LABORATORY FOR CHEMICAL TECHNOLOGY
Technologiepark 125, 9052 Gent, Belgium

Coach	**Supervisor(s)**	**Funding**
Dilan Tunçer Max Bols	Mark Saeys	D2M2

Vanadium Tug of War: Engineering catalyst redox properties for CO_2-Assisted Propane Dehydrogenation

Aim

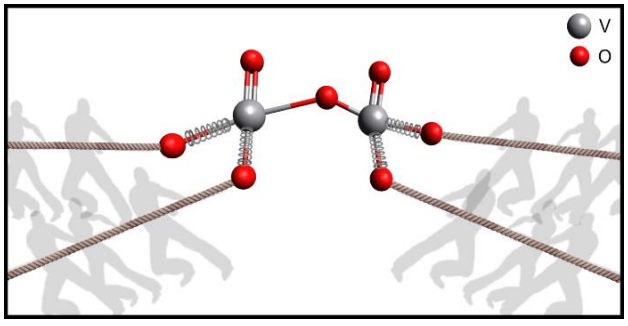
Discovery of design opportunities to tune vanadium active sites in heterogeneous catalysis for CO_2 assisted propane dehydrogenation into propylene and CO.

Justification

CO_2-assisted oxidative propane dehydrogenation (CO_2-OPDH) has several advantages over traditional industrial propane dehydrogenation processes. These include the use of milder reaction conditions, decreased overoxidation of the products, and net consumption of CO_2. A commercially viable catalyst is yet to be discovered and developed for this process, with major issues in selectivity and stability remaining. Vanadium supported on a wide range of materials has been explored and is reported as a promising class of catalysts. Promising features include the relative abundance and low toxicity of vanadium, and the versatility of vanadium as a transition metal with flexible redox properties.

The catalytic activity of vanadium is related to its reducible nature and its ability to easily change its oxidation state between 3+/4+/5+, thus enabling a redox cycle. This also leads to its popular use in batteries and as sacrificial oxidant. In a catalytic cycle, the redox behavior will dictate the mechanism that can be followed and hence the catalytic activity and selectivity. In this thesis, you will conduct *ab initio* computational chemistry calculations to investigate how the environment of vanadium moiety modifies its redox properties. The starting point will be last year's successful Master's thesis on this topic, which established a highly accurate computational methodology. You will use this methodology to engineer vanadium sites that enable a favorable catalytic cycle for CO_2-OPDH. These sites will be implantable into actual supported catalysts that can be tested in the lab (associated project with an experimental doctoral student in the group).

This thesis offers an excellent opportunity to be trained in computational catalysis, with the use of a selection of software packages (Gaussian 16, Orca), and high-performance computing, working on a topic with a significant and energy-efficient CO_2-reduction potential. You will gain fundamental insight in redox catalyst design and use this knowledge to guide catalyst design.



Program

- Literature study on vanadium redox properties relevant to (O)PDH catalysis and methods to engineer them
- Rational *in-silico* modification of cluster models to establish structure-performance relationships
- Discussion of the underlying structural drivers of redox properties and connection to catalysis
- Transfer insight gained from computational modeling into real-life catalyst synthesis