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Chemoselective Catalytic Hydrogenation of Acrolein on Ag(111): Effect of Molecular Orientation on Reaction Selectivity

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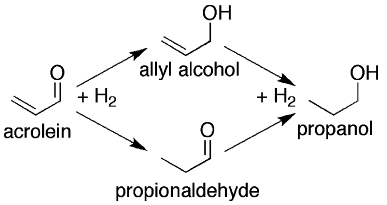
Abstract: The adsorption and hydrogenation of acrolein on the Ag(111) surface has been investigated by high resolution synchrotron XPS, NEXAFS, and temperature programmed reaction. The molecule adsorbs intact at all coverages and its adsorption geometry is critically important in determining chemoselectivity toward the formation of allyl alcohol, the desired but thermodynamically disfavored product. In the absence of hydrogen adatoms (H(a)), acrolein lies almost parallel to the metal surface; high coverages force the C═C bond to tilt markedly, likely rendering it less vulnerable toward reaction with hydrogen adatoms. Reaction with coadsorbed H(a) yields allyl alcohol, propionaldehyde, and propanol, consistent with the behavior of practical dispersed Ag catalysts operated at atmospheric pressure: formation of all three hydrogenation products is surface reaction rate limited. Overall chemoselectivity is strongly influenced by secondary reactions of allyl alcohol. At low H(a) coverages, the C═C bond in the newly formed allyl alcohol molecule is strongly tilted with respect to the surface, rendering it immune to attack by H(a) and leading to desorption of the unsaturated alcohol. In contrast with this, at high H(a) coverages, the C═C bond in allyl alcohol lies almost parallel to the surface, undergoes hydrogenation by H(a), and the saturated alcohol (propanol) desorbs.

Introduction

The chemoselective hydrogenation of α,β-unsaturated aldehydes to form the corresponding unsaturated alcohols is difficult, fundamentally interesting, and important both in the research laboratory and in chemical technology. Such alcohols are valuable and versatile intermediates in the production of fine chemicals and pharmaceuticals, and as is well-known, thermodynamics favors hydrogenation of the C═C bond to form the (unwanted) saturated aldehyde as illustrated in Scheme 1 for the particular case of acrolein. Thus, chemoselective C═O hydrogenation requires the manipulation of kinetic effects by means of a suitable catalyst in order to obtain the thermodynamically disfavored unsaturated alcohol.

Many different supported metal particle catalysts (including Pt, Pd, Cu, Ag, Au, Ir, and Os) which exhibit a wide range of chemoselectivity have been investigated[1] though relatively little has emerged in terms of fundamental understanding. Previously, by means of single crystal studies,[2] we showed that sulfur adatoms strongly perturb the adsorption geometry and electronic structure of crotonaldehyde on hydrogenated copper, resulting in major enhancement of hydrogenation chemoselectivity, in agreement with experiments of conventional supported Cu catalysts. Dispersed silver catalysts are known to be effective for the closely related chemoselective hydrogenation of acrolein under a variety of conditions of pressure and silver particle morphology.[3−6] Very recently, Kliewer et al. investigated the hydrogenation of acrolein, crotonaldehyde, and prenal on Pt(100) and Pt(111) and found that the adsorption state of the reactant strongly influenced reaction selectivity.[7] In the case of acrolein, significant decarbonylation to yield ethylidyne was observed. Here we report a study of acrolein chemoselective hydrogenation carried out under very well-defined conditions on an Ag(111) surface under ultra high vacuum. By means of temperature

Scheme 1. Possible Hydrogenation Products of Acrolein



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programmed reaction, high resolution XPS, and NEXAFS, we show that coverage-dependent effects on the adsorption geometry of both the reactant (acrolein) and the desired product (allyl alcohol) strongly affect overall chemoselectivity. Moreover, under our conditions, the system exhibits "clean" behavior in that no decarbonylation of the reactant occurred.

