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 (UMR 7197)
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Equipe d'accueil / *Hosting Team :*

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Responsable équipe / *Team leader* : Xavier CARRIER
Site Web / *Web site : https://lrs.sorbonne-universite.fr/*
Responsable du stage (encadrant) / *Direct Supervisor :* Xavier CARRIER
Fonction / *Position :* Professor
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Période de stage / *Internship period** : 1st of February – 30th June 2024

Titre / *Title*

Design of advanced carbide nanocatalysts for substitution of noble metals in heterogeneous catalysis

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

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

Highly selective catalytic materials are essential for increasing atom economy and reducing the carbon footprint of industrial processes, contributing to greener chemistry. Additionally, the substitution of critical metals, particularly noble metals, is a significant scientific, environmental, and geopolitical challenge in the development of such sustainable processes [1]. **T**ransition **m**etal **c**arbide (**TMC**) catalysts, primarily based on molybdenum (Mo) or tungsten (W), present attractive alternatives due to their abundance, affordability, and the coexistence of metallic and acidic/oxophilic

* **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.

functionalities from readily available metals [2]. Interest in TMCs was sparked in the 1980s when Boudart discovered that metal carbides exhibit catalytic properties similar to platinum-group metals [3]. The coexistence of metallic and acidic functionalities in TMCs makes them especially promising for selective hydrogenolysis and hydrogenation, as the oxygen content can simultaneously inhibit the metallic function and enhance the acidic character [4]. Hence, the metal-acid bifunctionality of TMCs can be tuned through oxygen modification due to the inherent oxophilicity of these materials. As a result, TMCs are highly versatile catalysts, ranging from monofunctional (either metallic or acidic) to bifunctional (metallic-acidic), depending on the synthesis method and/or reaction conditions

The main objective of the internship is to design innovative supported carbide bimetallic heterogeneous catalysts from purely base metals (Mo, W) with optimized metallic and oxophilic properties, as well as nanoscale proximities, for selective hydrogenolysis/hydrogenation. The bifunctional metallic and oxophilic properties of carbides will be fine-tuned through bimetallic Mo-W carbide formulations, where tungsten oxides (WO_x) or oxycarbides (WO_xC_γ) will impart oxophilicity to the metallic molybdenum carbide. Comprehensive characterization techniques will be employed to establish the structure-activity relationship of the prepared catalyst materials.

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

In the first step, catalysts will be synthesized using both conventional **t**emperature-**p**rogrammed **r**eduction (**TPR**) and more advanced sol-gel-based methods. The synthesized catalysts will be characterized using various techniques, including X-ray diffraction (**XRD**), high-resolution transmission electron microscopy (**HRTEM**), X-ray photoelectron spectroscopy (**XPS**), inductively coupled plasma optical emission spectroscopy (**ICP-OES**), X-ray fluorescence (**XRF**), N_2 physisorption, CO and NH_3 chemisorption, mass spectrometry, thermogravimetric analysis (**TGA**), point of zero charge (**PZC**) measurements. The catalytic performance of the synthesized materials will be evaluated through selective hydrogenation of acetylene, simulating the front-end purification process of alkene streams.

3. Références / *References*

[1] Paul T. Anastas, Mary M. Kirchhoff, Tracy C. Williamson, Catalysis as a foundational pillar of green chemistry, Appl. Catal. A: General, 2001, (221) 3

[2] J. Pang, J. Sun, M. Zheng, H. Li, Y. Wang and T. Zhang, Transition metal carbide catalysts for biomass conversion: A review, Appl. Catal. B, 2019, (254), 510

[3] Levy and Boudart, Platinum-Like Behavior of Tungsten Carbide in Surface Catalysis, Science, 1973, (181), 547

[4] M. M. Sullivan et al., Catalytic deoxygenation on transition metal carbides, Catal. Sci. Technol., 2016, (6), 602