

Development of X-ray emission spectroscopy in single site catalysis

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The local electronic configuration of the metal ion is reflected in the pre-edge region of the XAS spectrum, which arises from resonant excitations into the lowest unoccupied orbitals. Detailed XANES studies on transition metal complexes have demonstrated the sensitivity of X-ray absorption K edges and their (pre)edge features to their chemical environment, e.g. oxidation state, site symmetry, crystal field splitting. However, XANES is still not fully understood, and has been used mainly as a fingerprint for metal oxidation states or geometries. Here, developments in X-ray emission techniques, i.e. resonant inelastic X-ray spectroscopy (RIXS), are pursued.

In RIXS spectroscopy, the emitted energy is measured as function of the incident energy using a secondary spectrometer, thus yielding 2-dimensional (2D) X-ray information. The 2D picture is crucial to identify the correlation between the incident and emitted energies, and gives information on the electronic density of states of the system. Information similar to L- and M-edge spectroscopy is obtained because similar final states can be reached. The advantage of RIXS is that both incident and emitted energies are relatively high in energy, thus allowing in situ measurements on working catalysts. When different emission lines can be resolved and assigned to specific chemical environments, selective XAFS can be performed.

Initially, systematic RIXS studies using structurally known reference compounds, in combination with theory and complementary techniques like the direct L- and K-edge XANES, have been performed obtaining fundamental insights in the X-ray data obtained. The technique was explored from the previously studied 3d transition metals to the unexplored 4d and 5d transition metals. Full RIXS planes have been acquired as a function crystal orientation angle to determine the orientation of the molecular orbitals (MOs) and assign the different XANES features. In addition, important insights in charge transfer within the systems have been obtained.

We are currently studying the electronic properties of catalytic materials, i.e. single site homogeneous systems, in detail. Information on the orientation of MOs, the charge transfer between them, and their accessibility for reactants, is obtained, providing insights in the properties required for (enantio)selective catalysis. Additionally, preliminary results on in situ, flow-chemistry catalytic studies will be presented.

References

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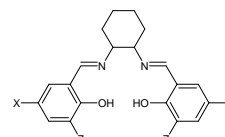
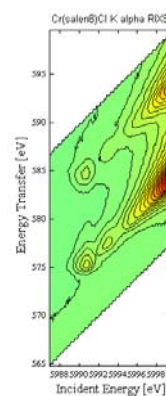


Figure 1: Example of Cr 1s2p RIXS for a Cr(salen) catalyst.