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

Laboratoire d'accueil / *Host Institution*

Intitulés / *Name* : Laboratoire de Réactivité de Surface (LRS) – UMR 7197
Adresse / *Address* : Campus Pierre et Marie Curie, Tours 43-33, 43-44 et 43-53, 3ème étage
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Equipe d'accueil / *Hosting Team :*

Adresse / *Address :* Campus Pierre et Marie Curie, Tours 43-33, 43-44 et 43-53, 3ème étage
Responsable équipe / *Team leader* : Hélène Pernot
Site Web / *Web site :* http://www.lrs.upmc.fr
Responsable du stage (encadrant) / *Direct Supervisor :* Josefine Schnee
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Période de stage / *Internship period* * : February - July 2023

Titre / *Title*
Iron exsolution from iron-substitutable materials: a way to get faultless single-iron catalysts?

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

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

For an efficient transformation of reactants into products over a heterogeneous catalyst, the catalytically active sites need to be accessible, thus well-dispersed. However, at the ultimate stage of atomic dispersion, although the latter generally boosts the catalytic performance, the properties of the catalytic sites may sometimes be affected in such a way that the activity/selectivity decreases.[1] To be able to investigate how the reactivity of molecules is impacted by the isolated character of catalytic sites, and ultimately to optimize this reactivity by designing the catalyst properly, one must succeed in 1) isolating the catalytic sites homogeneously, without introducing a different kind of neighboring sites, and by preventing the possibility of sintering/leaching under reaction conditions, and 2) controlling the surface density of these isolated sites, i.e increasing it to the highest possible extent, if beneficial. The hitherto reported approaches to bring active metals onto supports (e.g surface organometallic chemistry, ion exchange, non-hydrolytic

* 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).*

sol-gel) sometimes meet the first above requirement.[2,3,4] They however hardly meet the second one, or have not been sufficiently explored for that purpose.

Recently, mainly in the literature on perovskite materials, a phenomenon called "exsolution" was reported. The latter consists in the migration of metals incorporated on bulk sites of the material towards the surface under a reducing thermal treatment. It leads to metal nanoparticles having a controlled size and distribution (depending on the temperature, the composition of the reducing atmosphere, etc.), and being socketed at the surface, thus unable to agglomerate under catalytic reaction conditions.[5] On the other hand, in preliminary works carried out at LRS, it was shown that exsolution of metals can also occur within another type of materials, namely hydroxyapatite. In that case, the exsolution leads to highly dispersed metal sites at the surface, even to isolated atoms, rather than to nanoparticles.

Iron is the most abundant transition metal in the Earth's crust, and thus, it is considerably cheaper than the precious noble metals often used in catalysis. Because of its low toxicity, iron-catalyzed reactions have become an integral part of environmentally benign sustainable chemistry.[6] In the present internship, the aim will be to transpose the exsolution approach to various iron-substitutable materials, and see whether it allows obtaining single-iron-atoms being both resistant to sintering/leaching and achievable at high surface densities.

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

Materials will be prepared by various approaches, and their physicochemical properties will be characterized by multiple techniques such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), infrared, UV-Visible and Raman spectroscopies, nuclear magnetic resonance (NMR) spectroscopy, X-ray (thermo-)diffraction ((thermo-)XRD), X-ray photoelectron spectroscopy (XPS), transmission and scanning electron microscopies, N_2 physisorption, H_2-temperature programmed reduction, catalytic activity tests, etc.

3. Références / *References*

1. Mitchell, S.; Pérez-Ramírez, J., Single atom catalysis: a decade of stunning progress and the promise for a bright future. *Nature Communications* **2020,** *11* (1), 4302.
2. Avenier, P.; Taoufik, M.; Lesage, A.; Solans-Monfort, X.; Baudouin, A.; de Mallmann, A.; Veyre, L.; Basset, J. M.; Eisenstein, O.; Emsley, L.; Quadrelli, E. A., Dinitrogen Dissociation on an Isolated Surface Tantalum Atom. *Science* **2007,** *317*, 1056 – 1060.
3. Akri, M.; Zhao, S.; Li, X.; Zang, K.; Lee, A. F.; Isaacs, M. A.; Xi, W.; Gangarajula, Y.; Luo, J.; Ren, Y.; Cui, Y.-T.; Li, L.; Su, Y.; Pan, X.; Wen, W.; Pan, Y.; Wilson, K.; Li, L.; Qiao, B.; Ishii, H.; Liao, Y.-F.; Wang, A.; Wang, X.; Zhang, T., Atomically dispersed nickel as coke-resistant active sites for methane dry reforming. *Nature Communications* **2019,** *10* (1), 5181.
4. Debecker, D. P.; Bouchmella, K.; Stoyanova, M.; Rodemerck, U.; Gaigneaux, E. M.; Hubert Mutin, P., A non-hydrolytic sol–gel route to highly active MoO_3–SiO_2–Al_2O_3 metathesis catalysts. *Catalysis Science & Technology* **2012,** *2* (6), 1157-1164.
5. Kwon, O.; Sengodan, S.; Kim, K.; Kim, G.; Jeong, H. Y.; Shin, J.; Ju, Y.-W.; Han, J. W.; Kim, G., Exsolution trends and co-segregation aspects of self-grown catalyst nanoparticles in perovskites. *Nature Communications* **2017,** *8* (1), 15967.
6. Lopez-Tejedor, D.; Benavente, R.; Palomo, J. M., Iron nanostructured catalysts: design and applications. *Catalysis Science & Technology* **2018,** *8* (7), 1754-1776.