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

Laboratoire d'accueil / *Host Institution*

Intitulés / *Name* : Laboratoire de Réactivité de Surface
Adresse / *Address* : Campus Pierre et Marie Curie ; Tour 33-43, 4, place Jussieu, 75005 Paris
Directeur / *Director (legal representative)* : Hélène Pernot
Tél / *Tel* : 01 44 27 25 77
E-mail : helene.pernot@sorbonne-universite.fr

Equipe d'accueil / *Hosting Team :*

Adresse / *Address :* Campus Pierre et Marie Curie ; Tour 33-43, 4, place Jussieu, 75005 Paris
Responsable équipe / *Team leader* : Xavier Carrier
Site Web / *Web site :* http://www.lrs.upmc.fr/fr/l-unite-de-recherche.html
Responsable du stage (encadrant) / *Direct Supervisor :* X. Carrier, L. Delannoy, C. Guibert, C. Sayag
Fonction / *Position* :Professeur
Tél / *Tel* : 01 44 27 38 27
E-mail : xavier.carrier@sorbonne-universite.fr

Période de stage / *Internship period* * : Février-Juin 2023

Design of emerging nano-carbide heterogeneous catalysts as substitute for noble metals

Scientific Project (maximum 1 page):

1. *Description of the project*

The chemical industry has been facing new challenges since the beginning of the 21st century for the development of environmentally friendly processes and sustainable production of valuable chemicals. In this context, highly selective catalytic materials are a prerequisite for industrial development in order to reduce the carbon footprint and energy consumption of industrial processes (green chemistry). For example, in order to produce "drop-in" molecules derived from biomass with similar properties to those currently produced from fossil resources, selective deoxygenation through C-O cleavage of polyols as well as selective C=O hydrogenation appear as strategic reactions [1]. The design of selective catalytic systems for these reactions should allow one to increase the atom economy, reduce or eliminate waste which will circumvent waste treatment and disposal.

As a typical example, Palladium-based catalysts are recognized as the most efficient systems for industrial semi-hydrogenation reactions. However, Pd is a noble metal with limited resources (0.015 ppm in the earth crust) and its production is concentrated in a small number of countries (Russia and South Africa),

* min. 5 mois à partir du 30 janv 2023 / *min. 5 months not earlier than January, 30st 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).*

giving rise to highly fluctuating prices and geopolitical concerns (Pd is on the list of the critical raw material of the European Union). Replacing Pd could decrease the dependency to these rare metal resources. Transition metal carbide or nitride (TMC or TMN) catalysts (i.e. MoC, WC, MoN…) are attractive alternatives due to their metallic functionality from readily available metals [2].

The main objective of the project is to design innovative carbide and nitride nanocatalysts with optimized metallic properties for selective hydrogenation. The synthesis route will involve simple, non-toxic, procedures in order to develop environmentally-friendly, cost-effective and earth-abundant alternatives to Platinum-Group Metal catalysts (namely Pd). Extensive characterization as well as reactivity tests will be carried out in order to derive structure/activity relationships.

2. *Specific techniques or methods*

The research will be organized along two directions.

1st task. ***Catalyst design and characterization.***

This task will consist in the synthesis of new carbide/nitride catalysts including monometallic Mo or W carbide/nitrides as well as bimetallic systems (MoWC…) and more unusual ones such as Fe_2MoC in order to tune the hydrogenation selectivity.

- Benchmark systems will be first prepared through Temperature-Programmed Carburizing/Nitriding reactions largely applied in the literature. This classic and robust method [3] will produce an array of reference catalysts but with little flexibility on the composition and particle size.
- Second, an original pathway of synthesizing Transition metal carbide or nitride catalysts (TMC/TMN) with a sol-gel like urea glass method will give us an increased flexibility in the composition and particle size leading to an advanced design of nanocatalysts [4]. Oxide-supported TMC and TMN phases will be prepared via the same route. This original procedure has never been reported to our knowledge for supported catalysts.
- Various advanced characterization techniques will be used all along the synthesis (XRD, TEM, XPS…) with a potential of synchrotron-based characterization if time permits.

2nd task. ***Catalytic reactions.***

The TMC/TMN materials prepared will be tested in the selective hydrogenation of acetylene in an excess of ethylene and in the selective hydrogenation of butadiene in the presence of an excess of propene. The reactions conditions mimic the front-end process of purification of a stream of alkene (ethylene or propene) containing traces of alkyne or alkadiene (acetylene or butadiene) in the presence of a high concentration of H_2.

Correlation of the reactivity of the catalyst (Task 2) with the structure of the material (Task 1) will be a key point of the internship in order to improve the performance of the obtained nano-catalysts.

This project is based on a larger project funded by the French National Research Agency (ANR) in collaboration with the Universities of Lyon and Grenoble. A PhD will start at the Laboratoire de Réactivité de Surface in October 2023.

3. *References*

[1] K. Tomishige, Y. Nakagawa and M. Tamura, *Green Chem.*, **2017**, (19), 2876.
[2] M. Führer, T. van Haasterecht, J. Bitter, *Catal. Sci. Technol.*, **2020**, (10), 6089.
[3] P. Bretzler, M. Huber, A. Rane, R. E. Jentoft, K. Köhler, F. C. Jentoft, *J. Catal.* **2022**, (405), 60.
[4] C. Giordano, M. Antonietti, *Nano Today* **2011**, (6), 366.