate that on Pt(111), at low coverages, both molecules adsorb with C=C and C=O parallel to the metal surface while at high coverages new structures are favoured in which the C=O function is strongly directed towards the surface. Our experiments provide direct confirmation that such pronounced coverage-dependent effects do indeed occur.

Thus chemoselectivity in the catalytic hydrogenation of crotonaldehyde and structurally related  $\alpha,\beta$ -unsaturated aldehydes, appears to be influenced by the adsorption geometry of the



**Fig. 5** Suggested adsorption geometries of crotonaldehyde on Pt(111) at low (left) and high coverage (right). C=C shown in red; =O atom shown in black.

reactant. Strong re-orientation of the C=O function, as illustrated below, promotes its hydrogenation. It is possible that this change in adsorption geometry is accompanied by increased separation of the C=C bond from the surface, as suggested by the simple model shown in Fig. 5, which could also act to increase selectivity towards formation of the unsaturated alcohol. Photoelectron diffraction experiments are planned in order to test this latter possibility.

In summary, spectroscopic observations unambiguously demonstrate that the adsorption geometry of crotonaldehyde on platinum is highly coverage dependent. The C=C bond remains parallel to the surface under all conditions whereas the C=O bond switches from parallel to strongly tilted geometry as coverage increases. These findings provide insight into the way in which conformation

of the adsorbed reactant determines its subsequent catalytic behaviour.

FJW acknowledges financial support from the Leverhulme Trust. The authors thank Dr S. Lizzit and Dr L. Petaccia for their assistance during the synchrotron experiments.

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