Symposium for Data-Driven Approaches in X-ray Absorption Spectroscopy (DataXAS)

Contribution ID: **17**

Type: **Poster and Flash Presentation**

Interpreting Non-Redox Responses in Modulation-Excitation XAS

Monday 5 January 2026 16:11 (3 minutes)

Introduction

While operando X-ray absorption spectroscopy (XAS) offers valuable insights into the dynamics of catalysts, it remains a bulk technique. This poses a challenge given that catalysis is a surface phenomenon. To address this limitation, a modulation excitation (ME) experimental design combined with phase-sensitive detection (PSD) analysis can be used. This approach enables the separation of the active fraction of the material from the inert background.1 Traditionally, PSD results are interpreted by comparing the in-phase component to experimentally measured difference spectra. However, with the advent of faster and higher-resolution measurements we are beginning to observe dynamic, non-redox events that cannot be adequately described by conventional difference spectra. This highlights the need for more advanced analysis strategies that go beyond oxidation states, aiming to capture subtle electronic and structural changes. In this work, we explore such an approach by linking PSD results to changes in the electronic structure of the reactive Ni species.

Results & Discussion

We applied ME-XAS to investigate a Ni/SiO$_2$ catalyst with 16 nm Ni particles at the ROCK beamline of SOLEIL.2 To probe the dynamic response of the catalyst, two modulation periods were applied with CO$_2$ vs H2 in one case and O$_2$ vs H2 in the other.
As shown in Figure 2a, the O$_2$-modulation induces a strong response. Comparison with the a Ni-NiO difference spectrum (Figure 2c) confirms that the observed spectral changes are a transition from Ni^0 to Ni^{2+}. During 1 period, the NiO fraction varies from 21% to 35%. Likely only the outer shell of the Ni nanoparticles is involved.
On Figure 2b, the response to the CO2-modulation is shown. Here, the Ni-NiO difference spectrum does not match the in-phase response. It suggests non-redox changes. These could be caused by adsorbate formation, change in charge transfer at the metal–support interface or slight coordination changes that do not correspond to bulk oxidation. A new approach for interpretation is to link the observed spectral variations with changes in the electronic structure of Ni. An understanding of these phenomena allows for the incorporation of such effects into simulated XANES spectra, allowing the generation of theoretical difference spectra for direct comparison with experimental data.

References

1 D. Ferri et al., Top. Catal., 2011, 54, 1070
2 Briois, V et al., J. Phys. Conf. Ser. 2016, 712, 012149

Author: Mr LIPS, Servaas (Ghent University)

Co-authors: Dr POELMAN, Hilde (Ghent University); Mr D'OOGHE, Lennert (Ghent University); Prof. SABBE, Maarten (Ghent University); Prof. GALVITA, Vladimir (Ghent University)

Presenter: Mr LIPS, Servaas (Ghent University)

Session Classification: Flash Presentations