Catalyst Design Guided by XAS Spectroscopy

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Rational synthesis of catalytic materials plays a pivotal role in the industry due both to the enormous economic impact of these materials and their requirement for establishing more sustainable chemical processes, reducing pollution and producing energy. Despite this considerable economic and environmental importance, catalyst preparation has long relied on trial-and-error approaches. Innovative synthesis strategies are now being developed to achieve a truly rational design of catalytic materials, for example, to enable nanoscale control over the size and growth of supported active-phase particles. One of the most suitable molecular-level characterization techniques for guiding this rational design is X-ray absorption spectroscopy, which combines unique advantages (namely element specificity and insight into the electronic and local environment of the probed element). The purpose of this presentation is to present several examples of heterogeneous catalysts preparation (metals, sulfides, carbides) for which XAS experiments performed at French synchrotron beamlines (notably under operando conditions thanks to the Equipex funding for the ROCK project) have played a key role in the design of improved catalytic formulations

The atomic distribution of metals is of particular importance in catalysis, as surface atoms play a key role in catalytic performance. Furthermore, when bimetallic nanoparticles are exposed to various gas atmospheres (including reaction conditions) and heated to high temperatures, atomic redistribution may occur. Two examples obtained using ROCK [1] will be presented (Au-Ag nanorods and Au-Cu nanoparticles): they allow us to track the redistribution of metals (Au-Ag) and the onset of reduction (Au-Cu) to demonstrate that the kinetics of these processes depend strongly on the metal composition and particle volume.

A 2nd example will focus on sulfide catalysts (MoS_2) supported on alumina, which are key components in hydrodesulfurization (removal of sulfur from petroleum feedstocks) and in the conversion of biomass for biofuel production. In this case, a surface-science approach was developed to enable better control of the speciation of surface sorption sites, using α-Al_2O_3 single crystals with different orientations as model supports. Polarization-dependent surface EXAFS experiments [2], conducted on SAMBA and DIFFABS, revealed a preferential orientation of MoS_2 slabs on surfaces exhibiting reduced metal-support interactions. The metal-support binding strength appears to be a decisive descriptor for surface speciation and, consequently, for describing the surface-dependent volcano plot for hydrotreating activity.

Finally, HERFD XANES experiments conducted on FAME-UHD [3] using carbon-supported Mo and W carbide catalysts will be presented to investigate the role of the carburization sequence in the formation of these Mo-W carbides. A clear carburization order is observed, governed not only by the intrinsic reducibility of the metals but also by the extent of overlap between the predominant domains of reduced MoO_2 and WO_3-x. These results show that the material can be tailored to produce either homogeneous bimetallic nanoparticles or phase-separated carbides, thereby laying the foundation for a rational design of catalysts.

REFERENCES

1. J. van der Hoeven *et al. ACS Nano* **12**, 8467−8476 (2018); A. Nasseredine et al. ChemCatChem. **17**, e202500379 (2025)
2. A. Tougerti et al., *Angew. Chem. Int. Ed.* **51**, 7697-7701 (2012), C. Bara et al., *J. Am. Chem. Soc.* **137**, 15915-28 (2015), R. Garcia de Castro et al. *J. Catal.* **403**, 16-31 (2021), C. Chizallet et al. *J. Catal.* **394**, 157-166 (2021).
3. P. Azimov et al. *ChemCatChem* **18**, e0006 (2026)