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In situ X-ray studies of crotyl alcohol selective oxidation over Au/Pd(1 1 1) surface alloys

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ABSTRACT

The selective oxidation of crotyl alcohol to crotonaldehyde over ultrathin Au overlayers on Pd(1 1 1) and Au/Pd(1 1 1) surface alloys has been investigated by time-resolved X-ray photoelectron spectroscopy (XPS) and mass spectrometry. Pure gold is catalytically inert towards crotyl alcohol which undergoes reversible adsorption. In contrast, thermal processing of a 3.9 monolayer (ML) gold overlayer allows access to a range of AuPd surface alloy compositions, which are extremely selective towards crotonaldehyde production, and greatly reduce the extent of hydrocarbon decomposition and eventual carbon laydown compared with base Pd(1 1 1). XPS and CO titrations suggest that palladium-rich surface alloys offer the optimal balance between alcohol oxidative dehydrogenation activity while minimising competitive decomposition pathways, and that Pd monomers are not the active surface ensemble for such selox chemistry over AuPd alloys.

1. Introduction

The application of modern surface science and synchrotron methodologies has led to rapid advances in our current understanding of chemical phenomena at the solid-gas/liquid interfaces, and has impacted particularly on mechanistic and kinetic studies of heterogeneous catalysis [1]. However, the development of new catalytic materials still proceeds by largely empirical trial-and-error methodologies. To a large degree this reflects the dearth of quantitative experimental techniques suitable for identifying surface intermediates and tracking dynamic catalyst restructuring under reaction conditions; an approach that has acquired the sobriquet of operando spectroscopy [2]. A variety of new methodologies currently under development, including high-speed scanning probe microscopy [3], are making progress towards this goal. However all individual techniques suffer drawbacks, being either localised measurements, or exhibiting poor spatial/temporal resolution, surface sensitivity, or most problematic, a lack of chemical specificity.

Over the past decade the potential of time-resolved (Fast) X-ray photoelectron spectroscopy (XPS) for studying molecular adsorption processes has been demonstrated for a range of industrially relevant catalytic processes [4]. The success of this technique hinges on the high photon flux and high-resolution now available at third-generation synchrotrons [5]. These permit rapid XP spectral acquisition during chemical adsorption, or while the catalyst temperature is ramped to initiate surface chemistry [6]. Fast XPS represents a chemically specific, quantitative surface probe for following adsorption/reaction over catalytically active surfaces with a sensitivity of ~1% of a monolayer (ML). This technique allows the determination of threshold temperatures and activation barriers for surface reactions, and the elucidation of associated reaction pathways and configurational changes within surface adlayers [7]. New, differentially pumped electron analysers that are coming onstream at select brilliant light sources, also open the possibility for high pressure XPS studies. These allow volatile molecular adlayers, mimicking those formed at the surface of practical catalysts in solution phase or high pressure gas phase reactions, to be stabilised and characterised in real time at solid surfaces.

The heterogeneously catalyzed aerobic selective oxidation (selox) of hydrocarbons offers alternative, environmentally benign routes to a diverse range of valuable oxygenates for the fine chemical, pharmaceutical and agrochemical sectors [8]. These powerful catalytic technologies have the potential to replace stoichiometric inorganic oxidants such as Cr^{VI} salts or expensive

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homogeneous complexes (e.g. Mn salens), and their associated process disadvantages and safety issues [9]. Supported Platinum Group Metal particles are particularly promising partial oxidation catalysts [8,10], able to activate a range of alcohols and carbohydrates under mild conditions employing either neat substrate or green solvents including ionic liquids [11] supercritical fluids [12] and even water [13]. We recently showed that even isolated palladium centres anchored within a transitional alumina framework are efficient selox catalysts for alcohols [14]. The recent discoveries of Ru [15] and promoted Au catalysts [16] for such reactions is especially noteworthy, as these systems offer high turnover frequencies even during scale-up, although some require radical initiators and high air/O_2 partial pressures [17]. These reactions are highly regioselective (often >95%) towards the aldehyde product, even in the presence of diverse functionalities including aryl, allylic groups.

However, the generally poor intrinsic performance of heterogeneous catalysts relative to their homogeneous counterparts has often necessitated *ad hoc* promotion by non-noble metals to achieve even moderate yields [18]. To a large degree this reflects uncertainty over the active site responsible for the (widely held to be rate-limiting) oxidative dehydrogenation step. In an exciting breakthrough in this field, Hutchings and co-workers recently discovered a range of bimetallic AuPd catalysts that show exceptional activity and selectivity towards the oxidative dehydrogenation of diverse alcohols [16]. Combining these precious metals over a titania support confers up to 25-fold rate enhancements for alcohol aerobic oxidation under mild solvent-free conditions, while the introduction of Au also improves selectivities to aldehydes and ketones over those achievable with Pd alone. High-resolution STEM chemical mapping indicates the active nanoparticles possess a Pd-rich shell encapsulating a Au-rich core, and it is likely that surface Au atoms are crucial in regulating the electronic structure and thereby promoting selox chemistry over surface Pd. However, details of the active surface ensemble and role of Au in promoting selox remain uncertain; questions perfectly suited for investigation by in situ XPS.

