

Operando studies of nanoparticulate palladium catalysts for environmentally-benign selective aerobic oxidation of allylic alcohols

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This proposal addressed the aerobic selective oxidation of alcohols, which represent atom-efficient clean catalytic technologies widely employed in industry for sustainable chemicals production. Palladium clusters show promise for such reactions, however, their mode of operation has been ambiguous, presenting a challenge to successful commercialization.

Our team used ID24 and a novel in-situ reaction cell recently developed by Dr Mark Newton (**Figure 1**), to undertake dynamic, in-situ X-ray absorption and surface IR measurements in parallel with mass spectrometry to probe the nature of the active catalyst site during the vapour phase oxidation of crotyl alcohol to crotonaldehyde over Pd nanoparticles dispersed on mesoporous Al₂O₃.

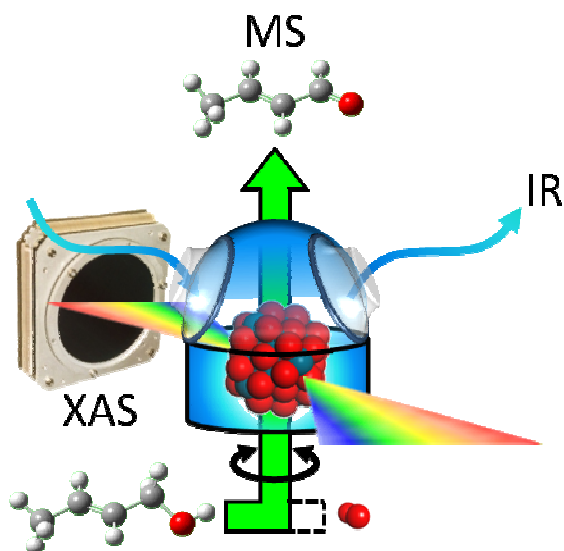


Figure 1 | Schematic of ESRF reaction cell. Synchronous DRIFTS/MS/XAS measurements were recorded in a stainless steel reactor with vitreous carbon windows permit high X-ray transmission with minimum interference to the XAS signal. Heated inlet and outlet gas lines prevent condensation of less-volatile components.

Cycling studies reveal oxidative dehydrogenation to crotonaldehyde is favoured over non-reducible PdO_x clusters, with gas phase oxygen promoting product desorption (**Figure 2**).

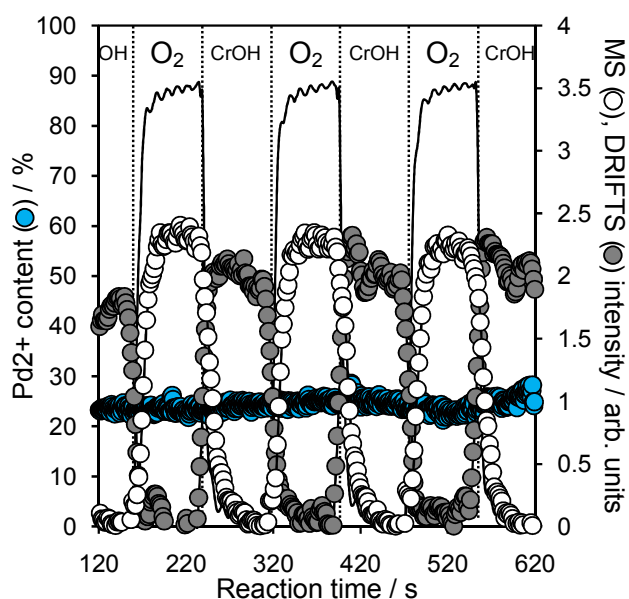


Figure 2 | Low temperature catalytic behaviour. DRIFTS/MS/XANES intensities as a function of alternating CrOH/O₂ cycles over 2.37 wt% Pd/meso-Al₂O₃ catalyst at 80 °C: ● 1712 cm⁻¹; — O₂ (m/z = 32), ○ crotonaldehyde (m/z = 70), ● fitted XANES Pd²⁺ concentration.

High temperatures facilitate reversible cycling of the Pd oxidation state under reducing or oxidising conditions, which in turn favour decarbonylation and combustion pathways associated with metallic clusters. Control of palladium redox properties emerges as a key experimental parameter for future optimisation, with Pd²⁺ species identified as crucial for high selectivity. These experiments have enabled us to construct a detailed picture of reaction-induced restructuring in this system (**Figure 3**), and to identify surface PdO_x as the active species. A full manuscript describing this work has just been submitted to Science (August 2010).

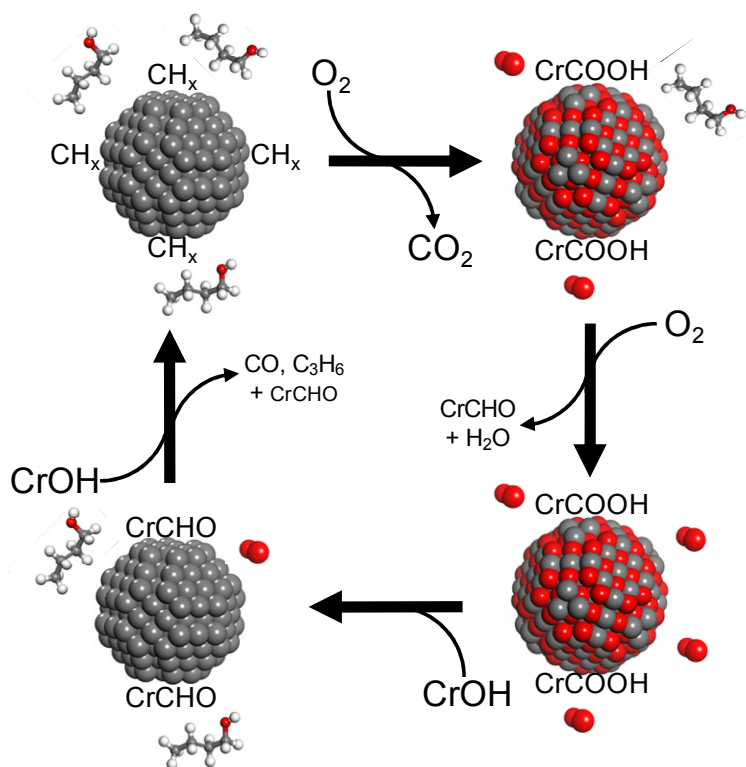


Figure 3| Reaction-driven restructuring. Proposed reaction network highlighting interdependency of catalyst phase (oxidation state) and associated selectivity towards CrOH oxidation upon surrounding reducing/oxidising reactant feedstream.