'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
Team if applicable :
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Number of phD under supervision : 0.5 Participation to supervisor training? no Year
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Research unit : LRS International co-supervision ? No
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Keyword 1 : Nanoparticles Keyword 2 : Catalysis
Keyword 3 : Polyoxometalates Keyword 4 : Mesoporous
Select co-funding programme if applicable : select

Project title : Design of new heterogeneous bi-functional catalysts affording an in-situ activation of oxygen for a greener oxidation of organic molecules

Hydrogen peroxide and dioxygen are considered as two "green" oxidants. However, dioxygen is disadvantaged due to its low kinetic reactivity, which, in the past, has largely contributed to the development of various processes working with hydrogen peroxide to convert alcohols into carbonyl derivatives or alkenes into epoxides. Reactions involving hydrogen peroxide have been extensively studied in the presence of heterogeneous catalysts, but in most cases, this oxidant with nucleophilic properties is leading to the leaching of active species and significant losses of activity, especially when amorphous mesoporous supports are used. Moreover, the current production of hydrogen peroxide from dioxygen and dihydrogen is dominated worldwide by a not so green process which greatly increases the environmental footprint of oxidation reactions working with commercial hydrogen peroxide. Significant research efforts are currently being made to find alternative methods to produce hydrogen peroxide [1]. Catalysts based on gold nanoparticles (NPs) or coupled with photo-catalysts, the combination of the two making it possible to work from visible photons, are among the most interesting approaches proposed. This project aims at coupling such production mode of peroxide or of other reduced forms of dioxygen like superoxides with oxidation catalysts known to be efficient in the oxidation of alcohols or alkenes by hydrogen peroxide. We will choose here soluble and covalently supported tungsten-based polyoxometalates (POMs) such as those we have worked on recently with R. Villanneau (IPCM) [2]. POMs do not behave only as oxidation catalysts but are also able to stabilize metal NPs. In this work, we will take advantage of this demonstrated proximity of POMs and metal NPs to couple the reduction of dioxygen with the oxidation of alcohols or alkenes. Metal colloids stabilized by POMs will be used as such or after deposition onto mesoporous oxides, the latter allowing a great optimization of both the dispersion and the accessibility of the active sites, a better recovery of the catalysts but also some possibilities of photo-catalytic activation. So, the proposed work aims at building and characterizing assemblies of POMs and nanoparticles in suspension or onto a porous support, studying their ability to reduce oxygen and to activate its reduced forms in order to perform the aerobic oxidation of organic model molecules under mild conditions.

To do so, we are looking for a candidate strongly interested in materials chemistry and applications in catalysis.

[1] R. J. Lewis, G. J. Hutchings, ChemCatChem, 2019, 11, 298.

[2] F. Bentaleb, O. Makrygenni, D. Brouri, C. Coelho Diogo, A. Mehdi, A. Proust, F. Launay, R. Villanneau, Inorg. Chem., 2015, 54, 7607.