

ClustOxSulf – Molecular Modeling of Photo-catalysts for CO₂ Reduction

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❖ Description of the problem

The photo-catalytic activity of transition metal clusters, bonded via oxygen/sulphur bridge or oxygen/sulphur-terminated, have a detrimental role for the process of CO₂ reduction. The reduction to HCOOH is a two-proton, two-electron process, $\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \Rightarrow \text{HCOOH}$. We study the reaction mechanism for clusters of different size and structure via quantum-chemical methods as implemented in Gaussian 16 [1]. The density functional theory methods are included in the software package and allow us to study reaction paths in gas phase, in solution, on solid surfaces and in porous materials.

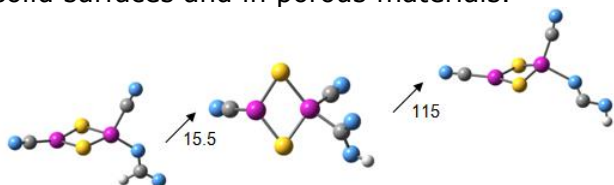


Figure 1: Binding of intermediates to Co₂S₂(CO)₂ in the first steps of CO₂ reduction and their relative stability (kJ mol⁻¹)

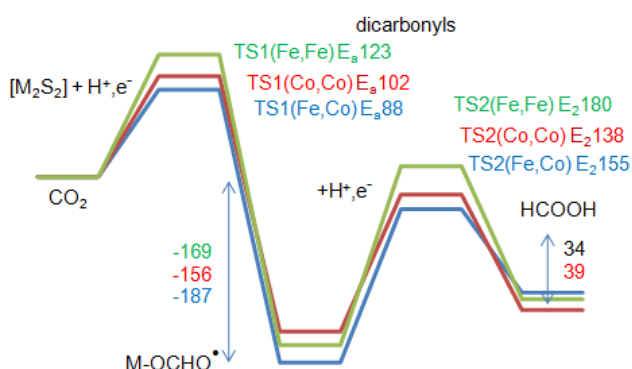


Figure 2: Reaction path of CO₂ reduction via OCHO* intermediate on dicarbonyls of Fe₂S₂, Co₂S₂ и CoFeS₂.

The role of the metal-metal chemical bond for the redistribution of partial charges in the clusters and for tuning their catalytic properties is studied on dicarbonyl complexes of sulphides. Photo-activation is detrimental for the CO₂ reduction process on carbonyl complexes, because it can compensate the high activation barrier.

These studies are performed by the laboratory of Theoretical and computational Chemistry of IGIC-BAS.

❖ Use of HPC Infrastructure

The Avitohol supercomputer was used to obtain the results on molecular modelling. It is located in the HPC center of ICT-BAS [2] and it is maintained by the National Center for High-Performance and Distributed Computing (NCHDC), subject to the National Roadmap for Research Infrastructures (NRI) [3].

The results were obtained using up to 12 HP Cluster Platform SL250S GEN8 servers, each with 2 Intel Xeon E2650 v2 CPUs and 2 Intel Xeon Phi 7120P coprocessors.

❖ Results and Future Work

In order to elucidate transition states, considerable computer time is required, exceeding 100 hrs. The main results on the simulation of CO₂ reduction on carbonyls of transition metal sulphides can be summarized as following:

1. Upon substitution of iron for cobalt the activation energy of the reaction is lowered substantially (Fig. 2).
2. For the intermediate OCHO* the energy barriers are lower as compared to COOH*.
3. The availability of light induced electron transitions, comparable by energy to the reaction barriers was determined, so that irradiation in the visible or near IR spectrum range should entirely compensate the activation barrier.

The work on this topic continues with halogen ligands and on selenide clusters already under study [4].

1. <https://gaussian.com>
2. <http://www.iict.bas.bg/avitohol/>
3. <http://nchdc.acad.bg/>
4. Sizemat 3 conference 2021; <http://twinteam.igic.bas.bg/Sizemat>