Unique *operando* Quick-EXAFS characterization of bimetallic heterogeneous catalysts used for hydrodesulfurization

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Introduction and Objectives

The catalytic reaction of hydrodesulfurization (HDS) producing fuels with low sulfur content needs to use bimetallic catalysts which consist of Mo and Ni (or Co) dispersed on a high surface area support [1]. Information on the formation of the active phases and their evolution under reaction conditions are crucial for designing catalysts with enhanced performances. Thus the aim of this study is to perform *operando* X-ray Absorption Spectroscopy (XAS) in order to unravel the sulfidation processes of molybdenum and its promoter. Such characterization still represents a significant challenge and requires the development of analysis cells operating with harsh reaction conditions (temperature, pressure, gas…). A new suitable XAS analysis cell [2] mimicking phenomena that take place in fixed bed reactors under reactive atmosphere at pressure up to 50 bar and temperature up to 500°C is presented.

Results and Discussion

For the first time, Quick-EXAFS technology enabled to characterise, under realistic working conditions, simultaneously molybdenum and nickel (cobalt) K-edges taking advantage of the time resolution and the edge-hopping capabilities available with the Quick-EXAFS monochromator installed at the SAMBA beamline [3].

During the activation phase under H_2S/H_2 flow, we observed concurrently the sulfidation of nickel (or Co) and molybdenum forming the mixed Ni(Co)MoS active phase. Depending of the catalyst pre-treatments (drying or calcination), we highlighted different mechanisms of sulfidation. In particular we observed for dried catalysts two molybdenum intermediate species: isolated MoO_4^{2-} and oxysulfide $\{MoOS_2\}$ (Figure), while for the calcined catalysts only the oxysulfide species are formed during the activation treatment. We also showed that the sulfidation of Ni (or Co) is greatly dependent of molybdenum.

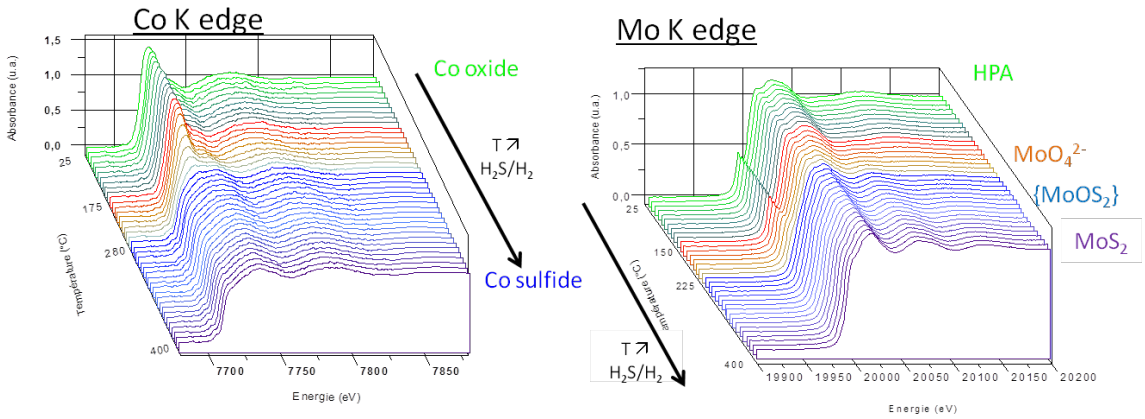

Figure: Simultaneous Quick-EXAFS studies at the Co and Mo K edges of the activation of a CoMo based catalyst under H_2S/H_2 (heating ramp 2°C/min).

Then the latter catalysts were characterized during the first hours of HDS reaction with model molecules (thiophene) using Quick-EXAFS combined to a mass spectrometer on line. Correlations between the evolution of active phases and the catalytic properties of our material are presented.

Conclusions

Simultaneous characterization of two metal species, accessible by the QEXAFS setup installed on the SAMBA beamline, which allowed an accurate description of the activation processes of bimetallic catalysts for hydrodesulfurization. We focused our study on the comparison of catalysts with similar formulations with different pre-treatments (dried/calcined) and two catalysts promoted by different metals: cobalt and nickel.

References

[1] H. Topsøe and B. S. Clausen, Catal. Rev. - Sci. Eng. 26 (1984) 395.
[2] A. Rochet, V. Moizan, V. Briois, and C. Pichon. Diamond Light Source Proceedings, 2010, Oxford, 1, e130 1.
[3] V. Briois, E. Fonda, S. Belin, L. Barthe, C. La Fontaine, F. Langlois, M. Ribbens, and F. Villain. UVX 2010, EDP Sciences, 2011, 41.