SORBONNE UNIVERSITÉ | **PSL UNIVERSITÉ PARIS**

MASTER DE CHIMIE DE PARIS CENTRE - M2S4
Proposition de stage 2024-2025
Internship Proposal 2024-2025

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
Adresse / *Address* : 4 Place Jussieu, Case 178, Tour 43, 3ème étage
Directeur / *Director (legal representative) : Vincent VIVIER*
Tél / *Tel* : +33 1 44 27 25 77
E-mail : vincent.vivier@sorbonne-universite.fr

Equipe d'accueil / *Hosting Team :*

Adresse / *Address :* 4 Place Jussieu, Case 178, Tour 43, 3ème étage
Responsable équipe / *Team leader* : Guylène Costentin
Site Web / *Web site :*
Responsable du stage (encadrant) / *Direct Supervisor : Guylene Costentin et Cyril Thomas*
Fonction / *Position :Chercheurs CNRS*
Tél / *Tel* : 01 44 27 36 32
E-mail : guylene.costentin@sorbonne-universite.fr, cyril.thomas@sorbonne-universite.fr

Période de stage / *Internship period* * : 27 January- -11th July (5 months minimum)

Préparation d'écocatalyseurs bio- et géo-inspirés pour une réactivité multi-fonctionnelle
Synthesis of bio- and geo-inspired ecocatalysts for multi functionnal reactivity

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

1. Description du projet / *Description of the project*

Hydroxyapatite (HAp) is a well-known calcium phosphate ($Ca_{10}PO_4)_6(OH)_2$ found in biomaterials, being the major mineral component of bones and teeth,[1] and also in the sedimentary phosphate deposits formed over time from marine animal skeletons. Close examination of these eco-compatible materials reveals a variability of textural properties (morphologies and specific surface areas) and compositions associated with the incorporation of defects. For example, biological apatites are enriched in carbonates, while natural apatites exhibit a wide range of colours, reflecting the particular ability of their structure to trap metals from water runoff. Mimicking these geochemical processes, synthetic apatites prepared by precipitation are original sorbents used in industry for the remediation of contaminants from wastewater and soils.[2,3] HAps are also attractive multifunctional catalysts that uniquely combine both intrinsic acid-base properties,[4] which can be tuned by controlling the defects (cationic and anionic vacancies, HPO_4^{2-}, CO_3^{2-}, NO_3^-) induced by the conditions of the precipitation process,[5] and redox properties provided by

* **min. 5 mois, maximum 6 mois à partir du 27 janv 2025 / *min. 5 months and max. 6 months not earlier than January, 27th 2025.***
Fin des conventions de stage au plus tard le 15/07/2025 ou le 15/09/2025 et le 15 novembre 2025.
End of internship at the latest July 52, 2025 or September. 15, 2025 and 15 November, 2025.

the incorporation of transition metals (M). M can be introduced by one-pot coprecipitation leading to solid solutions ($Ca_{10-x}M^{II}_x(PO_4)_6(OH)_2$) or by exchanging the surface calcium cations of HAp for metallic cations (geo-inspired approach).[6] The combination of the acid-base properties of Haps together with the (de)hydrogenation ability of Co and Ni makes this system very promising for the conversion of bioethanol into high value-added products such as *n*-butanol, an efficient gasoline additive,[7] and/or butadiene for the production of green tyres.[8] Indeed, this cascade reaction network follows a succession of steps catalysed by basic (or dehydrogenating), acid-base, and hydrogenation and acidic functions.

