<table>
<thead>
<tr>
<th></th>
<th>Master Thesis Subjects - 2019/2020</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>A combined experimental and modeling study of (mini)emulsion radical polymerization</td>
</tr>
<tr>
<td>5</td>
<td>Development of promoted La2O3 based catalysts for oxidative coupling of methane</td>
</tr>
<tr>
<td>6</td>
<td>High emissivity coatings in steam cracking furnaces</td>
</tr>
<tr>
<td>7</td>
<td>Kinetic study of plastic (wastes) gasification reactions</td>
</tr>
<tr>
<td>9</td>
<td>Combining the strength of experimental study and modeling tools to lift the field of Polymer Brushes</td>
</tr>
<tr>
<td>10</td>
<td>Analysing Big Data: QXAS on Pt-Fe catalysts</td>
</tr>
<tr>
<td>11</td>
<td>Kinetic Modeling of Fast Pyrolysis of Solid Plastic Waste</td>
</tr>
<tr>
<td>12</td>
<td>Fast Pyrolysis of Polyolefins in the Gas-Solid Vortex Reactor</td>
</tr>
<tr>
<td>13</td>
<td>Pt-based propane dehydrogenation catalysts: effect of In promotion, support and synthesis route</td>
</tr>
<tr>
<td>14</td>
<td>Design and Synthesis of Catalysts for CO2 Hydrogenation to Methanol</td>
</tr>
<tr>
<td>15</td>
<td>Relating sol-gel synthesis to flow behaviour</td>
</tr>
<tr>
<td>16</td>
<td>Big Data Meets Chemistry – Neural Network Based Property Estimation</td>
</tr>
<tr>
<td>17</td>
<td>Tri-reforming of hydrocarbon mixtures for the production of syngas</td>
</tr>
<tr>
<td>18</td>
<td>Impact of the spatial distribution of active material on the performance of n-hexane hydrocracking with a bifunctional catalyst</td>
</tr>
<tr>
<td>19</td>
<td>Solar thermochemical splitting of H2O and/or CO2 to generate H2 and/or CO</td>
</tr>
<tr>
<td>20</td>
<td>Reactor design for a gas-solid reaction to produce H2</td>
</tr>
<tr>
<td>21</td>
<td>Reactor design for a gas-solid reaction to capture CO2</td>
</tr>
<tr>
<td>22</td>
<td>Proton-mediated energy storage</td>
</tr>
<tr>
<td>23</td>
<td>Selective oxidation of bio-methane to formaldehyde: core-shell catalyst approach</td>
</tr>
<tr>
<td>24</td>
<td>Effect of feedstock on propylene yield in alcohol-to-olefins conversion</td>
</tr>
<tr>
<td>25</td>
<td>Gas radiative properties model development for oxy-fuel combustion</td>
</tr>
<tr>
<td>26</td>
<td>Genesys: Automatic generation of kinetic models for hetero-atomic compounds</td>
</tr>
<tr>
<td>No.</td>
<td>Title</td>
</tr>
<tr>
<td>-----</td>
<td>-------</td>
</tr>
<tr>
<td>27</td>
<td>Coke formation simulation during steam cracking</td>
</tr>
<tr>
<td>28</td>
<td>Pyrolysis of small hydrocarbon and oxygenated compounds: a combined modelling and experimental study</td>
</tr>
<tr>
<td>29</td>
<td>Continuous flow investigation of acid-catalyzed aldol condensations</td>
</tr>
<tr>
<td>31</td>
<td>First principles prediction of transfer and secondary reactions kinetics in free radical polymerization of industrially viable monomers</td>
</tr>
<tr>
<td>32</td>
<td>A combined experimental and modeling study of plasma polymerization and decomposition</td>
</tr>
<tr>
<td>33</td>
<td>Pulsed laser (co)polymerization to enhance industrial polymer synthesis</td>
</tr>
<tr>
<td>34</td>
<td>Unravelling lignin pyrolysis chemistry using phenolic model compounds</td>
</tr>
<tr>
<td>35</td>
<td>Design and Synthesis of Catalysts for CO2 Hydrogenation to Formic Acid</td>
</tr>
<tr>
<td>36</td>
<td>Design of bimetallic catalysts for CO2 hydrogenation</td>
</tr>
<tr>
<td>37</td>
<td>Kinetic Monte Carlo modeling of amyloid beta peptide polymerization</td>
</tr>
<tr>
<td>38</td>
<td>Experimental study of a gas-solid vortex reactor for oxidative coupling of methane</td>
</tr>
<tr>
<td>39</td>
<td>CFD based design of a gas-solid vortex reactor for oxidative coupling of methane</td>
</tr>
<tr>
<td>40</td>
<td>Automated extraction of kinetic information in the era of Open Data</td>
</tr>
<tr>
<td>41</td>
<td>Upgrading of a bio-refinery stream via hydrodeoxygenation: a kinetic study</td>
</tr>
<tr>
<td>42</td>
<td>Reductive Coupling of CO2 with Ethylene using Homogeneous Catalysts</td>
</tr>
<tr>
<td>43</td>
<td>Mitigating butadiene popcorn formation in industrial olefin units</td>
</tr>
<tr>
<td>44</td>
<td>The impact of hydrocarbon chain length on mixture effects in alkanes and cycloalkanes hydrocracking</td>
</tr>
<tr>
<td>45</td>
<td>Reducing Coking During Steam Cracking Of Hydrocarbons</td>
</tr>
<tr>
<td>46</td>
<td>New criteria for the instantaneous regime for gas-liquid reactions</td>
</tr>
<tr>
<td>47</td>
<td>Experimental study on the influence of reactor alloys on coke formation on a newly developed setup</td>
</tr>
<tr>
<td>48</td>
<td>Transient kinetics: development of a general non-steady state solver for plug flow reactors</td>
</tr>
<tr>
<td>49</td>
<td>Chemo-catalytic production of butadiene of bio-based feedstock: kinetics of butanediol dehydration</td>
</tr>
<tr>
<td>50</td>
<td>Directe afvang van CO2 uit lucht</td>
</tr>
<tr>
<td>Project Title</td>
<td></td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Unravelling NP-fertilizer digestion</td>
<td></td>
</tr>
<tr>
<td>Synthesis of Urea-Formaldehyde Resins from CO2</td>
<td></td>
</tr>
<tr>
<td>CO2 utilization through Super-Dry Reforming: process simulation</td>
<td></td>
</tr>
</tbody>
</table>
A combined experimental and modeling study of (mini)emulsion radical polymerization

Aim
Controlling (mini)emulsion polymerization conditions to enable nanoparticle production for nanostructured materials such as nanofibers with functionality loading.

Justification
Emulsion polymerization is an interesting technique to synthesize nanostructured materials in a sustainable way and susceptible to scale-up. A challenge is the complete understanding of the multiphase character of the reaction medium with on the one hand reactions in micelles/polymer particles and the other hand reactions in the aqueous continuous phase. Mass transport between both phases further complicates the polymerization kinetics. At LCT an experimental set-up is available to study emulsion polymerization at different reaction scales and based on different nucleation mechanisms, including the special case in which the polymerization commences in small droplets in the absence of micelles thus under so-called miniemulsion conditions. Equipment is available both for the measurement of the particle size distribution (PSD) and the chain length distribution (CLD). Key challenges are a control of the solid content and the polymerization degree in view of process intensification but also product properties upon further downstream processing. A novel route is here e.g. electrospinning of emulsions with a portfolio of novel morphologies within reach.

Program
1. Experimental study of mini- and macroemulsion to better understand the relation between process parameters and PSD/CLD.
2. Model-based design of the average particle size and chain length based on the experimental data set in 1.
3. Linkage of the emulsion morphologies to final product properties such as fibers spun from polymer emulsions.

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Supervisors
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Funding
-
Development of promoted La$_2$O$_3$ based catalysts for oxidative coupling of methane

Aim

Oxidative coupling of methane (OCM) is a promising one-step route to convert methane to more valuable chemicals most notably ethylene. The aim of thesis is to investigate the influence of different metal oxides in the performance of La$_2$O$_3$ for OCM.

Justification

Methane is the principal constituent of natural gas, with proven reserves estimated to be around 186 trillion m$^3$.\(^1\) Today, only about 10\% of the produced natural gas produced, is used as industrial feedstock by the chemical industry. Ethylene is a key building block for the chemical industry, and is mostly produced from crude oil via energy intensive steam cracking. Oxidative coupling of methane presents an attractive alternative route to produce ethylene from methane, reducing the dependence on crude oil. In the OCM reaction, CH$_4$ reacts with O$_2$ at high temperatures, forming ethane, ethylene, CO, CO$_2$ and H$_2$O. Currently, the use of OCM is limited by low ethylene yields. In practice the C$_2$ yields obtained from OCM are less than 30\%.\(^2\)

La$_2$O$_3$ based catalysts are among the more active catalysts for OCM, with strontium being a very good promoter.\(^3\) However, the C$_2$ selectivity obtained using La$_2$O$_3$ based catalysts are rather low (less than 40\%). In this thesis, we focus on the development of promoters for La$_2$O$_3$ based catalysts, employing a combination of kinetic measurements and catalyst characterization. Few different catalysts will be synthesized and kinetic performance is assessed. Various characterization techniques will be employed to study the physicochemical properties of the synthesized catalysts. Finally the role of promoters will be elucidated, utilizing acquired experimental data.

Program

- Literature survey on La$_2$O$_3$ based catalysts and kinetics of OCM
- Synthesis, characterization and kinetic testing of selected catalysts
- Understanding the role of the promoter based on the experimental evidence.

References

High emissivity coatings in steam cracking furnaces

Aim
The goal of this thesis is to investigate the effect of coating the furnace walls on the energy efficiency of steam cracking furnaces. Based on experimental results, the wavelength dependency of the boundary wall emissivity will be taken into account when modelling the radiative heat transfer in a steam cracking furnace.

Justification
Steam cracking is one of the most important petrochemical processes in which hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons. It is the principal industrial method for producing ethylene, propylene and butadiene. Steam cracking is also the most energy-consuming process in the chemical industry and globally uses approximately 8% of the sector’s total primary energy. Improving the energy efficiency has an immediate pay-out because energy cost counts for approximately 70% of production costs in typical ethane- or naphtha-based olefin plants. A more recent research topic is related to the radiant section of a steam cracking furnace, where the major part of heat transfer occurs by radiation. The radiation is emitted by the refractory walls towards the process radiant coils. Application of high emissivity coatings on the external surface of the refractory walls could improve the energy consumption in several ways. Less firing is required to reach the same process temperatures in the radiant coils and high emissivity coatings are observed to suppress the formation of hot spots which acts as a precursor for coke formation. A comprehensive study on high emissivity coatings will lead to a better understanding of the effect of high emissivity coatings on radiative heat transfer in steam cracking furnaces.

Program
- Literature survey on steam cracking furnaces in general and in more detail on the application of high emissivity coatings.
- A (CFD) model will be developed, simulating the radiative heat transfer in a simplified furnace.
- The model will have to be extended in order to more accurately account for the spectral dependency of emissivity based on typical emissivity profiles found in scientific literature.
- The absorptivity of the flue gas will have to be accounted for, different grey and non-grey models will have to compared.

Figure 1: Spectral normal emissivity of refractory brick at 800 °C in the 1.8 – 25.0 µm wavelength range. Constant boundary wall emissivities, $\varepsilon_{w,i}(T)$, at the gas phase absorption bands, typical for industrial furnaces, have been calculated.
Kinetic study of plastic (wastes) gasification reactions

Aim
Understanding the gasification reaction mechanisms for different plastic wastes, generation of reaction kinetic schemes and finally reduction of the reaction mechanisms using 1-D model

Justification
Over the recent decades, technological advances, population increase and lifestyle changes, have increased the annual amount of municipal solid waste (MSW), including plastic wastes. These wastes have to be treated wisely to close the circular economy loop (Figure 1), as well as decreasing the environmental impact. Landfilling is one of the easiest and oldest methods to discard plastic wastes. However, land shortage and environmental impact make this option the least desirable one. Gasification reactions, the goal of which is to crack large plastic polymer molecules and convert them preferably to syngas (H₂+CO), is considered as one of the promising (thermo)chemical recycling routes of plastic wastes [1].

Apart from the intrinsic gasification reactions, it is crucial to design the process efficiently so that production rate increases while equipment volume and environmental impact decreases (Process Intensification). This goal is going to be achieved through realization of Gas Solid Vortex Reactor (GSVR) concept [2] in plastic waste gasification at LCT, UGent. Implementing centrifugal force instead of gravity against the drag force, results in high slip velocity between phases and consequently, increasing the rates of heat and mass transfer. Hence GSVR is a possible methodology of PI in plastic waste thermochemical recycling.

