

In-situ Quick-XAS investigation of citric acid effect on the liquid sulfidation of HDS catalysts

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Improvement of hydrotreatment catalysts to obtain cleaner fuels requires the development of more efficient cobalt-promoted MoS₂ catalysts supported on alumina. One way to increase their efficiency is by improving the performances of the HDS catalyst (cobalt-promoted MoS₂ supported on alumina) with the addition of a chelating agent like citric acid (CA). A deeper understanding of the activation step, i.e. the sulfidation of cobalt and molybdenum, is necessary to explain the origin of a better activity for additivated catalysts activated under a gas/liquid mixture of H₂/gasoil/Dimethyldisulfide at 30 bar. The addition of CA in the impregnation solution might create a complex with Co and/or Mo in the solution which remains after the impregnation on the support¹. The presence of this complex during the catalyst activation would delay the sulfidation of the promoter and enable a simultaneous sulfidation of Co and Mo, leading to an improved active phase, as confirmed by *Fujikawa et al.*³. If the effect of CA addition on the gas sulfidation was widely studied², its effect on the liquid sulfidation mechanism is still unknown and has been studied in depth herein.

A dried catalyst and two different additivated (Co-impregnation and Post impregnation) catalysts with CA were synthesized and their liquid sulfidation was studied simultaneously at Co and Mo K edges thanks to the edge jumping operation mode available at the Quick-XAS ROCK beamline (SOLEIL Synchrotron)⁴. To this purpose, a new analytical cell was designed to reproduce the industrial conditions of the liquid sulfidation (350°C and 30 bar). The data were analyzed by principal component analysis and multivariate curve resolution by alternating least square minimization (MCR-ALS) in order to determine the concentration profiles of the species involved during activation and the XAS spectra of these pure species.

The EXAFS spectra of the oxide phases show a clear effect of the CA addition. Furthermore, for the co-impregnated and the dried catalysts at least 2 intermediate species are identified between the oxide phases and the final MoS₂ species at the Mo K-edge; while the sulfidation mechanism of the post-additivated catalyst goes through only one intermediate. Refinements of Fourier Transformed EXAFS spectra of the pure species isolated by MCR-ALS are on-going to precisely identify these compounds.

The combination of time resolved data collected at both edges with chemometric analysis and the characterisation of the oxide and sulfided phases (via XPS, MET and Raman spectroscopy, IR and ATG/IR) allowed us to give a first insight into the effect of the CA on the liquid sulfidation mechanism and to determine the different chemical species involved.

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