MASTER DE CHIMIE DE PARIS CENTRE - M2S2
Proposition de stage 2023-2024
Internship Proposal 2023-2024

Parcours type(s) / *Specialty(ies) :*
☐ Chimie Analytique, Physique et Théorique / *Analytical, Physical and Theoretical Chemistry*:
☐ Chimie Moléculaire / *Molecular Chemistry*:
☐ Chimie et Sciences Du Vivant / *Chemistry and Life Sciences*:
☒ Chimie des Matériaux / *Materials Chemistry:*
☒ Ingénierie Chimique / *Chemical Engineering:*

Laboratoire d'accueil / *Host Institution*
Intitulés / *Name* : Laboratoire de Réactivité de Surface – Sorbonne Université – UMR CNRS 7197
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Equipe d'accueil / *Hosting Team :* Approche moléculaire des sites actifs et de leur réactivité
Adresse / *Address :* 4 Place Jussieu, Case 178, Tour 43, 3ème étage
Responsable équipe / *Team leader* : Guylène COSTENTIN
Site Web / *Web site : http://www.lrs.upmc.fr/fr/l-unite-de-recherche/organigramme.html*
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Période de stage / *Internship period* * : 1th of February – 30th June (5 months minimum)

Titre / *Title*
Tuning surface termination of platelet-like biomimetic hydroxyapatite to optimize their catalytic reactivity.

Projet scientifique (1 page maximum) / *Scientific Project (maximum 1 page):*

1. Description du projet / *Description of the project*
Hydroxyapatite, the main mineral component of bones and teeth, is an eco-compatible calcium phosphate material, which surface properties can be tuned to the prerequisites of numerous classes of catalytic reactions. The simultaneous presence of acidic and basic sites in tunable proportions makes it an original system[1] that enables the valorisation of bio-ethanol towards different products of interest such as n-butanol, an efficient gasoline additive,[2] or butadiene used for the production of green tires.[3] In addition, their structure also gives them a particular ability for immobilizing metals as highly dispersed particles, or even monoatomic sites,[4] making them an attractive system for bifunctional basic and redox catalysis, whether for the selective oxidation of alcohols or propane,[5] the selective hydrogenation of unsaturated hydrocarbons,[6] or the synthesis of NH_3 (for hydrogen storage)[7].
Until now, catalytic activity studies have been carried out on particles precipitated at high pH that crystallized in the form of hexagonal rods. Biomimetic apatites synthesized under milder pH conditions, on the other hand, take the form of platelets, a morphology expected to develop a higher surface-to-

* min. 5 mois à partir du 30 Janvier 2024 / *min. 5 months not earlier than January, 30th 2024.*
Fin de stage au plus tard le 13/07/2024 ou le 29/09/2024 (dates de validation de diplôme). / *End of internship at the latest July 13, 2024 or Sept. 29, 2024 (dates of graduation).*

volume ratio, an important parameter for surface reactivity. Unlike rods, which show well-organized surface termination, these platelets show crystalline core embedded by a thin amorphous hydrated layer.[8] From preliminary studies at LRS, this hydrated layer enhances metal immobilization capacity, but makes the control of surface reactivity more complex to achieve.

The aim of the internship is to tune the surface termination of these platelets by modifying their preparation conditions to optimize their catalytic properties. The strategy will be based on the recent identification of the formation mechanism of these platelets, namely the precipitation of a precursor of hydroxyapatite, a calcium phosphate with monoclinic symmetry which further hydrolyzes more or less completely into the hydroxyapatite structure.[9] The use of an automated synthesis robot will enable us to finely explore, in a reproducible way, the impact of synthesis parameters (temperature, pH, rate and sequencing of addition of reagents during the precipitation step and maturation time) on the kinetics of the precipitation and hydrolysis steps.

In particular, we will seek to finely evolve, on the one hand, the size of the particles, the crystallinity and the surface composition and, on the other hand, the accessibility of the metals (cobalt and copper) which will be either incorporated in the automated reactor during the precipitation and/or maturation, or deposited post-synthesis on hydroxyapatite supports by impregnation or cation exchange. The structure, morphology, texture, bulk and surface compositions of the dried and thermally treated materials will be characterized using complementary techniques (see below) and their catalytic properties evaluated for different reactions implemented in the gas phase. The impact of the surface structuring of platelets modified or not by cobalt or copper on their acid-base properties, and for those modified by metals, on their performance in bifunctional catalysis will be discussed. The performances will be compared to those obtained for rod-shaped hydroxyapatites.

2. Techniques ou méthodes utilisées / *Specific techniques or methods*

- Synthesis: Automated reactor
- Characterizations: XRD, Raman, SEM, HRTEM, N_2 sorption, ICP, XPS, CO_2-TPD, NO-TPD, H_2-TPR,
-Catalytic properties: conversion of 2-methylbut-3-yn-2-ol (as model reaction for acid-base properties) and ethanol, butadiene hydrogenation.

3. Références / *References*

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