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Tilt the Molecule and Change the Chemistry: Mechanism of S-Promoted Chemoselective Catalytic Hydrogenation of Crotonaldehyde on Cu(111)**

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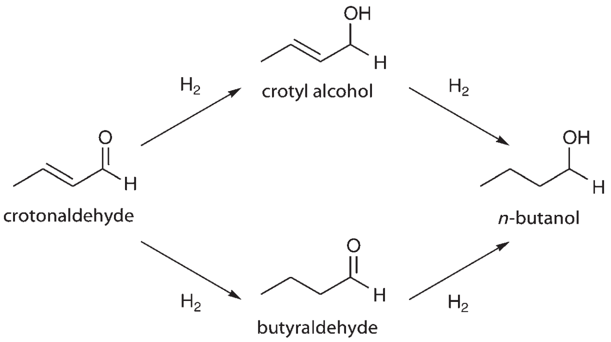
The chemoselective hydrogenation of α,β-unsaturated carbonyl compounds to form unsaturated alcohols is challenging, fundamentally interesting, and important both in the research laboratory and on a technical scale, as these materials are valuable and versatile intermediates in the production of fine chemicals and pharmaceuticals. Thermodynamics favors hydrogenation of the C=C bond to form the (unwanted) saturated aldehyde or ketone as shown in Scheme 1, which refers to the particular case of crotonaldehyde. Thus chemoselective C=O hydrogenation is a demanding process that requires the manipulation of kinetic effects by means of a suitable catalyst.



Scheme 1. Possible hydrogenation products of crotonaldehyde.

A variety of supported metal-particle catalysts (including Pt, Pd, Cu, Ag, Au, Ir, and Os) that exhibit a wide range of chemoselectivity have been investigated for this purpose,[1] though very little has emerged in terms of fundamental understanding. Theoretical studies[2] suggest that the adsorption geometry of the reactant molecule may be a key

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parameter in these systems, although direct experimental evidence for such effects is almost wholly lacking. Prompted by the striking findings of Hutchings and co-workers,[3] who reported that adsorbed sulfur strongly promoted the selectivity of practical dispersed Cu catalysts for production of crotyl alcohol from crotonaldehyde, we recently carried out a limited preliminary investigation[4] into the effects of a high coverage of sulfur (κ_S) on the adsorption and reactivity of crotonaldehyde on Cu(111). It was found that at a fractional surface coverage of $\kappa_S = 0.43$, sulfur activated the otherwise inert copper surface towards the formation of crotyl alcohol, albeit with very low efficiency, and an approximate evaluation of its effects on reactant adsorption geometry was performed, however, interpretation was restricted by the presence of a mixture of chemisorbed states.

Here, we present the results of a comprehensive investigation of crotonaldehyde hydrogenation on Cu(111) under very well defined conditions that enable determination of the reaction mechanism and elucidation of the mode of promoter action. By means of high-resolution X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption on fine structure (NEXAFS) studies, it is found that a very low sulfur coverage can induce 100 % conversion of adsorbed crotonaldehyde into crotyl alcohol, with essentially 100 % selectivity. By isolating the S-modified state and by taking advantage of the specificity of NEXAFS for the detection of double bonds and the ability of synchrotron photoemission to resolve chemically distinct species, we were able to follow the conversion of reactant into product and determine the orientation of both species with respect to the surface. This is an unprecedented observation of the evolution of a relatively complex surface-catalyzed reaction by these techniques, or indeed by any other technique.

Synchrotron radiation experiments were performed at the ELETTRA synchrotron radiation facility in Trieste (Italy). Deposition of sulfur and crotonaldehyde was monitored directly by using fast-XPS. Crotonaldehyde was dosed by backfilling the vacuum chamber with an accurately measured pressure of the vapor, and sulfur was produced as a beam of S_2 molecules generated by a solid-state electrochemical source.[5] Because dissociative chemisorption of dihydrogen on Cu(111) is significantly activated, hydrogen was supplied by means of a collimated hot filament atomizer.[6] This delivered a flux of hydrogen atoms directly to the sample surface, thus enabling the deposition of hydrogen with high coverages on a convenient timescale. NEXAFS intensity data were analyzed by following established standard methodology.[7]

