MASTER DE CHIMIE DE PARIS CENTRE - M2S4
Proposition de stage 2019-2020
Internship Proposal 2019-2020

Domaine de formation visé / *Field of training targeted :*
☐ Chimie Analytique, Physique, et Théorique */ Analytical, Physical and Theoretical Chemistry* :
X Chimie Moléculaire / *Molecular Chemistry* :
X Matériaux / *Materials:*
X Ingénierie Chimique / *Chemical Engineering:*

Laboratoire d'accueil / *Host Institution*
Intitulés / *Name* : Laboratoire de Réactivité de Surface
Adresse / *Address* : Campus Pierre et Marie Curie, 4 place Jussieu, 75005 Paris
Directeur / *Director (legal representative) :* Pr H. Pernot
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Equipe d'accueil / *Hosting Team : Ingénierie des surfaces nanostructurées et fonctionnelles*
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Responsable équipe / *Team leader* : Pr F. Launay & Dr C. Louis
Site Web / *Web site :* http://www.lrs.upmc.fr/fr/l-unite-de-recherche.html
Responsable du stage (encadrant) / *Direct Supervisor :* F. Launay
Fonction / *Position :* Professor
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Période de stage / *Internship period* * : February to june 2020
Gratification / *Salary* : Yes

Exploration of the potential of highly dispersed nickel-silica catalysts for wastes valorization

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

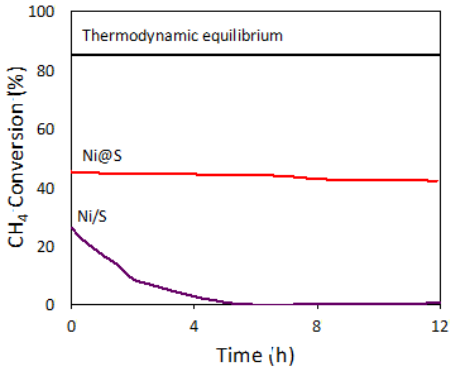
1. Projet / *Project*

For cost efficiency reasons, non-noble metals, including nickel, are increasingly considered as active phases in catalysis. However, the substitution of noble metals by Ni is not so simple. In 1922, the famous scientist and Nobel Laureate Paul Sabatier wrote that nickel-based catalysts have "an excessive activity along with maximum alterability", but the latter also indicated that "changing the catalyst preparation conditions may produce nickel that can do all kinds of work" and "maintains its activity for a long time" **[1]**.

Recently, we have been confronted with this problem in our work aiming at developing heterogeneous nickel-on-mesoporous silica catalysts for the dry reforming of methane ($CO_2 + CH_4 \rightarrow 2\ CO + 2\ H_2$), a reaction that allows the production of syn gas with proportions well adapted to the Fischer-Tropsch reaction **[2-3]**. Among the different approaches, a synthesis pathway Ni@S tested in collaboration with Pr A. Bleuzen and Dr G. Fornasieri (ICMMO Paris Sud) afforded monoliths of materials that are stable

* 5 à 6 mois à partir du 13 janv 2020 / *5 to 6 months not earlier than January 13, 2020.*

over time (continuous flow) and more active than average despite the drastic conditions imposed by the thermodynamics of the reaction **[4]**.



CH_4 conversion at 650°C during 12 h on stream under GHSV = 960 L g^{-1} h^{-1} using 10% CH_4, 10% CO_2 and 80% Ar (black: calculated thermodynamic values, red: with the best material prepared at ICMMO and purple: with a reference material)

The first objective of this internship is to reproduce the synthesis and characterization of these materials in order to test them under even more drastic conditions (extended durations and with less diluted gases than before). The pore structure in those samples is hexagonal but other materials with different pore structures will be synthesized to test this parameter. In the best case, the stability of the nickel (0) particles during the reactivity test will be monitored *in situ* using transmission electron microscopy. For this part of the work dealing with the valorization of wastes such as methane (biogas) and carbon dioxide, the catalysis experiments will be performed in collaboration with an external laboratory.

The catalytic activity of the same series of materials will also be examined on site as part of the valorization of lignin from biomass wastes using reductive depolymerization (with H_2). Lignin is an important source of aromatic molecules that could replace petroleum in the long term provided that the depolymerization process is well controlled **[5]**. Monitoring the reaction, which is a rather difficult task, will rely on the methods recently developed in our group **[6]** and in collaboration with Dr. B. Rousseau of the "Equipe Polymères" at IPCM/Sorbonne Université.

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

During this internship, the candidate will synthesize mesoporous silica-based nickel catalysts by using sol-gel pathways, characterize the samples by N_2 physisorption, X-ray diffraction, H_2 chemisorption and Temperature Programmed Reduction experiments. The depolymerization tests of the lignin will be carried out in pressurized reactors and will be monitored by the analysis of the solutions by HPLC and GC-MS after derivatization while the residual lignin will be characterized by NMR.

3. Références / *References*

[1] V.P. Ananikov, Nickel: The "Spirited Horse" of Transition Metal Catalysis, ACS Catal. 5 (**2015**) 1964-1971.
[2] O. Daoura, M.N. Kaydouh, N. El Hassan, P. Massiani, F. Launay and M. Boutros, Mesocellular silica foams-based Ni catalysts for dry reforming of CH_4 (by CO_2), Journal of CO_2 Utilization 24 (**2018**) 112-119.
[3] O. Daoura, S. Daher, M.N. Kaydouh, N. El Hassan, P. Massiani, F. Launay and M. Boutros, Influence of the swelling agents of siliceous mesocellular foams on the performances of Ni- based methane dry reforming catalysts, International Journal of Hydrogen Energy 43 (**2018**) 75205-75215.
[4] Thèse O. Daoura, Sept. **2019**, Sorbonne Université (LRS), Towards anti-coking and anti-sintering Ni@Silica based catalysts for the dry reforming of methane.
[5] C. Chio, M. Sain, W. Qin, Lignin utilization: A review of lignin depolymerization from various aspects, Renewable and Sustainable Energy Reviews 107 (**2019**) 232-249.
[6] Thèse L. Al Hussaini, Oct. **2019**, Sorbonne Université (LRS), Use of unconventional methods for the oxidative cleavage of lignin by dioxygen.