

# Sulfur, normally a poison, strongly promotes chemoselective catalytic hydrogenation: stereochemistry and reactivity of crotonaldehyde on clean and S-modified Cu(111)<sup>†</sup>

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**Sulfur adatoms strongly activate the otherwise inert Cu(111) surface towards chemoselective hydrogenation of crotonaldehyde by electronically perturbing and strongly tilting the reactant.**

Unsaturated alcohols are valuable intermediates in the fine chemicals and pharmaceuticals industries. Their production by chemoselective heterogeneous hydrogenation of the corresponding unsaturated aldehydes is difficult<sup>1</sup> because thermodynamics favours C=C hydrogenation over C=O hydrogenation. Therefore, the desired selectivity can only be achieved by exercising kinetic control over the competing reaction pathways. Previously, in the case of Pt(111), we showed by means of NEXAFS that single crystal studies can provide insight into the observed dependence on reactant partial pressures of C=C/C=O hydrogenation chemoselectivity.<sup>2</sup> However, in that case we were unable to investigate the reactive properties of the system under vacuum conditions due to decomposition of crotonaldehyde on platinum at  $T > 300$  K. Here, with Cu(111) we are able to examine both the reactive behaviour and the corresponding adsorption geometries of crotonaldehyde in the presence of (i) H(a) alone and (ii) H(a) + S(a). It is found that sulfur, normally a potent catalyst poison, strongly activates the otherwise inactive copper surface towards crotyl alcohol formation, a result that is understandable in terms of its effect on the electronic structure and orientation of the C=C and C=O bonds. Our findings are in excellent accord with, and provide an explanation for, the observations of Hutchings *et al.*, who showed that addition of sulfur to Cu/Al<sub>2</sub>O<sub>3</sub> catalysts operated at atmospheric pressure greatly increased selectivity towards crotyl alcohol production.<sup>3</sup>

Crotonaldehyde hydrogenation was studied in an ultra-high vacuum chamber (Cambridge) by means of temperature programmed reaction (TPR;  $3 \text{ K s}^{-1}$ ) with mass spectrometric detection of the desorbing species. The data are corrected for mass spectrometer sensitivity, molecular ionisation cross-sections, and fragmentation patterns. High resolution X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure spectroscopy (NEXAFS) were used to examine surface composition, adsorbate electronic structure and orientation of the C=C and C=O bonds in crotonaldehyde in the presence of H(a). These

measurements were carried out on the SuperESCA beamline at the ELETTRA synchrotron radiation facility in Trieste, Italy using well-established procedures detailed elsewhere.<sup>4</sup> The data were processed in accordance with standard methodology.<sup>5</sup>

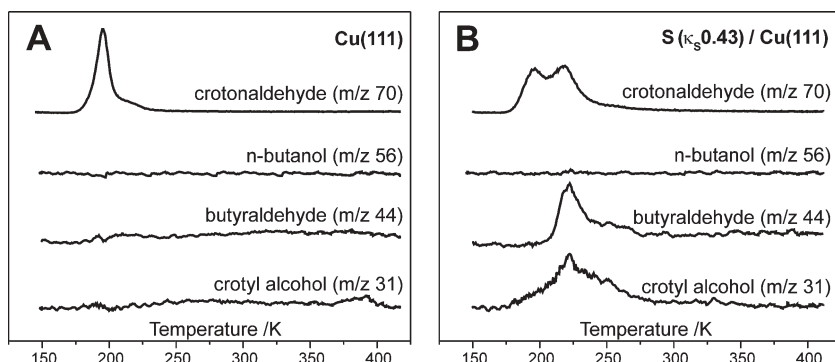
The Cu(111) surface was cleaned by Ar<sup>+</sup> bombardment at 800 K, followed by annealing in vacuum at 800 K. Surface integrity was checked by LEED and Auger electron spectroscopy in Cambridge, and by XPS in Trieste. Reagent grade crotonaldehyde (>99.9%, Sigma Aldrich) was purified before use by means of freeze-pump-thaw cycles; surface coverages were calibrated by temperature programmed desorption (Cambridge) and by fast XPS (Trieste) as shown in the supplementary information.<sup>†</sup> The monolayer point was easily identifiable by both techniques, enabling crotonaldehyde doses to be delivered with good accuracy ( $\pm 5\%$ ). Dissociative chemisorption of dihydrogen on Cu(111) is activated and therefore extremely slow under ultra-high vacuum conditions; accordingly a hot filament source<sup>6</sup> was used to generate a flux of H atoms, thus enabling the required hydrogen coverages to be achieved on a convenient timescale. Sulfur was deposited using an electrochemical source<sup>7</sup> that produced a beam of (largely) S<sub>2</sub> molecules, enabling precise control of S coverage.