Experimental Methods

Temperature programmed desorption and reaction measurements (TPD, TPR) were carried out in Cambridge, UK; high-resolution X-ray photoelectron (XPS) and near-edge X-ray absorption fine structure spectroscopy (NEXAFS) were performed at the ELETTRA synchrotron radiation facility in Trieste, Italy using the SuperESCA beamline. The TPD and TPR experiments were carried out in an ultrahigh vacuum chamber of conventional design. A linear ramp of 4 K s^{-1} was used in all experiments, with data acquisition by means of a quadrupole mass spectrometer whose ionizer was positioned 0.5 cm from the front face of the sample. Data are corrected for mass spectrometer sensitivity, molecular ionization cross sections and fragmentation patterns. Adsorbate coverages were estimated by means of uptake experiments in which observation of the low temperature TPD characteristic multilayer desorption feature enabled identification of the monolayer point. Coverages are quoted in terms of monolayers (ML). Experimental details pertinent to the synchrotron experiments have been described previously[8] and the data were processed following standard methodology.[9] XPS binding energies are corrected for monochromator error. NEXAFS photon energies are uncorrected: this does not affect the derivation of molecular tilt angles, which depends on intensity ratios measured under the same conditions within a single run. Uncertainty in derived tilt angles is mainly due to systematic error peculiar to the experimental configuration rather than in the random error associated with measured intensities. It is generally agreed that the former is in the order of ±5°,[9b] the implication being that all derived tilt angles will be systematically higher or lower than the true value. As will be seen, our conclusions depend mainly on *changes* in tilt angle. Adsorbate coverages were estimated by monitoring the C 1s XPS signal continuously during exposure to each adsorbate: in every case the monolayer point was clearly marked by shifts in C 1s peak position. The Ag(111) sample was cleaned by cycles of Ar^+ bombardment at room temperature, 600 K, 800 K and again at room temperature, followed by annealing in vacuum at 800 K. Surface integrity was verified by LEED and Auger electron spectroscopy in Cambridge and by XPS at ELETTRA.

Acrolein (90%) and its three hydrogenation products, allyl alcohol (≥99%), propionaldehyde (97%), and *n*-propanol (≥99.5%), were obtained from Sigma Aldrich, further purified by freeze−pump−thaw cycles and dosed by backfilling the vacuum chamber. Atomic hydrogen was supplied by means of a hot filament atomizer[10,11] that generated a flux of H atoms directed at the Ag(111) surface. This approach,[2] was necessary because dissociative chemisorption of dihydrogen on Ag(111) is an activated process that proceeds to a negligible degree at the impingement rates accessible under UHV conditions. Hydrogen exposures are quoted as fractions of a monolayer. An exposure of 60 Langmuirs to H_2(g) with the atomizer switched on gave a coverage of ~1 ML of H(a). Except where stated otherwise, the dosing sequence was (i) organic molecule and then (ii) hydrogen - done at 140 K (Cambridge) or 123 K (ELETTRA).

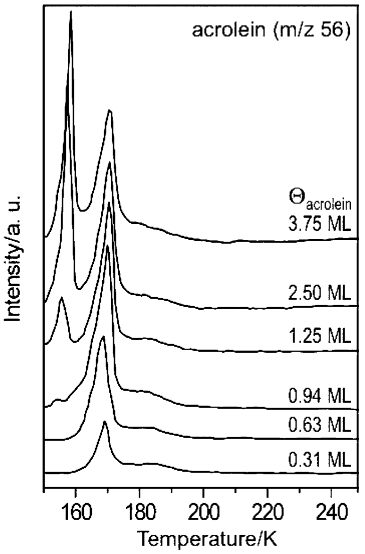

Figure 1. TPD spectra of acrolein on Ag(111) as a function of acrolein coverage (Θ).

