

### Self-absorption free HEROS method applied to a time-resolved study following oxidation of single site Ta catalysts

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Keywords: synchrotron radiation, time-resolved high energy resolution off-resonant X-ray spectroscopy, catalysts

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In this work we employed the high energy resolution off-resonant spectroscopy (HEROS) technique [1] for a time-resolved study of the density of unoccupied states of Ta atoms in a chemical system under reaction conditions [2]. In the HEROS approach, off-resonant X-ray emission spectra, which carry information on the density of unoccupied states [3,4], are recorded at a single incident beam energy fixed below the absorption edge of interest. As a result, the impact of the self-absorption effect on the density of unoccupied states data obtained from the measured HEROS spectra is reduced to only the probability of reabsorption of the emitted fluorescence radiation in the target which is usually nearly constant in the measured emission energy range [5]. We show that the self-absorption freeness and swiftness of the HEROS approach make it a powerful tool to study the chemical surrounding of the given atoms in chemical systems under reaction conditions [2].

The measurements were carried out at the SuperXAS beam line, Swiss Light Source, PSI, Switzerland. The investigated silica supported Ta complexes, Ta(V) carbene bisalkyl and Ta hydride, were loaded into a quartz-capillary reactor at a 20 ppm O<sub>2</sub> atmosphere. The Ta(V) carbene bisalkyl complex was prepared at the University of Lyon and the Ta hydride was obtained by subjecting Ta(V) carbene bisalkyl to reaction with 10% H<sub>2</sub>/He gas mixture at the temperature increased slowly in the range 20 °C – 140 °C. The samples were exposed to the synchrotron radiation beam (~10<sup>11</sup> photons/s) of energy 9.863 keV and 9.867 keV for Ta(V) carbene bisalkyl and Ta hydride, respectively (i.e. 18 eV and 14 eV below the Ta L<sub>3</sub>-edge binding energy, respectively). The induced fluorescence was detected in the energy range around the Ta La<sub>1</sub> emission line (8.146 keV) by means of a wavelength-dispersive von Hamos-type spectrometer consisting of two cylindrically

curved segmented-type Si(444) crystals [6] and a two-dimensional PILATUS 100K detector. The HEROS spectra were collected one by one with an acquisition time of 40 s each. From the full width at half maximum (FWHM) of a Gaussian fit to the elastic scattering peak an experimental resolution of 1.6 eV was found.

For both studied complexes the fingerprint Ta La<sub>1</sub> HEROS spectra were recorded before and after oxidation to determine temporal changes in the species' concentration. Analysis of the fingerprint spectra revealed formation of dimeric Ta species caused by the reaction with oxygen. As can be seen in Figure 1(a), during reaction of Ta(V) carbene bisalkyl with oxygen only about 20% of the sample first turned into its oxidized form and the remaining 80% transformed afterwards. The demonstrated step-wise transition is an effect of different reaction rates for oxidation and dimerization. Such a behavior was not observed in the case of Ta hydride which was found to oxidize suddenly after about 6800 s, as shown in Figure 1(b).

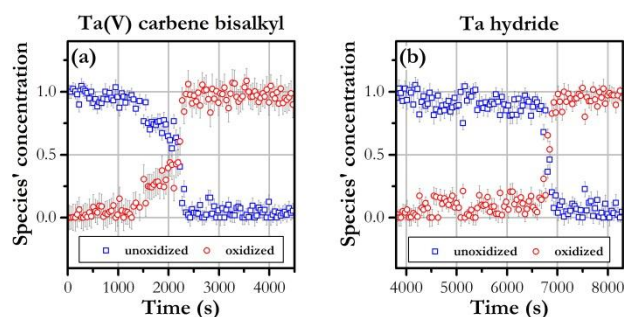


Figure 1. Relative concentration of Ta(V) carbene bisalkyl [2] (a) and Ta hydride (b) during oxidation as a function of time.

The present study demonstrates that HEROS allows probing the density of unoccupied states with high temporal resolution. In particular, since the HEROS spectra are not affected by the self-absorption effect, HEROS is a powerful tool to perform time-resolved studies on systems under reaction conditions.

**Acknowledgments:** This work was performed at the Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland. Some of us (W. B., J. H., J.-Cl. D., F. Z. and Y. K.) also acknowledge the financial support of the Swiss National Science Foundation.

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