Production of formate from CO_2 gas under ambient conditions: towards flow through enzyme reactors

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Carbon dioxide should not be seen anymore as a waste but as an alternative carbon feedstock to produce platform chemicals and energy carriers. In this context, hydrogenation processes, producing formate/formic acid, methanol, dimethyl ether or hydrocarbons from CO_2 and H_2, have been largely studied and demonstrated at the pilot plant scale. Especially, formic acid has been seen as a promising and safe hydrogen energy carrier and its worldwide demand is expected to grow significantly in the context of renewable energy. Usually, catalytic hydrogenative conversion involves high pressures and temperatures (> 20 bar and 140°C) and requires the compression / concentration of CO_2 and H_2. As far as storage and safety are concerned, the use of high-pressure hydrogen gas might be a major issue. CO_2 is thermodynamically stable and its difficult chemical activation has incited the scientific community to seek sustainable catalytic processes running at milder conditions.

Amongst emerging strategies to produce valuable chemicals from CO_2, biocatalytic processes have been seen as promising as they run on relatively mild conditions (25°C, 1 atm), are ecologically-friendly and highly selective.[1,2] In this context, we have demonstrated the ability of the formate dehydrogenase from *M. extorquens* AM1 (*Me*FoDH1) and a phosphite dehydrogenase mutant from *Ps. stutzeri* (PtDH) to work in a tandem reaction, with a clean *in situ* regeneration of the NADH cofactor (Figure 1).[3,4] The use of poly(ethylene glycol) diglycidyl ether (PEGDGE) as a cross-linking agent and carbon monolith as a porous support, both selected to promote CO_2 localization in the vicinity of *Me*FoDH1, was demonstrated to significantly increase productivity in formate. A flow through bi-enzymatic reactor was developed to produce formate from CO_2 gas leading to a space-time yield of 0.6 $mmol_{formate}.min^{-1}.L^{-1}_{reactor}$ and a turnover frequency (TOF) of 166 $mol_{formate}.mol_{MeFoDH1}.min^{-1}$, superior to most of the organometallic-based hydrogenation catalysts reported in literature. Considering the harsh conditions at which operate those last processes (*i.e.* 80-140°C and 80 bars of CO_2/H_2), we believe that the development of such enzymatic reactors in continuous flow could represent a sustainable alternative to organometallic catalysts in batch, enabling a safer, low energy consuming process with no separation of catalyst, no filtration, no compression of CO_2 and above all no pressurized H_2.

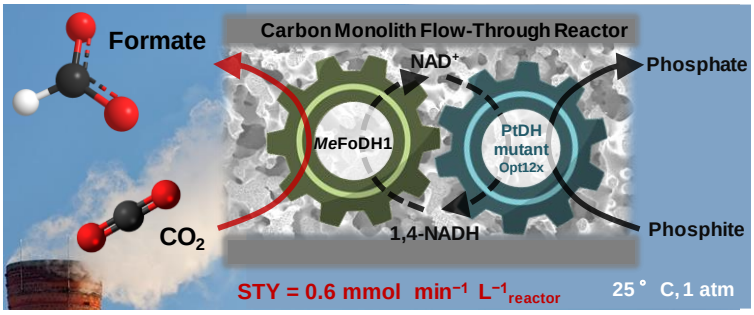

Figure 1: Schematic representation of the flow through bi-enzymatic reactor developed in our group.

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