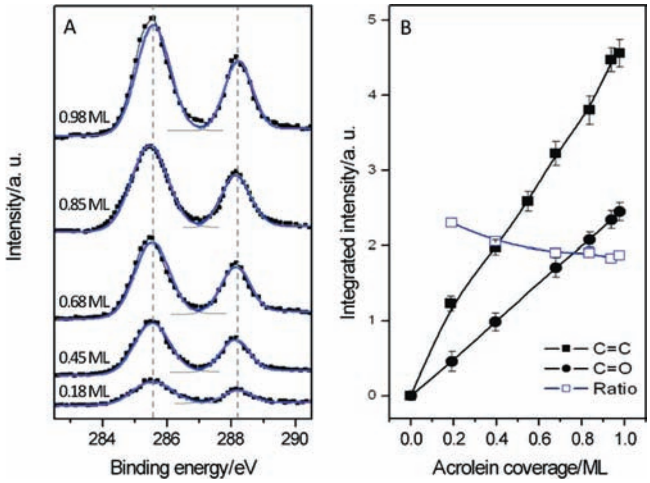

Figure 2. (A) C 1s fast XPS uptake of acrolein by Ag(111), and (B) coverage dependence of normalized integrated XPS peak intensities and of the ratio of these intensities.

Results and Discussion

Acrolein: Coverage Dependence of Adsorption Geometry. Figure 1 shows TPD spectra as a function of acrolein exposure: desorption from the contact layer and from multilayers gave rise to peaks at ~170 K (~42 kJ mol^{-1}) and ~156 K (~39 kJ mol^{-1}) respectively. The peak associated with chemisorbed acrolein shows a distinct increase in temperature with increasing coverage, consistent with attractive interactions between the adsorbed molecules.[12] Figure 2A shows the corresponding C 1s synchrotron XP spectra acquired during continuous exposure to acrolein (5×10^{-9} mbar). Two peaks whose integrated intensity ratio was almost constant are evident (Figure 2B), consistent with the presence of intact acrolein molecules. The 285.3 eV feature is assigned to the carbon atoms in the C═C bond;[13] the 287.8 eV emission is attributed to the carbonyl carbon atom.[13]

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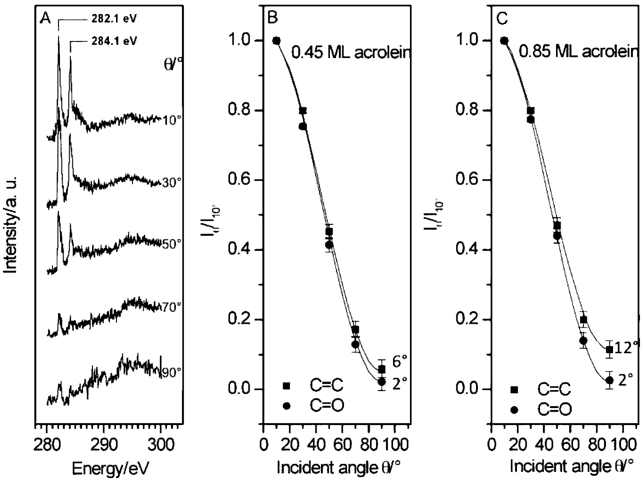

Figure 3. (A) C K-edge NEXAFS of 0.45 ML acrolein on Ag(111). (B) and (C) Analysis of normalized π^* resonance intensities as a function of photon-incidence angle (θ) for acrolein coverages of 0.45 and 0.85 ML, respectively. Bond tilt angles with respect to the surface are indicated.

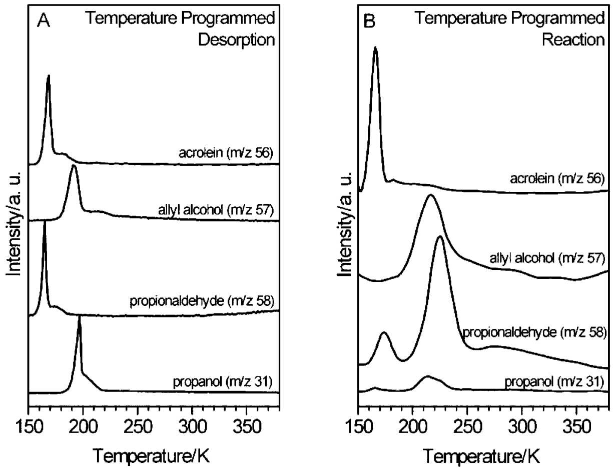

Figure 4. (A) TPD spectra after adsorption of 0.63 ML acrolein, 0.63 ML allyl alcohol, 0.57 ML propionaldehyde, and 0.55 ML propanol, and (B) TPR spectra for 0.63 ML acrolein + 1 ML H(a) on Ag(111), *m/z* 56 data scaled by 1/20; *m/z* 58 is scaled by 1/2.