Our recent XPS study of crotyl alcohol (2-buten-1-ol) oxidative dehydrogenation to crotonaldehyde over Pd(1 1 1) identified secondary decarbonylation reactions as a major factor in the deactivation of practical monometallic Pd selox catalysts [19]. Here we extend these methodologies to the Au/Pd(1 1 1) alloy system to explore the impact of Au incorporation on the surface chemistry of crotyl alcohol and explore the above questions. Au/Pd(1 1 1) alloys have been previously characterised in vacuo by conventional photoelectron spectroscopy [20,21], LEED [22], LEIS [23] and STM [22]; epitaxially deposited gold overlayers form apparently random substitutional surface alloys upon annealing above 600 K, reflecting the small lattice mismatch and bulk miscibilities of the metal components. It should be noted that recent theoretical analyses for Au/Pd(1 1 1) alloy surfaces suggests weak repulsion between Au and Pd atoms may drive local ordering [24]. The promotional effect of gold incorporation into Pd(1 1 1) has previously been demonstrated for ethyne cyclotrimerisation to benzene [25], wherein the genesis of Pd_6Au ensembles reduced hydrocarbon decomposition and promoted benzene desorption, in agreement with analogous studies on dispersed AuPd colloids [26], and for the enantioselective oxidative dehydrogenation of aliphatic alcohols to ketones [27]. In this paper we report the first surface science study of an allylic alcohol over AuPd alloys, and use in situ XPS to show that even small amounts of Au can promote the selective oxidation of crotyl alcohol while suppressing crotonaldehyde decarbonylation, and that isolated Pd sites are not the active site for such catalysis in extended alloys.

2. Experimental

Synchrotron XPS measurements were carried out at the SuperESCA beamline of the third generation Elettra light source using Pd(1 1 1) single-crystal samples prepared by standard procedures and maintained under ultra high vacuum ($\sim 1 \times 10^{-10}$ Torr). Quoted exposures are given in Langmuirs (1 $L = 1 \times 10^{-6}$ Torr s) and are uncorrected for ion-gauge sensitivity. Crystals were held at 95 K during dosing unless otherwise stated. Temperature-programmed reaction data were acquired by application of a linear heating ramp (~ 0.4 K s^{-1}) to the exposed sample. Crotyl alcohol (Aldrich 99%) was purified by repeated freeze-pump-thaw cycles prior to use. Sample dosing was performed by backfilling the vacuum chamber. Gold films were grown via room temperature deposition from an EFM3 Omicron evaporation source with integral flux monitor incorporating a tungsten-wrapped 1 mm Au rod. Typical gold growth rates were 10 min per monolayer. C 1s, Au 4f and Pd 3d XP spectra were acquired at a photon energy of 400 eV. The overall spectral resolution was $\sim$150 meV. Individual spectra were acquired approximately every 30 s during Fast XP measurements and all presented spectra have been Shirley background-subtracted. A common lineshape derived from graphitic carbon was adopted for all C 1s components, based on a Duniach Sunjic profile convoluted with a Gaussian/Lorentzian (4:1) mix, with a FWHM between 0.35 and 0.5 eV and asymmetry index = 0.0618. Fitting was performed using CasaXPS Version 2.3.15. Au/Pd alloy compositions were derived from the Au $4f_{7/2}$ and Pd $3d_{3/2}$ XP intensities, corrected for their respective photoionisation cross-sections at 400 eV, and were in excellent agreement with the corresponding Au NVV and Pd MNN AES signals. The variation in alloy composition with annealing temperature is shown for a 3.9 ML Au/Pd(1 1 1) surface in the Supporting Information. Annealed surfaces were held at the stated temperature for 1 min and cooled to 100 K for analysis. Simple Monte–Carlo simulations of Au/Pd alloys were conducted on a 144 atom 2D lattice assuming random substitution of non-interacting atoms at 300 K. Thermal desorption spectra were acquired in a separate ultra-high vacuum system, equipped with LEED/AES and sample cleaning facilities, using a VG 300 amu quadrupole mass spectrometer with a heating rate of $\sim$12 K s^{-1}.

