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Advanced Operando XAS Methodologies for Active-Site Identification and Quantification in Materials with Complex Speciation

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Quantitative structural identification of active sites in heterogeneous catalysts under reaction conditions using bulk spectroscopic techniques remains fundamentally limited. This is particularly true for Fe-exchanged zeolites, which exhibit isolated Fe ions co-existing with oligomers, and larger aggregates. This poses several challenges: (i) distinguishing active sites from spectators, (ii) quantifying the active sites, and (iii) disentangling changes in oxidation state and coordination environment under reaction conditions.

To address this challenge, we currently implement a suite of experimental protocols and data analysis methods coupled with operando X-ray absorption spectroscopy (XAS). Typical experiments consist of heating the sample to induce dehydration while acquiring spectra, followed by cooling to experiment/reaction temperature. We perform transient step-changes (addition/cut-off) of individual reactants or reactant mixtures to probe kinetics and redox properties. For transient measurements, a chemometric approach combining principal component analysis (PCA) and multivariate curve resolution (MCR) analysis is typically employed. PCA first identifies the minimum number of independent spectral components that reproduce the original data, while also obtaining an evaluation of the residuals. Then MCR decomposes overlapping spectral contributions, allowing us to track the evolution of Fe species during dehydration and reaction, and, when feasible, to extract kinetic parameters that can be correlated to online mass spectrometry and plug-flow reactor tests.

Upon reaching steady-state conditions, we can apply modulated excitation coupled with phase-sensitive detection (ME-PSD). Applying a gas pulse as a stimulus that selectively perturbs the catalytically active sites improves our ability to discriminate between them and spectator species. Stochastic noise is diminished by averaging the response over multiple modulation cycles, which enhances spectral sensitivity. Subsequently, the implementation of a lock-in amplification algorithm enhances signals that are phase-correlated with the applied perturbation, simultaneously suppresses static background contributions, and thereby enables the isolation of periodic, kinetically relevant spectral features.

When time resolution is limited, we combine modulation excitation with the step-scan technique by fixing a single energy point for each gas cycle and repeating this across an entire energy range. This generates an energy–intensity matrix from which spectra can be reconstructed, enabling, in some cases, unprecedented time resolution.

This combined advanced operando methodology and chemometric approach provides a robust basis for future integration with machine learning techniques. Neural networks trained on such decomposed spectral datasets could enable prediction of Fe K-edge XAS spectra from relevant reaction conditions (e.g., temperature, gas composition, redox environment) much faster than quantum chemical calculations. This could facilitate the screening of Fe coordination environments for experimental design and potentially optimize the usage of synchrotron beamtime.

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