Title: Computational CO_2-Reduction Catalysis: From Mechanistic Insights to the Development of New Simulation Tools

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Abstract:

This lecture will present recent advances in the computational modelling of photocatalytic CO_2 reduction mediated by polyoxometalates (POMs). POMs are polynuclear metal-oxide clusters constructed from early transition metals such as W, Mo, and V, typically in their highest oxidation states. A defining feature of POMs is their ability to reversibly accept multiple electrons with minimal structural distortion, enabling them to function as efficient electron reservoirs and relays. This property makes POMs particularly attractive for reduction catalysis and, in particular, for photocatalytic CO_2 conversion, where they can store and deliver the electrons required for multi-electron reduction processes.

We will discuss a few photocatalytic CO_2 reduction systems investigated computationally in our group, illustrating how detailed mechanistic insight and rationalization of experimental activity trends can be achieved by combining density functional theory (DFT), molecular dynamics (MD) simulations, and microkinetic modelling. These case studies include a Ni(II)-containing POM catalyst and two POM@MOF host-guest porous materials, in which encapsulation of the POM significantly enhances the catalytic performance of the MOF host.

Finally, we will introduce SURFXsim, a newly developed computational approach from our group that enables cost-effective atomistic simulations of spin-forbidden processes in realistic catalytic models. This method is designed to capture changes in spin multiplicity along the reaction coordinate (events often involved in photoredox catalysis) and opens thus new avenues for modelling complex reaction mechanisms involving spin-forbidden events accounting for explicit and dynamically evolving environments.