3. Results and discussion

3.1. CO adsorption over Au/Pd(1 1 1) surface alloys

In order to assess the impact of AuPd alloying on the resulting surface ensembles available for crotyl alcohol oxidation, we first probed the surface composition via CO adsorption as an active chemical titrant. The CO/Pd(1 1 1) adsorption system has been the subject of numerous surface science investigations, reflecting the diverse molecular bonding modes, balance of attractive and repulsive lateral interactions, and associated ordered structures formed at different CO coverages. Various adsorption sites have been proposed for well-defined CO arrays at one third $\{(\sqrt{3} \times \sqrt{3})R30^\circ\}$ and half monolayer $\{c(4 \times 2)\}$ coverages. For the latter phase, preferential occupancy of either bridge or fcc/hcp hollow sites has been proposed on the basis of respective vibrational [28] and photoelectron diffraction studies [29]. A recent STM investigation by Salmeron and co-workers suggest that both models are partially correct, with co-existing domains of bridge-bonded and hollow bound CO at half a monolayer [30].

This coverage-dependent adsorption was first tracked by time-resolved XPS over clean Pd(1 1 1) in order to fingerprint the chemical shifts associated with these different CO bonding modes. Fig. 1 shows the resulting C 1s XP spectra from which it is evident

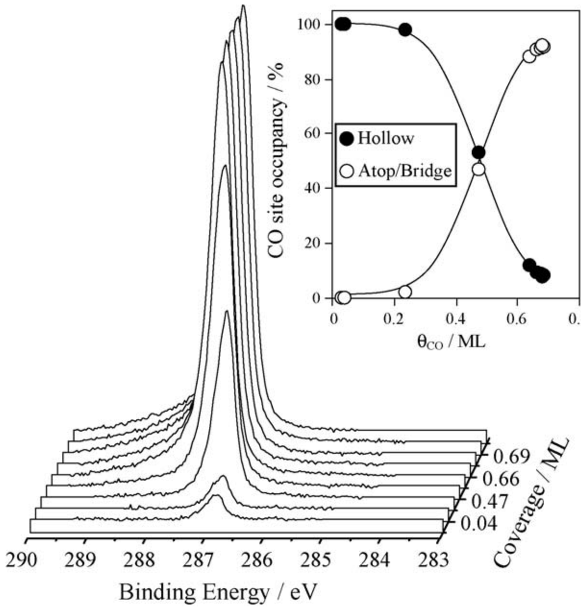

Fig. 1. In situ C 1s XP spectra during adsorption of a CO adlayer over Pd(1 1 1) at 100 K. Inset shows fitted intensities of CO components as a function of coverage illustrating coverage-dependent site switching.

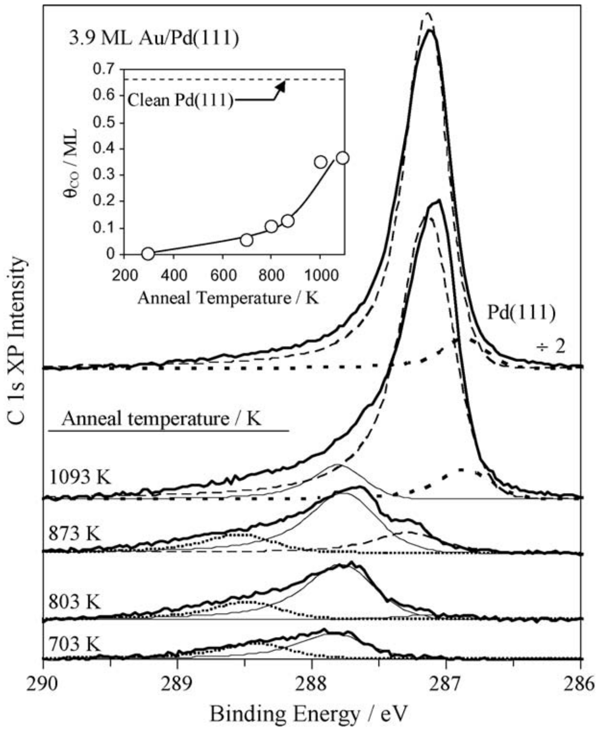

Fig. 2. C 1s XP spectra of saturated CO adlayers prepared over a 3.9 ML Au/Pd(1 1 1) surface at 100 K as a function of pre-annealing temperature. Surface Au strongly perturbs the chemical shift of chemisorbed CO. Inset shows saturation CO coverage as a function of pre-anneal temperature.

