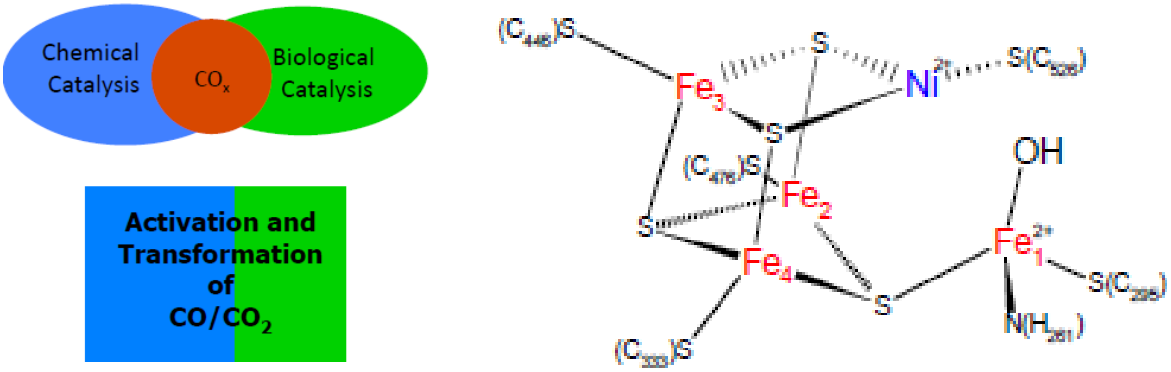
Biological catalysis – COx conversion studied by XAS



COx conversion studied within the Unicat Cluster of Excellence Berlin (left) and structural model of the active site in carbon monoxide dehydrogenase (CODH) (right).

Summary:

In this project biological systems, involving ligand conversion reactions at protein-bound metal centers, are investigated by X-ray spectroscopy (CO_2/CO). Nature uses diverse strategies for hydrocarbon transformation, e.g., harnessing the power of reduced oxygen species at iron-containing sites. The global carbon cycle depends on $C(O_x)(H_x)$ conversions such as CO_2-reduction to CO or formate using sophisticated metal cofactors in FDHs and CODHs. FDHs may reveal common strategies to dispose harmful oxygen species.

Atomic level structural information and electronic parameters in reaction intermediates are required to understand the mechanisms of the metal cofactors and to unravel general principles of biological small molecule catalysis. Such information will here be obtained by X-ray absorption spectroscopy (XAS), leading to improved structures of the cofactors, which allow to elucidate the reaction pathways. Metal- and ligand-centered XAS measurements will be performed on the metalloenzymes to focus on key questions related to the metal site structure, reaction mechanism, and oxygen tolerance:

CO_2/CO conversion is catalyzed by Mo/W formate dehydrogenases (FDH), the Ni/Fe or Mo/Cu carbon monoxide dehydrogenases (CODH) and acetyl-CoA synthase and corrinoid iron/ sulfur protein harboring Ni/Fe/Co containing cofactors The FDHs from *Rc* and *E. coli* contain a molybdenum-cofactor (moco), but only *Rc* FDH shows O_2-tolerance; incorporation of Mo or W may bias the direction of CO_2/formate conversion. Metal- and ligand- (Se) XAS on CO_2/CO/O_2 reaction intermediates will reveal structural changes for different metallations and S/Se-ligand exchange, related to the reactivity, catalytic bias, and O_2-tolerance. XAS will reveal structural differences in wildtype and mutant proteins, reflecting the functional alterations.

Combining spectroscopic, crystallographic, and theoretical results from all involved research teams will contribute to a comprehensive molecular picture of the metal cofactor structures and function.