Innovative chemical imaging speciation methodology for studying the impact of the impregnation and maturation of CoMoP/ Al_2O_3 HDS catalysts by Raman and XAS spectroscopies

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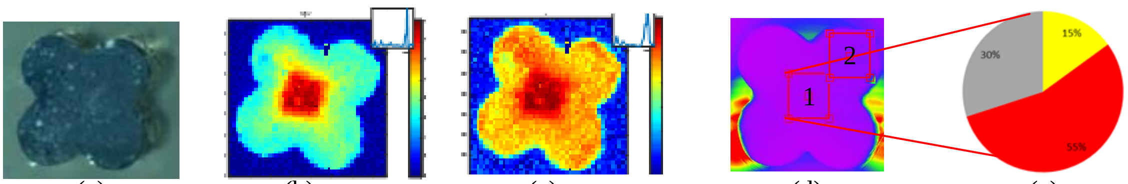
As restriction policies for sulfur emissions become stricter, in Europe allowing only up to 10 ppm of sulfur [1], there is a rise in demand for more efficient hydrodesulfurization (HDS) catalysts. The efficiency of these catalysts depends strongly on its preparation, the impregnation and maturation steps being considered of great importance [2]. In parallel, the development of chemical imaging tools has been shown to be essential for providing an insight into the chemical transformations occurring during these stages but also for revealing the complexity of the catalysts, which are made of a mixture of different oxide species [3].

In this study, an innovative analysis methodology was developed, providing a few microns spatially resolved chemical images and revealing speciation of Mo-based species for dried CoMoP/ Al_2O_3 HDS catalysts. The focus of the study was the location and quantification of two main groups of species that are present in the oxide phase of the catalyst: polymolybdates and heteropolyanions (HPAs), as deposited on quadrilobe-shaped alumina extrudates. HPAs are known to be related to an higher catalytic activity than polymolybdates [4], which explains the interest to identify them and above all quantify them, which cannot be carried out by Raman only. For that, the cross section of the same catalyst extrudate was analyzed by micro-beam Raman and macro-beam X-ray Absorption (XAS) spectroscopies. The species distribution was determined by Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) fitting analysis, a chemometric method allowing to isolate the spectral fingerprints of the different components within the mixture [5].

The in-depth use of MCR-ALS to the analysis of thousands of Raman hyperspectral images has resulted in a set of spectral components identified, by comparison with bulk references, as HPAs and polymolybdates species deposited on the support and whose mapping provided qualitative chemical images with a 16.2x16.2 µm resolution. In addition, XAS analysis, with a 300x300 µm resolution, provided quantitative speciation through linear combination fitting of spectra recorded on existing bulk references. An example of a sample can be seen in Figure 1(a). The Raman mappings of $AlMo_6$ and polymolybdates are presented in (b) and (c) respectively, showing that the species are more concentrated towards the core. XAS analysis was performed in the core (d1) and lobe (d2) of the extrudate. The core analysis (d1) provided an average quantification of the species, summarized in (e). In addition, XAS clarified the type of polymolybdate, octamolybdate, thus representing an important source of complementary information to the Raman imaging. The impact of other parameters, such as the P/Mo ratio or the additivation with citric acid, were also studied with the same methodology. The Raman imaging and XAS speciation provided insights on the impact of these parameters, constituting an important tool for improving the synthesis of the catalysts. Finally, hyperspectral XAS imaging with a similar resolution to the Raman imaging and applied to the same catalysts is under development and principles will be briefly presented.



(a) (b) (c) (d) (e)

Figure 1: (a) Example of a catalyst extrudate (b) Raman mapping of $AlMo_6$ (c) Raman mapping of polymolybdates (d) squared regions analyzed by EXAFS (1) core and (2) lobe (e) EXAFS average speciation in the core square in relative molar percentage of Mo in the species, legend: ■ 15% $AlMo_6$, ■ 55% octamolybdate, ■ 30% MoO_4^{2-}. Note: CoMoP/Al_2O_3 with 8 wt.% MoO_3, P/Mo 0.56, Co/Mo 0.4

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