MASTER DE CHIMIE DE PARIS CENTRE - M2S2
Proposition de stage 2023-2024
Internship Proposal 2023-2024

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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Site Web / *Web site :* https://lrs.sorbonne-universite.fr/
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Période de stage / *Internship period* * : 29 janv 2024 – 30 juin 2024

Synthesis of catalysts and study of their restructuring under reaction conditions

1) Project description.

The design of high-performance, selective catalytic materials - capable of accelerating a very specific reaction - opens up the prospect of highly efficient, sustainable chemical production. Historically, many catalysts have relied on the reactivity properties of mono-metallic nanoparticles (NPs) deposited on high-surface-area supports. It is now possible to combine several metals within NPs to take advantage of the specific properties of each of them to create tailor-made multi-metallic catalysts. However, this approach greatly complicates our understanding of the reaction behaviour of these catalysts. Indeed, the presence of several metals adds to parameters such as the size and shape of the NPs new parameters such as the composition and arrangement of the metals within the NPs (e.g. alloy, core-shell) or the chemical nature of the different metals (metallic, oxide). Added to this is the fact that NPs are liable to restructure during the reaction [1, 2], a phenomenon which can be positive if it results in an increase in catalyst activity and/or selectivity, but which can also lead to its deactivation.

The CO_2 methanation reaction [3] (also known as Sabatier reaction: $CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$) is one of the many catalytic reactions for which the high potential of multi-metallic NPs has been recently

* **min. 5 mois maximum 6 mois à partir du 29 janv 2024 /** ***min. 5 months and max. 6 months not earlier than January, 29th 2024.***
Fin des conventions de stage au plus tard le 12/07/2024 ou le 17/09/2024 et le 15 novembre. ***End of internship at the latest July 12, 2024 or September. 17, 2024 and 15 November, 2024.***

revealed. CO_2 methanation is a key reaction of the Power-to-Gas technology which aims at using excess electrical energy from renewable sources to produce gaseous chemical energy carrier. Although the CO_2 methanation reaction is thermodynamically feasible under practical conditions, it faces limitations in terms of kinetics. An efficient catalyst is needed to accelerate the methanation reaction, displaying high activity, selectivity, and stability within a suitable temperature range, all while considering economic constraints such as limiting the use of active and selective but too expensive metals such as Rh, Ru or Pd. The stability is specifically challenging, due to the exothermic nature of the methanation reaction. In this context, CO_2 methanation reaction could potentially benefit from all the distinctive advantage of multi-metallic NPs highlighted by pioneering research.

2) Techniques and methods used.

The first objective of the internship is to master and optimize the synthesis of multi-metallic NPs using a new method involving the gradual injection of a solution containing all constituent metal salts into oleylamine (which plays the dual role of reductant and stabilising) and octadecene at a temperature of 275°C [4].

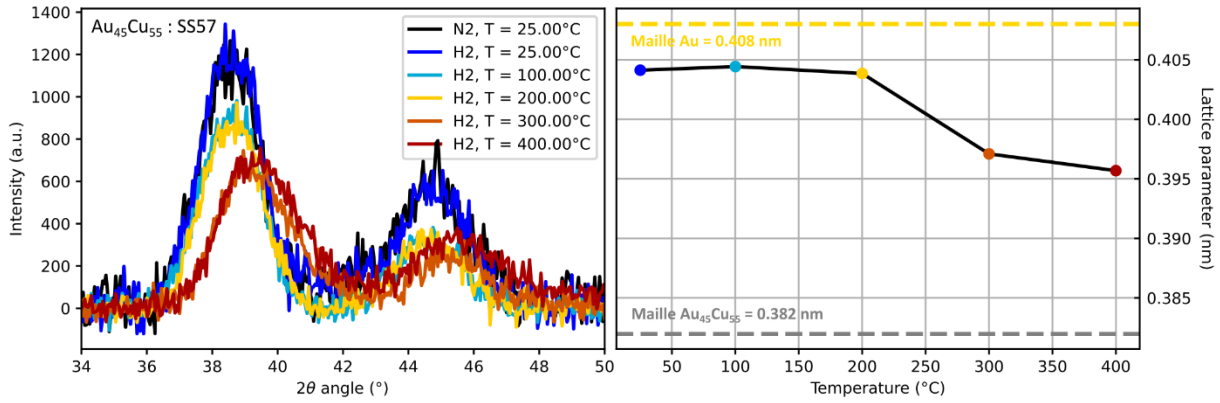

Figure 1 : Evolution du signal de diffraction de l'échantillon $Au_{45}Cu_{55}$ sous environnement neutre à température ambiante (noir) et à 5 paliers de température entre température ambiante et 400°C. b) Evolution du paramètre de maille des NPs obtenue à partir de la position du fit du pic 111 aux alentours de 39° en fonction de la température. La ligne horizontale jaune correspond au paramètre de maille de l'Au volumique. La ligne horizontale grise correspond au paramètre de maille d'un alliage de volume $Au_{45}Cu_{55}$.

The second is to characterize the structural properties of the NPs using high-resolution transmission electron microscopy (HRTEM). The third objective is to carry out a detailed study of the catalytic properties of NPs obtained after impregnation on a support by carrying out catalytic tests within the framework of the CO_2 methanation reaction. The final objective is to study in situ and operando the evolution of the catalyst structure under reaction conditions. These experiments will be carried out using X-ray diffraction on new state-of-the-art equipment, which makes it possible to circulate high-temperature gases through a catalyst while continuously monitoring the X-ray signal diffracted by the sample.

3) References

[1] Wilson *et al.*, *Nanoscale*, **11**, (2019), 752−761. https://doi.org/10.1039/C8NR07645F

[2] Delannoy *et al.*, *Phys. Chem. Chem. Phys.*, (2014), **16**, 26514-26527. https://doi.org/10.1039/C4CP02141J

[3] Daniel Schmider et al., *Ind. Eng. Chem. Res.* 2021, 60, 5792-5805, https://doi.org/10.1021/acs.iecr.1c00389

[4] Gaurav R. Dey et al., *ACS Nano* 2023, **17**, 5943−5955, https://doi.org/10.1021/acsnano.3c00176