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Selective Oxidation of Crotyl Alcohol over Pd(111)

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Received: October 12, 2007; In Final Form: November 14, 2007

The selective oxidation of crotyl alcohol has been explored over a Pd(111) model catalyst. At low temperatures, the alcohol adsorbs intact with the C=C bond parallel to the surface. Activation likely proceeds through an allyl alkoxide intermediate that follows two distinct reaction channels. Over the clean surface, ∼90% of the alcohol oxidizes to surface bound crotonaldehyde above 200 K, which subsequently all decarbonylates to propene and CO at room temperature. The minor reaction channel involves C−O scission to 2-butene and water. While some of these undesired reactively formed alkene products desorb around 300 K, the majority dehydrogenate to irreversibly bound carbon above 380 K. This latter decomposition pathway is unlikely to be important at the low temperatures utilized in liquid-phase crotyl alcohol oxidation over supported palladium catalysts. Adsorbed CO persists until 430 K and is likely responsible for site-blocking and deactivation of dispersed metallic Pd clusters. Coadsorbed oxygen suppresses crotonaldehyde decarbonylation and promotes its release from the surface.

Introduction

The direct, aerobic selective oxidation of alcohols over supported Pd catalysts has been the focus of considerable recent attention.[1−3] Allylic alcohols are important synthetic intermediates in the fine chemicals and notably fragrance/flavorings sector, and their selective oxidation presents particular challenges requiring preferential activation of the H_2C−OH group in the presence of reactive olefin centers. However the development of one-step heterogeneously catalyzed oxidative dehydrogenation routes from alcohols to the corresponding allylic aldehydes would offer great process, safety, and environmental rewards over current industrial syntheses employing hazardous stoichiometric reagents.[4] Palladium clusters show excellent activity and selectivity toward a range of primary alcohols but are prone to rapid on-stream deactivation.[5] Our own research on carbon and alumina-supported Pd clusters has provided strong evidence that deactivation is linked to the formation of metallic palladium surfaces,[6,7] while recent in-situ attenuated total reflection-infrared (ATR-IR) experiments have implicated irreversibly bound side products including CO in catalyst self-poisoning.[8−9] Here, we examine whether crotyl alcohol oxidative dehydrogenation to crotonaldehyde occurs over Pd(111) surfaces, and whether reactively formed products could be responsible for site-blocking and catalytic deactivation.

Allylic alcohols are capable of complex surface interactions, with the possibility for coordination via the C=C or C−OH bonds, however their surface chemistry remains poorly understood. Near-edge X-ray absorption fine structure (NEXAFS)[10] and temperature-programmed desorption (TPD)[11] of allyl alcohol over Ag(110) reveal nondissociative adsorption predominantly through the C=C bond, which is almost coplanar with the surface, but no surface reaction. On Rh(111),[12] vibrational and TPD analysis suggests the low temperature formation of an allyl alkoxide intermediate, coordinated through both oxygen and olefin functions, evidencing a strong C=C surface interaction that ultimately leads to decarbonylation. In contrast, allyl alcohol undergoes oxidation to acrolein and hydrogenation to *n*-propyl alcohol and propanal over Cu(110),[13] possibly via a surface alkoxide and oxametallacycle intermediates anchored through the terminal oxygen. Density functional theory (DFT) calculations[14] suggest allyl alcohol should adopt a di-σ adsorption mode over both Pd(111) and Pt(111), augmented by a weaker interaction between an atop metal site and the −H_2C−OH function. Such multipoint bonding may account for the competing reaction pathways observed experimentally: allyl alcohol decarbonylates over both Pd(111)[15] and Pd(110),[16] liberating ethene, accompanied by alcohol dehydration, that is, C−O scission, to propene and water over the Pd(111) face. To our knowledge, no higher allylic alcohols have ever been investigated, although there are are recent reports of crotonaldehyde adsorption and hydrogenation over Cu[17,18] and Pt[19−23] single-crystal surfaces that confirm a strong surface-olefin coordination.

Here we report the first study on the surface chemistry of crotyl alcohol. High-resolution time-resolved X-ray photoelectron spectroscopy (XPS) has allowed us to investigate the commercially important oxidative dehydrogenation route to crotonaldehyde over the catalytically relevant Pd(111) surface, which is a good model for the low index facets dominating large metallic Pd clusters.