C K-edge NEXAFS spectra for an acrolein coverage of 0.45 ML were recorded at 123 K at five photon incidence angles (θ, defined relative to the surface plane) and the results are presented in Figure 3A. The π^* resonances centered at 282.1 and 284.1 eV may be reliably assigned to the C=C and C=O bonds,[14] confirming the presence of intact acrolein molecules on the metal surface. These resonances exhibited very similar dependences on photon incidence angle: maximum at near-grazing incidence, vanishing at $\theta = 90°$, indicating that both double bonds are almost parallel to the metal surface. A more accurate evaluation of the tilt angles (α) of the C=C and C=O bonds with respect to the metal surface was carried out following the established procedure[9,15] which involves fitting the observed θ dependence of the normalized intensity to the theoretically calculated dependence for a series of trial α values. This gave tilt angles (α) of 2° for the C=O bond and 6° for the C=C bond, relative to the metal surface, as indicated in Figure 3B. That is, at relatively low coverage, *both* the carbonyl and the alkene functionalities are almost parallel to the metal surface: the molecule lies essentially flat, in accord with IRAS results for acrolein adsorption on (111) surfaces of Ag and Au.[16,17] Corresponding measurements and analysis carried out at high acrolein coverage (0.85 ML, Figure 3C) revealed a clear change in adsorption geometry. The C=O bond orientation with respect to the surface was unaffected whereas the C=C tilt angle increased to 12°. We infer that at high coverages increased intermolecular interactions (already implied by the TPD data) cause the C=C bond to tilt away from the surface.[3,18,19]

Acrolein Hydrogenation. Figure 4A shows reference TPD data for acrolein and its three possible hydrogenation products: allyl alcohol (the desired but thermodynamically disfavored product) propionaldehyde and propanol. Comprehensive fragment ion TPD data as a function of adsorbate coverage (not shown) confirmed that in each case the only desorbing species was the initially dosed molecule (i.e., allyl alcohol, propionaldehyde, or propanol).

Figure 4B shows TPR spectra acquired after *coadsorption* of 0.63 ML acrolein followed by 1 ML H(a). All three partially and fully hydrogenated products were formed and desorbed, along with unreacted acrolein. All three reactions are also observed with practical dispersed Ag catalysts operated at atmospheric pressure,[3−5] indicating that our measurements should be pertinent to an understanding of such systems, as we shall endeavor to show below.

Comparison of Figure 4A and B shows that the desorption temperatures of all three *reactively formed* molecules are substantially higher than those of the same molecules when the latter are simply preadsorbed on the silver surface. This implies that a surface reaction, rather than product desorption, is the rate-limiting step in all three hydrogenation processes.

Quantification of the TPR data via calibration of the mass spectrometer showed that with a conversion of ~30% the selectivities toward formation of allyl alcohol, propionaldehyde, and propanol were ~27%, ~68%, and ~5%, respectively. Figure 5 summarizes the trends in reactant conversion and product selectivity for acrolein coverages between 0.3 and 1.0 ML and for hydrogen coverages between 0.25 and 1 ML as well as a saturated coverage corresponding to 1.33 ML. Acrolein conversion (Figure 5) varied between 0% and 60%, increasing with decreasing acrolein coverage and increasing hydrogen coverage. Figure 5 also shows the corresponding trends in selectivity toward allyl alcohol formation which varied between 22 and 47%. Although these conversion and selectivity values do not refer to turnover under steady state conditions, it is noteworthy that they are broadly in line with the results of studies carried out at much higher pressure using both dispersed Ag catalysts and single crystals.[3−6] Consistent with references,[3,4] moreover, we find that allyl alcohol formation increased with acrolein coverage, which is at least consistent with the behavior of practical dispersed Ag catalysts that exhibited higher chemoselectivity with increasing acrolein partial pressure.[3,4] This may be rationalized in terms of the NEXAFS data (Figure 3) which show that at high coverages steric crowding forces the acrolein molecules to change their orientation, *increasing the tilt of the alkene function away from the surface*. Plausibly, the

