In situ XPS studies of crotyl alcohol selective oxidation over Pd(111) and Au/Pd(111) surface alloys

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Introduction
The heterogeneously catalyzed aerobic selective oxidation (selox) of hydrocarbons offers alternative, environmentally benign routes to valuable oxygenates for the fine chemical, pharmaceutical and agrochemical sectors [1]. These powerful catalytic technologies have the potential to replace stoichiometric oxidants or homogeneous complexes e.g. Mn oxides, and their associated process disadvantages and safety issues. Supported Platinum Group Metal nanoparticles are promising selox catalysts, able to activate diverse alcohols and carboxydrates under mild conditions employing either neat substrate or green solvents such as ionic liquids. We recently showed that even isolated palladium centres anchored within a transitional aluminia framework are efficient catalysts for the aerobic oxidative dehydrogenation of alcohols [2]. These reactions are highly regioselective towards the aldehyde product. Hutchings and co-workers recently discovered a range of bimetallic AuPd catalysts that show exceptional activity and selectivity for allylic alcohol selox [3]. However, the nature of the active surface ensemble and role of Au in promoting selox remain uncertain; questions well-suited to investigation by in situ X-ray photoelectron spectroscopy (XPS). Here we report the first study of crotyl alcohol selox over Pd(111) and Au/Pd(111) alloys, and show that trace Au suppresses the decarbonylation of reactively-formed crotonaldehyde, and that isolated Pd sites are not the active site for such catalysis in extended alloys.

Materials and Methods
Synchrotron XPS was performed at the Elettra SuperESCA beamline on a Pd(111) single-crystal ultra-high vacuum. Au films were grown at 500 K using an Omicron EFMS source. Crotyl alcohol was purified by freeze-pump-thaw cycles and background dosed at 95. Temperature programmed reaction data were acquired every 30 s during application of a linear heating ramp. C 1s XP spectra were acquired at 400 eV photon energy with a spectral resolution of 150 meV, and Shirley background-subtracted prior to analysis. C 1s spectra were fitted adopting a common Dunitz Sunjic lineshape convoluted with a Gaussian/Lorentzian mix. Alloys were generated by annealing a 3.9 ML Au film for 1 minute. Alloy compositions were calculated from Au and Pd AES signals corrected via published LEIS data [4]. Thermal desorption spectra were acquired with a quadrupole mass spectrometer and ramp of 12 K/s.

Results and Discussion
Crotyl alcohol (CH2=CH-CH2-OH) undergoes extensive oxidative dehydrogenation to crotonaldehyde over unpromoted Pd(111). However, all the reactively-formed aldehyde decarbonylates at 300 K, leaving chemisorbed CO and propylene, which may cause the on-stream deactivation seen for Pd selox catalysts. In contrast, pure Au films on Pd(111) suppress crotyl alcohol surface chemistry, with only reversible desorption observed. Thermal processing of ultrathin Au adlayers accesses a range of Au/Pd surface alloys which are extremely selective towards crotonaldehyde production, and greatly reduce the extent of hydrocarbon decomposition and eventual carbon laydown compared with Pd(111). Figure 1 shows temperature-programmed C 1s XP spectra of a reacting crotyl alcohol adlayer over a Au/Pd(111) surface. The transformation from adsorbed alcohol to aldehyde occurs between 170-350 K, coincident with desorption of the desired crotonaldehyde product.

Figure 1. Left) C 1s XP spectra of crotyl alcohol reacting on a Au/Pd surface alloy

The optimum surface alloy is Au3Pd. For this composition, Pd-rich ensembles facilitate 100 % efficient crotyl alcohol selox, while the presence of surface Au disrupts the secondary decarbonylation pathway, eliminating the formation of CO and carbon surface poisons. This contrasts with Pd(111) wherein 70 % of the alcohol reactant fully decomposes.

Significance
We have shown that small amounts of surface Au can promote palladium selox catalysts by suppressing decomposition of both alcohol reactant and aldehyde product. The optimum composition for synthesising high performance Au/Pd bimetallic selox catalysts is identified.

References