To assist with design of the process, coupled computational fluid dynamics (CFD) with kinetic models of plastic (waste) gasification in gas solid vortex reactor will be needed. The CFD framework is required to predict the fluid dynamic behaviour of the system. However, it is not possible to predict the process outcome unless fully predictive kinetic models are developed and coupled to the CFD framework. In this work, upon reaching the reasonable understanding of gasification reaction kinetics through literature study, the generation of reaction kinetic schemes, and afterwards reduction of the reaction mechanisms to be integrated with the CFD framework will be done.

Program
1. Literature study on kinetics of different plastic waste gasification reactions
2. Generation reaction mechanisms using Genesys [3, 4]
3. Creating 1-D kinetic model for the desired reaction using ANSYS Chemkin / Cantera
4. Mechanism reduction with the goal of being coupled with CFD framework


Combining the strength of experimental study and modeling tools to lift the field of Polymer Brushes

Aim
A combined experimental and modeling study of reversible addition-fragmentation chain transfer polymerization of styrenes, acrylates and methacrylates monomers using a trithiocarbonate-based chain transfer agent is explored. Experimental as well as model-based studies will be performed in order to determine the optimal conditions to conduct the synthesis of the desired polymer brushes with well-defined properties.

Justification

Polymer brushes are a class of polymeric assemblies in which the individual polymer chains are tethered to planar or curved surfaces by one chain end, and in which the grafting density (σ) of the polymer chains is higher than the radius of gyration (R_G). Modification of surface properties with the introduction of polymer brushes allows for various applications including the production of coatings for corrosion protection, novel adhesive materials, protein-resistant biosurfaces, chemical lubricants, and polymer carriers for controlled-release of active compounds.

Reversible addition-fragmentation chain transfer (RAFT) polymerization is one of the main approaches to synthesizing polymer brushes with well-established structure and polymer composition as well as controlled molar mass and narrow molar mass distributions over a wide range of monomers. Upon using RAFT polymerization, the synthesis of polymer brushes can be conducted by anchoring either a radical source (initiator) or the chain transfer agent (CTA) on the surface, although the latter option is the most widely used and more common approach.

One of the most important challenges to deal with during the preparation of polymer brushes is to have complete information regarding important characteristics such as molar mass and dispersity of the tethered polymers as well as the variation of polymer layer thickness as a function of polymerization time and grafting density. This information cannot be easily accessed simply by conducting experimental studies which only allow the determination of average properties of free polymer chains in solution. However, this limitations can be circumvented through a combination of advanced computational modeling techniques with meticulous experimental analysis and the main goal of this project is to develop a computational tool based on the Method of Moments to solve the polymerization system considering diffusional limitations. This code has to be able to account for average properties of polymer chains either in solution or tethered to a surface.

Program
1. Concise literature review on RAFT polymerization technique for the optimal synthesis of polymer brushes as well as modeling strategies of surface-initiated polymerization processes.
2. Developing a computer code based on the Method of Moments capable of describing the synthesis of polymer brushes via RAFT polymerization. Special attention will be focused on the potential influence of diffusional limitations on the reaction system.
3. Validation and benchmarking of the code in 2 against experimental data obtained at the Laboratory for Chemical Technology as well as data reported in the literature.
4. Application of the modeling tool developed in 2 for the identification of optimal experimental conditions for the synthesis of well-controlled polymer brushes.
Analysing Big Data: QXAS on Pt-Fe catalysts

Aim
As measurements become more complex and acquisition times get reduced, BIG data are increasingly encountered in research. This is for instance the case for Quick X-ray Absorption Spectroscopy measurements, where full spectra are recorded in less than seconds, quasi-simultaneously for several elements. In order to master these large amounts of data, new analyses methods are required, allowing for swift data visualisation, automated data treatment and accessible interpretation.

Justification
Promoted Pt catalysts are very effective to catalyze propane dehydrogenation, a major route to selectively produce propene. By adding a small amount of CO\textsubscript{2} to the feed as soft oxidant, carbon formation can be reduced and the equilibrium shifted to enhance selective production. Ni-Fe catalysts are known to rearrange under oxidizing or reducing conditions. Pt-based catalysts are expected to behave similarly, but so far, their behavior under oxidizing conditions has hardly been examined. In order to identify their restructuring and the Fe promoter role, two Pt-Fe catalysts have been examined using Quick-X-ray absorption spectroscopy (QXAS) at both the Pt-L\textsubscript{III} and Fe-K edge. XAS allows to examine the local environment around Pt and Fe in these bimetallic catalysts, even during treatment or reaction (reduction, oxidation, reverse water gas shift, redox cycling), see Figure.

As faster measuring techniques are developed and characterization methods are often combined with each other, the result of one measurement can soon encompass several MB of data. A Pt and Fe QXAS dataset forms the playground for this thesis. Data analysis will focus on pre-treatment, adequate comparison and plotting to visualize results, quantification of changes observed and the use of new analysis methods, e.g. statistical techniques like PCA, LCF, …, to get the most out of these data.

Program
The tasks proposed for this thesis include:
- Literature research on promoted Pt catalysts for propane dehydrogenation
- Theoretical background study on (Q)XAS
- Get familiar with Big Data techniques
- Data treatment, statistical analysis using LCF, PCA, … and interpretation of QXAS spectra.
- Combining and interpreting results.

Joining a XAS campaign at a synchrotron might be possible.

Figure: XANES spectra during H\textsubscript{2}-TPR of 3wt\%Pt-1wt\%Fe/MgAl\textsubscript{2}O\textsubscript{4} at the (a) Pt-L\textsubscript{III} and (b) Fe-K absorption edge.
Aim
Develop a detailed understanding of the underlying reaction mechanism for the pyrolysis of solid plastic waste by means of kinetic Monte Carlo modelling using plastic waste model compounds. Validate simulated model results through experimentation.

Justification
Polymers are so widespread all around the globe mainly because of their superior properties such as lightweight, durability, low cost, and ease of production. For more than 50 years, global production of plastics has continued to rise steadily and nowadays nearly 8% of the petroleum consumed worldwide is being used for the production of plastics and to power plastic manufacturing processes. It should be critically noted that the amount of solid plastic waste (SPW) being generated goes hand in hand with the escalation of the production and utilization of plastics. The global SPW production has steadily increased over the years to reach a value of 150 million tonnes per year as reported in 2017. Chemical recycling technologies, which can convert the SPW into alternative fuels or useful chemicals, are recently getting increasing attention in the scientific community. Pyrolysis is one of the simpler and cheaper thermochemical routes to process the SPW in the absence of a catalyst. To design and optimize a suitable reactor for the chemical recycling of the SPW, it is important to understand the intrinsic chemical reaction network of the fast pyrolysis process. Given the inhomogeneity of the SPW together with the complex product distributions, experimental and theoretical studies are generally performed starting with model compounds, such as long chain linear alkanes which can imitate linear polyethylene behavior. Fast pyrolysis of plastics proceeds through a free radical mechanism, which comprises of hundreds of different chemical compounds involved in thousands of distinct chemical reactions. A single-event microkinetic (SEMK) model will help obtaining a detailed description of these radical reactions and the corresponding overall product distributions.

The micro-pyrolyzer setup at the LCT has been designed to study the intrinsic kinetics of plastic materials. The GC x GC and the customized RGA coupled with the micro-pyrolyzer reactor allow a detailed analysis of the pyrolysis product spectrum. Moreover, the TOF-MS with “select eV” feature enhances the molecular ion ratios, and thereby, provides accurate identification of the heavy hydrocarbons in the product stream.

Program
- Detailed literature study on pyrolysis of solid plastic waste (SPW) as well as pure polymer feedstock such as PE, PS, and PP. Comprehensive understanding of the different experimental and modeling approaches for the fast pyrolysis of model plastic compounds.
- Experimental study of the pyrolysis of several plastic waste model compounds, using the tandem micro-pyrolyzer setup, to obtain detailed information on the product distribution and underlying reaction kinetics.
- Apply and extend the currently available in-house kinetic models to accurately simulate the experimental data. Special emphasis will be given on the reactor modeling aspect together with the competition between volatilization and degradation. Produced models will provide insights on the operating parameters for the scale-up of the pyrolysis process.
Fast Pyrolysis of Polyolefins in the Gas-Solid Vortex Reactor.

Aim.
Obtain pyrolysis oil from particulate polyolefins in the reactive Gas-Solid Vortex Reactor demonstration unit and carry out its elemental and compositional characterization.

Justification.
Polyolefin are considered as one of the key feedstocks to advance the circular economy by increasing their recycling. Mechanical recycling combines sophisticated high-end sorting systems together with in-depth remotion of contaminants like pigments, colorants and products leftovers. The significant fraction of plastic waste that cannot be recycled mechanically is a potential feedstock for chemical recycling. Several reactor technologies have been proposed to carry out plastic pyrolysis: continuous stirred tank, rotary kiln, auger, static fluidized bed, circulating fluidized bed and spouted bed reactors. These reactor technologies are hindered by limited interfacial heat transfer, presence of hot spots inside the reactor and slow removal of pyrolysis vapors from the reaction zone. The focus here is on the Gas-Solid Vortex Reactor (GSVR), a novel reactor technology that can potentially overcome those issues. In the GSVR a dense and uniform bed of particles is generated in a centrifugal field, which allows to sustain significantly larger gas-solid slip velocities and to gain temperature control. In the GSVR unit shown in Figure 1 gas is injected at high velocity via tangentially oriented inlet slots in a cylindrical chamber in which polyolefin pellets are continuously fed. Momentum transfers from the gas to the pellets, causing the latter to rotate, thus generating a large radially outward centrifugal force which opposes the radially inward gas-solid drag force.

A GSVR demonstration unit has been designed, constructed and tested at cold flow conditions at the Laboratory for Chemical Technology (LCT). A broad range of operation conditions in the GSVR can be evaluated. Particulate flow experiments revealed that the designed GSVR achieves a sufficiently high centrifugal-to-drag force ratio sustaining a rotating fluidized bed within a broad range of operation conditions and shows great potential for plastic pyrolysis.

Program.
- Survey literature on lumped kinetic models for the thermal pyrolysis of polyolefins (PE, PS, ...)
- Select the feasible ranges of mass flow rate and inlet temperature of carrier gas based on mass and energy balances
- Perform pyrolysis experiments in the GSVR demonstration unit with a polyolefin mass flow rate of 0.3 g s⁻¹
- Characterize the obtained pyrolysis oil by means of elemental and comprehensive two-dimensional gas chromatography analysis.
Pt-based propane dehydrogenation catalysts: effect of In promotion, support and synthesis route.

Aim
This thesis aims at analysing the influence of three factors upon the performance of a Pt propane dehydrogenation (PDH) catalyst: the addition of In as a promoter element, the effect of the support material and the synthesis method. This can be achieved by in situ monitoring the bimetallic catalyst with characterization techniques, through which understanding of the synergy between the two elements and the support will be acquired. The latter can lead to better design of industrial catalysts.

Justification
Due to the importance of alkenes in the chemical industry, the catalytic dehydrogenation of alkanes into pure alkenes has been studied extensively. Supported Pt nanoparticles seem to be very appropriate as catalyst. Their stability, activity and selectivity can be improved by adding In as a promoter, to form bimetallic Pt-In particles. The promotor in a bimetallic Pt cluster significantly influences the catalytic behaviour. Parameters such as atomic concentration and process temperature have a strong effect on the detailed structure of the nanocluster and as such, on the functioning of the catalyst. The support on the other hand can influence the activity and selectivity in a reaction based on its inherent properties (acidity, porosity, surface area, etc).

Pt-In catalysts can be prepared by wet chemical impregnation on a series of supports, like SiO₂, MgO, Al₂O₃, MgAl₂O₄, which can then be tested to study the support influence on the bimetallic performance. This can be compared with results from similar tests for samples prepared by a physical vapour synthesis, Atomic Layer Deposition (ALD), to assess the effect of both preparation methods on performance.

The interplay between the active element, promotor element and the support will be examined by means of characterization techniques (Figure 1, 2) and catalyst testing in reaction (Figure 3). The first will yield a physical description of the bimetallic catalyst in different conditions. The latter will elucidate the influence of promotor and support upon the catalytic behaviour.

Program
- Literature study on Pt-In catalysts and propane dehydrogenation.
- Synthesis of several supported PtₓInᵧ bimetallic particles.
- Sample characterization including, (S)TEM, TPR, TPD, TPO, NH₃-TPD, in situ XRD and DRIFTS measurements, to obtain the physicochemical characteristics of the catalysts.
- Reaction testing of the prepared catalysts in propane dehydrogenation (PDH).
- Time permitting: activity and carbon control by CO₂-assisted PDH.

