

Phase Sensitive Detected XAS to study real industrial oxidation catalysts

PhD position at

Université de Lille (Unité de Catalyse et Chimie du Solide, UCCS) and

Synchrotron SOLEIL (ligne de lumière ROCK)

Ecole Doctorale Sciences de la Matière du Rayonnement et de l'Environnement (104)

Context. The characterization of heterogeneous catalysts by X-ray Absorption Spectroscopy (XAS) is particularly suitable for the study of supported heterogeneous catalysts since it makes it possible to determine the speciation of the absorbing atom in the analyzed sample by giving access to structural parameters: distance, nature and number of nearest neighbors. Nevertheless, given the small interaction cross section between X-rays and matter, XAS is not a surface technique but rather a volume technique. Thus the *in situ / operando* characterization of catalysts which are in the form of bulk materials, e.g. most of the heterogeneous catalysts used for partial oxidation, by XAS is very limited. Indeed, the recorded signal will correspond to a global signal containing the species exposed to the surface of the catalyst where the catalytic reaction takes place, and the species found in the volume of the material (spectator during the catalytic reaction). To overcome this difficulty, we propose in this PhD to use the experimental set-up developed on the ROCK beamline. It consists of a set of fast switching valves allowing to use XAS spectroscopy in "Modulation-Excitation (ME)" regime. The modulation-excitation spectroscopy consists in applying a periodic perturbation to the sample and recording the response of the system to this excitation. This periodic perturbation will only influence the concentration profile of the active species to be probed (in our case the active species exposed at the surface of the catalyst). After a certain number of periodic excitations, the active species will reach a steady state in which their concentration will oscillate at the same frequency as the periodic excitation but with a phase delay. The amplitude and phase shift of the system response depend both on the frequency of the excitation and on the active species present in the sample (i.e. the species that are sensitive to excitation). A mathematical treatment makes it possible to trace the spectra not as a function of time, but of the phase (phase sensitive detection: PSD). This allows to get rid of the signal of the spectator species and to keep only the contribution of the active species.

Methodology. We propose in this PhD to study the correlation between structure and reactivity/selectivity of industrial $\text{Fe}_2(\text{MoO}_4)_3$ bulk catalyst. The latter is used in the partial oxidation of methanol (production of formaldehyde or of dimethoxymethane according to the conditions). Preliminary experiments have shown that if the absorption spectra for the $\text{Fe}_2(\text{MoO}_4)_3$ do not show significant variations during the pulses, the demodulated analysis allows evidencing significant variations.

The first year of the thesis will be held at the UCCS and will be dedicated to the treatment of standard EXAFS data of the different phases at the iron and molybdenum K-edges as well as the DFT modelling of the different surfaces of the catalysts to identify the potential active sites and calculate their spectroscopic signatures. During this first year, the student will be asked to make a bibliographic study of the different approaches used in various spectroscopies for the interpretation within the modulation-excitation mode.

The second year will be spent at SOLEIL (ROCK beamline) to acquire spectroscopic data within the ME setup during dedicated sessions. Different periodic perturbations will be considered for the quick

change of the reactive atmosphere: i) pulses of O₂ and methanol saturated atmosphere (He/CH₃OH), ii) pulses of O₂ and atmosphere saturated in methanol/O₂ reaction mixture (O₂/He/CH₃OH), iii) pulses of O₂ and H₂. Together with the X-ray absorption spectroscopy, mass spectrometry as well as gas chromatography data will be recorded. The main objective of this second year is to go beyond a qualitative interpretation of demodulated spectra: i) determination of the number of species present during the perturbation sequence and ii) isolation of the pure spectra of these species. This first part should be tractable with existing chemometric tools (principal component analysis, multivariate analysis) with some adaptations. A method of analysis of the pure spectra thus isolated will be developed (method quite close to a standard EXAFS analysis if the pure spectra have been effectively isolated). Another approach would be to generalize the method presented by Nachtegaal et al. (J. Catal. 2013 vol 305, p 92) which consists in performing an EXAFS refinement on spectra differences. The applicability of this method in the case of more than two components remains to be demonstrated. The bibliographic methodological survey performed during the first year will of course open new approaches to treat these data.

Gathering of the spectroscopic and the modelling data will be performed during the last year of the PhD. The active sites determined via the interpretation of the ME XAS spectra will be confronted to the results obtained by DFT calculations. The location of the work during this last year will be defined during the second one.

Profile: Master in Material Science, Physical Chemistry or Inorganic Chemistry with knowledge in Spectroscopy and/or Modelling.

PERSONS TO CONTACT BY CANDIDATE

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