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Speciation of Ru Molecular Complexes in a Homogeneous Catalytic System: Fingerprint XANES Analysis Guided by Machine Learning

Identifying the true active species in homogeneous catalytic systems remains one of the most demanding challenges in modern spectroscopy. Low metal concentrations and dynamic reaction environments often make conventional EXAFS analysis impossible, leaving XANES as the only accessible technique for probing local structure.

In this work, we combine machine learning with fingerprint XANES analysis to reveal the speciation of Ru molecular complexes that can be formed *in situ* in homogeneous systems. Ruthenium-based catalytic systems can be used to hydrogenate sugar alcohols to alkenes, offering an efficient pathway toward environmentally friendly and sustainable chemical processes. The system based on RuX_3 salts (X = Cl, Br) dissolved in the ionic liquid (Bu_4PBr) has been proposed as a catalyst for this type of reaction.

A comprehensive database of theoretical Ru K-edge XANES spectra was generated using *ab initio* simulations (FDMNES), systematically varying Ru-Br/Ru-Cl and Ru-CO distances, as well as CO coordination numbers. The resulting data were processed using a descriptor-based machine learning approach trained to predict both ligand type and interatomic distances from selected spectral features such as edge position, curvature of the white line, and PCA-derived components. The work was carried out using the original program codes written in Python, using the PyFitIt library.

The trained models achieved $R^2 > 0.98$ in cross-validation and accurately reproduced both Ru-Br/Ru-Cl and Ru-CO bond lengths and CO coordination numbers for experimental spectra measured at ESRF BM23. Remarkably, even mixed or previously uncharacterized species were correctly identified.

This study demonstrates how combining spectral descriptors with physical modeling can overcome sensitivity limitations of XAS in homogeneous catalysis. The methodology provides a general framework for extending fingerprint analysis beyond qualitative interpretation, enabling the direct identification of molecular catalyst species from XANES spectra.

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