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Operando synchronous DRIFTS/MS/XAS as a powerful tool for guiding the design of Pd catalysts for the selective oxidation of alcohols

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ABSTRACT

The selective aerobic oxidation of crotyl alcohol to crotonaldehyde was investigated by time-resolved synchronous DRIFTS/MS/XAS over silica and alumina supported Pd nanoparticles. Alcohol and oxygen reactant feeds were cycled through the catalyst bed while dynamic measurements of the palladium oxidation state, molecular adsorbates and evolved product distribution were made simultaneously on a sub-second timescale. Highly dispersed palladium nanoparticles remained in a partially oxidised state <100 °C, independent of the redox environment, and were selective for crotonaldehyde formation. Higher temperatures facilitated rapid catalyst reduction on exposure to crotyl alcohol, with palladium metal driving crotonaldehyde decarbonylation to propene and CO, while slower (surface diffusion-limited) re-oxidation on exposure to oxygen re-opened selective oxidation pathways. Surface palladium oxide is identified as the desired active species.

1. Introduction

Recent years have seen significant progress in the development of atom efficient heterogeneous catalysts for the aerobic selective oxidation (selox) of alcohols to desirable carbonyl products [1–6]. The chemical synthesis of allylic aldehydes in particular, has presented a valuable testing ground for fundamental concepts in catalysis and surface science such as structure-sensitivity and the relative importance of geometric versus electronic influences, while affording commercially valuable molecules. Crotonaldehyde, produced by the low temperature oxidative dehydrogenation of crotyl alcohol (CrOH), is a termite repellant, and precursor to sorbic acid, an important food preservative [7], while cinnamaldehyde is widely used to confer a cinnamon aroma in the food and fragrance sectors, and as an insecticide to prevent the spread of mosquito larvae [8]. In the past, allylic aldehydes were synthesised via oxidation of their alcohol analogues by stoichiometric oxidants such as permanganates and chromates [9,10], with concomitant poor atom efficiencies and high environmental disposal costs [11–13]. Gold, platinum, ruthenium and palladium have also shown promise for allylic and/or benzyl alcohol selox when dispersed on high surface area supports [14–25], however there have been few systematic studies to understand the surface reaction mechanism, and identify the catalytically active site in order to guide future research and produce more active, selective and critically stable catalyst formulations.

The most extensive studies of alcohol selox have been conducted over Pd catalysts, wherein liquid phase X-ray Absorption Spectroscopy (XAS) and ATR-IR measurements have uncovered important changes in the palladium oxidation state on-stream [16,17,26–28]. The first such time-resolved, operando investigation of cinnamyl alcohol selox highlighted a direct relationship between the PdO content and resultant catalytic activity [28,29], noting catalyst reduction to palladium metal was accompanied by deactivation. A potential explanation for the latter observation was advanced through time-resolved X-ray photoelectron spectroscopy (XPS) and thermal desorption studies of crotyl alcohol [30,31] and crotonaldehyde [32] over Pd(1 1 1) and Au/Pd(1 1 1) model single crystal catalysts which indicate that surface oxygen decreases the adsorption energy of both reactant and product, minimising their decomposition and subsequent site-blocking by strongly bound CO and carbonaceous residues. The hypothesis that surface Pd^{2+} sites are responsible for allylic and benzyl alcohol selox gained additional support from ex situ XPS and XAS measurements of high activity Pd atoms and nanoparticles on mesoporous alumina [16,17] and silicas respectively [14].

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We recently explored whether dynamic structure-reactivity measurements in the vapour phase would shed further light on the roles of palladium oxide and metal in crotyl alcohol selox [33], and demonstrated the benefits of coupling multiple operando spectroscopies with on-line mass spectrometry to detect reaction-induced restructuring (in the absence of competitive solvent adsorption or mass-transport limitations) and relate this to the nature of reactively formed adsorbates and evolved products. Expanding upon this initial synchronous, time-dependent DRIFTS/MS/XAS communication we conclusively demonstrate that crotyl alcohol selox is favoured over partially oxidised Pd nanoparticles, while undesired combustion and crotonaldehyde decarbonylation pathways are exclusive to reduced Pd metal formed in situ under oxygen deficient conditions.

2. Experimental

2.1. Catalyst synthesis

Mesoporous alumina (meso-Al_2O_3) was prepared using the method reported by Vaudry et al. [34]. Aluminum sec-butoxide (87.5 g) was hydrolysed with de-ionized water (20.6 g) in propan-1-ol (550 g). Lauric acid (21.6 g) was added after 1 h of stirring. The mixture was aged (static) at room temperature for 24 h, and then heated for 48 h at 110 °C. The resulting solid was filtered and washed with ethanol and dried at room temperature. The lauric acid template was removed by calcination under static air at 550 °C for 2.5 h, through heating to 250 °C at 25 °C min^{-1} and then to 550 °C at 5 °C min^{-1}.

SBA-15 was synthesised via the method reported by Zhao et al. [35]. Pluronic P123 (10 g) was dissolved in water (75.5 cm^3) and HCl (2 M, 291.5 cm^3) and stirred at 35 °C. Tetramethoxysilane (15.5 cm^3) was then added and the mixture left for 20 h under agitation. The resulting gel was aged for 24 h at 80 °C without agitation. The remaining solid was filtered, washed with water (1000 cm^3) and dried at room temperature before calcination at 500 °C for 6 h in air (ramp rate 1 °C min^{-1}).