Previous work established that the hydrogen-covered Cu(111) surface was completely inert towards crotonaldehyde hydrogenation,[4] and control experiments showed that maximum chemical activity occurred at a sulfur coverage of $\kappa_S = 0.16$ ($\kappa = 1$ corresponds to the atom density of Cu(111), 1.77×10^{15} atoms cm^{-2}). Accordingly, all the data were acquired with $\kappa_S = 0.16$. Figure 1 A shows C 1s fast-XPS data acquired during exposure of the sulfur-predosed Cu(111) surface to crotonaldehyde at 153 K. The spectra consist of two peaks in 3:1 intensity ratio, consistent with the presence of intact crotonaldehyde.[4,8] The peak with higher intensity that appears at lower binding energy is assigned to the three carbon atoms of the CH_3CHCH moiety: the lower intensity, higher binding energy peak is attributed to the carbonyl carbon atom, in agreement with expectation. It is clear that the molecule binds in two chemically distinct states, one associated with S-modified sites (285.10 eV) and the other being characteristic of adsorption at unperturbed sites (285.55 eV). Figure 1 B shows a decomposition of the C 1s spectrum into its two components. The S-modified state, which is populated first, is the more strongly adsorbed state of the two and could therefore be isolated by carrying out the adsorption at 173 K (Figure 1 C). Both states exhibit a 3:1 peak intensity ratio, indicating the presence of two distinct kinds of intact crotonaldehyde molecules.

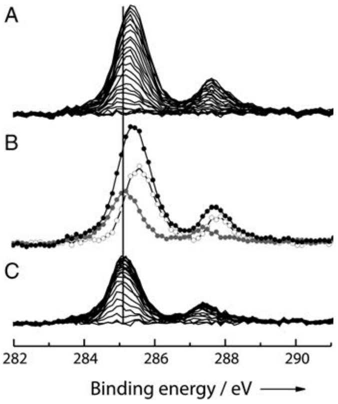

Figure 1. C 1s fast-XPS uptake of crotonaldehyde on the S-promoted Cu(111) surface ($\kappa_S = 0.16$) at 153 K (A) and 173 K (C). The S-bound state is isolated at 173 K. The decomposition of A into two components is shown in B: gray filled circles denote the S-bound state, and unfilled circles denote the unperturbed state.

C K-edge NEXAFS spectra for the isolated S-modified state were recorded at five photon-incidence angles (θ, defined relative to the surface plane) to determine the orientation of the C=C and C=O bonds with respect to the surface. (It is known that in the absence of S, the molecule lies essentially flat on Cu(111).[4]) Figure 2 A shows the raw data, which exhibit two π^* resonances centered at 282.30 and 284.45 eV: these may be assigned with confidence to the C=C and C=O bonds, respectively.[4,8–9] Simple inspection shows

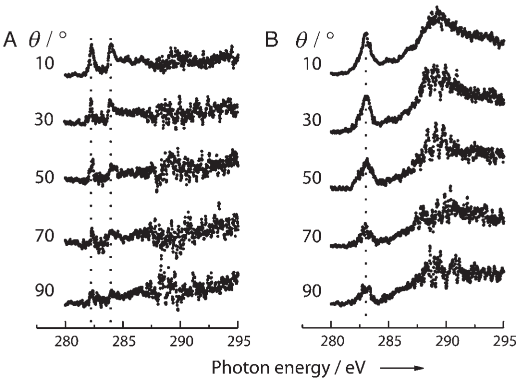

Figure 2. A) C K-edge NEXAFS of crotonaldehyde on Cu(111) predosed with S atoms ($\kappa_S = 0.16$). B) NEXAFS of the same surface taken immediately after dosing H atoms.

that both resonances are most intense at near-grazing photon incidence; moreover, on going towards normal incidence the relative intensity (I_θ) of the 284.45 eV resonance decreases fastest. We may immediately infer that both double bonds are tilted with respect to the surface, with the C=C bond significantly more tilted more than the C=O bond.