that two distinct CO environments are distinguishable at 286.9 and 287.2 eV. Only the low binding energy (BE) state is populated below 0.5 ML CO, and can therefore be confidently assigned to CO bound in fcc or hcp hollow sites. At the half monolayer point the hollow occupancy falls at the expense of the higher BE state, with the 50:50 population of both states (Fig. 1, inset) in excellent agreement with STM observations [30], from which this new state can be assigned to bridge bound CO. This site-switching becomes much more pronounced close to saturation coverage, with the hollow sites heavily depleted. Such extreme depopulation of hollow sites is not seen for high coverage ordered CO structures on Pd(1 1 1), wherein hollow and atop bound CO are proposed. However, the sensitivity of this adsorption system to surface crowding means that slight coverage differences, in our case the introduction of relatively few additional molecules, can drive the formation of disordered structures with preferential occupancy of less sterically-demanding bridge and atop sites. Even at the highest coverages we could not distinguish a third C 1s component attributable uniquely to atop sites, hence we believe the 287.2 eV state contains contributions from both bridge and atop CO. The relative energies of these two species is consistent with initial state expectations from the Blyholder model of charge donation from the CO 2σ orbital into the surface, and back donation from the metal d-orbitals into the CO π^* orbital; the latter contribution increasing with surface coordination number with hollow > bridbridge > atop.

The surface ensembles available for CO adsorption over a range of AuPd surface alloys were subsequently explored via progressive annealing of a thick (3.9 ML) 300 K deposited Au overlayer (Fig. 2) and subsequent exposure to a saturation CO dose. It should be noted that Au does not thermally desorb from Pd(1 1 1). In contrast to previous reports, CO did not adsorb over the pure Au adlayer at 100 K [21]. Anneals above 600 K, sufficient to begin Au dissolution into the Pd(1 1 1) substrate, facilitated weak CO chemisorption into two high binding energy states at 287.7 and 288.5 eV. Higher temperature anneals, which drive further Pd surface enrichment, increase the saturation CO coverage (Fig. 2, inset), and promote the re-emergence of the two CO adsorption states at 286.9 and 287.2 eV characteristic of clean Pd(1 1 1). Surface compositions are derived from AES measurements of the overall gold mole fraction in the outermost several layers, corrected using recently published LEIS data from reference 23 to determine the actual gold coverage in the terminal surface layer. This correction is significant for alloys containing less than 90% Au in the selvedge since strong gold surface segregation occurs in dilute Au/Pd alloys [23]. It is interesting to note that significant (~16%) surface Au was retained even following the highest annealing temperature in this study. The coverage-dependent fitted intensities of these four CO surface species are shown in Fig. 3a. A Monte–Carlo simulation was subsequently undertaken to model the distribution of surface ensembles available as a function of Au/Pd composition, and thereby help assign the new high CO states observed on gold-rich surface alloys. The predicted concentrations of pure Pd hollow and bridge/atop sites in Fig. 3b are in good agreement with the experimental trends, confirming that even 10% gold is sufficient to switch off binding at threefold hollows. As expected $Pd_2(Pd)$ bridge and $Pd(Pd_2)$ atop sites decay more slowly, with significant populations present up to ~50% gold. The corresponding growth of $Pd_2(Au)$ bridge and $Pd(Au_2)$ sites quantitatively tracks that of the respective 288.5 and 287.7 eV CO states, enabling their assignment to perturbed bridge and isolated Pd ensembles. The chemical shift of both CO alloy adsorption states is consistent with charge donation from Pd to Au, as previously reported within the Au/Pd(1 1 1) system [21,31], and associated reduced metal back donation into the CO π^* orbital.

3.2. Crotyl alcohol adsorption over Au/Pd(1 1 1) surface alloys

The adsorption and thermal chemistry of crotyl alcohol ($CH_3CH{=}CHCH{-}OH$) over an unannealed 3.9 ML gold film was first examined to benchmark the reactivity of bulk gold surfaces

