

## Bioinspired and Heterogenized Molecular catalysts for the Reduction of CO<sub>2</sub>

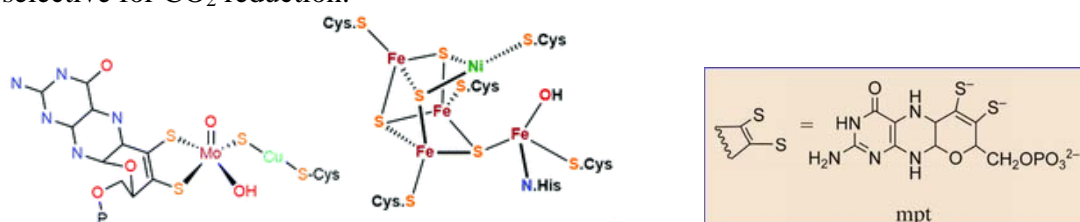
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The reduction of carbon dioxide into carbon-containing molecules is an original strategy for storing low-carbon energies and for using CO<sub>2</sub> as a source of carbon in organic chemistry, instead of fossil resources. Molecules such as carbon monoxide and formic acid but also more complex molecules (methanol, methane, and ethylene) can be formed during CO<sub>2</sub> reduction.

The challenge is great because CO<sub>2</sub> is thermodynamically very stable. Its reduction involves with multi- electrons and protons processes, which are kinetically unfavorable and the reactions are most often not very selective. The development of efficient, stable and selective catalysts is therefore essential. It is a bio-inspired approach that is followed in our laboratory to develop new molecular catalysts based on non-noble metals for the photo-/electro-reduction of CO<sub>2</sub>. For example, taking inspiration from formate dehydrogenases, we have in recent years synthesized dithiolene ligands mimicking natural molybdopterin ligands (mpt, see figure below) and developed a whole series of molybdenum / nickel dithiolene complexes that are active and selective for CO<sub>2</sub> reduction.<sup>1-4</sup>



Active sites of CODHs (Mo-Cu and NiFe) and molybdopterin ligand (mpt)

We propose here a new direction for this research topic. Our goal is to mimic another class of enzymes, the CO dehydrogenases (CODH), which catalyzes of the reduction of CO<sub>2</sub> into CO. The active sites of CODH contain the heterobinuclear sites, based on Mo and Cu or based on Ni and Fe, in which one metal ion catalyzes electron transfers and the other acts as a Lewis acid, involved in the polarization of a C-O bond of CO<sub>2</sub>. The figure above (left) shows the MoCu site of a CODH in which the Mo ion is chelated by an mpt ligand, as well as the NiFe site of a second class of CODH (right). In the latter case, the Ni ion, inserted in a Fe-S cluster, catalyzes the transfer of electrons to the CO<sub>2</sub> molecule while the exogenous Fe ion serves as a Lewis acid. So far, only three bioinspired heterobinuclear complexes have been reported as catalysts for CO<sub>2</sub> electroreduction. One of which originated from laboratory work.<sup>5-7</sup> We propose to explore further this family of catalysts (synthesis of binucleating ligands and corresponding complexes, mechanistic studies).

Furthermore, the use of molecular complexes in electrochemical devices requires that they be grafted on the surface of the cathode. This PhD project will also involve the modification of the ligands in order to introduce functionalities allowing covalent or non-covalent grafting of the catalyst on carbon electrodes which are nanostructured (carbon nanotubes). Our laboratory also has expertise in this area.<sup>8-10</sup>

The objective of this project is therefore the development of molecular complex systems, specifically heterobinuclear systems, their coupling with the pyrene (or analogs) function and their grafting onto electrodes. The study will focus on Mo-Cu or Ni-Fe couples but may also be extended to other combinations of metal ions: for example by using other redox metals (such as Co) or other Lewis acid ions (Zn, alkaline-earth,...), always non-noble. All these complexes will be evaluated for their ability to catalyze the reduction of CO<sub>2</sub> by electrochemical and photochemical means. Our laboratory has the necessary equipment for these studies.

The student will therefore have the opportunity to deal with very diverse questions of organic synthesis (the ligands), organometallic (the complexes) as well as questions of catalysis. More specifically, he/she will be confronted with the techniques of electrochemistry and photochemistry. The very multidisciplinary content of this project constitutes an excellent basis for training through research in molecular chemistry.

## References

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