Results and Discussion

The reactivity of crotyl alcohol (CH_3−CH=CH−CH_2OH) over clean Pd(111) was followed by C 1s XPS, NEXAFS, and mass spectrometry (experimental details are provided in the Supporting Information). Figure 1 shows the C 1s XP spectra

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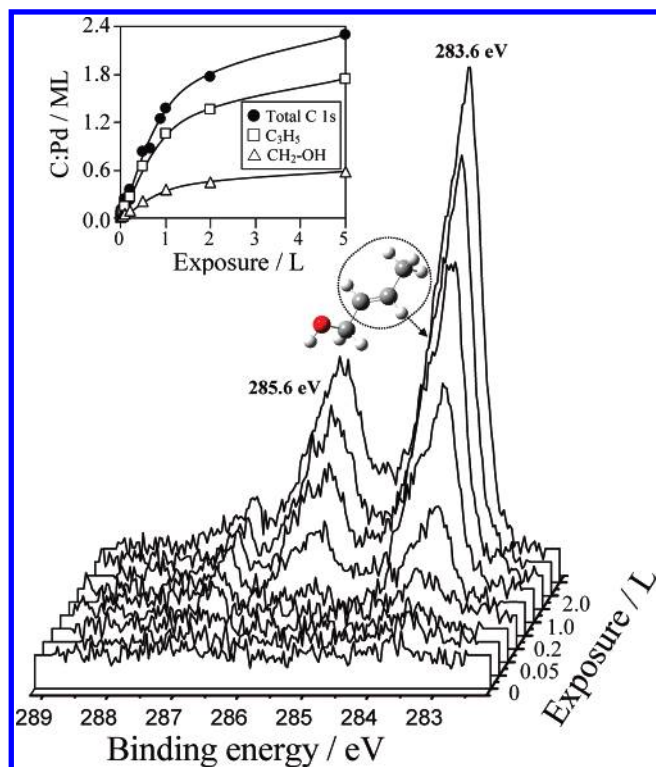
Figure 1. C 1s XP uptake of crotyl alcohol on Pd(111) at 95 K. Inset shows total surface carbon coverage and integrated intensities of individual fitted components.

Figure 2. Temperature-programmed C 1s XP spectra of a reacting saturated crotyl alcohol adlayer adsorebd over Pd(111) at 95 K. Inset shows 3D chemical map showing transformation from alcohol to aldehyde and subsequent decarbonylation.

during low-temperature crotyl alcohol adsorption. These exhibit two well-resolved features, readily assigned to the respective $CH_3CH=CH-$ and $-H_2C-OH$ functionalities in the parent molecule, whose intensities saturate around 1.5 L exposure. This is indicative of nondissociative adsorption into a single bound state within the monolayer. The saturation monolayer coverage of 0.15 ML is somewhat lower than that reported for crotonaldehyde over Cu(111)[18] and may reflect both the longer C−O bond and conformational flexibility of the alcohol and therefore greater steric footprint. The alcohol peak positions are in excellent agreement with those reported for crotonaldehyde on Pt(111),[22] albeit with the alcohol carbon slightly downshifted (by 0.3 eV) relative to the carbonyl as expected from simple initial state considerations. Higher exposures result in peak broadening to higher binding energy associated with crotyl alcohol multilayers.

The molecular orientation within the monolayer was probed through angular dependent C K-edge NEXAFS measurements (see Supporting Information). Crotyl alcohol exhibits a number of resonances associated with C 1s transitions to π^* and σ^* lowest unoccupied molecular orbitals (LUMOs). The $\pi^*_{C=C}$ resonance is strongest at grazing incidence and vanishes at normal incidence, while the σ^*_{C-H} and $\sigma^*_{C-C/C-O}$ resonances show the opposite angular intensity variation. These trends are consistent with an essentially coplanar allyl moiety akin to that reported for allyl alcohol on Ag(110)[10] and crotonaldehyde on Pt(111)[22] and Cu(111).[17] This geometry presumably provides for strong bonding with the palladium surface, as proposed for allyl alcohol on Ag(110),[10] Rh(111),[12] and Pd(111).[15]