The S-promoted hydrogenation reaction was studied by preadsorbing crotonaldehyde at 173 K followed by dosing with atomic hydrogen ($\kappa_H \approx 0.7$), immediately after which the XPS and NEXAFS data were recorded. Hydrogen treatment caused a remarkable change in the NEXAFS spectra (Figure 2 B). The resonances at 282.30 and 284.45 eV corresponding to C=C and C=O bonds, respectively, were replaced by a single resonance at 282.92 eV. Clearly, a reaction had occurred leading to the hydrogenation of one of the double bonds: the question is, which one? XPS provided an unambiguous answer as illustrated in Figure 3, which shows C 1s and O 1s XPS before (top) and after (bottom) addition of hydrogen. The spectra obtained before addition of hydrogen are exactly as expected for crotonaldehyde; the positions of the carbonyl C 1s emission peak and the O 1s emission are characteristic of the C=O double bond.[10] After dosing with hydrogen, the C 1s and O 1s spectra were both markedly different: the entire C 1s spectrum shifts to lower binding energy, and crucially, the carbonyl peak shifts by a substantially greater amount. Conversely, the O 1s emission shifted to higher binding energy, consistent with S-induced valence charge transfer away from the oxygen atom thus activating the C=O bond towards hydrogenation. Both observations are diagnostic of the formation of a C–O single bond,[10] demonstrating unequivocally that chemoselective hydrogenation to form crotyl alcohol had occurred. We may therefore assign the single NEXAFS resonance in Figure 2 B to the C=C bond of the unsaturated alcohol. Note that the chemoselective reaction occurred on a timescale that was short compared with the observation time (≈10 min) with 100 % conversion of the reactant at 100 % selectivity.

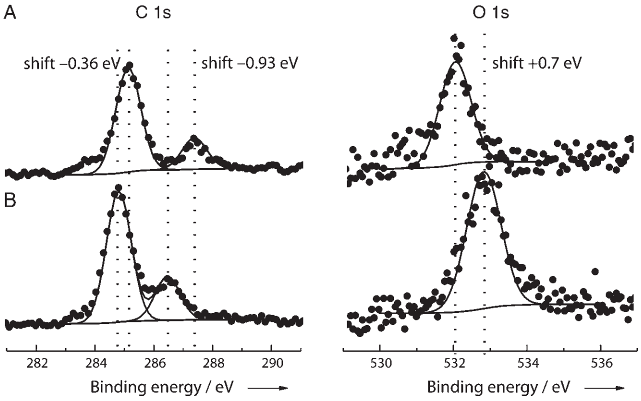

Figure 3. C 1s and O 1s XPS recorded before (A) and after (B) the hydrogen dose. Clear shifts in the spectra indicate that the formation of crotyl alcohol is achieved with 100 % conversion and selectivity.

The tilt angles of all three double bonds were evaluated by standard procedures,[9] which involved fitting the observed photon-incidence-angle dependence (normalized to $I_{10°}$) to the theoretically calculated dependence for a series of trial bond orientations. The optimum fits are shown in Figure 4, from which it is apparent that the C=C bond in crotonaldehyde is tilted with respect to the surface by approximately 36° whereas the C=O bond is tilted by about 23°. These results, taken with the XPS data, provide a plausible explanation for the activation of Cu by S and the observed 100 % selectivity towards crotyl alcohol formation (see below). Sulfur strongly perturbs the carbonyl function of crotonaldehyde (XPS), activating it towards hydrogenation whilst also inducing a pronounced tilt of the C=C function away from the surface (NEXAFS), rendering it immune from attack by hydrogen atoms, thus favoring formation of the unsaturated alcohol. Interestingly, a similar pronounced C=C tilt angle is also present in the crotyl alcohol product (≈39°) suggesting that this bond in the unsaturated alcohol should also be protected against hydrogenation, inhibiting its further hydrogenation to yield *n*-butanol, which would be the thermodynamically favored product. As we shall see, this ultraselective behavior was observed over the entire range of reactant conversion. (Note that Wahlström et al.[11] reported an ordered ($\sqrt{43}\times\sqrt{43})R7.5°$ S overlayer structure in the sulfur coverage regime relevant to the present work. Whether S-crotonaldehyde steric repulsion or some other type of interaction is responsible for C=C tilting can only be determined by theory, and such calculations are planned.[12])