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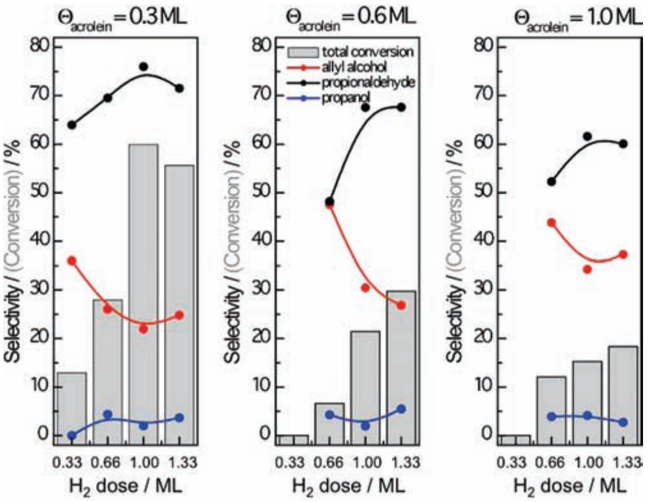

Figure 5. Summary of TPR data over a range of acrolein and hydrogen coverages. Selectivities toward allyl alcohol, propionaldehyde, and propanol are plotted as points, overlaid onto data for total conversion, shown as gray bars.

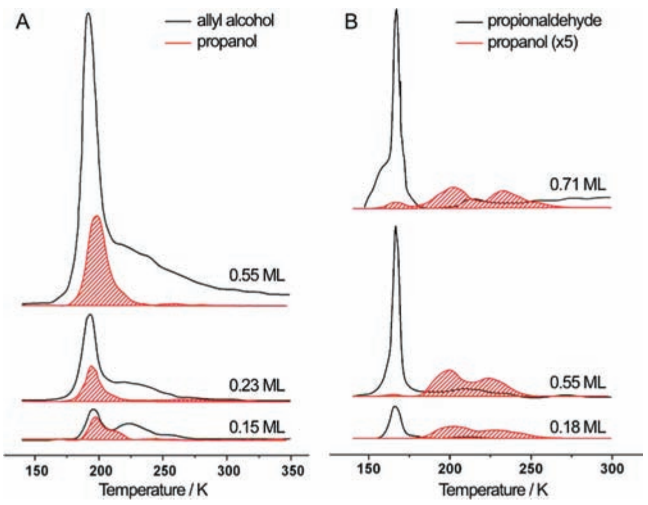

Figure 6. Desorption of reactively formed propanol from (A) TPR of allyl alcohol (0.15, 0.23, and 0.55 ML) and hydrogen (60 L) and (B) TPR of propionaldehyde (0.18, 0.55, 0.71 ML) and hydrogen (60 L). Masses shown for allyl alcohol, propionaldehyde, and propanol are 57, 58, and 31, respectively.

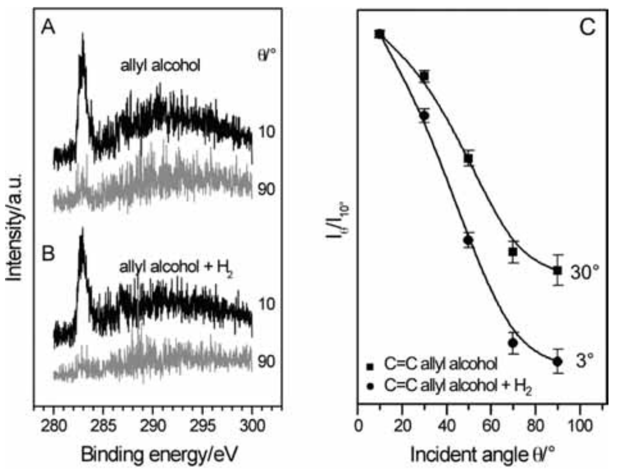

Figure 7. (A) C K-edge NEXAFS spectra for allyl alcohol recorded before, and (B) after ∼430 L H_2 dose. (C) Normalized π^* intensities as a function of photon-incidence angle (θ) indicating tilt angles of the C=C bond with respect to the surface.