Figure 2 shows the temperature-programmed C 1s XP spectra of a reacting crotyl alcohol adlayer over clean Pd(111) and reveals three important temperature regimes. At low temperature, the surface is dominated by the intact parent molecule. Between 200 K and room temperature, the major low binding energy peak associated with the hydrocarbon backbone sharpens,
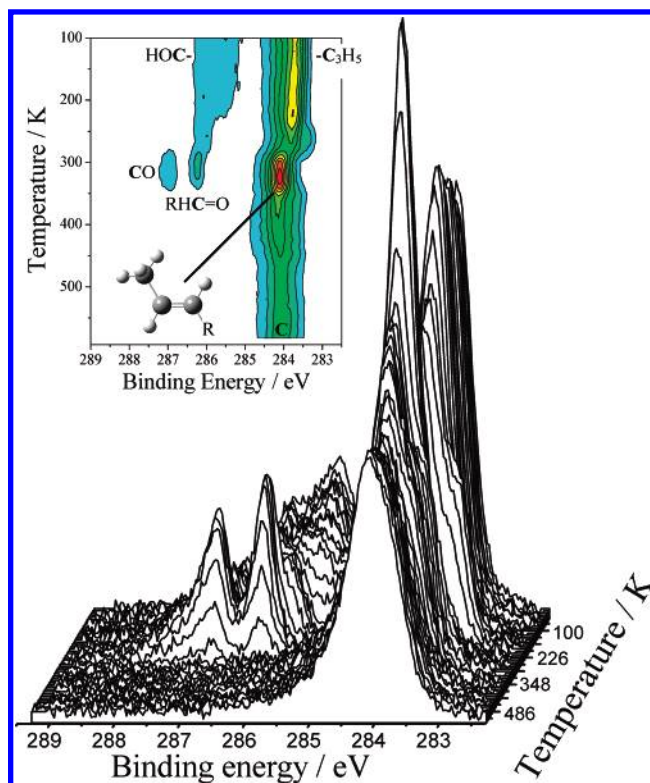
accompanied by a small +0.4 eV peakshift, and the resulting line shape and peak position are strongly reminiscent of alkylidynes over Pt(111).[24,25] Simultaneously, the 285.6 eV peak associated with the $-H_2C-OH$ carbon shifts to higher energy and splits to give two new well-resolved chemical states at 286.2 and 287 eV. In light of their chemical shifts and the following mass spectrometry data, these are assigned to respective $-HC=O$ and molecular CO environments. Surface carboxylate groups derived from ethanol over oxygen precovered Pd(110) exhibit a similar high energy (287 eV) carbon state around 300 K.[26] Annealed crotyl alcohol adlayers also exhibit signature crotonaldehyde NEXAFS spectra (Supporting Information) evidencing an efficient selective oxidation pathway to the aldehyde below room temperature. Further heating above ∼340 K results in loss of first carbonyl and then CO surface species and concomitant broadening and intensity loss within the CH_x region, resulting in a peak characteristic of graphitic surface carbon.