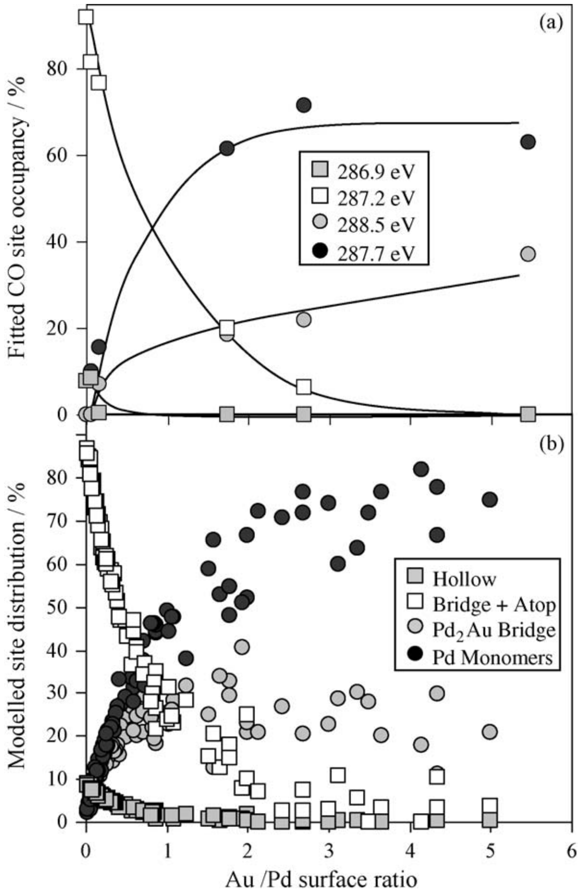

Fig. 3. (a) Integrated C 1s XP intensities of fitted CO components for saturated CO adlayers adsorbed at 100 K over AuPd alloys prepared by annealing a 3.9 ML Au/Pd(1 1 1) surfaces and (b) simulated variation in select Pd ensembles available for CO adsorption over AuPd alloys. Surface Au rapidly supresses CO adsorption over larger Pd ensembles.

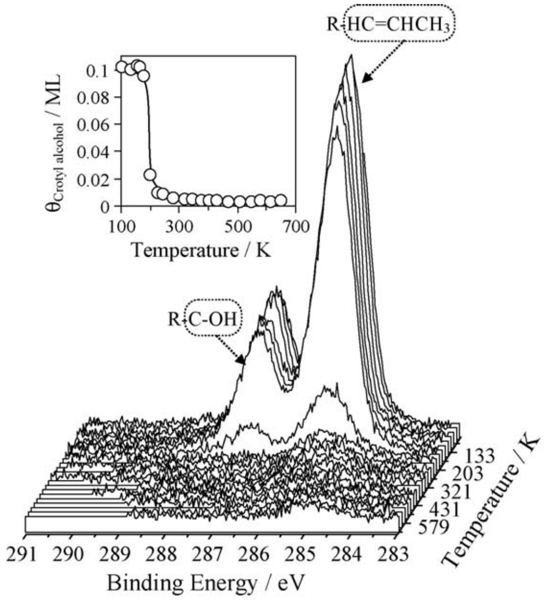

Fig. 4. Temperature-programmed C 1s XP spectra of a saturated crotyl alcohol adlayer prepared over an ultrathin 3.9 ML Au/Pd(1 1 1) film at 100 K. Inset shows crotyl fitted alcohol coverage as a function of temperature illustrating fully reversible chemisorption over pure gold.

towards allylic alcohols. As observed over clean Pd(1 1 1), low temperature alcohol adsorption gives rise to two distinct C 1s environments at 285.2 and 286.8 eV in a 3:1 ratio, associated with the respective –H_2–C–OH and propylidene functionalities. The saturation crotyl alcohol coverage over the thick Au overlayer is around two-thirds that over Pd(1 1 1) at 0.1 ML. The lower coverage may reflect more disordered packing arrangements due to the weaker molecular interaction with gold. There is some debate over the threshold temperature at which Au/Pd surface alloying commences, with early LEIS studies on the reverse Pd/Au(1 1 1) system indicating that Pd diffusion occurs at the interface at 300 K [32]. However, a recent LEIS and LEED investigation by Tysoe and co-workers on Au/Pd(1 1 1) reveals negligible intermixing below 600 K [23], in accordance with our preceding CO chemisorption measurements which show no titratable surface Pd sites on an as-deposited gold film. These latter observations are important since they open the possibility of following the thermal evolution of a crotyl alcohol adlayer by temperature-programmed XPS, without complications from simultaneous changes in the surface metal composition. Fig. 4 reveals that crotyl alcohol does not undergo any surface chemistry over the pure gold adlayer, simply desorbing above 170 K, and leaving only trace carbon behind amounting to ~3% of the saturated monolayer. This suggests that the selective alcohol oxidation activity reported for supported [17,33,34] and stabilised [35] Au nanoparticles is not associated with extended (1 1 1) gold terraces, and must be confined to higher surface energy facets/defects or electronically perturbed (1 1 1) ensembles decorating clusters only a few nanometres across.