The aim of the internship is to prepare hydroxyapatite and metal modified hydroxyapatite to be tested for the bio-ethanol upgrading. HAps will be obtained by precipitation by controlling finely the influence of the operating parameters (pH, order and rate addition of Ca and P precursors, temperature) using an automated Mettler Toledo reactor. As calcium nitrate is often used as a calcium source, traces of nitrates have been detected by infrared spectroscopy, but it is not yet documented how these impurities affect the acid-base balance and the metal immobilisation process. Particular attention will be paid to the washing and calcination steps to reduce the impact of nitrates. The $Ca(OH)_2$ precursor will also be used in the synthesis as a Ca nitrate precursor alternative. M^{2+} (Co, Ni) will be incorporated considering coprecipitation (bulk and surface modification) and deposition in excess of solution and impregnation approaches (surface modification). We will attempt to evaluate the influence of the immobilisation process on the thermal evolution of M^{2+} species under air or reducing atmosphere, paying attention to the final speciation and dispersion of the metal. The synergistic effect between the acid-base properties of hydroxyapatite and the M^{2+} or M^0 functions on the conversion and selectivity of the ethanol conversion network will be discussed using a structure-reactivity relationship approach.

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

The controlled precipitation of the HAp and M-modified HAps will be achieved using an Automated Mettler Toledo reactor. Post metal immobilization will be achieved by cationic exchange and by impregnation methods in the excess of solution.

Structural characterizations will be based on XRD, Infra-red and Raman data; the morphology of HAp particles and M^0 nanoparticle size will be characterized by electron microscopy (SEM, TEM), while specific surface areas will be measured by N_2 sorption; the elemental composition of HAps will be determined by ICP, the reduction temperature of M^{2+} cations will be investigated by temperature programmed reduction (H_2-TPR). The surface properties of M-HAps will be characterized by combining XPS and NO-TPD, acid-base properties will be evaluated by the model gas phase conversion of 2-methylbut-3-yn-2-ol and the performance of the prepared catalysts will be tested in the of ethanol conversion to *n*-butanol and butadiene.

3. Références / *References*

1 N. Vandecandelaere, C. Drouet, Biomimetic apatite-based biomaterials: on the critical impact of synthesis and post-synthesis parameters, J. Mater. Sci. Mater. Med. 2012, 23, 2593–2606, https://doi.org/10.1007/s10856-012-4719-y

2 Ibrahim et al., Hydroxyapatite, a multifunctional material for air, water and soil pollution control: A review, J. Hazard. Mater. 2020, 383, 121139, https://doi.org/10.1016/j.jhazmat.2019.121139

2 Delplanche et al., Removal of contaminants from water effluent using a hydroxyapatite composite WO/2019/10617617

4 S. Diallo-Garcia, M. Ben Osman, J.M. Krafft, S. Casale, C. Thomas, J. Kubo, G. Costentin, Identification of Surface Basic Sites and Acid-Base Pairs of Hydroxyapatite, *J. Phys. Chem. C* **2014**, *118*(24), 12744-12757, (2014), https://doi.org/10.1021/jp500469x

5 C. Reynaud, C. Thomas, G. Costentin, On the Comprehensive Precipitation of Hydroxyapatites Unraveled by a Combined Kinetic-Thermodynamic Approach**,** Inorg. Chem., 2022, 61, 7, 3296–3308, https://doi.org/10.1021/acs.inorgchem.1c03884

6. C. Reynaud, C. Thomas, D. Brouri, Y. Millot, A. Miche, G. Costentin, Surface immobilization mechanisms of cobalt ions on hydroxyapatite catalyst supports. *Catal. Today*, *432*, 114621 (2024), https://doi.org/10.1016/j.cattod.2024.114621

7 M. Ben Osman, J.M. Krafft, C.Thomas, G. Costentin, Importance of the Nature of the Active Acid/Base Pairs of Hydroxyapatite Involved in the Catalytic Transformation of Ethanol to *n*-Butanol Revealed by Operando DRIFTS, ChemCatChem 2019, 11, 1765-1778, https://doi.org/ 10.1002/cctc.201801880

8 Pomalaza et al., Ethanol-to-butadiene: the reaction and its catalysts, Catal. Sci. Technol. 2020, 10, 4860-4911. https://doi.org/10.1039/D0CY00784F