The dynamic behaviour of Pt-group metal nanoparticles during liquid- and gas-phase catalysis

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Supported metal nanoparticles (NPs) used in heterogeneous catalysts have been demonstrated to be far from structurally passive in the presence of adsorbates and under reaction conditions. Understanding the structural response of NPs to their environment can give in-depth insights into reaction mechanisms as well as how catalyst design affects their reactivity, selectivity, and stability, and potentially their regeneration once deactivated. Nowadays, fourth-generation synchrotrons provide the high-quality structural data and the time resolution necessary for mechanistic studies of heterogeneously catalysed reactions. The results presented here exemplify the possibility to capture subtle structural effects on a timescale of seconds using high-energy X-ray diffraction (XRD), Pair Distribution Function (PDF) analysis, and X-ray Absorption Spectroscopy (XAS). One example shows how PDF analysis allied to Pt-$L_{2,3}$ edge XAS was used to determine that Pt NPs are reactive at room temperature in manners that are not a priori expected from the traditional Langmuir explanation of the CO oxidation by O_2 on Pt surfaces. These results, obtained under repeated exposures of a commercial, 3-4 nm Pt/Al_2O_3 catalyst to CO and O_2 atmospheres [1], reveal the reversible formation of reactive Pt surface oxides, whose appearance and removal from the system are highly correlated to the production of CO_2 during redox cycling.

Time-resolved PDF analysis on another commercial Pt/Al_2O_3 catalyst provided experimental evidence of structural modulations in Pt NPs occurring simultaneously with their movement relative to the alumina support: two phenomena previously only predicted through computational studies. These fully reversible effects were induced by exposure to H_2 not only in gas-phase environments, as indicated by computational results, but also in the liquid phase and to a degree largely dependent on the size of the nanoparticles [2].

However sensitive to the structural modifications induced by reactive environments these techniques may be, an atomistic description of the involved nanostructures remains challenging, especially in the presence of complex background scattering from sample environment and catalyst support. Multivariate analysis techniques have recently emerged as a means to partially sidestep this problem and extract chemically sensible information from time-resolved XAS, XRD, and PDF data. Here we show some examples of their application to the identification and kinetic profiling of intermediate species during the reduction of Ru- and Pd-based catalysts [3,4].

[1] S. Checchia et al, under review in ACS Catal.
[2] D. Bonavia et al, Nat. Commun. (2025) 16, 9591.
[3] P. Lazzarini et al, ACS Catal. (2025) 16, 2, 1077-1090.
[4] D. Bonavia et al, under review in ACS Catal.

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