Au–Pd intermixing at temperatures below 1000 K has little impact on the overall saturation coverage of crotyl alcohol, or upon the degree of subsequent thermally induced decomposition and carbon laydown. However surfaces containing ≥15% Pd in the outermost layer (achieved for anneals above 873 K) are sufficient to switch on a new reaction pathway for the alcohol. This new chemistry is illustrated for the 973 K annealed surface in Fig. 5, which evidences pronounced sharpening of the 286.8 eV component above 170 K, accompanied by a +0.3 eV peakshift. The low BE component also sharpens, but shifts in the opposite direction by a similar magnitude. The resulting C 1s spectral fingerprint between 170 and 350 K matches that of crotonaldehyde on Pd(1 1 1), and this assignment is confirmed by mass spectrometry (see below). Crotonaldehyde features disappear rapidly above 350 K, coincident with the emergence of a broad, low energy carbon state reminiscent of alkylidyne fragments on Pt(1 1 1) [36]. The latter in turn diminish above 600 K to leave only trace carbonaceous residue. Representative snapshot spectra highlighting this transformation are shown in the Supporting Information, and the associated fitted surface component intensities for the 973 K annealed, Au_2Pd_3 surface alloy presented in Fig. 6. These in situ XPS measurements clearly show that the selective oxidation of crotyl alcohol to surface bound crotonaldehyde occurs with 100% efficiency over this alloy composition at room temperature. Although some of the desired crotonaldehyde product decomposes at higher temperatures, only 3% of the initial alcohol is left behind. This contrasts with unpromoted Pd(1 1 1) wherein over 70% of a crotyl alcohol monolayer fully decomposes [19].

Analogous thermal desorption mass spectra were recorded for a range of AuPd alloy surfaces in order to identify the stable reaction products evolved from these alloy surfaces. Only the parent crotyl alcohol desorbed from the unannealed thick Au overlayer, giving rise to 153 K multilayer and 183 K monolayer desorption states (see Supporting Information). These temperatures are slightly below those observed over Pd(1 1 1) [19] in line with the

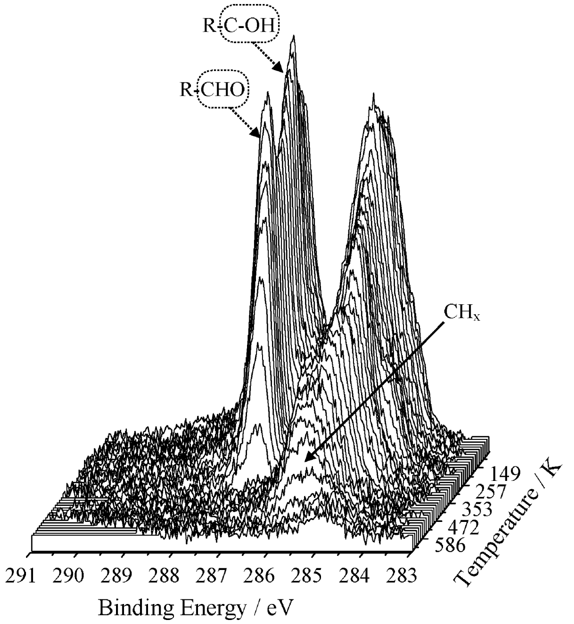

Fig. 5. Temperature-programmed C 1s XP spectra of a saturated crotyl alcohol adlayer over an ultrathin 3.9 ML Au/Pd(1 1 1) film annealed to 973 K. Oxidative dehydrogenation and subsequent crotonaldehyde desorption is strongly promoted over a Pd-rich surface alloy.

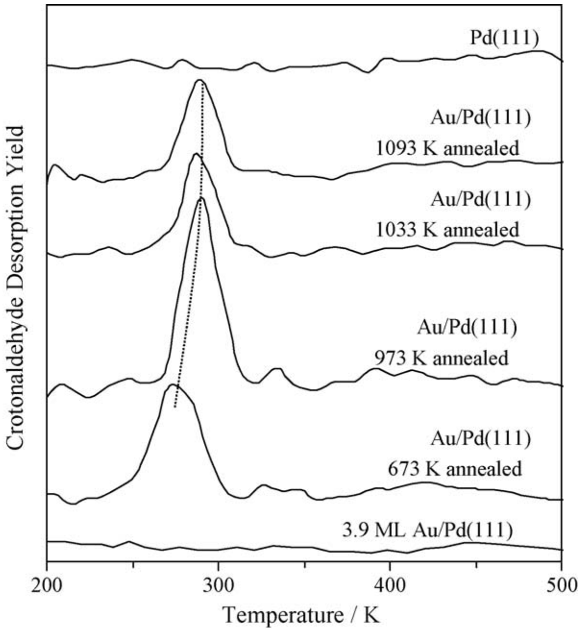

Fig. 7. Thermal desorption mass spectra of reactively-formed crotonaldehyde from a saturated crotyl alcohol adlayer adsorbed at 100 K over 3.9 ML Au/Pd(1 1 1) films. A comparative spectrum is shown for Pd(1 1 1). Optimal crotonaldehyde production occurs over Pd-rich surface alloys.