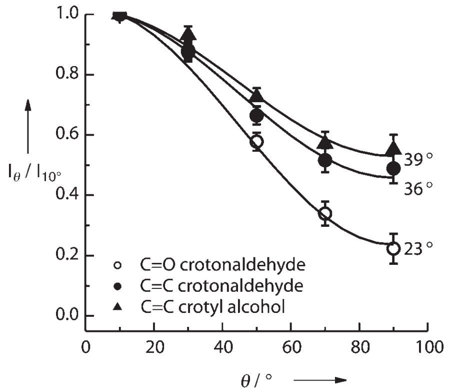

Figure 4. Full analysis of normalized π* intensities plotted against the photon-incidence angle (θ), showing the tilt angles of each double bond with respect to the surface.

The S-promoted surface reaction was studied in more detail by stepwise incremental addition of hydrogen atoms to preadsorbed crotonaldehyde at 173 K, with XPS and grazing-incidence NEXAFS data recorded after each dose of hydrogen (Figure 5). It is apparent that successive doses of hydrogen resulted in progressive changes in shapes and positions of the π* resonances. At 4 minutes hydrogen exposure, the intensity of the C=O peak diminished whilst the C=C resonance broadened. Eventually, with increasing amounts of added hydrogen, the carbonyl resonance disappeared altogether and the C=C resonance shifted to 282.92 eV, characteristic of crotyl alcohol.

The corresponding C 1s and O 1s XPS data shown in Figure 6 A and C are in excellent accord with the NEXAFS

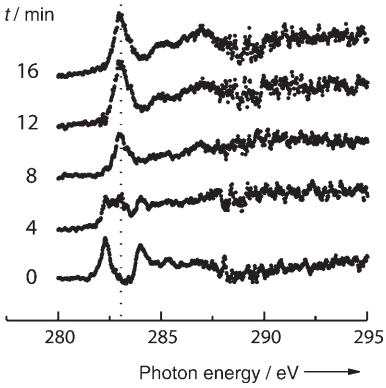

Figure 5. C K-edge NEXAFS acquired at $\theta = 10°$ after each hydrogen atom dose.

results and serve to illustrate the changes in electronic structure of the surface species during progressive conversion of reactant into product. As the conversion proceeds, both the C 1s and the O 1s emission initially broaden and then converge on the characteristic spectra of crotyl alcohol. These results permit estimation of the reaction selectivity. By fitting the spectra with two Gaussian components, the separate contributions from crotonaldehyde and crotyl alcohol may be quantified. The corresponding integrated intensities are plotted in Figure 6B, from which it is clear that at every stage of reaction, conversion of crotonaldehyde into crotyl alcohol proceeds with 100 % chemoselectivity, leading ultimately to 100 % conversion of the reactant. Note that C 1s and O 1s data mirror each other extremely closely, providing strong confirmation of these conclusions. Finally, Figure 7 shows a plausible structural model that is consistent with our findings.

In summary, we have shown that X-ray absorption spectroscopy and photoemission may be used to elucidate the mechanism of a demanding, interesting, and relatively complex catalytic reaction in considerable detail. The chemoselective process in question is prototypical of an important class of heterogeneous reactions that are of potential technical importance. Sulfur strongly promotes catalytic activity by electronically perturbing the target C=O bond and at the same time strongly tilting the C=C bond away from the surface, rendering it immune to attack by hydrogen adatoms, thus favoring chemoselective hydrogenation. The strongly tilted C=C configuration is retained in the product molecule, similarly inhibiting its further hydrogenation to the thermodynamically favored saturated alcohol. The success of the strategy used here suggests that many other catalytic systems of fundamental interest and practical importance could be similarly investigated.

