

Enhancing the sensitivity of X-ray based techniques by pulse experiments

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X-ray based synchrotron methods are invaluable tools for materials characterization under relevant process conditions. In the particular case of heterogeneous catalysis, these methods have become indispensable to obtain key structural information on catalytic materials under in situ and operando conditions. High energy X-rays further enable larger cross sections and sufficient time-resolution to follow rapid structural changes in the sub-second regime.

Despite the enormous advantages over traditional characterization methods, the large majority of the X-ray based techniques remain bulk-sensitive. Thus subtle structural changes, which could be associated to near surface variations, are obscured by bulk structural changes. This issue is further hampered by the fact that typical experiments are carried out at steady state under static conditions. Pulse experiments offer a possibility of improvement because the catalyst is stimulated to perform a specific event and to exhibit the structural changes associated with that event. Repetition of the event, thus repeated pulses (modulation), already improve the signal-to-noise ratio of any spectroscopic/diffraction method. Further enhancement can be achieved by filtering out the static signals, e.g. the unresponsive bulk, by phase sensitive analysis (Figure 1) [1]. It should be emphasized that this approach is valid irrespective of spectroscopy/diffraction method. Pulse experiments not only represent a powerful analytical method to increase sensitivity of a given characterization technique to small changes. From a catalytic view point, they can also simulate the operation of some specific automotive catalysts but also the regeneration of catalysts in large scale industrial plants.

The potential of pulse experiments is demonstrated in the specific cases of X-ray absorption spectroscopy (XAS) and high energy X-ray diffraction (XRD) of catalysts based on precious metals (Pd, Rh) used in automotive catalysis. In the case of XAS, pre-reduced 2 wt% Pd/Al₂O₃ and 2 wt% Rh/Al₂O₃ are compared during repeated CO-NO pulses at 300°C [2]. Partial re-oxidation of both metals in the presence of NO can be followed only after phase sensitive analysis of the time-resolved spectra. Moreover, generation of carbidic species, which are necessarily formed at the surface of

Pd nanoparticles, is also enhanced by analysis of the phase-resolved data and by the EXAFS fit of Pd/Al₂O₃.

In the case of high energy XRD, the advantage of using this approach is emphasized in the case of 2 wt% Pd/CeZrO₂ (Pd/CZ) [3] that is typically silent in the XRD with respect to the Pd-PdO phase. The time-resolved high energy XRD data collected during CO-O₂ experiments at 300°C display the reflections of the bulk material but hardly display any tangible change. Given the fine dispersion of PdO induced by CZ, no information is available about the state of Pd. The XRD data after phase sensitive analysis exhibit only the very subtle changes associated with the signals responding to the modulation experiment. Besides providing information on the dynamics of reduction and re-oxidation of the Ce³⁺/Ce⁴⁺ pair, the data also shows additional broad features corresponding to reflections of Pd nanoparticles of 2 nm. The sole intensity change is associated with the relative increase of long range order attributed to PdO reduction. Therefore, the modulation data can capture simultaneously the dynamic reduction and re-oxidation of PdO and CZ.

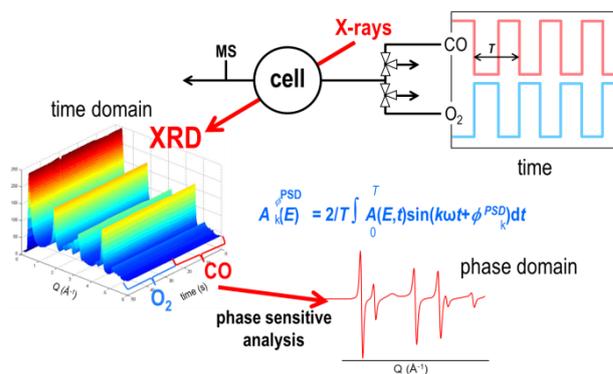


Figure 1. Layout of a high energy XRD modulation experiment.

In conclusion, subtle structural changes in XAS spectra and XRD patterns can be captured and their temporal response precisely assessed by performing modulation experiments. This provides access to detailed structural-dynamic behaviour of catalytic systems.

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- [1] D. Baurecht, U. P. Fringeli, *Rev. Sci. Instrum.* **72** (2001) 3782.
- [2] D. Ferri, S. K. Matam, R. Wirz, A. Eyssler, O. Korsak, P. Hug, A. Weidenkaff, M. A. Newton, *PCCP* **12** (2010) 5634.
- [3] D. Ferri, M. A. Newton, M. Di Michiel, G. L. Chiarello, S. Yoon, Y. Lu, J. Andrieux, *Angew. Chem.* **53** (2014) 8890.