anticipated lower enthalpy of adsorption. Gold-rich alloys reduce the amount of reactant desorption, and simultaneously promote the evolution of crotonaldehyde at room temperature (Fig. 7). This is a striking contrast to the surface chemistry of Pd(1 1 1) for which only dehydration (butene and water) and decarbonylation (CO and propene) desorption products are seen. The crotonaldehyde desorption yield rises with increasing surface Pd content, reaching a maximum for the 973 K annealed Au_2Pd_3 surface. This enhanced oxidation performance is accompanied by an increase in the desorption peak temperature from 270 to 290 K. Since C 1s XPS reveals crotonaldehyde is formed on the surface of AuPd alloys below 200 K (see Fig. 6), this aldehyde evolution must be desorption-rate limited. The stronger binding of crotonaldehyde to more palladium-rich surfaces may reflect either a different adsorption mode (e.g. flat-lying versus tilted, or π-bonding through both C=C and C=O moieties) or reduced electronic perturbation as gold atoms diffuse subsurface. It is interesting to note that even high temperature anneals, sufficient to drive the vast majority of deposited gold subsurface and generate a terminating surface alloy containing 70% Pd, only result in limited aldehyde decarbonylation. Both propene and CO desorb from AuPd alloy surfaces at 300 and 350–400 K, respectively. Their desorption profiles are slightly perturbed compared to Pd(1 1 1), with propene evolving in a single state in the presence of surface gold. This decarbonylation pathway operates as a minor route over Au-rich alloys, but accounts for ~50% of the reactively-formed crotonaldehyde for compositions above Au_2Pd_3.

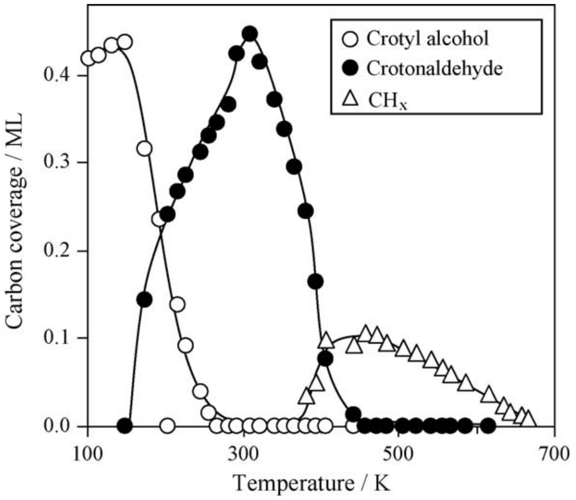

Fig. 6. Integrated C 1s XP intensities of fitted crotyl alcohol, crotonaldehyde and carbonaceous components for a saturated crotyl alcohol adlayer adsorbed at 100 K over a 973 K pre-annealed 3.9 ML Au/Pd(1 1 1) surface. Selective alcohol oxidation is followed by competitive aldehyde desorption (major pathway) or dehydration (minor pathway).

The impact of the bulk (mol fraction) and surface AuPd alloy compositions on the surface catalysed selox and decomposition pathways of adsorbed crotyl alcohol, and corresponding evolution of crotonaldehyde into the gas phase is summarised in Fig. 8. Limitations of the individual metal components for alcohol oxidation are immediately apparent. Pure palladium shows good low temperature conversion of crotyl alcohol to crotonaldehyde [19], but is also very active towards subsequent aldehyde decarbonylation, and dehydrogenation of the resultant surface propylidyne fragments. Consequently no crotonaldehyde desorbs intact from extended Pd(1 1 1) ensembles in the absence of additional co-adsorbed oxygen [19]. This may account for the rapid deactivation of monometallic Pd nanoparticles [16,37]. At the other extreme, pure gold is able to chemisorb crotyl alcohol into both monolayer and multilayer desorption states, but is unable to initiate the crucial C–H/O–H activation steps. In a clear example of a strong synergetic interaction, the incorporation of a relatively small number of gold atoms, which CO chemisorption suggests is sufficient to disrupt palladium hollow sites, dramatically suppresses crotonaldehyde decomposition, while actually enhancing its formation from the parent alcohol.

