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

Laboratoire d'accueil / *Host Institution*

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Equipe d'accueil / *Hosting Team :*

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Période de stage / *Internship period* * : Février-Juin 2021

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

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

1. Description du projet / *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 the 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). In this respect, catalytic semi-hydrogenation is the main current process for reducing impurities (alkynes, dienes…) in light alkenes feeds which are the key chemicals for the synthesis of Polyethylene (PE) and polypropylene (PP), the world leading thermoplastics.

Palladium-based catalysts are recognized as the most efficient systems for industrial semi-hydrogenation reactions. However, their selectivity towards alkenes decreases drastically at high conversion of alkynes or dienes. Moreover, 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), giving rise to highly fluctuating prices and geopolitical concerns (Pd is on the list of the critical raw material of the European

* 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).*

Union). Replacing Pd for selective hydrogenation could decrease the dependency to these rare metal resources. Transition metal carbide or nitride (TMC or TMN) catalysts (i.e. MoC or WC) are attractive alternatives due to their metallic functionality from readily available metals.

The main objective of the project is to design innovative carbide and nitride nanocatalysts with optimized metallic properties for selective hydrogenation of alkynes and dienes. The synthesis route will involve simple, non-toxic, procedures in order to develop 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. Techniques ou méthodes utilisées / *Specific techniques or methods*
The research will be organized along two directions.
1st task. ***Catalyst design.***
This task will consist in the synthesis of new carbide/nitride catalysts including monometallic Mo or W carbide/nitrides as well as bimetallic systems (Fe_3MoC, $FeWN_2$…) and more original ones such as Fe_3C or Ni_3C 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 [1] will produce an array of reference catalysts but with little flexibility on the composition and particle size.
- Second, an original pathway of synthesizing 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 [2,3]. Oxide-supported TMC and TMN phases will be prepared via the same route. This original one-pot procedure has never been reported to our knowledge.
Conventional characterization techniques in the lab will be used all along the synthesis (XRD, TEM, XPS…).
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. Propene has been chosen for replacing butene for analytical reasons.

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.

3. Références / *References*

[1] G. Djéga-Mariadassou, M. Boudart, G. Bugli, C. Sayag, *Catal. Lett*. **1995**, *31*, 411-420.
[2] C. Giordano, M. Antonietti, *Nano Today* **2011**, *6*, 366-380.
[3] C. Giordano, C. Erpen, W. Yao, B. Milke, M. Antonietti, *Chem. Mater*. **2009**, *21*, 5136-5144.