In every case, the dosing sequence was (a) sulfur at room temperature (if used), (b) hydrogen at 200 K and (c) crotonaldehyde at 150 K. The effects of sulfur were studied by working with the ( $\sqrt{7} \times \sqrt{7}$ )R19°-S surface, its formation being monitored by LEED and Auger spectroscopy. Adsorbate fractional coverages ( $\kappa_X$ ; X = crotonaldehyde, S, H) are specified relative to the number density of metal atoms in the Cu(111) surface.

Fig. 1A shows TPR spectra acquired after co-adsorption of crotonaldehyde and hydrogen ( $\kappa = 0.23$  and  $0.67$  respectively) on clean Cu(111). It is apparent that no hydrogenation reactions occur in this case: all the initially adsorbed crotonaldehyde desorbed intact at  $\sim 200$  K, accompanied by dihydrogen desorption at  $\sim 325$  K. Fig. 1B shows the corresponding TPR data obtained from the sulfur pre-dosed ( $\sqrt{7} \times \sqrt{7}$ )R19°-S surface ( $\kappa = 0.43$ ). A mixture of partial hydrogenation products desorbed; crucially, crotyl alcohol, the desired and thermodynamically disfavoured product was formed, along with the saturated aldehyde. Quantification of these data *via* appropriate calibration of the mass spectrometer showed that the selectivities towards crotyl alcohol and butyraldehyde formation were  $\sim 56\%$  and  $\sim 34\%$  respectively. This is in remarkable agreement with the findings of Hutchings *et al.*<sup>3</sup> who investigated the same reaction with S-promoted Cu/Al<sub>2</sub>O<sub>3</sub> catalysts operated under practical conditions and found that S caused a substantial increase in

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**Fig. 1** TPR spectra for (A) crotonaldehyde + H(a) ( $\kappa = 0.23$  and  $0.67$ ) and (B), the same as A, in the presence of S ( $\kappa = 0.43$ ).  $m/z$  70 is scaled by  $1/30$ .

selectivity towards crotyl alcohol formation. Specifically, at the lowest temperature they used ( $\sim 330$  K) which is closest to the temperature regime of our experiments, they observed selectivities towards crotyl alcohol and butyraldehyde formation of 44% and 25% respectively. It is also apparent from Fig. 1 that S induced a more strongly bound state of adsorbed crotonaldehyde, which desorbed at  $\sim 225$  K. We suggest that this is the catalytically active species—stronger binding of the molecule to the surface is accompanied by a weakening of the intramolecular bonding, thus activating the molecule to hydrogenation;<sup>8</sup> as we shall see, this view accords well with the XPS results.

