Monitoring the Formation of a Single-Atom Catalyst with *Operando* Quick XAFS

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ABSTRACT

Single-atom catalysts (SACs) have demonstrated their ability to enhance selectivity,[1] reduce the need for expensive metals,[1,2] and even replace molecular catalysts.[2,3] Among SACs, M-N-C materials, which consist of isolated metal (M) atoms stabilized by nitrogen dopants in a carbon matrix, are the most widely studied, with applications spanning electro-, photo- and thermo-catalysis. These catalysts are typically synthesized via impregnation-pyrolysis methods, where processing parameters dictate the final metal coordination and thus the catalytic performance.

In this study, we investigated the thermal evolution of Pt and Co precursors initially adsorbed on a carbon powder, using established synthesis protocols[4,5] and X-ray absorption spectroscopy (XAS) at the SOLEIL ROCK beamline. Multivariate curve resolution – alternating least squares (MCR-ALS) analysis of the spectra reveals complex interconversion processes, with pyrolysis temperature and flowing gas (N_2 or H_2) as critical parameters.

As an illustration, Figure 1 presents the XAS evolution and MCR-ALS decomposition results for the formation of a Co-N-C catalyst, which exhibited high activity and selectivity in CO_2 electroreduction. The process begins with decomposition of adsorbed cobalt(II) acetate, followed by gradual cobalt reduction and single-atom formation (6.3±2.5 light neighbors – optimal fraction around 350 °C) in parallel with the separate development of slightly oxidic cobalt dimers and few-atom clusters (1.0±0.4 and 2.6±0.6 Co neighbors, respectively), and concludes with the appearance of large nanoparticles (8.3±1.6 Co neighbors). These findings offer valuable guidelines for the rational synthesis of SACs.

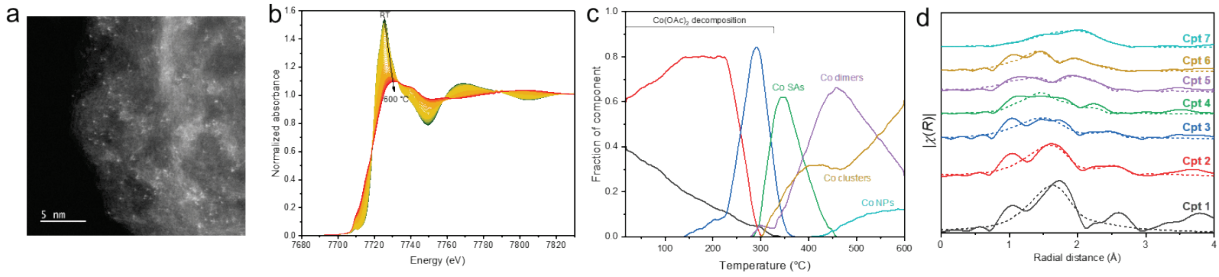

Figure 1. a) STEM-HAADF image of a Co-N-C SAC. b) Evolution of Co-K edge XAS spectra during pyrolysis of $Co(OAc)_2$ and 1,10-phenanthroline on carbon black, from RT to 600 °C under N_2 flow. c,d) Corresponding MCR-ALS component fractions and XAFS FT moduli of components (extracted from full RT-600-RT-900°C sequence).

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