Figure 1: (left) In situ XRD patterns during H₂-TPR of Pt-In₂O₃/SiO₂ with varying Pt/In ratio. (right) 2θ XRD scans.

Figure 2: HAADF-STEM image of a Pt-In/Mg(Pt)(In)(Al)Oₓ grain and corresponding EDX elemental maps.

Figure 3: performance of Pt-In/Mg(In)(Al)Oₓ in terms of space time yields. Inset: STEM image of Pt-In particle.
Design and Synthesis of Catalysts for CO₂ Hydrogenation to Methanol

Aim
The aim of this thesis is to design and synthesize new highly selective heterogeneous catalysts for methanol synthesis active at milder reaction conditions as well as benchmark the activity of the commercial Cu-Zn catalysts. This project is part of a wide Flemish effort towards the design of an integrated CO₂ to Methanol prototype and involves collaboration from researchers from KULeuven, VITO and VUB as well as 14 different companies.

Justification
The discovery of efficient technologies that enable the use of carbon dioxide as a starting material for chemical synthesis is one of the biggest scientific challenges of our time. Carbon dioxide capture and utilization (CCU) has the potential to reshape the European Chemical Industry, and as such, has been recognized by the European Chemical Industry Council and by the European Union as one of the top research priorities of the EU to reach its 2050 climate objectives in a cost-effective way.

There are several challenges and opportunities in the design of new catalysts for CO₂ reduction. The first one is controlling the selectivity to Methanol. Given the large number of intermediates and the different reaction pathways (See Figure 1), selectivity control requires an in-depth understanding of the reaction mechanism and nature of the active sites. Although the detailed mechanism for this reaction is highly controversial,[73-74] four overall reactions have been identified for the hydrogenation of CO₂: methanol synthesis, reverse water gas-shift, Sabatier reaction and formic acid synthesis. Due to the highly exothermic and exergonic nature of the Sabatier reaction, and the endothermic and endergonic nature of the water gas-shift reaction, the biggest challenge when designing new methanol-synthesis catalyst is achieving the right combination of productivity and selectivity by creating a catalyst active at mild temperature that does not catalyse the Sabatier or the water gas shift reaction.

Program
1. Literature survey on the hydrogenation of CO₂ the methanol using heterogeneous catalysts.
2. Benchmark the catalytic activity of the commercial Cu-Zn catalysts.
4. Screening of reaction conditions using the high-throughput setup.
Relating sol-gel synthesis to flow behaviour

Aim
The understanding of the flowability of sol-gel synthesis in view of applications such as electrospinning.

Justification
Ceramic materials are known for their high chemical and thermal stability, as well as their good corrosion resistance and excellent mechanical properties of a bulk material in compression. One way to produce them is by using the sol-gel technique. A sol-gel process is a wet chemical technique used in the production of solid glasses and ceramics starting from small molecules, especially metal oxides of silicon and titanium. With this process, a very diverse range of materials can be obtained, such as dense ceramic fibres, uniform particles, aerogels and dense films.

One always starts from a solution, often referred to as a sol, which acts as a precursor to form an integrated network, or gel. This gel-like system can be seen as a system consisting of two phases, a liquid part and a solid part, which are both evolving over time from a colloidal suspension of very small particles (1-1000 nm) to a polymer-like network.

A challenge remains to understand how the chemical synthesis conditions influence the processability and thus flowability of sol-gel solutions. Limited focus has however been put on this task from a rheological point of view, explaining the current Master thesis.

Program
1. Performing a literature study on sol-gel synthesis parameters.
2. Experimental work to enable a broad set of sol-gel structures in view of further application.
3. Rheological analysis of the structures synthesized in 2., considering also model developments in a first instance using the method of moments.
4. Relating the insights in 3. to the actual manufacturing of sol-gel based membranes at the Centre for Textile Science and Engineering.

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Supervisors
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prof. dr. ir. Karen De Clerck

Funding
-
Big Data Meets Chemistry – Neural Network Based Property Estimation

Aim
The aim of this master thesis is to develop models for the prediction of various thermodynamic and physical properties such as enthalpies and entropies of formation, and solvation energies. These models can then be used in kinetic model generators to predict reaction rate parameters such as activation energies and pre-exponential factors. Depending on the used data, the model could also be used to predict yields and product concentrations in a retrosynthesis tool. Development of these models will require the generation and/or extraction from literature of data for a large number of organic molecules.

Justification
Detailed kinetic models are essential in the development and optimization of various chemical processes. Currently, kinetic model generation tools such as Genesys [1, 2] and RMG [3, 4] rely on group additivity [5] and libraries to estimate reaction rate coefficients for the various encountered reactions. While this has proven to be an efficient and fairly accurate estimation method, there are still several drawbacks. One is the necessity of a reference reaction for each set of group additive values. This increases the complexity of the group additive database and requires some basic user experience when generating the input. Another issue is that of data consistency. When using group additivity it is important that all the used data has similar sources or has been calculated at the same level of theory. Hence the obtained values depend on the data source. These problems can be circumvented by using a less strict estimation approach. Neural networks can handle data from various sources. Moreover, assuming that no single source is 100% accurate, having several data points for one reaction can even improve the overall prediction accuracy of the network. With vast amounts of available reaction data – both experimental and ab initio – it is possible to train a well-designed neural network to learn certain phenomena and their contributions towards the kinetics of a reaction. Examples are ring strain corrections and non-nearest neighbour effects. In the group additivity approach, additional correction factors have to be determined to account for these effects. These often require additional efforts and are not always easily generalized. Using a neural network for the estimation of kinetic parameters fits in the context of developing a self-learning kinetics estimator.

Program
- Literature survey on existing Artificial Intelligence-based methods for property prediction
- Generation of clean datasets of thermo-physical properties of a wide range of organic molecules.
- Potentially supplement (literature) data with ab-initio (or other) calculated values.
- Draw up the architecture for and training of an artificial neural network for the prediction of thermo-physical properties.

Tri-reforming of hydrocarbon mixtures for the production of syngas

Aim
Tri-reforming of a hydrocarbons mixture utilizing CO₂, H₂O and O₂ is an emerging technique for the production of synthesis gas and CO₂ abatement. Nevertheless, formulation and design of a low-cost, active and stable catalyst is a major challenge due to the complex reaction network and rapid catalyst deactivation. The goal of this work is to establish the optimum conditions and optimum catalyst (Ni supported on perovskite) for the tri-reforming process.

Justification
Syngas (CO+H₂) plays an important role as an intermediate in the production of several industrial products, such as Fischer–Tropsch liquids, methanol and ammonia. Currently, syngas is produced from fossil fuels, mainly coal, natural gas and naphtha. Syngas from renewable resources, such as biomass, exhibits a promising perspective, because it is a CO₂ neutral resource, which is distributed extensively in the world. However, after the biomass gasification process, next to CO and H₂ there is a mixture of unreformed hydrocarbons (CH₄ + C₂H₄ + ...) + (tar), which still contains 50% of the product energy potential. The most critical challenge is to reform these hydrocarbons to syngas. Steam reforming is one of the main technologies for hydrocarbon conversion to syngas. The endothermic reaction between CₓHᵧ and H₂O typically proceeds over a nickel-based catalyst at high temperature. Although nickel catalysts are effective for steam reforming of hydrocarbons mixtures, improvement is needed in terms of activity, stability, suppression of coke deposition, and regeneration.

The tri-reforming process is a synergetic combination of steam reforming, CO₂ reforming (carbon dioxide from power plants, ...), and partial oxidation of hydrocarbons in a single reactor for more efficient production of syngas. The process has several potential advantages compared to steam and dry reforming: high hydrocarbon conversion can be achieved, CO₂ is utilized, the desired ratio H₂/CO can be controlled, and coke formation minimized. The main challenges in bringing this reforming technology to practice rest in novel catalysts development and the understanding of the reaction mechanisms for kinetic modeling and process optimization. How can this be tackled?

In recent studies, perovskite-type oxides have been used as catalyst precursor and support for tri-reforming. The general formula of perovskite is ABO₃, where the A site contains rare or alkaline earth metals, while the B site holds 3d transition metals. Moreover, perovskites allow easy modification of its oxidation states, oxygen mobility within the lattice, oxygen vacancies, and redox properties by partial substitution at the A or B sites, thereby improving catalytic activity, stability and suppressing carbon formation.

Program
- Energetic and exergetic analyses will be applied to the tri-reforming process in order to assess the suitability of this reaction for the production of syngas with a desired H₂/CO molar ratio for the Fischer–Tropsch process and methanol production;
- Synthesis of perovskite materials (LaCeO₃, LaFeO₃, FeCeO₃, LaNi₀.₈Fe₀.₂O₃, La₀.₉Ca₀.₁Ni₀.₅Fe₀.₅O₃, La₃-xCeₓNi₀.₅Fe₀.₅O₃);
- Catalyst characterization by BET, H₂-TPR, O₂-TPO, CO₂-TPO, TEM, XRD, in situ XRD;
- Evaluation of the effect of the perovskite type and role (precursor vs. support) on the Ni catalyst’s performance in the tri-reforming of a hydrocarbons mixture.
Impact of the spatial distribution of active material on the performance of n-hexane hydrocracking with a bifunctional catalyst

Aim
To study the influence of the spatial arrangement of catalyst particles and the distribution of active sites on the catalytic performance of the hydrocracking of n-hexane over a bifunctional catalyst with metal and acid sites. Transient and steady-state experiments with the Temporal Analysis of Products (TAP) reactor system will give the necessary understanding of the role that the active material distribution plays in catalyst activity and performance. Furthermore, experimental data can also give detailed information regarding the reaction mechanism for modelling purposes and can serve as a basis for introducing the distribution of active material as a design factor in catalyst optimization.

Justification
The chemical industry faces the challenge of satisfying the production demand for a steadily increasing world population while minimizing the overall environmental impact. Due to the prominent role of catalysis in the industry, an improvement of catalytic technologies would enable the use of alternative feedstocks, reduce unwanted byproducts or increase overall efficiency. A possibility for improvement lies within the optimized design of catalysts for achieving optimal activity and selectivity.

The spatial distribution of active material is a factor that strongly affects performance and thus, it can be considered in the design of a tailored catalyst. An optimal active material distribution can be advantageous for increasing the conversion and selectivity, or smoothing temperature gradients. Understanding the role of active material distribution could be beneficial in the design of optimized catalysts.

Program
- Literature review on hydrocarbon hydrocracking with bifunctional catalysts.
- Steady-state experiments with various catalyst samples under different flow, temperature and pressure conditions.
- Transient pulse experiments with different degrees of catalyst dilution and particle placement inside a tubular reactor.
- Transient pulse experiments with bifunctional catalyst samples containing different distributions of active sites.
Solar thermochemical splitting of H₂O and/or CO₂ to generate H₂ and/or CO

Aim
Solar thermochemical water splitting to generate hydrogen is emerging as a viable alternative to solar photochemical splitting. The kinetics of H₂O/CO₂ splitting are largely controlled by the inherent redox properties of the oxygen storage materials used. The objective of this thesis is to study the effect of dopants on the thermal reducibility, H₂O/CO₂ oxidation and stability of a perovskite storage material.

Justification
In the following decades, direct solar energy conversion is likely to gain increasing global importance. Such a process makes use of solar heat as energy source to break or form chemical bonds using a solid metal oxide as intermediate oxygen carrier material. Recently, researchers have developed a novel material for which thermal reduction occurs as low as 1200K. After reduction, the oxygen carrier can be regenerated by extracting oxygen from CO₂ or H₂O with production of CO or H₂. An important advantage is that solar heat can be generated by the whole spectrum of solar radiation, as opposed to solar electricity which uses only specific spectral regions. Hence, the production of H₂ or CO₂ via solar heat has the potential of being far more efficient than photoelectrical H₂ or CO production.

The high operating temperature, however, poses several challenges: (i) In terms of equipment cost and design, solar heating can be very demanding. (ii) Solid oxygen carrier materials may lose specific surface area due to sintering at high temperature. The design of materials which can be thermally reduced at temperatures below 1200K would therefore be an immense step forward towards commercialization of a direct solar energy conversion process for H₂ or CO production.

The above thermochemical process proceeds in two steps: 1) oxide dissociation using solar heat with oxygen release and 2) reoxidation/regeneration using H₂O/CO₂. Stoichiometric oxides can be used, yielding redox pairs such as e.g. ZnO/Zn, SnO/SnO₂, In₂O₃/In, and Fe₂O₃/FeO, but these suffer from low melting points and hence severe sintering and/or volatility. Among nonstoichiometric materials, CeO₂₆/₇CeO₂ is the standard. However, even when modified with metal ions, drawbacks of CeO₂-based oxides are the poor reducibility even at 1700K as well as sublimation of the oxides at high temperatures.

