

MS37-2-1 Complementarity of hyperspectral XAS imaging and Raman spectroscopy for studying the impregnation and drying of supported CoMoP / Al₂O₃ HDS catalysts
#MS37-2-1

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Abstract

With strengthened environmental regulations in oil fractions¹, there is a demand for more efficient hydrodesulfurization (HDS) catalysts. The preparation of these catalysts starts with the impregnation of a solution containing Mo and Co and usually P on an alumina support, followed by maturation and drying. Upon impregnation/maturation, there is a change in the equilibria between the Mo-species in the acidic impregnation solution due to the contact with basic alumina, leading to an heterogeneous distribution of different Mo species further transformed upon drying into mono, polymolybdates and P-HPAs (Heteropolyanions)². As the catalytic activity is improved with P-HPAs³, a rational design of the catalyst requires an *in situ* spatially and time-resolved chemical speciation to better understand the underlying adsorption processes for *in fine* mastering those unitary preparation steps.

Our methodology is based on the complementary use of *in situ* X-ray Absorption Spectroscopy (XAS) and *ex situ* Raman spectroscopy hyperspectral imaging. At the ROCK-SOLEIL beamline, Full Field (FF) time-resolved Mo K edge XAS imaging has been developed, consisting in the recording of space-energy resolved 3D data cubes using a pixelated CMOS camera (1.625µm pixel size)⁴. The rate of spectra collection is 1 cube/11s, each cube corresponding to 580 images/energies, recorded with a Field of View of 1.6mm x 1.2mm. These performances perfectly match the resolution required for the characterization of the preparation of a mm-sized industrial alumina extrudate. Optimized cells for *in situ* impregnation/maturation and *in situ* drying have been specifically developed. The first one allows the injection of ~0.1µL solution inside the cell cavity containing an extrudate (1.5mm x 1.6mm), followed by 3h-maturation. Inside the drying cell, the same extrudate is heated from RT to 120°C followed by 1h isothermal plateau.

Processing of the hyperspectral XAS data is performed in Jupyter notebooks followed by linear combination fitting (LCF) of the EXAFS spectra using a library of EXAFS spectra of bulk references⁵, results in the quantification of Mo-based species dispersed on the support, given in relative fraction of spectrum.

The work presented herein enables for the first time the dynamic monitoring of the Mo-speciation changes during the key preparation steps of a catalyst with 8 wt.% MoO₃, Co/Mo 0.4, P/Mo 0.56 after a dry impregnation (Fig.1(a)-(b)). Whereas only the Strandberg's HPA is measured in the impregnation solution, the speciation obtained by FF XAS imaging shows that Anderson's AlMo₆O₂₄, Dawson monomer's, lacunary Keggin's HPAs, monomolybdate and the pristine Strandberg's HPA are dispersed on the extrudate after *in situ* impregnation/maturation (3h). The maps suggest an heterogeneous spatial distribution of the species, with an increasing HPAs concentration from the core to the edges of the extrudate (Fig.1(c)-(d)). After drying (2h, 120°C), the dispersion of species reflects the heterogeneity obtained at the end of the maturation.

References

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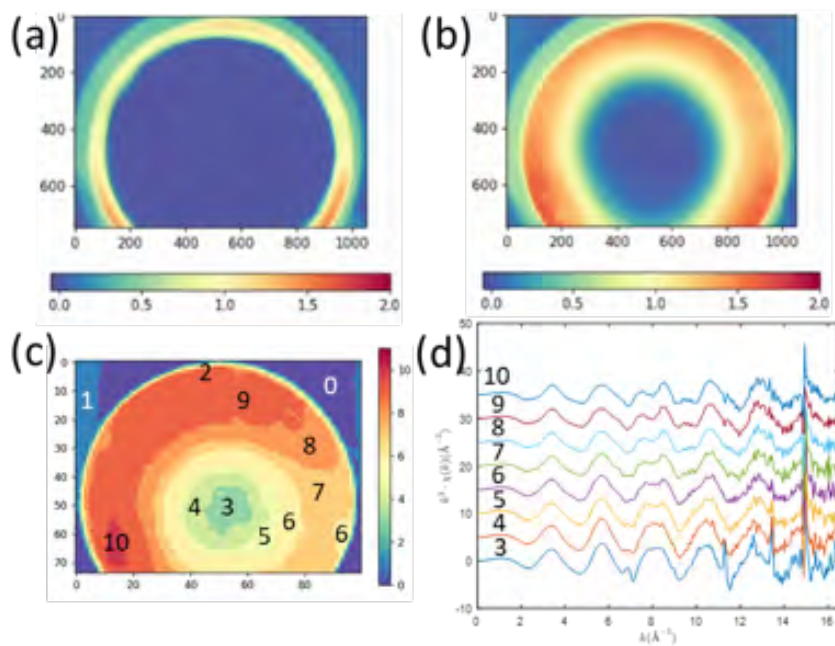


Fig. 1: Approximate absorption maps at (a) 2 min (b) 46 min after impregnation. (c) Edge jump slicing of a map at the end of 3h maturation and (d) EXAFS spectra from the slices in (c).