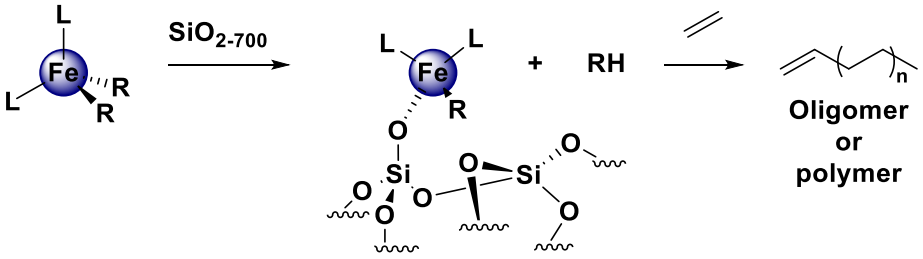
M2 Internship Proposal:
Supported iron catalyst for the oligo-/polymerization of ethylene

Context: Iron, a naturally abundant and inexpensive metal, is widely used in ethylene oligomerization and polymerization. [1] However, several limitations remain: iron complexes, being coordinatively unsaturated and highly reactive, tend to deactivate during the reaction. To overcome this problem, iron complexes can be immobilized on a surface, thereby limiting bimolecular deactivation reactions. Fe(II)-supported species (the preferred oxidation state for oligo- and polymerization reactions) remain scarce in the literature.[2]

Research project and Objectives: The objective of this project is to expand the Surface OrganoMetallic Chemistry (SOMC) of Fe(II) species in order to: 1) gain a better understanding of the structure of intermediates during catalyst preparation, 2) elucidate the mechanisms of ethylene polymerization involving species that are unstable in molecular form, such as iron–allyl complexes, and 3) study the effect of steric hindrance on a surface in relation to a bulky ligand. The presence of bulky ligands around the iron centre is known to limit, to some extent, deactivation pathways during ethylene polymerization.[3]

Using the SOMC approach, and similar to the supported Ni(II) species already developed by the CADICOM host team,[4] the goal of this internship project is to synthesize, characterize, and evaluate new supported Fe(II) species as catalysts. Molecular Fe(II) precursors (alkyl iron,[5] allyl iron[6]) will be synthesized and then grafted onto a surface (pure silica with a specific surface area of 200 $m^2 \cdot g^{-1}$, partially dehydroxylated under high vacuum at 700 °C, $SiO_{2\text{-}700}$) (Scheme 1). The new grafted species will be characterized by DRIFTS, ICP, and EPR, and their reactivity with ethylene for oligomerization or polymerization will be evaluated. The resulting products will be characterized by GC (oligomers) or HT-SEC.



Scheme 1: Synthesis of supported Fe(II) complexes and their application in catalysis for the oligo- and polymerization of ethylene

Profile of the candidate: The project will involve the preparation, characterization, and evaluation of catalysts; among other things, the candidate will develop their ability to work in an inert atmosphere and to use various analytical methods. The candidate must demonstrate great enthusiasm and enjoy working as part of a team.

Proposed internship date: Starting from January/February until July 2027

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Reference:

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