In search of alternative materials to ceria for the solar thermochemical process, recent attention went to perovskite-type oxides, driven by their proven thermodynamic and structural tunability and their reducibility under less extreme conditions. In perovskite oxides of the type Lnₓ₁.AₓMnO₃(LnAM₃), substitution of the trivalent Ln³⁺ by the divalent A²⁺ creates Mn³⁺/Mn⁴⁺ redox active pairs, which can assist in H₂O and CO₂ splitting.

Program
- Literature survey: (i) Thermochemical redox processes and redox behavior of metal oxides and perovskites, (ii) process kinetics
- Design of an oxygen carrier for thermal reduction (La₁₋ₓSrₓMnO₃, Y₁₋ₓSrₓMnO₃, Y₁₋ₓCaₓMnO₃, …)
- Characterization of the prepared materials by SEM, STEM-EDX, TPR, (in situ) XRD, TGA, …
- Activity and stability performance tests of the materials
- Kinetic study of the thermal reduction process and modelling of solid-gas reactions.
Reactor design for a gas-solid reaction to produce $\text{H}_2$

### Aim
Develop a **large-scale reactor** model for the **gas-solid iron looping** process to **produce $\text{H}_2$**

### Justification

A **hydrogen economy**

A hydrogen economy\(^1\) foreseen in the early 1970s with its bright prospects is fast becoming a reality (schematic displayed in ). Infrastructure for supply and storage of hydrogen is being setup in advanced economies like Japan, EU, and USA.

One promising means of producing $\text{H}_2$ from $\text{H}_2\text{O}$ is **chemical looping**, a two-steps process, with abundantly available iron oxide. Chemical looping offers not only the production of a high purity $\text{H}_2$ stream\(^2\) (ppm level impurities), but also the advantage of inherent separation of $\text{CO}_2$, a greenhouse gas. Applying this process, a gas stream with an atypical composition (for example, off gas streams from pyrolysis, gasification, or metallurgical industry) can be used for production of $\text{H}_2$ while simultaneously separating the $\text{CO}_2$ and other impurities (a schematic is displayed in Figure 2). Chemical looping as a means to produce high purity $\text{H}_2$ had been first developed on an industrial scale more than a century ago\(^3\) but modern reactors may prove to be more efficient for the envisioned approach mentioned herein.

### Program

- Literature review to select an appropriate reactor type and acquire reliable kinetic data.
- Development of a readable detailed reactor model (dimensions, heat/mass/momentum transfer, pressure drop, etc.) using Python/MATLAB (or any other programming language) for the selected reactor type and optimisation of the process conditions (temperature, pressure, gas composition, etc.).
- Economic assessment of the detailed reactor type with possible simulation of an industrial scenario on Aspen Plus.

The ideal candidate should have a strong interest in reactor design, process economics, and development of his/her programming skills.

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**Figure 1.** A schematic showing the move towards an $\text{H}_2$-based sustainable society

**Figure 2.** Iron looping for $\text{H}_2$ production with inherent $\text{CO}_2$ and impurities separation
Reactor design for a gas-solid reaction to capture CO₂

Aim
Develop a large-scale reactor model for the gas-solid calcium looping process to capture and separate CO₂ from an industrial gas stream.

Justification
Reducing CO₂ emissions is one of the main targets of the European Union for the transition from our current energy system to a neutral carbon energy system. To prevent releasing this greenhouse gas to the atmosphere, it is required to develop techniques focused in carbon capture, storage and utilization.

Currently, mature technologies for CO₂ capture include amine scrubbing, pressure swing adsorption (PSA) and membrane-based separation. Amine scrubbing provides a stream with high CO₂ purity, however the cost of the solvent is around ~$1000/ton¹, giving rise to high operational expenses. Membrane-based separation provides a more economic and practical technology but its selectivity towards CO₂ is not exceptionally high and in some cases secondary separation methods are required for higher CO₂ purity². The use of Calcium-based sorbents in a 2-steps looping process (schematics in Figure 2 below) provides an economic and efficient option for CO₂ separation; these materials have demonstrated to be highly reactive to CO₂ and, since the cost of limestone is ~$15/ton and the spent sorbent can be recycled back to the cement industry, it provides an alternative to costly separation processes. This technology has been demonstrated for post-combustion gases using fluidized bed reactors on a pilot scale³. It is, thus, of interest to find further opportunities for its application to pre-combustion gases and to evaluate the performance of potential reactor types through reactor modelling.

Program
- Literature review to select an appropriate reactor type and acquire reliable kinetic data.
- Development of a readable detailed reactor model using Python/MATLAB (or any other programming language) for the selected reactor type and optimisation of the process conditions.
- Economic assessment of the detailed reactor type with possible simulation of an industrial scenario on Aspen Plus.

The ideal candidate should have a strong interest in reactor design, process economics, and development of his/her programming skills.

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Proton-mediated energy storage

Aim
Energy is one of the most important topics in the 21st century as it is the foundation of today’s society. Novel renewable and clean energy sources can substitute fossil fuels to enable sustainable development. In this project, a proton-conducting material will be investigated as the supporting phase for an iron-based material as energy storage medium for solid-oxide metal–air redox batteries.

Justification
Energy can be stored in different forms: as mechanical energy; in an electric or magnetic field; as chemical energy of reactants and fuels. Today, energy storage becomes more complex and important, and high-performance energy storage techniques are required to enable efficient, versatile and environmentally friendly use of energy, including electricity. The metal–air battery is one such advanced energy storage and conversion technology. It converts the chemical energy in lithium (anode) and oxygen (cathode) into electric energy during discharge, and stores electric energy by splitting Li–O2 discharge products during charging using electricity (like an electrolysis device or a reversible fuel cell to generate hydrogen and oxygen by splitting water).

Recently, a combination of a regenerative solid oxide fuel cell (SOFC) and a chemical looping redox cycle was demonstrated as novel type of metal–air battery. Herein, the solid oxide electrochemical cell serves as the “electrical functioning unit”, switching between fuel cell and electrolyzer modes to realize the discharge/charge cycles. On the other hand, the redox cycle unit acts as the “energy storage system” to carry out reversible chemical–electrical energy conversion via H2/O2-mediated metal/metal oxide (Me/MeOx) redox reactions. In this way, chemical energy is stored in redox couples that are physically separated from the electrodes of the solid oxide electrochemical cell. A key component to the performance of such solid oxide metal–air redox battery is the energy storage medium. In the present project, Fe supported on proton-containing ceramics will be investigated as a hydrogen storage material (see Figure).

![Figure: Schematic illustration of energy storage in the proton-mediated Fe redox reaction.](image)

**Figure:** Schematic illustration of energy storage in the proton-mediated Fe redox reaction.

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<tr>
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<td>Hilde Poelman</td>
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Program
- Literature survey: Thermochemical redox processes and redox behavior of metal oxides and proton-conducting perovskites;
- Synthesis of proton-conducting perovskites (BaCeO3, BaZrO3, BaCeZrDyO3...) and supported FeOx materials;
- Characterization of the prepared materials by SEM, STEM-EDX, TPR, (in situ) XRD, TGA, …;
- Proton conductivity tests;
- Activity and stability performance tests of the materials;
- Test in a SOFC.
Selective oxidation of bio-methane to formaldehyde: core-shell catalyst approach

Aim
The selective oxidation of methane to formaldehyde, which avoids the production of carbon dioxide by full oxidation and is therefore important for the versatile utilization of methane, is still viewed as challenging. Here, we utilize catalyst synthesis followed by atomic layer deposition (ALD) and nanocoating to prepare an efficient and thermally stable catalyst based on SiO$_2$@V$_2$O$_5$@Al$_2$O$_3$ core@shell nanostructures.

Justification
Methane, the main component of biogas, is mostly used for heating and electricity generation. Recent progress in bio-methane technology presents a further stimulus for converting abundant methane to more valuable chemical feedstocks and thus reducing dependence on petroleum resources. Nevertheless, the four strong C-H bonds of methane (bond energy = 413 kJ/mol) present a serious obstacle to its chemical conversion. At elevated temperatures, methane can be catalytically converted to syngas, which can be used as a feedstock for the catalytic production of added-value hydrocarbons or alcohols. Although a number of indirect processes for the oxidative conversion of methane to formaldehyde (HCHO), methanol (CH$_3$OH), and ethylene (C$_2$H$_4$) have been developed and applied industrially, direct conversion of methane by partial oxidation is still challenging because of the above mentioned high C-H bond energy and the need to avoid carbon dioxide release as a greenhouse gas.

V$_2$O$_5$/SiO$_2$ was identified as a good catalyst for methane partial oxidation, achieving methane to HCHO conversion and selectivity of 10 and 65%, respectively, at 600°C. The thermal stability of the catalytically active surface species can be increased by protection/encapsulation with an oxide. In well-designed core@shell-type catalysts, highly disperse active species in the core can be protected against deactivation caused by sintering or coking during high-temperature reactions.

Atomic layer deposition (ALD) or nanocoating are considered attractive growth techniques for homogeneous encapsulation of active species, e.g. by Al$_2$O$_3$, allowing the surface of core species to be uniformly coated with layers of controlled thickness at an atomic scale. Here, we will design highly disperse V$_2$O$_5$ nanocatalysts supported on SiO$_2$ spheres with Al$_2$O$_3$ overcoating for the direct oxidation of methane to HCHO.

Program
Transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), in situ X-ray diffraction (XRD), Raman spectroscopy, H$_2$ temperature programmed reduction (H$_2$ TPR), and diffuse reflectance UV–vis spectroscopy analyses will be used to determine the mechanism of core vanadium species preservation at high temperature and the type of core@shell structure capable of achieving maximal methane-to-HCHO conversion without undergoing deactivation. New catalysts will be compared with conventional mesoporous silica supported V$_2$O$_5$, prepared by impregnation. The effect of the presence of CO$_2$ as well as using CO$_2$ as soft oxidant will be investigated.
Effect of feedstock on propylene yield in alcohol-to-olefins conversion

Aim
Understanding the effect of feedstock on the reaction mechanism in alcohol-to-olefin conversion processes.

Justification
Among the commercially relevant olefins, the global propylene demand has increased most significantly. One of the alternative processes to conventional naphtha steam cracking entails methanol transformation into olefins over a heterogeneous catalyst. Higher alcohols, often produced from bio-based sustainable feedstock, can also be converted into olefins. Typically, a zeolite catalyst with high porosity, such as H-ZSM-5, transforms methanol into light olefins and hydrocarbons with a wide range of applications as depicted in Figure 1 [1]. Further research remains of interest for methanol, to give guidelines for increasing propylene yield. For the higher alcohols, an academic interest exists as limited research has been conducted and no consensus regarding the reaction mechanism has been reached yet [2].

Over the last decades, many different reaction mechanisms for methanol-to-olefins conversion have been proposed [3]. Currently, the dual cycle mechanism involving aromatics and alkenes is getting widely accepted for methanol-to-olefins. The balance between the alkene and the aromatic cycle will determine the product distribution and the propylene yield and varies as a function of operating conditions. For the higher alcohols, ethanol and butanol, a higher importance of the alkene cycle is expected. By comparing activity, selectivity and catalyst deactivation, elucidation of the relation between alcohol feedstock and the reaction mechanism is aimed at. This insight will allow the construction of guidelines to increase the propylene yield.

Program
For elucidation of the reaction mechanism, intrinsic kinetic data will be acquired. At the start of this work, intrinsic kinetic data will have been gathered for methanol-to-olefins on H-ZSM-5. In this work, kinetic data will be acquired for ethanol and butanol to be compared to methanol conversion over the catalyst H-ZSM-5. A first goal is the proper selection of experimental conditions (temperature, pressure and space time) required to assess their impact. This selection is based on a literature research on the reaction mechanism. The catalytic testing of the feedstock over H-ZSM-5 will consequently be performed on the high-throughput mechanistic investigation set-up to give insights into the mechanism.

Gas radiative properties model development for oxy-fuel combustion

Aim
Developing flue gas radiative properties model for H₂O-CO₂ mixtures of the composition characteristics under for oxy-fuel combustion.

Justification
A main challenge for ethylene industry is the upcoming stronger environmental regulations relating to NOx emission in steam cracking furnaces. As the conventional flame burners almost reached their limits in NOx reduction, more attentions have been paid to alternative combustion technologies such as oxy-fuel combustion, which has a clear advantage because of no nitrogen present in the process (apart from leakages), therefore almost no NOx is produced. In addition, the produced flue gas of oxy-fuel combustion is a highly concentrated CO₂ stream that can be more easily captured, stored or used for other applications\(^1\).

