Bioinspired catalysis for the capture and valorization of CO_2 using supercritical conditions

Catalyse bioinspirée pour la capture et la valorization du CO_2 en conditions supercritiques

Level : PhD

Profile of the candidate : Hold a Master of Chemistry degree with at least 5 months internship in a research or industrial laboratory. Speaking basic French is required. Organic and organometallic synthesis. Handling of pressurized stainless steel reactors. Chromatographic and spectroscopic analysis (GC-FID, NMR, IR, UV-Vis).

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Keyword(s) : Coordination chemistry, homogeneous and supported catalysis

Scientific context : Even if anthropic carbon dioxide excess in earth atmosphere is a problem, this waste could be regarded as a largely available carbon source. The use CO_2 as a valuable substrate is actually an important challenge since its catalytic transformations can lead to valuable products such as urea, carboxylic acids, carbamates and carbonates. Organic carbonates are very useful compounds that can be linear (DMC, polycarbonates) or cyclic (solvents for Li batteries, polymer precursors). Our recent studies focus on the preparation of cyclic carbonates from the cycloaddition of CO_2 to epoxides, catalyzed by chromium or zinc complexes[1]. Moreover, this total atom economy reaction doesn't need any organic solvent since CO_2 can ensure this behavior when using supercritical conditions.

Missions : The capture of CO_2 can be achieved by amine based processes or enzymatic reactions. We developed a selective CO_2 capture procedure based on carbonic anhydrase[2] which active site is made of a zinc complex surrounded by histidine ligands. As this enzyme is too expensive and unstable to be used as catalyst in a more than 60°C process, we propose the synthesis of bio-inspired zinc complexes using histidine like ligands. As the enzymatic step is reversible, the driving force of the global process leads on the carbon dioxide transformation. To achieve this, the formation of stable cyclic carbonates will occur by the addition of epoxides. Moreover, the rate of this atom economy cycloaddition can be significantly increased under CO_2

supercritical conditions[3]. The main challenge of this PhD proposal is to find the specific conditions that will allow the coupling of both steps: CO_2 capture and cycloaddition to epoxides, using zinc-histidine catalysts. This may be achieved by tuning the reaction parameters, using a sapphire glass lined reactor, but also by modifying the histidine ligands on the active species. The second challenge is to fix the catalytic system on a support to allow its recyclability and further use in a fixed bed reactor to get a continuous process. To do so, the zinc species will be grafted *via* $Si(OR)_3$ groups[4] to SBA-15 silica support and characterized by XRD and solid NMR techniques.

Reference :

1- L. Christ *et al. J. Mol. Cat. A: Chemical* **2013**, 381, 161 & *Molecular Cat*. **2018**, 456, 87
2- L. Christ, A. Pierre *et al. J. Mol.Cat. B: Enzymatic* 2009, **60,** 163
3- M. Djoufak, *PhD thesis*, Université Claude Bernard, Lyon 1, **2013,** pp 124
4- A. Tuel e*t al. New* J. Chem. **1999**, 23, 473

Application: Please send CV, motivation letter, copy of M1 and M2 grades, one or two recommendation letters including contact information **until May 20th, 2020.**