C=C bond should then be less vulnerable toward reaction with hydrogen adatoms, kinetically favoring the formation of the otherwise thermodynamically disfavored unsaturated alcohol.

Secondary Chemistry: Further Hydrogenation of Allyl Alcohol and Propionaldehyde. The hydrogenation of allyl alcohol and propionaldehyde were studied to obtain further insight into the overall chemistry. Both molecules react with coadsorbed H(a) as shown in Figure 6A and B. Propanol formed by hydrogenation of allyl alcohol desorbed at ∼200 K. Control experiments showed that adsorbed propanol desorbed at the same temperature, indicating that the hydrogenation reaction is desorption rate limited. Propionaldehyde hydrogenation also gave a desorption peak at ∼200 K but with additional hydrogenation occurring at higher temperatures. In this connection, given that allyl alcohol and propionaldehyde are tautomers, one may advance an admittedly speculative explanation for the hydrogenation processes illustrated in Figure 6A and B, as follows. Allyl alcohol, an enol, adsorbs in the enol form which undergoes facile C=C hydrogenation at ∼200 K. Propionaldehyde adsorbs at 123 K to yield the keto form (see NEXAFS results below) but with increasing temperature some enol is formed, which it may or may not be in equilibrium with. The enol form hydrogenates at ∼200 K, giving rise to the same ∼200 K desorption peak as that observed for allyl alcohol hydrogenation, then, hydrogenation of the more resistant C=O bond present in the keto form occurs at higher temperatures.

Figure 7A and B shows step corrected C K-edge NEXAFS spectra recorded at 123 K for 0.3 ML allyl alcohol before and after coadsorption of hydrogen, for grazing and near normal photon incidence angles. The resonance at 282.9 eV may be assigned to the C=C bond of allyl alcohol[15,20] and evaluation of tilt angles as before[21] leads to the optimal fits shown in Figure 7C. It is apparent that in the absence of H(a) the C=C bond is quite strongly tilted with respect to the surface (∼30°) consistent with bonding to the surface via the alcohol function, in agreement with the TPD data of Solomon et al.[22] In marked contrast with this, the presence of H(a) markedly decreases the tilt angle to ∼3°, bringing the C=C bond nearly parallel to the surface.

Corresponding NEXAFS data for propionaldehyde reveal a similar trend in behavior. NEXAFS spectra of 0.15 ML propionaldehyde are shown in Figure 8A for various incidence angles from grazing to near normal. The C=O resonance appears as a sharp peak at 284.2 eV, its nonzero intensity at normal incidence indicating that the C=O bond is tilted with respect to the surface. Subsequently, the surface was exposed to 20 min of H flux and the NEXAFS recorded again. The angular dependence of peak intensities was analyzed as before and the results are shown in Figure 8B. Adsorbed hydrogen induced molecular reorientation, as was the case with allyl alcohol. The tilt angle of the C=O bond was 23° in the absence of hydrogen reducing to 10° after hydrogen exposure: the bond becomes more accessible to reaction consistent with the observation that propionaldehyde → propanol hydrogenation is favored at high hydrogen coverage.

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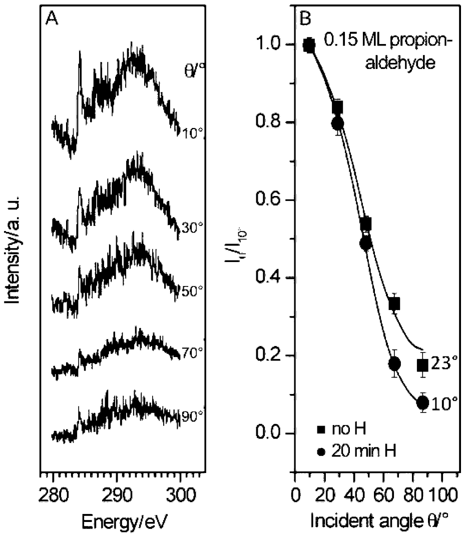

Figure 8. (A) C *K*-edge NEXAFS of 0.15 ML propionaldehyde in the absence of coadsorbed hydrogen. (B) Derived C═O tilt angles in the absence and presence of H(a).