Oxy-fuel combustion is characterized by a higher adiabatic flame temperature and faster burning velocity. Flue gas recirculation is often adopted to control the furnace temperature and achieve a similar radiative heat flux profile as the conventional air combustion. This allows the technology to be successfully applied without major modifications. To study the effect of oxy-fuel combustion on steam cracking furnace and determine the amount of gas recirculation, the radiative properties of the H₂O and CO₂ enriched flue gas should be properly accounted for. However, most of the previously established gas radiative properties models are corresponding to air-fired combustion scenario and can lead to inaccuracy\(^2\). Therefore it is necessary to develop a radiative properties model for H₂O-CO₂ mixtures of the composition characteristics under for oxy-fuel combustion.

Program
- Selecting the most important absorption bands of H₂O and CO₂ for the oxy-fuel combustion scenario based on the available HITEMP 2010 spectral emissivity database.
- Obtain total emissivities of the flue gas at different compositions which are typically encountered in oxy-fuel combustion using either line by line (LBL) or statistical narrow band (SNB) calculation.
- Develop a weighted sum of gray gas model (WSGGM) based radiative properties model using the total emissivities calculated in the previous step.
- Validation of the model against the benchmark solutions for some oxy-fired conditions.

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Genesys: Automatic generation of kinetic models for hetero-atomic compounds

Aim
The aim of this master thesis is to develop ab initio kinetic models for the pyrolysis of hetero-atomic (nitrogen, oxygen and sulphur) containing compounds via newly calculated group additive values.

Justification
In the European chemical industry, there is a strong drive to shift to renewable and alternative feedstocks in the pursuit of sustainability and increased profitability. These feeds entail a wide variety of hetero-atomic species, which have a different chemical behavior compared to hydrocarbon molecules. As these compounds can negatively influence the process, operability and quality of the products streams, having a mathematical model able to describe their influence is essential for the future development and integration of renewable and alternative process streams.

Accurate chemical kinetic models are extremely powerful and valuable. Many significant public policy and business decisions are and have been made on the basis of predictions using detailed kinetic models. However, for most technologically important systems constructing a reliable and sizable kinetic model remains to be very difficult and time consuming. Recent advancements in chemistry and informatics have enabled a new kinetic modelling approach of tracking each molecule and intermediate throughout the reaction process using fundamental kinetics information. Several tools have been developed to automatically build large kinetic models, such as the in-house developed automatic network generator Genesys. When constructing such large reaction networks, the availability of accurate thermodynamic data for all species and rate coefficients for all possible reactions is a prerequisite. For hetero-atomic compounds, lack of this type of information is in most cases the limiting factor of these network generation tools. A systematic approach to address this problem of data scarcity consists of the development of group additivity models based on high-level computational methods.

Program
- Evaluating the existing group additivity values from literature and collaborators in Genesys.
- Determining new thermodynamic and kinetic group additivity values from ab initio calculations and implementing them in Genesys.
- Building kinetic models for the pyrolysis of hetero-atomic species and validating them to experimental data.
Coke formation simulation during steam cracking

Aim
Understanding coke formation mechanism and constructing semi-empirical kinetic model to simulate the coke deposition during steam cracking process.

Justification
Steam cracking as the major olefin product process is discovered to further improve its performance, especially the coke deposition during this process. Coke formation has a deleterious influence on the energy efficiency and economic viability of steam cracking process. The low coke layer thermal conductivity leading to a higher coil surface temperature to maintain the feed conversion. Simultaneously, the cross area starts to decrease, leading to a higher pressure drop along the reactor coil. A higher feed inlet pressure is desired to satisfy the product specification. Once the coil surface temperature or inlet pressure exceeds the maximum material permissible value, the process has to be shut down to carry out the decoking process.

At present it is believed that carbon deposition occurs according to a combination of three main mechanisms, namely catalytic coke formation, free radical coke formation and condensation formation. Although extensive progress has been made in the fundamental modelling of the gas-phase chemistry, these existing models are not sufficient to simulate coke formation in different processes. Moreover, surface reaction mechanism is not well studied among these models. The only general coke formation model is constructed for ethane steam cracking process and the involved reactions are depicted:

Program
1. Literature survey:
   - Coke formation mechanisms and the corresponding kinetics simulation.
   - The influence of catalytic coke formation on the free radical coke formation.
   - Different coke deposition morphologies during the steam cracking process.
   - Surface reaction and gas-surface reaction mechanism.

2. Semi-empirical coke formation model construction based on existing experimental results, and the model will be validated through the experimental results from JSR and poilt setup.

3. Developing a general understanding of the Genesys code and Chemkin simulation.
Aim
The aim of this thesis is to understand the chemistry of the pyrolysis of small hydrocarbon and oxygenated compounds through combined theoretical calculations, kinetic modelling and experimental work.

Justification
In order to understand the pyrolysis of large hydrocarbon and oxygenated fuels for steam cracking, it is crucial to first have a detailed understanding of the pyrolysis kinetics of small and simple fuels. A study is done for the thermal decomposition of small hydrocarbons like methane, ethane, ethylene, acetylene, propane, propene, allene and propyne as well as for the formation of important aromatics like benzene, toluene and styrene starting from these fuels. To use these kinetics in the development of a kinetic model for the pyrolysis of oxygenated fuels, kinetics for small oxygenates need to be added. The knowledge of the thermal decomposition of oxygenates fuels is important when considering the steam cracking of bio-based feedstocks, but also during the steam cracking of fossil fuels oxygenated impurities are often present. The small oxygenates that will be considered are methanol, ethanol, butanol, formaldehyde, formic acid, methyl acetate, dimethyl ether, MTBE and cyclic ethers.

A kinetic model for small compounds can be constructed automatically with the use of Genesys. On-the-fly fast estimation techniques for thermodynamic properties and kinetic parameters, such as group additivity, often lead to bigger errors when used for smaller molecules. For this reason, some thermodynamic and kinetic parameters will be determined with quantum mechanical techniques automatically with Genesys. Literature based or in-house developed experimental data will be used to extensively validate the developed kinetic model.

Program
- Literature survey regarding experimental and modelling studies for the pyrolysis of selected model compounds.
- Pyrolysis experiments of model compounds on the bench scale set-up. Data collection under a broad set of experimental conditions in diluted and undiluted atmospheres.
- Automatic determination of thermodynamic properties and reaction rate coefficients with *ab initio* techniques implemented in Genesys.
- Generation of a kinetic model for the model compounds automatically with Genesys. Validation of the kinetic model with new or literature experimental datasets.
- Implementation of the developed kinetic models in the LCT base mechanism.
Continuous flow investigation of acid-catalyzed aldol condensations

Aim
Experimental investigation of zeolites as aldol condensation catalysts and assessment of the kinetic performance in the aldol condensation of furfural with acetone, furfural with cyclohexanone and/or the hydroxymethylation of cyclohexanone. Acquisition of a fundamental understanding of the reaction mechanism, potential deactivation effects, and catalyst property effects on the reaction rates of different types of aldol condensations via microkinetic modelling.

Justification
The aldol condensation is an important carbon-carbon coupling reaction, with applications in the pharmaceutical industry and fine chemicals production. By creating new carbon-carbon bonds, heavier and more complex molecules can be formed. As such, the reaction can play an important role in the valorisation of biomass-derived molecules, such as furfural, hydroxymethylfurfural and cyclohexanone.

Currently batch operation is the main industrial mode of operation for these types of reactions. However, the aldol condensation could benefit from the advantages offered by continuous flow. By an improved control over the reaction parameters, continuous flow operation can result in safer, more sustainable and more performant processes, especially in combination with heterogeneous catalysis. Moreover, continuous operation has also advantages at the laboratory scale, i.e., catalyst deactivation can be readily investigated by making use of a continuous flow set-up.

Zeolites are investigated as a heterogeneous alternative for the homogeneous base catalysts which are currently in use as aldol condensation catalysts. Preliminary experiments indicate the zeolite catalysts are active but suffer from deactivation and some competing side reactions are observed to occur. The development of a (micro)kinetic model, based on experimental data, and elaborate characterization of the catalysts will provide insight into the reaction behaviour and provide guidelines for further process, product and catalyst optimization.

Program
Different commercially available zeolites, e.g. zeolite Y, zeolite Beta, will be used in aldol condensation experiments under different conditions of temperature and feed composition. Different types of aldol condensations will be investigated, e.g. the cross-condensation of furfural with acetone, furfural with cyclohexanone and/or the hydroxymethylation of cyclohexanone. These experiments will be performed in both a batch-type reactor, as well as a continuous flow reactor. The gathered kinetic data will serve as a basis for a reaction model describing the kinetics. In order to get a better idea of the deactivation mechanisms, several characterisation techniques will be applied on the catalysts before and after reaction. Finally, a better understanding of the reaction behaviour will allow optimization and a better control over product selectivity and catalyst behaviour.
Aldol condensation experiments

Batch reactor

Continuous flow reactor

Kinetic modelling approach

Aldol condensation reactions

Cross-condensation of furfural with cyclohexanone

Hydroxymethylation of cyclohexanone

Cross-condensation of furfural with acetone

Zeolite catalysts
First principles prediction of transfer and secondary reactions kinetics in free radical polymerization of industrially viable monomers

Aim

Implementation of micro-kinetic modelling to obtain reliable kinetics of the occurrence of rare events and side reactions to assess the influence of the chemical structure on properties of the polymer.

Justification

Sophisticated macromolecular architectures that meet predefined end-use properties have a tremendous potential for a variety of high-tech applications and can, in principle, be synthesized using radical polymerization techniques that do not require industrially unattractive stringent oxygen or water free environments or highly purified reagents.

Full control of the detailed chemical structure of the individual macromolecules can only be accomplished within a very narrow window of process conditions since it requires that throughout the polymerization the rates of the various elementary reactions are carefully balanced which introduces the need for dynamic synthesis protocols that allow an instantaneous control of reactant concentrations and temperature.

To elucidate and quantify the effect of the molecular structure of the monomer on the chemistry and the reactions rates, cutting edge quantum chemical techniques can be used to assist in obtaining intrinsic rate coefficients as a complement to experiment and, hence, to contribute to an accelerated optimization of radical polymerization processes and design of functional polymer material.

Program

1) Computationally evaluate rate coefficients for possible rare events and side reactions during polymerization of potentially interesting styrene and vinyl monomers, focussing on vinyl monomers relevant for the synthesis of polymers with high-tech and biomedical applications.

2) Validation of the calculated rate coefficients in close collaboration with the ongoing experimental and model development work. Accurately model the kinetics by implementing the calculated rate coefficients in available micro-kinetic models to simulate conversion and (co)polymer microstructural characteristics.

3) An estimation of the improvement in prediction of polymer properties by knowing the kinetics well and inclusion of all relevant reactions.
A combined experimental and modeling study of plasma polymerization and decomposition

Aim
By combining experimental and modeling tools it is the aim to better characterize and design synthesis procedures for plasma polymerization and decomposition.

Justification
In plasma polymerization/decomposition, a monomer phase is inserted in a plasma discharge, giving rise to a complex interplay of fragmentation and chain growth reactions. A two-phase system is obtained with reactions in the gas phase and on the targeted substrate. The reaction product is a thin polymer layer that adheres under the correct conditions (e.g., power, flow rate, and pressure) to a suited substrate. Surface modification becomes therefore possible, allowing a wide range of high-tech applications (e.g., scaffolds for tissue engineering and ‘green’ coatings).

A key challenge remains a detailed characterization of the polymeric surface, with a different level of crosslinking density. Overall average properties such as the layer thickness and the surface atom composition are accessible, using for instance spectroscopic techniques. However, a detailed microstructural information is currently lacking as less focus has been put on the mapping of the kinetics as in conventional chemical/polymerization processes. A multidisciplinary research approach combining principles from chemical engineering and physics is thus recommendable.

Program
1. Literature study on diffusion of (macro)species in gas/liquid phase and on surfaces. The input is crucial to allow for a correct interpretation of the interaction of kinetics and transport phenomena in the two-phase reactive system (gas phase and substrate).
2. Experimental study (location: Technicum) on plasma-assisted deposition of acrylic acid on a polymer surface. In a first try, flat samples will be used to facilitate the analysis of coating properties such as thickness, chemical composition, homogeneity, etc.
3. Developing a computer code capable of describing and designing plasma polymerization/decomposition. Attention will be focused on deterministic and stochastic solvers. The code should be capable to operate both under conditions of low and high fragmentation rates.
4. Application of the computer code for supporting the identification of optimal experimental conditions.
Pulsed laser (co)polymerization to enhance industrial polymer synthesis

Aim

The determination of essential intrinsic rate coefficients for industrial radical (co)polymerization using pulsed laser polymerization experiments and simulations.

