# *Operando* Spatio-Temporal Study of CO oxidation reaction in Pd Catalysts using Full-Field Hyperspectral XAS imaging

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## ABSTRACT

The ROCK beamline at the SOLEIL synchrotron has recently implemented Full-Field (FF) hyperspectral Quick-XAS imaging, combining element-specific XAS with micrometer-scale spatial resolution and second-scale temporal resolution for investigating the reaction pathways of functional materials under *operando* conditions [1,2]. Hyperspectral cubes containing 170 to 580 images of the sample, recorded at energy values scanning an X-ray absorption spectrum, were acquired using a pixelated CMOS camera (1.625 µm pixel size over a 3.3 mm field of view) with acquisition times as short as 2.5 s for unraveling the spatial dynamics of hydride formation during $H_2$ pretreatment and their subsequent impact on the CO oxidation reaction over supported Pd nanoparticle catalysts.

Hyperspectral datasets were processed using in-house developed Jupyter notebooks and analyzed by Multivariate Curve Resolution with Alternating Least Squares, enabling extraction of transient species and their spatial concentration profiles. During $H_2$ pretreatment, the initial reduction of the oxidized catalyst led to the formation of $PdH_x$ species under 5% $H_2$ or metallic Pd under 0.08% $H_2$. Depending on the support ($Al_2O_3$ or $TiO_2$), these transformations propagated through the catalyst bed as reduction wavefronts. During CO oxidation reaction, the catalysts exhibited distinct spatial and temporal phase evolution, correlated with the reaction stage and the support–metal interactions that govern the spatial variations. Below 200 °C, the catalyst remained predominantly metallic, a state associated with high activity through a Langmuir–Hinshelwood reaction pathway [3]. As the temperature increased to 300 °C, the catalyst progressively evolved towards a highly oxidized state following the heater direction, suggesting a transition towards a Mars–van Krevelen-type reaction pathway [4].

Beyond these mechanistic insights, FF hyperspectral XAS imaging also uncovered pronounced beam-induced effects for the RT $H_2$ uptake that remain undetectable in conventional XAS measurements. These effects were significantly more pronounced for the $TiO_2$-supported catalyst, highlighting the strong interplay between the support properties, the X-ray beam, and catalyst reactivity. As the higher photon flux delivered by 4$^{th}$-generation synchrotron sources becomes increasingly available, spatially resolved *operando* XAS will be essential not only for distinguishing intrinsic catalytic behavior from probe-induced artefacts, but also for improving the reliability of *operando* catalyst characterization and guiding the design of more efficient and robust heterogeneous catalysts.

## REFERENCES

1. V. Briois *et al*., J. *Synch. Rad.*, **31**, 1-24 (2024)
2. V. Briois *et al*., ChemCatChem, **e202400352**, 1-14 (2024)
3. M.A. Spronsen *et al*., Chem. Soc. Rev., **46**, 4347-4374 (2017)
4. B. L. M. Hendriksen. *et al*., Nat. Chem., **2**, 730-734 (2010)