Bio-inspired catalyst design for small molecule activation in multi-electron reduction processes

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The activation of small molecules in multi-electron reduction catalysis has become an important area of research due to the challenges associated with the energy and environmental problems facing our society. These redox processes are generally promoted by metal ions. In our aim to develop efficient complexes for such catalytic processes, we focused on thiolate-based scaffolds, as thiolate-metal complexes are widely present in the active site of enzymes catalyzing the reactions of interest. Examples include the hydrogenases, which reversibly reduce protons to generate H_2 (see Figure). Our aim is to design innovative catalysts (for H_2 production and O_2 reduction) that are robust and active in water, based on the use of thiolate-based ligands and noble-free metal ions.

In particular, we will describe how we have designed our most efficient catalytic systems. This involved a systematic exploration of series of complexes to assess the impact of the metal, the first coordination sphere, particularly with regard to the pivotal role of the thiolate during catalysis, and the second coordination sphere, where a potential proton relay can be introduced. We will also present mechanism studies, including the generation and characterization of intermediate species, to unveil the key factors for enhanced activity. Finally, we will also discuss how we can modify the catalytic conditions to optimize the catalytic process (homogeneous or heterogeneous conditions, how to supply electrons, i.e., chemically, via electro-assisted or photo-assisted processes).