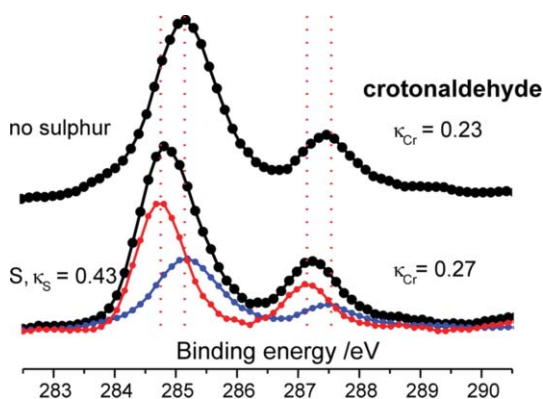
The synchrotron XPS data are also consistent with the presence of two distinct states of crotonaldehyde on the S-modified surface. Fig. 2 shows C 1s XP spectra acquired at 77 K for crotonaldehyde on the clean Cu(111) surface and in the presence of sulfur ( $\kappa = 0.43$ ). In both cases, two peaks appear with 3 : 1 intensity ratio consistent with the presence of intact crotonaldehyde molecules;<sup>2</sup> it is also apparent that S causes a very significant decrease in the apparent binding energy of both components, pointing to the presence of an S-perturbed state of crotonaldehyde. The emission due to the S-induced state may be extracted from the raw data as a difference spectrum, indicated by the red curve in Fig. 2 which shows that S causes an equal reduction in the binding energy of both components by  $\sim 0.38$  eV, consistent with  $S \rightarrow$  molecule charge transfer. This could imply partial population of the C=C

and C=O  $\pi^*$  orbitals, weakening these bonds and thus activating them towards hydrogenation.

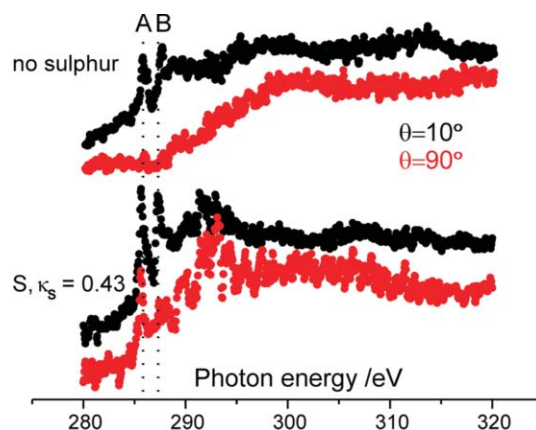
The presence of both C=C and C=O resonances in the NEXAFS (Fig. 3) provides strong confirmation that crotonaldehyde adsorbs intact on both the clean surface and the S-modified surface; their intensities were invariant with time indicating the absence of beam damage effects.

Crotonaldehyde C K-edge NEXAFS data were acquired at five photon incidence angles ( $\theta$ ) for both the clean and S-modified surfaces in the presence of hydrogen adatoms ( $\kappa_{Cr} \sim 0.25$ ;  $\kappa_S = 0.43$ ;  $\kappa_H = 0.67$ ); they should therefore be relevant to an understanding of the catalytic system. The dominant spectral features are two sharp peaks marked A and B (Fig. 3) assigned to the C=C and C=O  $\pi^*$  transitions, respectively.<sup>2</sup> From the characteristic changes in their intensities between  $\theta = 10^\circ$  and  $\theta = 90^\circ$  it is immediately apparent<sup>5</sup> that in the absence of sulfur both the C=C bond and the C=O bonds are essentially parallel to the metal surface. Strikingly, in the presence of S, it is clear that the molecular geometry is strongly altered (Fig. 3, bottom spectra) as discussed in detail below.

The results of a full analysis of the NEXAFS intensity data<sup>5</sup> are shown in Fig. 4 which permits an estimation of the C=C and C=O tilt angles ( $\alpha$ ) with respect to the metal surface. In the absence of S, both carbonyl and alkene functions are parallel to the surface—the molecule lies flat. In the presence of sulfur, detailed interpretation of the NEXAFS data is more complicated. Here, both the C=O and C=C intensities initially decrease with  $\theta$  but then increase



**Fig. 2** C 1s XP spectra at 77 K for crotonaldehyde submonolayer on clean Cu(111) (top) and S-treated surface (bottom). Energy scale referenced to the Cu  $3p_{3/2}$  line at 75.0 eV. Difference spectrum shown in red (scaled top spectrum (blue) subtracted from bottom spectrum).