The 2.4 wt% Pd/meso-Al_2O_3 and 2.2 wt% Pd/SBA-15 catalysts were prepared using tetraamine palladium(II) nitrate solution (Johnson Matthey assay 4.16% Pd) by incipient wetness impregnation. Dried samples were calcined at 500 °C (ramp rate 1 °C min^{-1}) in static air for 2 h, then reduced under flowing H_2 (10 cm^3 min^{-1}) at 400 °C (ramp rate 10 °C min^{-1}) for 2 h. Samples were stored in air and not re-activated prior to use.

Pd nanoicosahedra were synthesised by adapting the procedure of Xiong et al. [36]. PVP (0.534 g, 55,000 MW) and citric acid (0.900 g) were dissolved in water (120 cm^3) at room temperature under good mechanical stirring. A reflux condenser was set up and the reagents were heated to 90 °C in air. Na_2PdCl_4 (0.282 g) was dissolved in 45 cm^3 water at room temperature and added to the reaction mixture using a syringe pump at a rate of 85 cm^3 min^{-1}. After a further 5 h, the volume was reduced using a rotary evaporator, and the resulting stabilised colloid collected by centrifugation at 4000 rpm, washed once with acetone and three times with ethanol. The PVP-stabilised Pd nanoicosahedra (1 g) were subsequently re-dispersed in 5 cm^3 ethanol and slurried with 1 g of meso-Al_2O_3, then dried at 50 °C for 24 h to give a final palladium loading of 5 wt%.

2.2. Catalyst characterisations

Accurate Pd loadings were determined by MEDAC Analytical and Chemical Consultancy Service Ltd. Samples were digested in either HF or nitric acid prior to ICP analysis on a Varian Vista MPX inductively coupled plasma-optical emission spectrometer (ICP-OES).

Nitrogen porosimetry was undertaken on either a Quantachrome Nova 1200 porosimeter, with analysis carried out using NovaWin 2 v2.2 analysis software, or on a Micromeritics ASAP 2010 instrument. Samples were degassed at 120 °C for 2 h prior to recording N_2 adsorption/desorption isotherms. BET surface areas were calculated over the relative pressure range 0.02–0.2, where a linear relationship was maintained. Pore diameters and volumes were calculated applying the BJH method to the desorption isotherm, for relative pressures >0.35.

Powder X-ray diffraction (XRD) patterns were recorded on either a Panalytical X'pertPro diffractometer fitted with an X'celerator detector, or a Bruker D8 Advance diffractometer fitted with a LynxEye high-speed strip detector, both using Cu Kα (1.54 Å) sources calibrated against either Si (Panalytical) or SiO_2 (Bruker) standards. Low angle patterns were recorded for $2\theta = 0.3–8°$ with a step size of 0.01°. Wide angle patterns were recorded for $2\theta = 25–75°$ with a step size of 0.02 and volume-averaged Pd particle sizes calculated by Scherrer analysis.

Pd metal dispersions were measured by CO chemisorption on a Quantachrome ChemBET 3000 system, or H_2 chemisorption on a Micromeritics PulseChemisorb 2700. Samples were outgassed at 150 °C under flowing He (20 cm^3 min^{-1}) for 1 h, and then reduced at 100 °C under flowing hydrogen (20 cm^3 min^{-1}) for 1 h before analysis at room temperature. Note that this reduction protocol is far milder than that employed during the original catalyst syntheses, and control experiments show that it does not induce, e.g. particle sintering.

High resolution (scanning) transmission electron microscopy (S)TEM images were recorded on either an FEI Tecnai F20 FEG TEM operating at 200 kV equipped with a Gatan Orius SC600A CCD camera, or at the SuperSTEM 1 (Daresbury) facility with an instrument based on a Cambridge VG HB 501UX microscope operating at 100 keV with a cold-field emission source, a high-resolution pole piece and Nion Mark II spherical aberration corrector capable of achieving a spatial resolution of 0.1 nm [37]. Samples were prepared by dispersion in methanol and drop-casting onto a copper grid coated with a holey carbon support film (Agar Scientific Ltd.). Images were analysed using ImageJ 1.41 software. High-angle annular dark-field (HAADF) imaging, which is particularly sensitive to heavy atoms [38], was used to image Pd-impregnated supports. Conventional bright-field (BF) imaging was used to visualise unsupported icosahedra.

X-ray photoelectron spectra were acquired on a Kratos AXIS HSi spectrometer equipped with a charge neutraliser and monochromated Al Kα excitation source (1486.7 eV). Binding energy (BE) referencing was employed using the adventitious carbon peak at 285 eV, and valence band edge. Survey scans were recorded for surface elemental analysis (pass energy 160 eV), with high resolution spectra recorded at 40 eV pass energy. Spectral fitting was performed using CasaXPS Version 2.3.5 with a common lineshape based on a Gaussian/Lorentzian (50:50) mix as well as asymmetry based on a Donaich–Sunjic mix of 0.005, with a FWHM of 2.34 eV adopted for all Pd components. Two Pd chemical environments were present at 335.0 eV and 336.4 eV, assigned as Pd metal and PdO respectively. It is important to remember that the observation of metallic Pd does not mean the surface is only partially oxidised, since the inelastic mean free path of Pd $3d_{5/2}$ electrons is ~1.3 nm, and the XPS spectra will therefore contain a significant contribution from any underlying metallic palladium, lowering the apparent oxide surface concentration. In situ XPS measurements were performed following exposure to CrOH within the main sample analysis chamber: the sample was heated to either 80 or 250 °C (at 5 °C min^{-1}), and the temperature stabilised for 20 min, prior to background dosing 10 L CrOH (purified by freeze–pump–thaw cycles) through a leak valve. The sample was