Operando Synchronous DRIFTS/MS/XAS as a Powerful Tool for Guiding the Design of Heterogeneous Catalysts

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Introduction and Objectives

Catalysis is a rich, multidisciplinary field with a global socio-economic impact ranging from improved air quality to the design of new HIV therapies, and creation of bulletproof fabrics. Heterogeneous (solid) catalysis is currently experiencing a global renaissance, with interest soaring in new predictive quantum chemical models and experimental synthetic and analytical methodologies able to deliver tailored catalyst formulations offering precise activities, and selectivities, for diverse chemistries, including artificial photosynthesis. The rational design of new heterogeneous catalysts for sustainable chemical technologies can be accelerated by molecular level insight into surface chemistry [1], and nanoengineering approaches to achieve precise control over the structure and reactivity of novel functional materials [2,3]. Here we highlight how in-situ and time-resolved X-ray spectroscopies can be used to visualise chemistry in action and identify the active catalytic site responsible [4], and thereby help direct the design of tunable nanocrystalline and nanoporous catalysts for clean technologies such as the aerobic selective oxidation (selox) of allylic alcohols [5].

Experimental

Mesoporous silica[3] and alumina[4] supported Pd catalysts were prepared via surfactant-templating of the parent support and subsequent incipient wetness impregnation. Time-resolved, in-situ synchronous DRIFTS/MS/XAS measurements were recorded during vapour phase crotyl alcohol (CrOH) selox within an fixed-bed reactor upon exposure of catalysts to alternating CrOH or O_2 cycles under isothermal conditions. Pd K-edge energy dispersive XAS measurements were collected at beamline ID24 of the ESRF, with activity and selectivity followed by on-line MS, and DRIFTS.

Results and Discussion

Figure 1a shows the set-up for our synchronous DRIFTS/MS/XAS measurements. Below 140 °C , crotonaldehyde is reactively-formed over PdO_x nanoparticles upon

exposure to CrOH (Figure 1b), but only desorbs during O_2 adsorption. Higher reaction temperatures promote reversible nanoparticle surface restructuring, accopmanied by a concomitant loss of catalyst selectivity. Analogous liquid phase CrOH selox over Pd/mesoporous silicas reveals significant rate-enhancements associated with the use of 3D interconnected/penetrating support architectures.

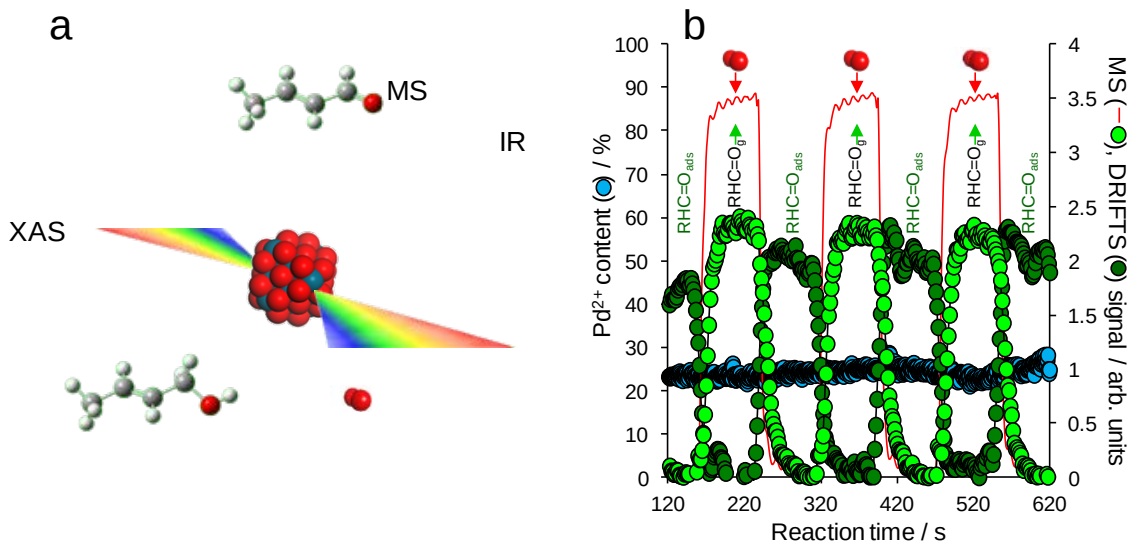

Figure 1. (a) Cartoon of stainless-steel in-situ reactor; **(b)** DRIFTS/MS/XANES intensities as a function of alternating CrOH/O_2 cycles over 2.37 wt% Pd/meso-Al_2O_3 catalyst at 80 °C: ● 1712 cm^{-1}; — O_2 (m/z = 32), ○ crotonaldehyde (m/z = 70), ● XANES Pd^{2+} concentration**.**

Conclusions

Synchronous DRIFTS/MS/XANES measurements have highlighted the importance of stabilising surface PdO, and minimizing catalyst reducibility, in order to achieve high allylic aldehyde yields, guiding the future design of Pd-derived catalysts for aerobic alcohol selox. This methodology is widely applicable to vapour phase organic synthesis.

References

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