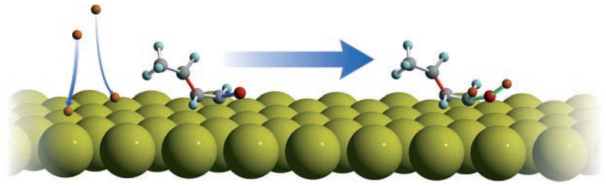

Figure 7. Schematic representation of the surface-mediated hydrogenation of crotonaldehyde to crotyl alcohol. The C=C and C=O bonds of crotonaldehyde are colored red and blue, respectively. When hydrogen atoms (orange) impinge upon the surface, the C=O bond is hydrogenated while the C=C bond is left intact; the newly formed single bonds are shown in green. Note that in this mechanism the geometry of the reactively formed crotyl alcohol is essentially the same as that of its parent crotonaldehyde.

Experimental Section

High-resolution XPS and 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 hydrogen atoms. These measurements were carried out on the SuperESCA beamline at the ELETTRA synchrotron radiation facility in Trieste (Italy). XPS and NEXAFS spectra were collected using a double-pass 32-channel hemispherical electron analyzer. The degree of linear polarization of the photons was 0.99. The angle between the entrance lens of the analyzer and the incoming photon beam was 70° in the horizontal plane. Photon-incidence and photon-detection angles during XPS experiments were fixed at 8° and 78°, respectively. The data were processed in accordance with standard methodology.[7] Note that the XPS binding-energy scale is referenced to the Cu $3p_{3/2}$ line at 75.0 eV (the NEXAFS photon-energy scale is uncor-

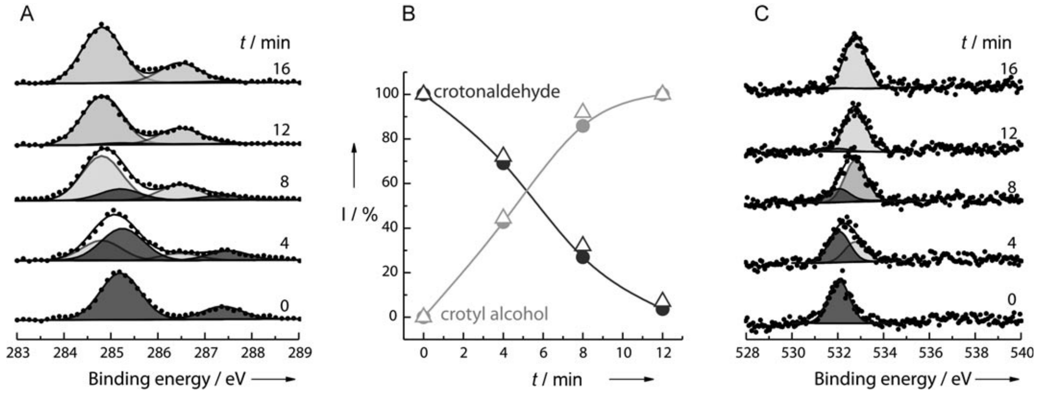

Figure 6. C 1s (A) and O 1s (C) XPS spectra acquired after each hydrogen dose; crotonaldehyde peaks are shaded dark gray, and crotyl alcohol peaks are shaded light gray. B) Normalized integrated XPS peak intensities (I) showing the evolution of crotyl alcohol with the consumption of crotonaldehyde (time of hydrogen dose plotted). Circles denote C 1s data, and triangles correspond to O 1s data.

rected). The Cu(111) surface was cleaned by Ar^+ bombardment at 800 K, followed by annealing in vacuum at 800 K. Reagent-grade crotonaldehyde (> 99.9 %, Sigma Aldrich) was purified before use by means of freeze–pump–thaw cycles and dosed by backfilling the vacuum chamber with an accurately measured vapor pressure; surface coverages were calibrated by fast XPS. Crotonaldehyde was dosed at 173 K to ensure the isolation of the desired surface state; subsequent XPS and NEXAFS spectra were recorded at 168 K to limit desorption from the surface. Dissociative chemisorption of dihydrogen on Cu(111) is activated and therefore extremely slow under ultrahigh-vacuum conditions; accordingly a hot filament source[6] was used to generate a flux of hydrogen atoms, thus enabling the required hydrogen coverages to be achieved on a convenient timescale (173 K). Sulfur was deposited (298 K) using a solid-state electrochemical source[5] that produced a beam of S_2 molecules, enabling precise control of S coverage.

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