The corresponding thermal desorption mass spectra are shown in Figure 3, alongside the fitted intensities of the key carbon species from Figure 2. At low coverages (<0.07 ML), crotyl alcohol underwent complete decomposition to CO and H_2. Higher exposures resulted in a sharp molecular desorption state at 209 K, which saturated around 1.5 L, co-incident with the appearance of a 200 K multilayer desorption. As evidenced from the C 1s XP data, partial desorption of the alcohol adlayer coincides with the threshold reaction temperature for the remaining chemisorbed alcohol, first resulting in simultaneous desorption of reactively formed C_4H_8 and H_2O at 265 K. Butene can only have formed via subambient C−O activation and scission, supporting an adsorption mode in which crotyl alcohol coordinates to the palladium surface via both allyl and terminal $-H_2C-OH$ functions, as for allyl alcohol.[10] Water and 2-butene evolution both require free surface hydrogen, and indeed room-temperature H_2 desorption is also observed (most likely gener-
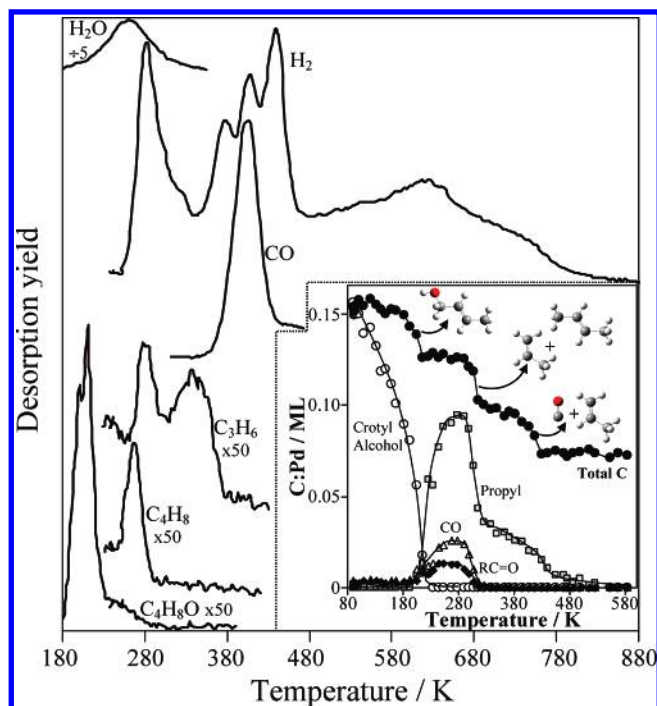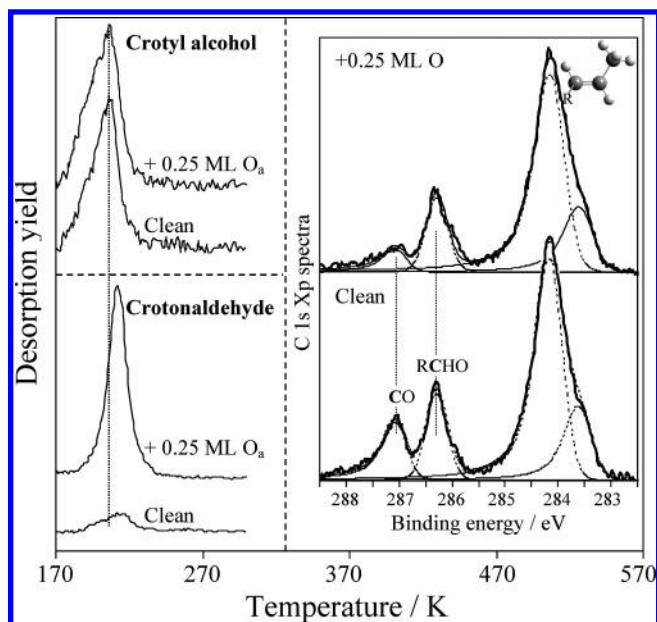
Figure 3. Thermal desorption mass spectra of 2 L crotyl alcohol adsorbed on Pd(111) at 95 K. Inset shows correlation with integrated C 1s XP intensities of fitted surface species.


Figure 4. Thermal desorption mass spectra following crotyl alcohol and crotonaldehyde from 2 L crotyl alcohol adsorbed on clean and oxygen precovered Pd(111) at 95 K. Inset shows corresponding fitted C 1s XP spectra for 2 L crotyl alcohol adlayer heated to 250 K over clean and oxygen precovered Pd(111).

ated from an allyl alkoxide surface intermediate). This hydrogen desorbs in parallel with significant propene at 280 K. The latter suggests a distinct reaction channel involving either butene decomposition or a decarbonylation mechanism analogous to ethene production from allyl alcohol over Pd(111).[15] Our high-resolution XPS provides unequivocal evidence for the existence of a separate decarbonylation route from the alcohol, via a (croton)aldehyde intermediate, operating between 200 and 300 K. Mass spectrometry and XPS confirm the CO coproduct remains surface bound until ~350 K. The absence of other side-reactions, for example, hydrogenation to butanol/al or loss of the terminal methyl to form allyl alcohol or ketene, is in line with the high selectivity toward the allylic aldehyde product seen experimentally over dispersed palladium particles.

The integrated C 1s signals show that approximately half of a saturated crotyl alcohol monolayer remains as irreversibly bound carbon following high-temperature processing. This is consistent with the sequential dehydrogenation evidenced by the series of H_2 desorptions at 380, 407, 441, and 620 K, which is typical of olefin decomposition to graphitic carbon over metal surfaces. Assuming CO is only derived directly from crotonal-dehyde, comparison of the combined C 1s [CO + crotonalde-hyde] with [total CH_x] intensities reveals that ~89% of the parent alcohol follows the oxidation and subsequent decarbo-nylation pathway. Dehydration to butene is a minor reaction channel.

