MASTER DE CHIMIE DE PARIS CENTRE - M2S2
Proposition de stage 2020-2021
Internship Proposal 2020-2021

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 (LRS)
Adresse / *Address* : Sorbonne Université (SU) - Campus Pierre et Marie Curie, Tour 33-43 3ème étage
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Equipe d'accueil / *Hosting Team :* Laboratoire de réactivité de Surface (LRS)
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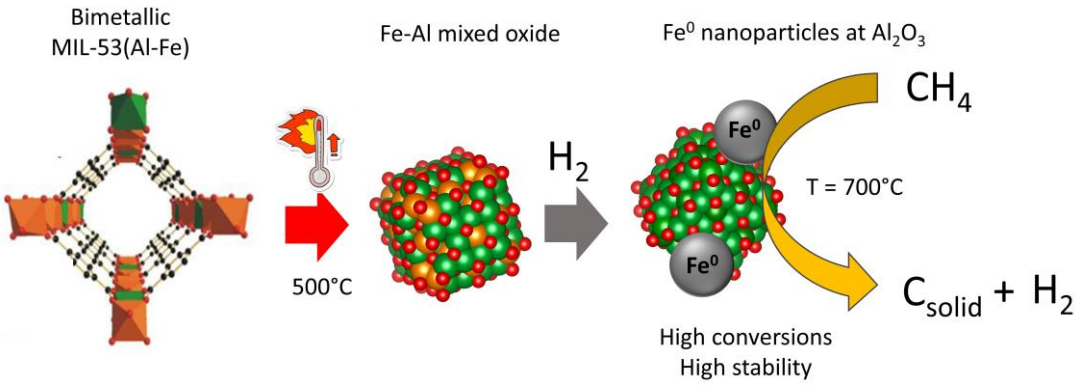
Période de stage / *Internship period* * : from 2021/01/18 to 2021/07/16

Synthesis and characterization of bimetallic Aluminum-Iron Metal-Organic Frameworks (MOF) employed as templates in the preparation of catalysts for catalytic decomposition of methane

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

1. Topic: Iron-based catalysts made of isolated iron oxide and metal iron nanospecies dispersed on a support such as alumina were shown to be highly promising to perform the catalytic decomposition of methane (CDM), a virtuous COx-free hydrogen production technology towards clean fuel widely used in fuel cells that generates only carbon nano materials (CNMs) as a high value-added by-product.[1] Similar to other endothermic reactions, CDM requires elevated temperatures that commonly lead to the sintering of the active Fe phase and in turn to the decrease of the catalyst performances.
Our team recently demonstrated a strategy to produce nickel-based catalysts made of stable Ni^0 nanoparticles homogeneously dispersed on porous alumina that do not sinter even under high temperatures (>700°C). This approach consists in impregnating the aluminum-terephthalate-based MOF named MIL-53(Al) with Ni^{2+} precursors, followed by the thermal removal of the MOF organic linkers. This results in an Al-Ni mixed oxide for which the reduction of the isolated Ni species leads to the formation of very small and stable Ni^0 nanoparticles.[2]
Inspired by these results, the goal of this internship is to develop a new method to produced CDM catalysts made of Fe^0 nanoparticles stabilized on a porous alumina support by using MIL-53(Al) MOF as template. The procedure will consist in: (1) the homogeneous dispersion of the Fe^{3+} cations in close proximity of the Al^{3+} of the MIL-53 framework, (2) the calcination of the MIL-53(Al-Fe) to obtain Fe/Al mixed oxide

and (3) the reduction of the Fe^{3+} to produce the Fe^0-Al_2O_3 catalyst. Two approaches will be explored to homogeneously disperse the Fe^{3+} cations within the MIL-53(Al): Fe^{3+} precursors will be either impregnated within the pores of MIL-53(Al) or included within the inorganic building unit of the MOF by substituting a part of the Al^{3+} cations by Fe^{3+} cations leading to bimetallic MIL-53(Al-Fe) (Scheme 1).



Scheme 1. Procedure for the synthesis of Fe^0-Al_2O_3 catalyst starting from the bimetallic MIL-53(Al-Fe). The catalytic decomposition of methane is also displayed.

2. Technics or methods: MIL-53(Al) and MIL-53(Al-Fe) will be synthesized under solvothermal conditions at LRS. The different materials will be characterized by standard techniques of characterization of hybrid porous and crystalline materials (thermogravimetry, N_2 adsorption, PXRD). The iron species within MIL-53(Al-Fe), Al-Fe mixed oxides and Fe^0-Al_2O_3 will be characterized by spectroscopy (FTIR, UV-Vis, DRIFT of adsorbed probe molecules, RAMAN, XPS), microscopy and temperature programmed reduction. Chemical compositions of the different materials will be determined by EDX, XPS for the surface species. All these techniques are available at LRS (except ICP). CDM catalysis will not be achieved in LRS. They will be achieved in the University of Balamand in Lebanon by our Lebanese collaborators who have the proper apparatus.

3. References :

[1] J. X. Qian et al. International Journal of Hydrogen Energy, 2020, 45, 15721-15743.
[2] Leila Karam, Julien Reboul et al. ChemCatChem 2020, 12, e190127.