Shifting the electrocatalytic reduction of CO_2 to MeOH, a computational study.

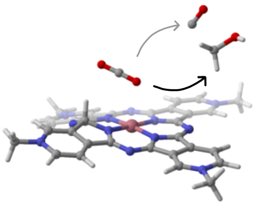
Context

The electrochemical transformation of carbon dioxide using electricity from a renewable energy source holds great promise for achieving carbon neutrality. Substantial progress has been made to improve the effectiveness of the catalysts towards CO_2 to CO conversion by taking inspiration for enzymatic processes for instance.

While CO is a useful building block for the production of various chemicals, there is a growing interest in direct reduction of CO_2 to more reduced products such as methanol. A recent study showed that a cobalt phthalocyanine (CoPc) could convert CO_2 to MeOH with faradic yields of 0.3%.[1] A mechanism was proposed on the basis of a spectroscopic study supported by DFT computation to rationalize this reactivity.[2] It involves a key species $[HPc\text{-}Co\text{-}CO]^-$ whose formation is limited under CO_2, but may be favored under CO atmosphere in basic medium.

In our group, we have demonstrated experimentally that with a pyridinium functionalized cobalt phthalocyanine $(Py^+)_4Pc\text{-}Co$, the yield of CO_2 conversion to MeOH can climb to 14%, which is the best result achieved so far with a molecular electrocatalyst. However, our catalyst does not allow the direct conversion of carbon monoxide, suggesting a different mechanism to that previously proposed.

Aims



Our hypothesis is that in our case, the CO_2 to MeOH conversion could involve the participation of the phthalocyanine as a hydride or proton relay. We therefore wish to elucidate the mechanism that allows this unprecedent activity. We also want to understand the difference in the binding mode of CO between CoPc and analogous ML systems (M=Fe,Co ; L=Por,Pc), that could explain its superior reactivity.

Methodology

This project follows previous studies of parent Fe porphyrin catalysts[3] and recently published methodologies.[4] We will optimize the geometry of several postulated intermediates in order to identify the most favored thermodynamical pathway. The activation energy of the key steps involving CO decoordination *vs* its further reduction at the catalyst will also be evaluated. In addition, we will make use of EDA analysis to propose a description of the $PcCo\text{-}CO_2$ binding mode. Computations will use Gaussian and ADF programs. We seek to valorize the result of this work in a publication.

Candidate

We're looking for a methodical and resourceful M1/M2 candidate, with a good knowledge in coordination chemistry/organometallic catalysis and an appetite to learn computation. We will teach the master student how to : investigate a mechanistic study, model 1st raw transition metal complexes, analyze metal-substrate interaction and implement her/his chemical intuition to interpret the result of her/his computation.

Internship condition

Paid internship, 5 months min, starting early 2024. Telework can be set up.

Contact

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