A plausible geometrical interpretation of the catalytic behavior in terms of the changes revealed by NEXAFS is as follows. The adsorption geometry of acrolein is dependent on coverage. Depending on the relative C═C and C═O tilt angles, allyl alcohol and propionaldehyde are formed with varying selectivities. Hydrogenation of either double bond necessarily depletes the surface of H(a). At low initial hydrogen coverages, this leads to the surface being denuded of H(a) so that the reactively formed allyl alcohol or propionaldehyde molecule adopts a configuration with the double bond strongly tilted away from the surface. These factors combine to favor desorption of the primary hydrogenation product, rather than its further hydrogenation to form propanol. Conversely, at high initial hydrogen coverages, hydrogenation of acrolein does *not* completely denude the surface of H(a). The newly formed allyl alcohol or propionaldehyde lies flat with the double bond parallel to the surface and further hydrogenation to propanol is favored. Note that while selectivities to allyl alcohol and propionaldehyde formation vary with respect to acrolein and hydrogen coverage, propanol selectivity remains approximately constant. We may infer this is because propanol is formed from both allyl alcohol and propionaldehyde: as selectivity toward allyl alcohol formation increases, propionaldehyde formation decreases, and vice versa.

Although the results presented here were obtained under well-defined conditions, comparison with earlier work is not straightforward. The performance of supported Ag nanoparticle catalysts is known to be influenced by support acidity,[6] or, in the case of TiO_2, by the intervention of strong metal support interaction.[5] Bron et al. investigated a range of Ag-based materials including Ag(111) single crystals, sputtered Ag, and silica-supported Ag nanoparticles, over a very wide pressure range (2 mbar to 20 bar). They too concluded that surface coverage played an important role in influencing adsorption geometry and hence selectivity. Their *in situ* XAS results indicated the presence of flat-lying acrolein at low pressure, again at least consistent with our observation of a parallel-oriented molecule at low coverage. They also found that a minimum pressure of ∼100 mbar was necessary for allyl alcohol formation at 550 K. This is not necessarily inconsistent with our data that were obtained under very different conditions of T and p. In our case, the allyl alcohol pulse occurred at ∼230 K while acrolein itself desorbed at ∼170 K and the starting coverages of reactants were preset by adsorption from vacuum. Therefore at 550 K it is to be expected that much higher gas phase pressures are needed to establish surface coverages of reactants in the submonolayer range. Lim et al.[23] carried out a DFT study of acrolein adsorption on Ag(110) and concluded that defect sites may play a role in the catalytic reaction. Defect sites do not appear to be of major significance in our case given that acrolein conversions of up to ∼60% of initial coverage could be achieved with selectivities around ∼40% or better.

Conclusions

One. The coverage dependent adsorption geometry of acrolein is critical in determining selectivity.

Two. In the absence of H(a) and at relatively low coverage, *both* the carbonyl and the alkene functionalities are almost parallel to the metal surface. At high coverages the C═C bond tilts markedly with respect the surface rendering it less vulnerable toward reaction with hydrogen adatoms, kinetically favoring the formation of the otherwise thermodynamically disfavored unsaturated alcohol.

Three. Reaction with coadsorbed H(a) results in formation of all possible hydrogenated products: allyl alcohol, propionaldehyde and propanol, consistent with the behavior of practical dispersed Ag catalysts operated at atmospheric pressure under steady state conditions. Formation of all three hydrogenation products is surface reaction rate limited.

Four. At low H(a) coverages, the C═C bond in the newly formed allyl alcohol is strongly tilted with respect to the surface, rendering it immune to attack by H(a)—and the unsaturated alcohol desorbs.

Five. At high H(a) coverages, the C═C bond in the newly formed allyl alcohol is almost parallel to the surface, undergoes hydrogenation by H(a)—and the saturated alcohol (propanol) desorbs. Propionaldehyde shows a lesser H-induced reorientation of the C═O bond which may contribute to its relative stability toward further hydrogenation compared to allyl alcohol.

Six. The observed trends in chemoselectivity toward allyl alcohol formation as a function of reaction variables are consistent with the behavior exhibited by practical Ag catalysts.

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