Study of the genesis of HDS catalysts by in situ photon in photon out spectroscopy

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The advent of in situ/operando spectroscopies in the field of heterogeneous catalysis was a key turning-point making possible a fundamental understanding of the relationship linking the active phase structure, reactivity, and selectivity. However conventional and widely applied X-ray spectroscopic techniques (e.g., X-ray Absorption (XAS), X-ray Photoelectron Spectroscopy (XPS)…) gives a weighted averaged signal over all the transition metal ion speciation and it is not possible to obtain a set of pure spectra corresponding to the numerous speciation (spin, covalency, oxidation state…) that the absorber undergoes during the synthesis/activation of the catalyst and the catalytic reaction. This last decade have seen the implementation of two complementary photon in photon out spectroscopies: High Energy Resolved Partial Fluorescence Detection XAS (HERPFD-XAS) and Resonant Inelastic X-ray Scattering (RIXS). By aligning the detector at an appropriate energy, HERPFD-XAS allow access to a pure XAS spectrum of only one speciation of the absorber metal. 1s-2p RIXS gives access to different electronic intermediate states of the XAS pre-edge structure whereas in classical XAS K edge, the pre-edge corresponds to the sum of these states.

We used these two spectroscopies to study the genesis of hydrodesulphurization (HDS) catalysts. The active phase of this class of catalyst is consisting of Co promoted nanometer scale MoS_2 particles dispersed on γ-alumina support. Combination of Mo with Co gives a synergetic effect in HDS activity due to the formation of the active CoMoS phase. However, the exact structure and localization of cobalt remains unclear due to the segregation of the Co element in different phases during the catalyst activation step. HERPFD XAS and 1s 2p RIXS spectra were recorded at SOLEIL synchrotron facility on GALAXIES beamline. To follow the genesis of the active phase, the catalyst was heated up to 400 °C in a ramp of 1 °C/min under a flux of H_2/H_2S. Using Co K edge HERPFD-XAS we were able to separate the sulfide and the reaming oxide phase. Thanks to the partial fluorescence detection and to the removal of cobalt oxide form the global signal, XAS spectrum of CoMoS shows sharper features compared to those published in the literature making comparison to theoretical XAS spectra possible. CoMoS structures showing S/M-edges were generated by DFT calculation and their corresponding Co K edge XANES spectra were calculated. The best agreement between experiment and theory is observed for tetrahedral Co localized at S-edges of the MoS_2 layers. *In situ* Co K edge 1s2p RIXS of the sulfided catalyst shows excitations to band-like unoccupied states revealing the metallic nature of the CoMoS active phase which questioning earlier XPS data processing A new XPS fitting procedure, considering the exact electronic structure of the active phase is proposed and gives rise to 20 % of Co in oxide phase and 80% in CoMoS phase. This fit is in agreement with HERPFD-XAS results unlike previous fit available in litterature where a disagreement between XAS and XPS is reported (XAS show an almost total sulfidation while XPS adjustment shows a sulfidation of 40-60% of Co oxide phase).

In conclusion HERPFD-XAS and 1s2p RIXS are very powerful to characterize selectively both electronic and geometric structure making possible the localization of Co in HDS catalysts (S-edge) and showed that the promotion rate is underestimated. These findings pave the way to future investigations on the impact of Co S/M-edges substitution on the final properties of the catalyst.