MASTER DE CHIMIE DE PARIS CENTRE - M2S2
Proposition de stage 2021-2022
Internship Proposal 2021-2022

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* :
x Chimie des Matériaux / *Materials Chemistry :*
x Ingénierie Chimique / *Chemical Engineering :*

Laboratoire d'accueil / *Host Institution*

Intitulés / *Name* : Laboratoire de Réactivité de Surface (LRS) – UMR 7197
Adresse / *Address* : Campus Pierre et Marie Curie, Tours 43-33, 43-44 et 43-53, 3ème étage
Directeur / *Director (legal representative) :* Hélène Pernot
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Equipe d'accueil / *Hosting Team :*

Adresse / *Address :* Campus Pierre et Marie Curie, Tours 43-33, 43-44 et 43-53, 3ème étage
Responsable équipe / *Team leader* : Hélène Pernot
Site Web / *Web site :* http://www.lrs.upmc.fr
Responsable du stage (encadrant) / *Direct Supervisor :* Josefine Schnee
Fonction / *Position :* Chargée de recherche CNRS
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Période de stage / *Internship period* * : February - June 2022

Titre / *Title*

Novel bottom-up route to prepare nickel-hydroxyapatite catalysts with ultrahigh and stable nickel dispersion

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

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

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, or HAp) is the main component of bones and teeth. It is thus an ecological, non-toxic and biocompatible material. Besides playing an important role in many clinical applications such as drug design and bone tissue regeneration, it has proved to be efficient as a support and co-active phase in heterogeneous catalysis. It actually has many advantages over other materials used in heterogeneous catalysis (perovskites, zeolites, MOFs), for instance its very good thermal and chemical stabilities. Its intrinsic surface acid-base properties can be easily tuned by varying its Ca/P ratio, and its framework Ca^{2+} cations can be substituted by catalytically active metals (Ni^{2+}, Cu^{2+}, Ag^{+}, etc.), which leads to multifunctional catalysts suitable for a broad range of applications.[1] When such Ca^{2+} substitution is done at the surface of the HAp through ion exchange, a widely used method in heterogeneous catalysis, it is however difficult to obtain a significant content of isolated metal atoms which often show particularly

* min. 5 mois à partir du 31 janv 2022 / *min. 5 months not earlier than January, 31st 2022.*
Fin de stage au plus tard le 15/07/2022 ou le 30/09/2022 (dates de validation de diplôme). / *End of internship at the latest July 15, 2022 or Sept. 30, 2022 (dates of graduation).*

high catalytic activities. Indeed, upon surface ion exchange, residual ions in solution generally induce a nucleation of monomeric sites at the surface which then grow up to bigger nanoparticles.[2] This is precisely the issue that the present internship will address. Rather than using the classical "top-down" approaches like ion exchange to load a metal onto the surface of the HAp, we propose to explore a novel "bottom-up" approach that has emerged very recently (in 2017) in the field of perovskites (being much less versatile and exhibiting a much lower specific surface area than HAp materials), and that has, to our knowledge, never been applied to HAp materials. The idea is to substitute framework Ca^{2+} cations by Ni^{2+} ones (catalyzing important hydrogenation reactions) both at the surface and within the bulk of the HAp by co-precipitation, and then to submit the resulting materials to reducing treatments which are reported, in the case of perovskites, to induce a migration of substituting metal cations from the bulk towards the surface. In the case of perovskites, which for the moment are used mainly in electrochemistry applications, this phenomenon is called "exsolution" and allows controlling the size, dispersion and anchorage of metal nanoparticles at the surface.[3] In the case of HAp materials, based on preliminary results obtained at LRS, exsolution of metals might occur at much lower temperatures and therefore is expected to yield much smaller nanoparticles, even isolated metal atoms. Compared to ion exchange, the exsolution approach promises to yield a considerably higher density of isolated metal atoms, which should lead to very interesting catalytic properties. In the context of resources management, nickel is of great interest nowadays as it is a non-noble/rather cheap metal.
The aim of the present internship will be to enlighten the key parameters which govern the exsolution of Ni in Ni-substituted HAp materials, in order to be able to make use of this phenomenon in a controlled way for designing highly performant catalysts. The internship will consist of preparing Ni-HAp materials by co-precipitation, by varying several parameters that are suspected of influencing the exsolution of Ni, then of probing the properties of the prepared materials by various physico-chemical characterization techniques, and finally of evaluating the catalytic performance of the prepared materials, for instance, in the selective hydrogenation of butadiene.

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

Ni-HAp materials will be prepared by co-precipitation thanks to an automated reactor with integrated pH meter allowing to prepare as much as 10 g of catalyst at a time in an accurate, systematic and reproducible way. The materials to be tested in the above-mentioned reaction will be characterized by physico-chemical techniques such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), infrared, UV-Visible and Raman spectroscopies, nuclear magnetic resonance (NMR) spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), electron microscopy, etc.

3. Références / *References*

1. Ibrahim, M.; Labaki, M.; Giraudon, J.-M.; Lamonier, J.-F., Hydroxyapatite, a multifunctional material for air, water and soil pollution control: A review. *Journal of Hazardous Materials* **2020,** *383*, 121139.

2. Campisi, S.; Galloni, M. G.; Bossola, F.; Gervasini, A., Comparative performance of copper and iron functionalized hydroxyapatite catalysts in NH_3-SCR. *Catalysis Communications* **2019,** *123*, 79-85.

3. Kwon, O.; Sengodan, S.; Kim, K.; Kim, G.; Jeong, H. Y.; Shin, J.; Ju, Y.-W.; Han, J. W.; Kim, G., Exsolution trends and co-segregation aspects of self-grown catalyst nanoparticles in perovskites. *Nature Communications* **2017,** *8* (1), 15967.