'Physique et Chimie des Matériaux' – ED 397 – année 2020

PhD project for funding (max 1p), to send to

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Research unit (full name + acronym) : Laboratoire de Réactivité de Surface (LRS) UMR7197
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Number of phD under supervision : 0.5 Participation to supervisor training? no Year
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Keyword 1 : MOF Keyword 2 : chemobiocatalysis
Keyword 3 : alcohol oxidation Keyword 4 : amination
Select co-funding programme if applicable : select

Project title : Creation of heterogeneous chemoenzymatic catalysts based on the use of Metal-Organic framework for the eco-compatible and selective amination of alcohols

Amines are essential building blocks for the synthesis of fine chemicals, agrochemicals, pharmaceuticals, dyes and food industries [1] Reductive amination is classically employed in industry to produce amines from ketones or aldehydes by using hydrogen (H2) as reducing agent, in the presence of metal catalysts [2]. Although efficient, this method generally results in a mixture of amines and displays side reactions. An interesting alternative to address these issues is the use of biocatalysts, thus avoiding the use transition metal catalysts while affording higher stereo- and region-selectivity. More, enzymes operate at ambient temperature, which saves energy and minimizes the use of toxic organic solvents [3]. Transaminases (ATAs) have proven to be efficient for the synthesis of important chiral amines from ketones and aldehydes [4]. On the other hand, thanks to the development of biorefinery as a step toward renewable carbon sources, many molecules with alcohol functional groups can be obtained from biomass and then used as building blocks to be subsequently converted to a number of high-value bio-based chemicals or materials.

In this project, we propose to address these two opportunities by implementing a chemoenzymatic “one-pot” process starting from alcohols as initial substrates. In this process, the alcohol will be first oxidized into a carbonyl intermediate in the presence of a chemical catalyst and subsequently transformed into an amine in the presence of a transaminase. Importantly, both chemical catalyst and enzyme will be attached on a same support, a Metal-Organic framework (MOF), resulting in a heterogeneous system. This virtuous system will merge efficiency and robustness of the chemical catalyst with the high enantio-, regio-, and chemo- selectivity of enzymes. In addition, it will positively impact amine formation towards green chemistry requirements in several ways : (1) reduction of reaction time, energy and amount of wastes, (2) use of alcohol from biomass, an abundant and cheap feedstock (3) the heterogenization of the system will greatly facilitate its recycling. MOFs, porous hybrid materials made of the regular assembly of coordination complexes, were shown to possess a great potential for heterogeneous catalysis and more recently as support to stabilize enzymes [5]. Here these materials will be used to immobilize both types of catalysts: the chemical catalysts, which will be inserted within the micropores of the MOF while and the transaminases that will be firmly attached on the external surface by covalent bonding.

This multidisciplinary project deals with both material chemistry and (bio)catalysis fields. MOFs will be synthesized by hydrothermal or microwave treatment. Catalytically active nanophases, namely metal nanoparticles, will be synthesized within the pores of MOF thus used as nanoreactors. This project will be co-supervised by Pr C. Jolivalt, an expert in biocatalysis and Dr J. Reboul, an expert in the synthesis of nanostructured materials (particularly MOFs) and nanoparticles.

Characterization of the catalysts will beneficiate of the extensive technical environment existing within the LRS and in the technical platform of the Institute of Material Paris Center (IMPC). The project, and thereby the candidate, will profit of the recognized experience of the LRS team that gathers strong expertise for the synthesis and fine characterization of inorganic and hybrid porous materials, metal nanoparticles, immobilization and implementation of biocatalytic systems.

[1] M. Breuer et al. Angew. Chemie - Int. Ed., vol. 43, no. 7, pp. 788–824, 2004.
[2] E. M. Dangerfield, et al. J. Org. Chem., vol. 75, no. 16, pp. 5470–5477, 2010.
[3] M. Höhne, U. T. Bornscheuer ChemCatChem, vol. 1, no. 1, pp. 42–51, 2009.
[4] F. Gu, P. Berglund Green Chem., vol. 19, no. 2, pp. 333–360, 2017.
[5] D. Yan B. C. Gates ACS Catal. Vol. 9, pp. 1779−179, 2019.