Justification

To optimize industrially applied radical polymerization processes and to develop new polymer materials kinetic modeling is indispensable. The success of kinetic modeling for these purposes depends largely on the accuracy of the intrinsic rate coefficients used. Since the joint estimation of these coefficients by multi-response regression to polymerization data is very demanding, an independent step-by-step determination is beneficial. Pulsed laser polymerization (PLP) (e.g. Marien et al., Macromolecules 2017, 50, 1371) is a very interesting well-accepted technique in the industrial community (e.g. Deglmann et al., Macromol. React. Eng. 2018, 12, 1800010), allowing to study individual reactivities. In PLP, photoinitiator radicals are generated at laser pulses with a frequency \( \nu \) (Figure 1; left). Depending on the PLP conditions and the monomer type, the molar mass distribution (Figure 1; right) can possess specific characteristics (e.g. repetitive inflection points), allowing the determination of intrinsic rate coefficients (e.g. Marien et al. Polymer Chemistry 2016, 7, 6521).

In this thesis, PLP is used for the determination of backbiting, \( \beta \)-scission and (cross)propagation rate coefficients that are essential to design industrial (co)polymerizations. Kinetic Monte Carlo (KMC) modeling is applied for the identification of optimal PLP conditions. Experimental data is obtained using the LCT PLP setup. (co)Monomers are selected in collaboration with industry.

Program

1. Performing a literature study on the available methods for the determination of individual rate coefficients in radical (co)polymerization.
2. An available computer code for the kinetic modeling of PLP is used to relate specific side reactions to characteristics of the PLP molar mass distribution as a function of the PLP conditions.
3. Extension of the available PLP computer code to penultimate copolymerization kinetics.
4. Experimental determination of intrinsic rate coefficients for industrial radical (co)polymerization processes using the LCT PLP setup.
## Unravelling lignin pyrolysis chemistry using phenolic model compounds

### Aim
To gain deeper insights into lignin pyrolysis chemistry through experimentation and kinetic modelling of fast pyrolysis of phenolic model compounds.

### Justification
Biomass fast pyrolysis is a route for generating alternative energy and fine chemicals such as levoglucosan, vanillin, catechol, resins and adhesives. Lignocellulosic biomass constitutes of cellulose (30-50 wt.%), hemicellulose (15-30 wt.%) and lignin (10-30 wt.%), and ash (5-10 wt.%) on a dry basis. Cellulose is a linear homopolymer of glucose, while hemicellulose is a branched heteropolymer made up of pentose and hexose sugars. Lignin, a complex polymeric structure made up of several oxygenated aromatic groups joined by ether linkages, constitutes about 10-30% of lignocellulosic biomass. Biomass fast pyrolysis, and thus lignin pyrolysis, involves a series of primary and secondary radical reactions, which lead to produce primary and secondary products. Moreover, in the kinetic models developed at present the conversion of solid biomass to gaseous products is not very well deciphered. The chemical transformations in the biomass structure during fast pyrolysis need to be investigated more thoroughly using model compounds.

An experimental and modeling study will help in better understanding the pyrolysis chemistry. The micro-pyrolyzer setup at LCT has been designed to understand the intrinsic kinetics of biomass and its model compounds. The GC x GC and customized RGA coupled with the micro-pyrolyzer reactor allow a detailed analysis of the pyrolysis product spectrum. Moreover, the TOF-MS with “select eV” feature enhances the molecular ion ratios, and thereby, provides accurate identification of the products.

### Program
- Literature study on experimental and modelling approaches for fast pyrolysis of lignin model compounds.
- Experimental study of the pyrolysis of mono and dimeric lignin model compounds, using the tandem micro-pyrolyzer setup to obtain information on the product distribution and reaction kinetics.
- Apply and extend the currently available kinetic models to simulate the experimental data. Thereby, provide insights on the operating parameters for scale-up of the pyrolysis process.
Design and Synthesis of Catalysts for CO₂ Hydrogenation to Formic Acid

Aim
The aim of this thesis is to design and synthesize new highly selective heterogeneous catalysts for formic acid synthesis. This project is part of a wide Flemish effort towards the development of technologies for the conversion of CO₂ to value-added chemicals using catalysis and renewable energy. To benchmark, compare and develop the various technologies, the formation of formic acid is selected as the initial target. This project involves collaboration with researchers from KULeuven, VITO and UAntwerp as well as 14 different companies.

Justification
The field of catalytic formic acid synthesis is heavily dominated by homogeneous catalysts, several noble metals including Ru, Rh, Ir and Pt have been identified as very active in this transformation. A few heterogeneous metal catalysts for the reduction of CO₂ to formic acid and formates have been reported in the literature. However, the catalytic efficiency of these catalysts is significantly lower when compared to state of the art homogeneous catalysts. Our efforts toward the development of heterogeneous catalysts will focus on the synthesis of layered double hydroxides (LDHs). LDHs are a class of anionic clays with brucitic sheets holding divalent and trivalent metallic cations situated in hydroxide octahedra. Due to the positive charge of the layers, hydrated anions are intercalated between them. Their general chemical formula is \( \text{M}^{\text{II}}_{\text{1-x}} \text{M}^{\text{III}}_{\text{x}}(\text{OH})_2(\text{A}^n^-)_{\text{xy}}\cdot \text{yH}_2\text{O} \), where \( \text{M}^{\text{II}} \) is a divalent metallic cation (Mg²⁺, Ca²⁺, Ni²⁺, ...), \( \text{M}^{\text{III}} \) a trivalent metallic cation (Al³⁺, Ga³⁺, Fe³⁺, ...), \( \text{A}^n^- \) an interlayer anion (CO₃²⁻, Cl⁻, NO₃⁻, ClO₄⁻, ...), and \( x \) the layer charge density ranges between 0.20 and 0.33 for most of the cationic couples.

Program
1. Literature survey on the hydrogenation of CO₂ the formic acid using heterogeneous catalysts.
2. Synthesis and characterization of new heterogeneous catalysts based on LDH
3. Screening of reaction conditions using the high-throughput setup.
Design of bimetallic catalysts for CO₂ hydrogenation

Aim
Investigation of various heterogeneous, bimetallic catalysts for the hydrogenation of CO₂ into methanol. Investigation of the kinetics of the most relevant elementary steps and determination of the kinetic role of both metal elements.

Justification
Carbon dioxide is one of the end products of combustion and its concentration in the atmosphere has reached unprecedented levels. A possible solution to the increasing CO₂ concentration is the recycling of carbon dioxide. One of the most promising technologies is the hydrogenation of CO₂ to methanol using renewable hydrogen. Methanol is a versatile platform molecule that can also be used as an alternative green fuel. The commonly applied catalyst for this reaction is Cu/ZnO/Al₂O₃. Palladium- and nickel-based alloys have emerged as promising low temperature catalysts for this reaction, but they have not been investigated extensively, therefore lacking optimization.

The existing dual site kinetic model for CO₂ hydrogenation on Cu/ZnO will be extensively evaluated, giving an in depth understanding in the mechanism on Cu/ZnO/Al₂O₃ and the role of the ZnO promoter. Detailed knowledge of the reaction mechanism allows insight in catalyst activity, selectivity and stability and will allow design and optimization of CO₂ hydrogenation catalysts. Subsequently, a microkinetic model will be constructed for CO₂ hydrogenation on Pd-based catalysts and compared to Cu/ZnO.

Program
The following activities will be performed during the master thesis:

- A literature review on the non-Cu-based bimetallic catalysts for CO₂ hydrogenation.
- Evaluation of the Cu/ZnO microkinetic model: identify what the role of the ZnO promoter is.
- Perform DFT calculations to complete the dataset for CO₂ hydrogenation on Pd-based catalysts.
- Construction of a microkinetic model for CO₂ hydrogenation on a Pd-based bimetallic catalyst.
Kinetic Monte Carlo modeling of amyloid beta peptide polymerization

Aim
LCT expertise in the field of polymer reaction engineering is applied to the polymerization of peptides leading to the formation of linearly growing fibrils. Peptide polymerization is important for a number of currently incurable diseases, such as Alzheimer’s disease (AD), where amyloid β (Aβ) peptides undergo ordered aggregation. Despite intensive research efforts, detailed kinetic mechanisms underlying this complex polymerization process are not well known and modeling will contribute to better understanding of basic molecular mechanisms and, in the long run, may contribute to better understanding of disease development mechanisms and may even expedite the development of treatment for AD.

Justification
The Karolinska Institute in Stockholm investigates the Aβ polymerization process, which involves two competing nucleation mechanisms (Figure 1). The fibril length distribution (FLD) was characterized using fluorescence correlation spectroscopy (FCS) and fibrilar structure by circular dichroism spectroscopy (CDS). Processing the data from both FCS and CDS leads independently to nearly identical values of the apparent rate coefficient of the overall polymerization. However, current modeling efforts are limited to (i) analytical solutions for specific cases or (ii) the method of moments, which only allows to calculate the average fibril length. Moreover, such modeling does not allow to easily discriminate between competing nucleation mechanisms. Kinetic Monte Carlo (kMC) modeling of the FLD will increase our understanding of the various competing mechanisms and may help us identify the factors accelerating the development of AD.

Program
- Concise literature study of experimental and modeling techniques for Aβ peptide polymerization.
- Adjusting and benchmarking an existing kMC polymerization code toward reactions of Aβ peptides and fibrils, using rate laws reported in the literature.
- Estimating elementary rate coefficients from an extensive data set provided by the Karolinska Institute.
- Understanding the competition between primary and secondary nucleation mechanisms, thereby identifying the factors accelerating the aggregation process.

Figure 1: Polymerization of peptides toward fibrils, involving competing nucleation mechanisms. The schematic represents some of the possible routes of amyloid formation through primary (black arrows) or secondary pathways (green arrows). Assembly commences from a monomeric precursor that could be unfolded, partially folded or natively folded (left-hand side). During the nucleation phase, dynamic equilibrium between these states is responsible for generating species with increased amyloid potential, which then self-assemble. Once the critical nucleus is generated rapid formation of β-rich amyloid fibrils starts (elongation phase). Secondary mechanisms, such as secondary nucleation on the surface of preformed fibrils (or aggregates), or fibril fragmentation, are also crucial determinants of the fate of assembly. The fluorescence of thioflavin T (ThT-blue trace), a dye that binds to cross-β aggregates, is commonly used to follow the progress of the reaction.
Experimental study of a gas-solid vortex reactor for oxidative coupling of methane

Aim
The objective of this work is to optimize the operating conditions in the gas-solid vortex reactor (GSVR) in order to obtain high product yields during oxidative coupling of methane (OCM) and use the exothermic reaction heat in an optimal manner.

Justification
Oxidative coupling of methane (OCM) is considered one of the most promising routes to directly convert methane into more valuable hydrocarbons. As a result of an increased methane supply since 2008 (because of the exploitation of shale and stranded gas reserves) and a significantly dropped methane price, petrochemical industry is actively investigating the OCM process for commercial/industrial application. However, the uncertain economics related to the tradeoff between conversion and C₂ selectivities is an important reason why OCM is currently not industrially applied. In the last decades, numerous studies have focused on developing a viable catalyst that has the potential to improve the low C₂ yields. But, next to the catalyst aspects, reactor design is of crucial importance for OCM as well. The lack of an appropriate reactor is one of the primary reasons why OCM has not been commercialized at industrial scale as well. Recent work has shown that an optimal OCM reactor combines good thermal backmixing with limited species backmixing. Both these characteristics can be obtained in a gas-solid vortex reactor (GSVR) making it the ideal candidate for OCM.

In this project, valuable experimental data will be gathered for OCM in the reactive GSVR setup available at the LCT. In a first set of experiments, non-catalytic particles will be used, serving as heat carrier and allowing autothermal operation of the reactor. Next, experiments including serveral types of OCM catalysts, or a combination thereof, will be performed. Finally, an optimization of operating conditions (combination of inlet temperatures, composition, inert/catalyst loading and residence times) will be performed in order to achieve a maximum heat transfer, methane conversion and olefin selectivity during OCM.

Program
- Literature study on the state-of-the-art for Oxidative Coupling of Methane: catalysts and reactor technologies.
- Non-catalytic experiments, where the solid particles only serve as heat carriers
- Catalytic experiments, potentially using a combination of different catalysts
- Optimization of operating conditions

Figure 1: Schematic representation of a GSVR.
CFD based design of a gas-solid vortex reactor for oxidative coupling of methane

Aim
The objective of this work is to optimize the design and operating conditions of the gas-solid vortex reactor (GSVR) in order to obtain high product yields during oxidative coupling of methane (OCM). Multiphase computational fluid dynamic (CFD) simulations will be performed in the open-source CFD package OpenFOAM.