**Fig. 3** C K-edge NEXAFS spectra at 77 K for crotonaldehyde and H(a) ( $\kappa_H = 0.67$ , crotonaldehyde and S coverages as in Fig. 2).

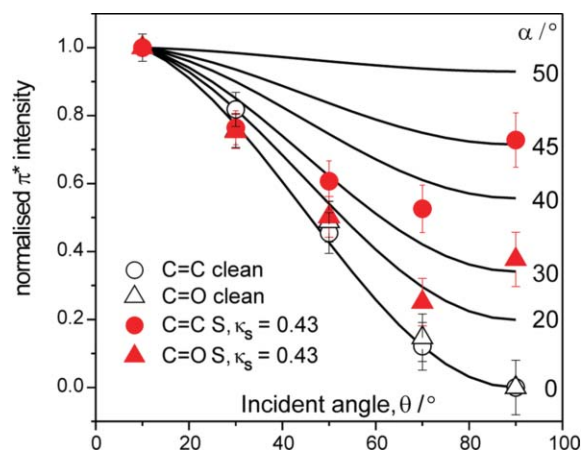


Fig. 4  $\pi^*$  resonance intensities normalised to intensity at  $10^\circ$  for the C=C and C=O bonds on clean Cu(111) and S/Cu(111) ( $\kappa_s = 0.43$ ).

again at normal incidence ( $\theta = 90^\circ$ ). This indicates the presence of more than one type of chemisorbed crotonaldehyde—as expected on the basis of the TPD and XPS results. Some molecules lie essentially flat and some, perturbed by S, have both C=O and C=C tilted with respect to the surface. Inspection of Fig. 4 shows that the manifestation of tilting at  $\theta > 60^\circ$  are much more pronounced for C=C than for C=O. The implications are that (i) in the tilted molecules C=C is much more inclined than C=O or (ii) there are some molecules in which only C=C is tilted and C=O is unaffected or (iii) a combination of both effects. We infer that co-adsorbed sulfur electronically perturbs crotonaldehyde (XPS) activating it for hydrogenation by strengthening its interaction with the surface (TPD) and weakening the intramolecular bonding. The NEXAFS results show that this process involves substantial tilting of the C=C bond accompanied by some C=O tilting. The result is an overall increase in reactivity. Possible adsorption geometries are shown in Fig. 5 which depicts the more tilted C=C bond and the less tilted C=O bond, a configuration that should favour carbonyl hydrogenation relative to alkene hydrogenation as observed under practical reaction conditions.<sup>3</sup>

In summary, S adatoms on Cu(111) promote the activation of crotonaldehyde towards hydrogenation, notably with respect to formation of the unsaturated alcohol, which is the desired product. This is the result of S-induced rehybridisation of the adsorbed reactant which results in weakening of the intermolecular bonding

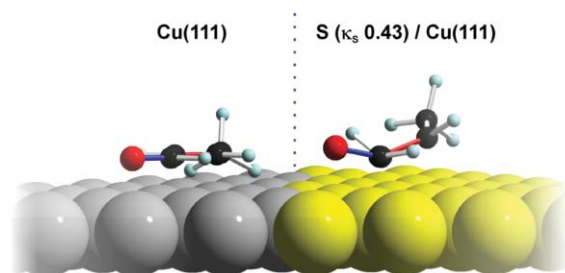


Fig. 5 Suggested adsorption geometries for crotonaldehyde on Cu(111) showing sulfur-induced tilting. The molecule is viewed down a C–C bond, with C=O shown in blue and C=C shown in red.

and tilting of the C=C and C=O groups with respect to the surface, thus facilitating interaction with adsorbed hydrogen. This re-orientation is most pronounced for the C=C bond, favouring the unsaturated alcohol, thus providing a plausible explanation for the effects of promotion by S on the performance of dispersed Cu catalysts operated at atmospheric pressure.<sup>3</sup> Our findings are also in harmony with earlier observations<sup>2</sup> on un-promoted Pt(111) in which case it was shown that increased reactant coverage induced tilting of the C=O bond thus favouring crotyl alcohol formation.

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