On the basis of the preceding in situ X-ray surface science studies we propose that high palladium surface concentrations

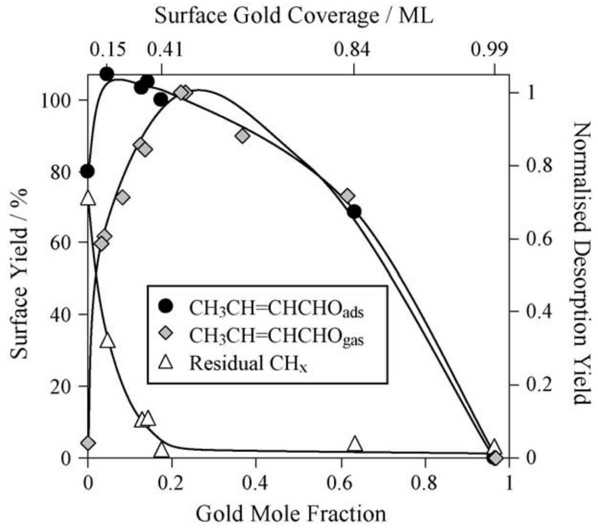

Fig. 8. In situ XPS derived crotyl alcohol conversion to surface-bound crotonaldehyde, and net decomposition to residual surface carbon as a function of Au alloy composition. Gold mol fraction determined from raw Au:Pd AES ratios and surface compositions from corrected AES signals [23]. The normalised desorption yields of reactively-formed crotonaldehyde evidence strong selox promotion by surface Au. Competitive product decomposition prevails over crotonaldehyde desorption over pure Pd(1 1 1).

should provide the optimum selox activity for dispersed AuPd alloy nanoparticles. This is consistent with recent studies on the aerobic oxidation of crotyl alcohol over PVP-stabilised bimetallic AuPd nanoparticles [35]. These exhibit maximum turnover frequencies and selectivities to the desired aldehydes for bulk Au:Pd ratios of 1:3 (c.f. a bulk ratio of 1:5 in this study), and also hydrogenation and isomerization side products characteristic of pure Pd-like surface character. Similar palladium surface segregation and associated excellent selox activity has been reported for Al_2O_3, TiO_2 and SiO_2 supported AuPd nanoparticles [16,38], wherein STEM and XPS indicate a Au-core, Pd-shell spontaneous partitioning upon calcination in air. We should note that the situation is more complex for carbon supported AuPd particles, wherein it is postulated that the selective oxidation of glycerol to glyceric acid proceeds over Au-rich alloy surfaces decorated with Pd monomers [39]. However, the bimetal distribution was very inhomogeneous between individual particles in this latter study, and did not utilise a surface sensitive spectroscopic method to model the terminating alloy composition. Although our own research has shown that atomically-dispersed Pd is extremely active for allylic alcohol oxidation when these monomers are tethered within an alumina matrix, the present work highlights the importance of the surrounding surface environment. Our earlier work on allylic alcohol selox has shown that strong adsorption of a proximate C=C bond is essential for subsequent activation of primary alcohols [40]. This observation is supported by our NEXAFS measurements on crotyl alcohol over Pd(1 1 1) [19] which reveal the C=C bond is bound parallel to the surface in both parent alcohol and aldehyde product. In the present system, it seems likely that extended gold ensembles within Au-rich surfaces are themselves inactive towards crotyl alcohol, while the probability of finding two Pd monomers in close proximity, able to tether the allyl function while activating the alcohol, is too small for significant oxidation. We should point out that gold chemistry does exhibit a pronounced particle-size dependency, hence Au-rich alloy nanoparticles may be more active than would be predicted from this model study. To date, no operando surface spectroscopy or (S)TEM studies have been conducted on such AuPd bimetallic catalysts during alcohol selox. Hence the true nature of the active surface ensemble, whether bimetal alloy, mixed metal oxide, or a composite metal–metal oxide, remains an elusive yet exciting challenge for new analytical techniques.

4. Conclusions

In situ XPS is a versatile technique for studying surface reactions over catalytically-relevant, model single-crystal substrates in real-time. Thick gold epitaxial overlayers prepared over a Pd(1 1 1) substrate reversibly chemisorb crotyl alcohol, but are unable to drive selective oxidation or decomposition. Gold-rich AuPd surface alloys show moderate activity for the oxidative dehydrogenation of crotyl alcohol to crotonaldehyde, which in turn desorbs intact at room temperature with minimal competing side-reactions. Palladium-rich alloy surfaces convert 100% of a crotyl alcohol adlayer to crotonaldehyde, although as much as half of this aldehyde subsequently decarbonylates to produce gas phase CO and propene, and leave small amounts of residual carbon ($\leq$30% of a monolayer). As previously reported, Pd(1 1 1) also shows good selox performance, however decarbonylation and dehydration are now the dominant process for reactively formed crotonaldehyde, resulting in high levels of surface carbon deposits. The optimum surface alloy composition for crotyl alcohol selox, with minimal decomposition of the resultant crotonaldhyde product, is Au_2Pd_3, associated with a bulk alloy composition of $AuPd_5$.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2008.10.034.

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