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| **MASTER DE CHIMIE DE PARIS CENTRE - M2S2**  **Proposition de stage 2022-2023**  **Internship Proposal 2022-2023** |
| **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 – Sorbonne Université – UMR CNRS 7197  Adresse / *Address*: 4 Place Jussieu, Case 178, Tour 43, 3ème étage  Directeur / *Director (legal representative) :* Hélène PERNOT  Tél / *Tel* : +33 1 44 27 25 77  E-mail : helene.pernot@sorbonne-universite.fr |
| **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*  Responsable du stage (encadrant) / *Direct Supervisor:* Cyril THOMAS, Guylène COSTENTIN  Fonction / *Position :* Chercheurs CNRS  Tél / *Tel* : +33 1 44 27 36 30  E-mail : [cyril.thomas@sorbonne-universite.fr](mailto:cyril.thomas@sorbonne-universite.fr), guylene.costentin@sorbonne-universite.fr. |

Période de stage / *Internship period* [[1]](#footnote-1) : 30th of January – 13th July (5 months minimum)

**Titre */ Title***

Hydroxyapatite-supported Ru nanoparticles for the chemical storage of H2 as ammonia.

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

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

As a “Never-Ending Story”1 associated with the increasing needs in ammonia (NH3) and the recent surge of interest on ammonia as an energy carrier,2 the development of improved materials for the catalytic synthesis of ammonia (N2 + 3 H2 = 2 NH3) remains of the utmost interest to increase the thermodynamic efficiency of this compound.1 Overall, Ru-based catalysts promoted by basic additives and/or supports have been reported to be the most active materials in the catalytic synthesis of ammonia.2 To our knowledge, however, one of the current most promising basic supports, namely hydroxyapatite (HAp), has not been reported yet as an oxide carrier of Ru nanoparticles for the catalytic synthesis of ammonia. HAps are environment-friendly calcium phosphates (Ca10-*x*(PO4)6-*x*(HPO4)*x*(OH)2-*x*) present as the main mineral of bones and teeth. It is assumed that the tunable morphological and acid-base properties of HAp will help design Ru-based materials of improved efficiency in the catalytic synthesis of ammonia and provide further insights into the fundamental comprehensive understanding of this reaction.

Ammonia is a key chemical compound for the production of mainly fertilizers,2 which remain of instrumental interest in the feeding of the world’s population, and to a lower extent of explosives and polymers. More recently ammonia has been identified as an energy vector, due to its high energy density and hydrogen content together with the existing storage and transportation infrastructure.2 NH3 could therefore be used as a chemical to store the hydrogen produced by water electrolysis powered by sunlight and wind renewable energies.2

Early 70s, it was found that ammonia synthesis could be catalyzed more effectively than with the Fe-based catalysts, i.e. at lower temperatures and pressures, by promoted Ru materials supported on activated carbons.2 These catalysts not only suffered from hydrogen poisoning due to its strong adsorption onto the Ru nanoparticles but also from a burying/sintering of the Ru nanoparticles into/onto the activated carbons due to the occurrence of the methanation reaction (Csupport + 2 H2 = CH4) at the interface between the carbon support and the Ru nanoparticles.2 The latter drawback led to the study of oxide-supported Ru catalysts. Overall, it was concluded in this field that the catalytic performance of the Ru catalysts was strongly dependent on the size of the Ru nanoparticles (structure-sensitivity concept) although this was the subject of controversy, and on the basicity of the promoters and/or support.2 As the rate-determining step of the ammonia synthesis catalytic reaction has been claimed to be the dissociation of N2,2 an increase in the basicity of the promoters and/or support should result in an increase in the electron density of the Ru nanoparticles and the electron transfer from these nanoparticles to the  anti-bonding orbital of N2, which in turn is supposed to be favoring the dissociation of N2.2

The synthesis of the materials of interest for the project will start with the investigation of the influence of the basicity of the HAp support (by varying the Ca/P ratio) of Ru nanoparticles for the catalytic performance in ammonia synthesis. A rod-like morphology3 will be targeted with a specific surface area of about 40 m2/g and the Ca/P ratio will be varied by changing the pH of the reaction medium between 6.5 and 10.0 (6.5, 8.0, 9.0, 10.0) at 80 °C. At pH 6.5, the synthesis will be performed with the introduction of the Ca solution into the P solution (Ca  P route) at 80 °C (Ca/P = 1.53), whereas at pH 9.0 the PCa route will be preferred (Ca/P = 1.71).4 The syntheses performed at pH 8.0 and 10.0 will be done via the PCa route. The materials will be calcined at 600 °C for 2 h under ambient air in a muffle furnace. Ru (2 wt%) will be deposited on the HAp supports by both dry and excess aqueous solution impregnations of Ru(NO3)3(NO) and RuCl3 precursors. In the case of the preparation of the samples with an excess of solution, the pH of the medium will be set to a pH close to the point of zero charge of the supports to avoid their dissolution-reprecipitation.4 After drying in air at 120 °C, the samples will be reduced under H2 for 2 h at 500 °C. The loading of Ru will eventually be varied on the most promising HAp support. The samples will be characterized by various techniques (see below) and their catalytic performance evaluated in the ammonia synthesis catalytic reaction. ***This proposal is part of the H2CASTORAMA ANR project for which a PhD is to be funded by October 2023. We are therefore already seeking for a very good and motivated candidate strongly interested in pursuing a PhD.***

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

- Automated reactor for the synthesis of HAPs

- Chemical analyses, N2 sorption, XRD, CO2-TPD, catalytic conversion of 2-methylbut-3-yn-2-ol (as a model reaction to characterize the basic properties), H2-TPR, TEM, H2 and/or CO chemisorption.

- Low-temperature N2 adsorption followed by FTIR (N2-FTIR)

- Catalytic equipment for ammonia synthesis

**3. Références / *References***

1. Schlögl, R., Catalytic Synthesis of Ammonia—a “Never‐Ending Story”? *Angew. Chem. Int. Ed.* **2003**, *42*, 2004-2008. <https://doi.org/10.1002/anie.200301553>.

2. Sato, K.; Nagaoka, K., Boosting Ammonia Synthesis under Mild Reaction Conditions by Precise Control of the Basic Oxide–Ru Interface. *Chem. Lett.* **2021**, *50*, 687-696. <https://doi.org/10.1246/cl.200855>.

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

4. Reynaud, C.; Thomas, C.; Casale, S.; Nowak, S.; Costentin, G., Development of a Thermodynamic Approach to Assist the Control of the Precipitation of Hydroxyapatites and Associated Calcium Phosphates in Open Systems. *CrystEngComm* **2021**, *23*, 4857-4870. <https://doi.org/10.1039/D1CE00482D>.

1. \* min. 5 mois à partir du 30 Janvier 2023 / *min*. *5 months not earlier than January, 30th 2023.*

   Fin de stage au plus tard le 13/07/2023 ou le 29/09/2023 (dates de validation de diplôme). / *End of internship at the latest July 13, 2023 or Sept. 29, 2023 (dates of graduation).*  [↑](#footnote-ref-1)