To mimic the full aerobic selective oxidation reaction (often conducted under solvent-free conditions[3]), a saturation crotyl alcohol exposure was dosed onto a p(2 × 2) oxygen precovered Pd(111) surface and then annealed. The resulting temperature-programmed MS and C 1s XP spectra are shown in Figure 4. The impact of surface oxygen on the stability of reactively formed crotonaldehyde is striking. Over bare Pd(111) aldehyde decarbonylation is complete and none desorbs. While coad-sorbed oxygen has no impact on the intrinsic reactivity of crotyl alcohol (the same fraction reacts over both surfaces), it promotes low-temperature crotonaldehyde desorption at 215 K, thereby

suppressing the decarbonylation route. XPS shows that this temperature is extremely close to that at which aldehyde is actually formed on the surface (>200 K), hence its appearance in the gas-phase is reaction-rate limited. Redhead analysis, whereby the sample heating rate and desorption peak maximum are utilized to obtain a desorption activation energy,[27] yields a reaction barrier toward reactively formed crotonaldehyde of 52 kJ mol^{-1}, comparable to that for allylic alcohol oxidation over large Pd clusters where apparent activation energies of 45−54 kJ mol^{-1} are reported.[3,28] This correspondence suggests that the initial intrinsic activity of practical Pd metal clusters catalysts is rate-limited by the surface oxidative dehydrogenation step, that is, C−H and O−H cleavage. However, the XPS spectra inset in Figure 4 show that coadsorbed oxygen still fails to stabilize a significant fraction of the desired aldehyde product with respect to CO at the mild temperatures under which tradi-tional palladium selective oxidation catalysts operate. Repeated catalytic turnover at temperatures below 350 K will therefore result in the rapid accumulation of adsorbed CO and conse-quential blocking of active Pd ensembles. Coadsorbed oxygen did not influence the minor dehydration pathway to butene. These two distinct pathways are summarized in the reaction network shown in Scheme 1. The mechanism by which oxygen promotes the selective oxidation of crotyl alcohol to crotonal-dehyde remains to be explored, but may reflect steric crowding of the more rigid aldehyde within the coadsorbed adlayer or substrate-mediated charge transfer away from the aldehyde conjugated π-system and associated weaker product binding.

In summary, we have shown that Pd(111) surfaces are active for the low-temperature selective oxidation of crotyl alcohol to crotonaldehyde. Alcohol dehydration to butene and water represents a minor side reaction pathway in competition with the dominant route to the desired allylic aldehyde. Subsequent room-temperature decarbonylation impacts in two ways on the overall catalytic process: it lowers the possible yield of crotonaldehyde released from the surface and facilitates self-poisoning and deactivation at the mild temperatures (333−373 K) typically employed in selox chemistry through the retention of CO and hydrocarbon fragments. Coadsorbed oxygen some-

Letters

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SCHEME 1: Reaction Network and Proposed Bonding Interactions of Cinnamyl Alcohol over Clean and Oxygen Precovered Pd(111)
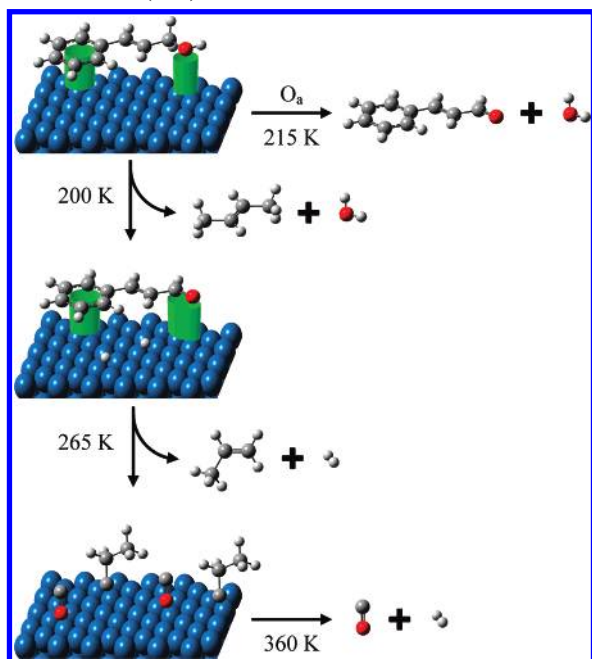
what ameliorates this process, promoting the release of free crotonaldehyde product. These findings also suggest that crotyl alcohol selective oxidation over supported Pd catalysts exposing a high fraction of (111) planes requires careful temperature control, being hindered by reversibly bound CO below 380 K and by irreversibly bound carbonaceous residues above 400 K.

Supporting Information Available: Crotyl alcohol TPD-MS uptake along with representative snapshot C 1s XP spectra and NEXAFS spectra and assignments This material is available free of charge via the Internet at http://pubs.acs.org.

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