

MASTER DE CHIMIE DE SORBONNE UNIVERSITE

Proposition de stage 2025-26

Internship Proposal 2025-26

Parcours type(s) / Specialty(ies) :

- ☐ Chimie Analytique, Théorique, Spectroscopies et Electrochimie/ *Analytical, Theoretical Chemistry, Spectroscopies, Electrochemistry*
- ☐ Chimie Moléculaire / *Molecular Chemistry*
- ☒ Chimie des Matériaux / *Materials Chemistry*
- ☒ 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, 3^{ème} étage

Directeur / *Director (legal representative)* : Vincent VIVIER

Tél / *Tel* :

E-mail : vincent.vivier@sorbonne-universite.fr

Equipe d'accueil / Hosting Team : Catalyse : du nanomatériau à la réactivité du site actif.

Adresse / *Address* : 4 Place Jussieu, Case 178, Tour 43, 3^{ème} étage

Responsable équipe / *Team leader* : Guylène COSTENTIN

Site Web / *Web site* : <http://www.lrs.sorbonne-universite.fr>

Responsable du stage (encadrant) / *Direct Supervisor* : Elizabeth VERA

Fonction / *Position* : Maître de Conférence

Tél / *Tel* :

E-mail : elizabeth.vera-bernal@sorbonne-universite.fr

Période de stage / *Internship period* * : 26 January – 15 July 2026 (6 months)

Titre / Title

Supported metal nanoparticles obtained by redox-exsolution for H₂ generation via water-gas shift.

Projet scientifique du stage (1 à 2 pages) / Internship scientific Project (1 to 2 pages):

1. Contexte de l'étude / Background

Hydrogen has surged as a vital fuel in the transition towards sustainable energy solutions. Currently, it is mainly produced through the reforming of hydrocarbons, which typically yields syngas, a mixture of H₂ and carbon monoxide (CO). The production of pure CO-free hydrogen, from syngas is mainly achieved industrially with the water-gas shift reaction (WGS, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$). Therefore, the development of efficient catalysts for this reaction is crucial.[1] Recently, Ni-based catalysts have been investigated as an alternative to traditional Fe-Cr catalysts, owing to their increased activity and lack of Cr-related toxicity. However, their H₂ selectivity is sometimes limited by CH₄ formation along with catalyst deactivation caused by metal sintering and coke formation. To overcome these drawbacks,

* min. 5 mois, maximum 6 mois à partir du 26 janv 2026 / *min. 5 months and max. 6 months not earlier than January, 26th 2026.*

Fin des conventions de stage au plus tard le 15/07/2026 ou le 15/09/2026 et le 15 novembre 2026.

End of internship at the latest July 15th, 2026 or September. 15th, 2026 and November 15th, 2026.

several approaches have been explored. In particular, the introduction of a secondary metal to form an alloy has proven effective in modifying the surface strain and electronic properties of catalysts, thereby enhancing their activity. [2]

In addition, redox-exsolution has emerged as a promising method for synthesising catalytically active supported metals. The process consists in the emergence (exsolution) of nanoparticles (NPs) directly from the bulk of the support. Transition metal ions are incorporated as B-site dopants of a perovskite lattice (ABO_3) during the synthesis step. Metal exsolution is then triggered by a high-temperature reduction step, which compensates for lattice destabilisation caused by oxygen-vacancy formation. Size and population of the exsolved NPs depend on the reduction conditions, and it has been shown that these exsolved NPs present strong interactions with the perovskite support. This strong anchoring promotes the resistance of the metal NPs to both agglomeration and coke formation.[3]

Therefore, redox-exsolution seems to be a promising route for the development of novel catalysts for the WGS reaction. In particular, it has been shown that exsolved Ni metallic NPs are more active and stable than commercial Fe-Cr catalysts. [4]

2. Description du projet / Description of the project

The objective of the project is to develop metallic and bimetallic NiCu-based catalysts for the WGS reaction via redox exsolution. A family of $\text{La}_{1-x}\text{Sr}_x\text{Ti}_{1-y}\text{M}_y\text{O}_{3+\delta}$ perovskites will be synthesized using the sol-gel method, to achieve specific surface areas of approximately 20-40 m^2/g . Ni and Cu will be incorporated as B-site (Ti) dopants to generate metallic (Ni) and/or bimetallic (NiCu) NPs with different Ni/Cu ratios. Catalyst reduction will be initially carried out at 700 °C under H_2 to perform exsolution. The morphology of the exsolved NPs will be characterised by electron microscopy and spectroscopy techniques to understand the relationship between reduction temperature, NP size, and electronic state. Both fresh and exsolved materials will then be tested for the WGS reaction in the 100-600 °C range. Once the optimal Ni/Cu ratio is identified, exsolution will be performed on the selected catalyst at different times and temperatures to evaluate the effect of NP morphology on the catalytic activity. Additionally, the regeneration properties of the catalyst will be evaluated by reduction/oxidation cycles. Finally, the evolution and stability of the exsolved bimetallic NPs will be examined using microscopy techniques.

Strong consideration will be given to motivated candidates who are interested in pursuing a PhD.

3. Techniques ou méthodes utilisées / Specific techniques or methods

- Synthesis of perovskites by sol-gel method.
- XRD, N_2 sorption analyses, H_2 -TPR, electron microscopy (SEM and TEM), XPS.
- Tests on catalytic bench
- Data analysis

4. Références / References

1. Dehimi L. et al., Hydrogen production by the water-gas shift reaction: A comprehensive review on catalysts, kinetics, and reaction mechanism, *Fuel Process Technol*, **2025**, 267, 108163. <https://doi.org/10.1016/j.fuproc.2024.108163>
2. Park Y. M., Roles of highly ordered mesoporous structures of Fe–Ni bimetal oxides for an enhanced high-temperature water-gas shift reaction activity, *Catal. Sci. Technol.*, 2021, 11, 3251. <https://doi.org/10.1039/d1cy00164g>
3. Vera E. et al., Comparative Study of Exsolved and Impregnated Ni Nanoparticles Supported on Nanoporous Perovskites for Low-Temperature CO Oxidation, *ACS Appl. Mater. Interfaces*, **2024**, 16, 7219-7231. <https://doi.org/10.1021/acsami.3c17300>
4. Huang R. et al., Exsolved metal-boosted active perovskite oxide catalyst for stable water gas shift reaction, *J. Catal.*, **2021**, 148-159. <https://doi.org/10.1016/j.jcat.2021.05.029>