Justification
The low natural gas price and the large amounts of shale and natural gas have created a renewed interest in methane as a source of liquid energy carriers or as a raw material for the chemical industry. In this work one of the most promising processes for valorizing methane to longer hydrocarbons, the oxidative coupling of methane (OCM), will be studied. Two key challenges have to be addressed before OCM can be considered as an alternative gas-to-chemical technology, namely the low yields of ethylene and what to do with the substantial heat release of the reaction. In order to prevent the unwanted propagation of the gas-phase reactions and efficiently address the large amount of heat released, reactors with short gas-phase residence time and efficient heat transfer are preferred for OCM. Hence the gas-solid vortex reactor (GSVR), developed at the Laboratory for Chemical Technology, emerges as an excellent reactor choice for demonstrating the OCM process.

In combination with modeling, valuable experimental studies can be carried out for different operating conditions. Nevertheless, these time intensive experimental studies can be drastically reduced by focusing on high level computational fluid dynamics (CFD) simulations. These simulations will allow to optimize the reactor geometry and operating conditions specifically for OCM.

In this project, both reactive and non-reactive CFD simulations of the GSVR are performed using the open-source CFD package OpenFOAM. The developed reactive CFD model takes into account a detailed OCM microkinetic model consisting of both homogeneous and heterogeneous reactions. The simulations are validated against the results obtained on the experimental setups available at the LCT.

Program
- Literature study on the state-of-the-art for oxidative coupling of methane: catalysts and reactor technologies.
- Getting acquainted with the OpenFOAM software package by performing some preliminary non-reactive CFD simulations, including validation with cold-flow experimental data.
- Reactive simulation of the GSVR for OCM and validation with experimental data.
- Optimization of operating conditions and design of the GSVR reactor specifically for the oxidative coupling of methane. Different microkinetic models will be tested for different catalysts. Benchmarking of the GSVR reactor technology through comparison with classical reactor techniques.

Figure 1. Catalyst volume fraction (top), and ethylene mole fraction (bottom) in a 16 slot GSVR.
Automated extraction of kinetic information in the era of Open Data

Aim
Boost the use and interpretability of Open Data for kinetic modelling by developing an algorithm able to maximize the extraction of kinetic information from historical experimental data.

Justification
The development of a whole new generation of catalysts suitable for sustainable processes is crucial. Kinetic modelling has frequently been postulated as the ideal tool for catalyst design. Indeed, the use of fundamental relationships, particularly when based on micro-kinetic (e.g. SEMK) models, enables the identification of the optimal catalyst structures, set of operating conditions, and reactor configuration; ensuring as well extrapolative properties [1]. However, the burdens of data collection and extraction of kinetic information, have limited the use of kinetic modelling for catalyst design up to now.

At the moment, both Belgium and Europe are creating and promoting open access databases in which scientists will store and share their experimental data [2]. The bottleneck will thus be on extracting information from that data for model development, as nowadays this step relies solely on the researcher’s prior knowledge and experience. This work aims at developing a methodology for automated extraction of kinetic information that can be retrieved in a set of experimental (open) data (Fig. 1). The resulting kinetic information will provide guidelines for the construction of a kinetic model.

Program
Develop a tool with the capability of extracting kinetic information the experimental data. In practice, this means that all kinetic features, i.e. variations in the dependent variables (e.g. decrease in conversion) must be identified and, preferably, classified in terms of relevance. Likewise for the experimental variables (e.g. partial pressure) that might explain the variability in the dependent variable (e.g. conversion). This can be achieved via the recognition of patterns and fingerprints [3], e.g. abrupt variations in the dependent variables of interest (e.g. conversion, selectivity, reaction rate). In order to automate this procedure, an algorithm will be developed in Python and applied to a biofuel production dataset.

Figure 1: Simplified flowchart for kinetic modelling. Top: current status (bottleneck in red). Bottom: future (innovations by master thesis in green).

Upgrading of a bio-refinery stream via hydrodeoxygenation: a kinetic study

Aim
Understanding the relationship between catalyst properties and reaction mechanism by means of micro-kinetic modelling of the hydrodeoxygenation of aldol condensation products.

Justification
Due to the continuously increasing demand for energy and chemicals, and the environmental concerns about the use of fossil resources, the search for renewable alternatives is more urgent than ever. Lignocellulose is a type of biomass which may constitute a viable option for the sustainable production of fuels as well as chemicals. A highly promising route consists of hemicellulose dehydration into furfural which is, subsequently, reacted with acetone to create new carbon-carbon bonds and yield larger and more valuable molecules [1]. To produce high-quality fuels, the thermal stability and the combustion properties of the condensation products should be upgraded by oxygen removal [2] (see scheme). The oxygen removal is usually carried out via hydrodeoxygenation (HDO) which is a heterogeneously catalysed reaction occurring in presence of hydrogen [3]. Up to now, the hydrodeoxygenation of such aldol condensation products has been barely reported in the literature. At the Laboratory of Chemical Technology, we have been investigating the hydrodeoxygenation of such products over catalysts comprising a Ni-Cu active phase deposited on supports with different acidities. This is expected to have an important effect on the reaction mechanism, as well as the pressure and temperature at which the reaction is performed.

Program
Experimental data on the hydrodeoxygenation of furfural condensation products with different catalysts and operating conditions will be available at the start of the thesis. To rationalize the complex nature of the reaction mechanism and the numerous experimental variables that were investigated (i.e. catalyst properties and operating conditions), a (micro-)kinetic model accounting for the elementary reaction steps will be developed. Aiming at discriminating between rival models and/or improve the quality of the selected model, additional experiments, planned through sequential experimental design techniques, might be performed in High-Throughput Set-Up at the LCT. The model should ultimately be used to provide guidelines to the design of new generation of hydrodeoxygenation catalysts.

Reductive Coupling of CO\textsubscript{2} with Ethylene using Homogeneous Catalysts

Aim

Our aim is to develop the first heterogeneous catalysts for the reductive coupling of CO\textsubscript{2} with ethylene using well-defined Ni-based catalysts.

Justification

The discovery of efficient technologies enabling the use of CO\textsubscript{2} as a starting material for chemical synthesis is one of the biggest scientific challenges of our time. The development of the reductive coupling of CO\textsubscript{2} with olefins could serve the dual purpose of reducing CO\textsubscript{2} emissions and producing value-added chemical building blocks, hence helping the environment while creating new opportunities for the chemical industry. The reductive coupling of CO\textsubscript{2} with alkenes is a highly desirable reaction, leading to the formation of acrylic acids and acrylates. Since ethylene and CO\textsubscript{2} can be obtained from renewable sources, and given the numerous industrial applications of acrylates, especially in the area of superabsorbent polymers, the development of this technology could represent a major breakthrough for the synthesis of renewable polyacrylates.

In our quest to develop efficient catalyst for this transformation, we will look into well-defined structured materials able to catalyse the most challenging step of the proposed reaction mechanism “The β-hydride elimination”. We will explore the catalytic activity of several well-defined commercially available catalysts. This could be done “in silico” using DFT calculations and modelling, “in vivo” using an experimental setup or as a combination. This project is part of a collaborative effort towards the development of Ni catalysts for the reductive coupling of CO\textsubscript{2} with ethylene and you are expected to work closely with other students focusing on the complementary project. It is ideal for students looking to gain experience working in interdisciplinary groups as it will involve interacting with professors and students from several departments within Gent University.

Program

1. Literature survey on the synthesis of well-defined Ni-NHC complexes.
2. Synthesis of Ni-NHC complexes and of screening reaction conditions.
3. Performing detailed mechanistic studies using NMR and kinetic measurements.
Mitigating butadiene popcorn formation in industrial olefin units

Aim
Mitigating butadiene popcorn formation in industrial olefin units.

Justification
Olefin units are subject to fouling and corrosion. Intrusion of molecular oxygen in distillation towers and overhead condensers forms peroxides, which initiate (and catalyze) butadiene polymerization. The mechanism is initiated by air or peroxides and promoted by rusty iron, oxygen and metal oxide catalysts. Butadiene polymer may appear in different forms, namely sheet, rubber, crystalline, or popcorn polymer. The latter is insoluble and hence detrimental to many unit operations. In addition, popcorn polymer presents a safety issue, as it rapidly and powerfully expands, building up pressure, resulting in popcorn particles “popping” and causing mechanical damage such as metal rupture, leading to loss of containment. Hence, olefin units typically have spare depropanizer reboilers to ensure a ca. 4 year on-line cycle, with a cycle time of ca. 12 months for the reboiler. Fouling occurs mostly in the reboiler and less in the depropanizer bottom. Since the 1940s, butadiene unit operators have learnt that certain process conditions exacerbate popcorn formation, yet no comprehensive model exists to predict reported popcorn reactivity behavior.

Program
1. Literature study to identify the industrial shutdown protocols which cause popcorn formation.
2. Improve the existing design of glass vials in order to mimick the conditions of e.g. industrial reboilers (in cooperation with EEPC members, in particular Dow Terneuzen).
3. Synthesize popcorn in glass vials to identify which industrial shutdown/cleaning protocols cause popcorn formation.
4. Determine the role of oxygen in the initiation mechanism responsible for popcorn formation.
5. Characterization of the morphology of the synthesized popcorn using Raman spectroscopy.

Figure 1: Reaction mechanism for 1,3-butadiene. Adopted from Levin et al. Journal of Hazardous Materials 2004, 115, 71–90.
The impact of hydrocarbon chain length on mixture effects in alkanes and cycloalkanes hydrocracking

Aim
Understanding of the impact of hydrocarbon chain length on the ideal/non-ideal hydrocracking regime transition within mixture effects in alkanes and cycloalkanes hydrocracking.

Justification
Besides everyday increase of use of alternative energy sources, fossil based fuels are supposed to remain the main energy source for heavy duty vehicles like airplanes or transoceanic ships. Due to more and more strict legislation with respect to air pollution, but, also, due to characteristics of crude oils, processing of oil streams still attracts large attention in research. Also, hydrocarbons originating from renewable sources require further upgradation to meet present-day quality standards.

Hydrocracking represents one of the processes used in petroleum refining industry for upgrading the oil streams for their use as fuels. To do so, the hydrocarbon structure is changed either by isomerization or by cracking of the molecule. Basically, this reaction takes place in a hydrogen atmosphere and is catalysed by a bifunctional material, containing a metal and an acid function.

The real industrial feeds are mixtures of alkanes, cycloalkanes and aromatic molecules. However, most of the research done on this topic assesses the reaction mechanism via single model molecule feed. Building further upon this, the present challenge is to investigate how the presence of several components impacts on the individual behaviour. The main impact is expected to be situated in competitive adsorption to active sites, both metal and acid, which can lead to partial inhibition. Furthermore, the presence of particular molecules might lead to poisoning of catalyst. The mixture effects on other phenomena in reaction mechanism will be also investigated. The particular focus of this thesis will be on impact of hydrocarbon chain length in mixture of alkanes and cycloalkanes.

Program
1 – Literature review : Introduction to the hydrocracking mechanism and to the principle of ideal hydrocracking;
2 – Experimental campaign on high-throughput setup : The goal is to determine the impact of chain size during the hydrocracking of mixture of alkanes and cycloalkanes. Experiments will be planned accordingly.
3 – Analysis of the results and determination of the hydrocarbon chain size impact;
4 – Potentially (if time allows), understanding of the impact of aromatic molecules presence on hydrocracking of the mixture with alkane and cycloalkane.

Recommended literature
Aim
The main goal is to experimentally study the coking behaviour of various coil alloys and coatings at high temperature (950°C) steam cracking of different hydrocarbon feedstocks. The influence of the feed and the coil material will be investigated. Analysis of the cracking effluent and of the fresh, coked and decoked samples will be performed to obtain a better insight into the factors that affect the coking rate on the various materials.

Justification
Lower olefins such as ethylene and propylene are industrially produced by steam cracking of hydrocarbons at high temperatures (above 800°C). The reactor coils need to be heat resistant and for that reason, they are constructed from Fe-Ni-Cr alloys. However, these alloys have the tendency to promote coke deposition on the inner surface of the coils, an undesired side reaction, due to the catalytic properties of their constituents, in particular of Ni and Fe. The formation of coke is influenced by many factors besides the coil material, such as the composition of the feed or the surface roughness of the coil. The accumulation of coke on the reactor wall leads to poor heat transfer and an increase in the pressure drop. These effects are finally translated into a decreasing production capacity and energy efficiency of the steam cracker and have a negative impact on the economy of the process. Reducing the coke deposition to the minimum level is a major challenge. Therefore several techniques are considered for industrial use: application of additives, development of new alloys and coating of the tube alloys.

The influence on the coke formation of various alloys will be tested. Therefore, steam cracking experiments will be performed with propane as a feedstock. The obtained results will be compared with previously acquired results from cracking experiments with ethane, so the influence of the feed can be evaluated. For a better understanding of the influence of the alloy on the coke deposition, the morphology and the composition of the coke formed on the samples can be analysed by SEM and EDX. In literature, several coking mechanisms are described. A study of these mechanisms, together with the experimental results can give a better insight of coking behaviour.

Program
- Experimental study of high temperature (950°C to 1050°C) aging procedure to mimic industrial conditions using a Plug Flow Reactor (PFR) followed by steam cracking simulations using Chemkin 17.0
- Focus will be on studying the pretreatment conditions (the type and form of oxide layers) before steam cracking and their effects on coke formation.
- To understand the effects of alloying elements (in the reactor coil material) on the structural integrity of produced oxide layers and their benefits on mechanical properties.
- Studying the role of sulfur on coke formation by varying the continuous addition of sulfur from 20 ppmwS/HC to 300 ppmwS/HC
- To study the effect of high temperature aging and different feedstocks (Ethane and butane) using a PFR/JSR by comparing their rate of coke formation, morphology and composition of the materials.
- In an effort to identify the elements S, chemical analyses of the JSR/PFR coked samples together with samples of the Pilot plant for steam cracking from LCT and industrial samples will be conducted by means of possible techniques such as TEM, SEM with EDX, XRD and XPS.
- By using the above mentioned techniques, the effect of inhibitor addition, temperature, coating or no steam dilution on the surface morphology and composition will be investigated in detail.

Coach
Ir. Manjunath Patil

Supervisor(s)
Prof. dr. Kevin Van Geem
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CO₂ utilization through Super-Dry Reforming: process simulation

Aim
Develop a detailed process simulation for CO₂ utilization from a steel industry’s gas to CO through Super-Dry Reforming.

Justification
Steel production is an energy- and carbon-intensive industry that requires a strong reductant to reduce the iron ore in the Blast Furnace. CO obtained from the reaction of metallurgical coke with hot air is typically used for this purpose. Even though steel production is a highly integrated process that reuses its intermediate streams, significant amounts of CO (50-70%) end up in the Basic Oxygen Furnace Gas, with CO₂ (10-20%), H₂ (1-2%) and N₂ (15-30%), as an unusable gas mixture for their iron ore reduction step due to the oxidizing power of the present CO₂.

In the Laboratory for Chemical Technology, a Super-Dry Reforming technology has been developed to upgrade CO₂ and CH₄ mixtures to high purity CO and water (schematics in Figure 1 above).

Program
- Literature review on chemical looping processes for dry reforming and CO₂ separation.
- Development of a process simulation in Aspen Plus involving kinetic data, reactor configurations and heat management.
- Evaluation of the process dynamic behaviour using Aspen Plus Dynamics.

The ideal candidate should have a strong interest in process design and optimization.

Figure 1. A schematic representation of the proposed Super-Dry Reforming process

Super-Dry Reforming is a chemical looping process, consisting of 2 cycles, 3 combined reactions and 3 solid materials (reforming catalyst, oxygen carrier and CO₂-sorbent) to maximize the CO yield. Overall, the process converts 3 molecules of CO₂ with 1 molecule of CH₄ to 4 molecules of CO and 2 molecules of H₂O. The CO from Super-Dry Reforming can be directly injected in ArcelorMittal’s Blast Furnace, significantly reducing the carbon footprint of steel production, not only by reducing the amounts of CO₂ released to the atmosphere but also by reducing the amount of coke required in the Blast Furnace to produce the same amount of steel. Therefore, it is of interest to develop a detailed process simulation for its future implementation in the steel industry.

New criteria for the instantaneous regime for gas-liquid reactions

Aim
Development of improved criteria for the occurrence of the so-called instantaneous regime for gas-liquid reactions. Elucidation of the apparent divergent predictions by the classical mass transfer models for a class of gas-liquid reactions.

Justification
General criteria for operation in the “instantaneous regime” for gas-liquid reactions are well known and can be found in many chemical reaction engineering textbooks:

\[ \text{Ha} > 2 \] and \[ \text{Ha} >> F_\infty - 1 \]

Ha being the Hatta number and \( F_\infty \) the infinite enhancement factor. However, for the class of gas-liquid reactions that aims at selective reactive removal of a component B, present in the liquid phase in relatively small amounts in a product stream P, we found that these classical criteria for the instantaneous regime are not sufficient. Even though the above criteria are fulfilled a numerical solution of the film model showed concentration profiles that do not correspond to those defined as “instantaneous”, see Figure 1.

Moreover, even though the above criteria are fulfilled, there can be a significant contribution of reaction in the “bulk”. This insight was obtained with the film model, one of the classical models for gas-liquid mass transfer, the other classical ones being the penetration model and surface renewal model. Generally, these are known to yield very similar results, both qualitatively and quantitatively. However, for our class of reactions preliminary results suggest they predict “divergent” results, i.e. qualitatively fundamentally different results.

Therefore, the goal of this project is to study the general case of irreversible gas-liquid reactions:

\[ A_{(g)} + B_{(l)} \rightarrow C_{(l)} \] \hspace{1cm} \[ A_{(g)} + P_{(l)} \rightarrow X_{(l)} \]

B being a component to be removed from a liquid stream that also contains a valuable product P. This represents for example selective chlorination or oxidation of organic product streams that contain small amounts of impurities, e.g. in a falling film reactor. Though relevant industrially, this class of G-L reactions seems not to have been studied nor that it has been reported that the classic criteria for the instantaneous regime are not sufficient.

Program
- Literature review of this class of G-L reactions and of criteria for the instantaneous regime.
- Develop and implement the relevant reactor models (film, penetration and surface renewal models).
- Compare the three different models and to validate whether or not the models yield opposite predictions in the limiting case of fully instantaneous reactions.
- Derive new criteria for the instantaneous regime for this class of reactions.
Aim

The goal of this thesis is to test and use a new experimental setup to study the effect of different coil alloys on coke formation in steam cracking reactors. The experimental setup is designed to test the performance of the alloys in a wide range of operating conditions.

Justification

Steam cracking of hydrocarbon feedstock remains one of the most important processes in the petrochemical industry. While cracking feed, cokes are produced on the wall of the cracker coils which are disadvantageous. Due to coke formation, the burners have to put more energy into the furnace and the diameter of the coils are decreased which causes a pressure drop and thus less yield of the wanted products such as ethylene and propylene.

There are typically four main categories of anti-coking technologies: additives, 3D geometries, coatings and reactor alloys. This master thesis focuses on the reactor alloys.

Reactor alloys have been upgraded over the years for two main reasons: to withstand higher temperatures and to increase their carburization resistance. Recently however, there is an increasing trend to improve the materials even further, focusing on decreased coke formation. This is for example done by adding alloying elements that create a stable oxide layer blocking the active sites for coke formation.

The combination of alloying elements needs to be tuned to form a stable, uniform oxide layer that does not crack or flake at the typically very high temperatures of steam cracking. The performance of these special alloys should be tested on a laboratory scale to see whether they are beneficial on the long run or not.

Program

1. Literature study on coke reduction techniques in steam cracking furnaces.
2. Testing of the newly developed setup.
3. Experimental study of the influence of different (industrial and synthetic) feedstocks on cokes formation.
4. Experimental study of the influence of different reactor alloys on cokes formation.
5. Investigate the surface morphology and composition of the different cokes samples with SEM and EDX measurements.
Transient kinetics: development of a general non-steady state solver for plug flow reactors

Aim
Implementation of a transient solver in the microKinetic Engine (µKE) for a set of differential equations with respect to space, such as a plug flow reactor (PFR). Validation of the new µKE feature via the execution and analysis of several known case studies.

Justification
The µKE, is a user-friendly software tool developed within the Laboratory for Chemical Technology at Ghent University [1]. The current version of the software allows the simulation and regression of steady-state processes via experimental intrinsic kinetic data [2][3]. However, industrial processes never operate at steady-state conditions as transient phenomena, due to variations in the operating conditions or catalyst deactivation, occur.

Through the incorporation in the software of the process time as an independent variable, the convergence to the steady-state solution is improved and accelerated. Furthermore, and on a more fundamental level, the integration of these dynamic effects can provide more information on reaction intermediates and the sequence of reactions in complex reaction networks obtained with transient kinetic data analysis [4].

Presently, µKE is under development to account for dynamic effects usually associated with industrial processes, such as start-up, shut-down, general disturbances and catalyst deactivation, as previously mentioned. For the moment, component mass balances can be described in transient terms for continuous stirred-tank reactor (CSTR). However, these will also be extended for PFR, thus expanding the versatility of the µKE for other processes.

Program
Firstly, a literature survey on solvers for systems of partial differential equations into the µKE will be done. This will be followed by the selection of the optimal solver according with the previous literature survey. Secondly, the solver will be embedded, in a generic manner, in the existing framework of the µKE. Finally, the validation of this feature will be performed, making use of several available case studies. A comparison with the steady-state solution may also be envisaged, in order to prove the potential of the unsteady state features.

Chemo-catalytic production of butadiene of bio-based feedstock: kinetics of butanediol dehydration

Aim
Unravelling the kinetics of the selective dehydration of 2,3 butanediol to 3-buten-2-ol by performing an experimental study and through the construction of a detailed kinetic model which is able to explain and predict the influence of varying operating conditions on the dehydration. Maximize the 3-buten-2-ol yield using the experimental information obtained and the kinetic model constructed.

Justification
Butadiene is the key building block for synthetic rubber production and is currently industrially produced starting from fossil fuels. Given the increasing importance of not only polybutadiene itself, but also acrylonitrile butadiene rubber and styrene butadiene rubber, among others, alternative bio-based production processes starting from sugar or sugar derived feedstock are considered. In the SPICY project the sugar will first be transformed to 2,3-butanediol which will be further converted to butadiene. In this process 2,3-butanediol will need to be selectively dehydrated to 3-buten-2-ol which will then be dehydrated to butadiene.

This master thesis is performed within the framework of the SPICY Project, a collaboration between KU Leuven, UGent, UHasselt, BBEPP and VITO.

Program
- Literature survey on bio-based production processes of butadiene with the specific focus on the conversion of 2,3-butanediol to 3-buten-2-ol and consecutively to butadiene.
- Experimental investigation of the selective dehydration of 2,3-butanediol to 3-buten-2-ol.
- Construction of a fundamental kinetic model and regression to the experimental data obtained in the laboratory.
- Maximize the 3-buten-2-ol yield using this model and the experimentally gained insights.
Directe afvang van CO₂ uit lucht

Doel
Ontwikkeling en karakterisering van materialen voor de directe afvang van CO₂ uit lucht en kinetische studie van dit proces.

Verantwoording
De nadelige effecten van grote hoeveelheden CO₂ in de atmosfeer op ons leefmilieu (oceaanverzuring, klimaatopwarming, extreme weersomstandigheden, …), worden steeds uitdrukkelijker erkend door maatschappij en regering. Maar zelfs indien we onze koolstofafgifte snel verlagen, dan nog zullen de atmosferische concentraties lange tijd hoog blijven omdat de oceaanen grote hoeveelheden CO₂ bevatten. Om de CO₂-concentraties onder controle te houden, is het onontbeerlijk om processen met lage koolstofimpact te ontwikkelen én volop in te zetten op directe afvang van CO₂ uit lucht, hetzij via herbebossing, hetzij via fysische en chemische adsorptie op industriële schaal. De gewonnen CO₂ kan herbruikt worden als chemische bouwsteen of energiedrager, met behulp van hernieuwbare energie.


Programma
- Literatuuroverzicht over de huidige stand van zaken van directe afvang van CO₂ uit lucht.
- Thermodynamische berekeningen om kandidaat materialen te selecteren.
- Synthese van verschillende vaste metaaloxide CO₂ sorptiemiddelen.
- Materiaalkarakterisering met N₂ adsorptie, X-stralendiffraactie, thermogravimetrische analyse, …
- Testen van de CO₂ sorptie: blootstelling van materialen aan (i) gecontroleerde, samengedrukte lucht in een reactor met online GC-MS analyse; (ii) ongecontroleerde luchtblootstelling (binnenshuis, buitenshuis, gedroogd) over verschillende tijdsperioden met regelmatige staalname en analyse met reactortests, thermische gewichtsanalyse en infrarood spectroscopie.
- Kinetiek: via een serie experimenten wordt een kinetische dataset samengesteld om door regressie een geschikt kinetisch model te fitten aan de data. Dit zal toelaten om de kinetiek van verschillende CO₂ sorptiematerialen te vergelijken en hieruit aanbevelingen te formuleren over het meest interessante materiaal voor directe CO₂ afvang uit lucht gebaseerd op Aspen Plus simulaties.