

Master Thesis Subjects- 2019/2020

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Coaches dr. ir. Van Steenberge	Supervisors dr. ir. Van Steenberge, prof. dr. ir. Dagmar D'hooge	Funding -
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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.

Coach Sepehr Madanikashani	Supervisor(s) Kevin Van Geem	Funding Interreg Europe
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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.



Figure 1 Schematic diagram of plastic waste gasification recycling route

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 (H_2+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

[1] K. Ragaert, L. Delva, K. Van Geem, Mechanical and chemical recycling of solid plastic waste, Waste Manage. (Oxford, U. K.), 69 (2017) 24-58.

[2] J. De Wilde, Gas-solid fluidized beds in vortex chambers, Chem. Eng. Process., 85 (2014) 256-290.

- [3] N.M. Vandewiele, K.M. Van Geem, M.-F. Reyniers, G.B. Marin, Genesys: Kinetic model construction using chemo-informatics, Chem. Eng. J. (Amsterdam, Neth.), 207-208 (2012) 526-538.
- [4] R. Van de Vijver, N.M. Vandewiele, P.L. Bhoorasingh, B.L. Slakman, F. Seyedzadeh Khanshan, H.-H. Carstensen, M.-F. Reyniers, G.B. Marin, R.H. West, K.M. Van Geem, Automatic Mechanism and Kinetic Model Generation for Gas- and Solution-Phase Processes: A Perspective on Best Practices, Recent Advances, and Future Challenges, International Journal of Chemical Kinetics, 47 (2015) 199-231.

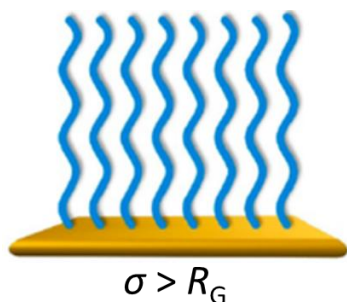
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Combining the strength of experimental study and modeling tools to lift the field of Polymer Brushes

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.

Coach Nadadur Srinath	Supervisor(s) Hilde Poelman, Vladimir Galvita	Funding FWO bimetallic
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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 CO₂ 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_{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

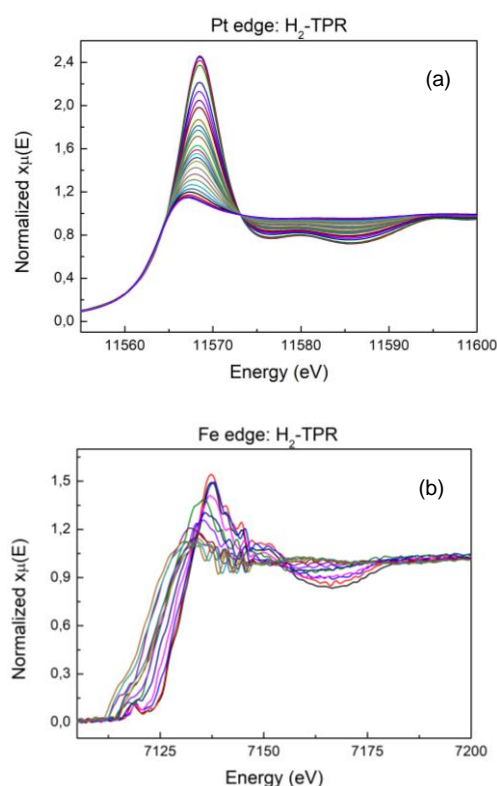


Figure: XANES spectra during H₂-TPR of 3wt%Pt-1wt%Fe/MgAl₂O₄ at the (a) Pt-L_{III} and (b) Fe-K absorption edge.

Coach ir. Onur Dogu	Supervisor(s) Prof. dr. ir. Kevin Van Geem, dr. ir. Paul Van Steenberghe	Funding FWO
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Kinetic Modeling of Fast Pyrolysis of Solid Plastic Waste

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.

Coach Dr. César A. Urbina Blanco	Supervisor(s) Prof. Mark Saeys	Funding CATCO2RE
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Reductive Coupling of CO₂ with Ethylene using Homogeneous Catalysts

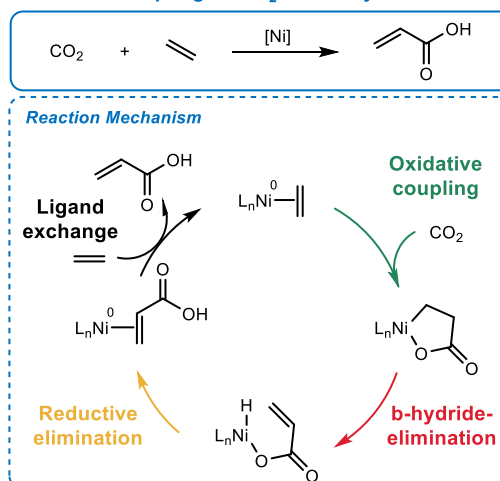
Aim

Our aim is to develop the first heterogeneous catalysts for the reductive coupling of CO₂ with ethylene using well-defined Ni-based catalysts.

Justification

The discovery of efficient technologies enabling the use of CO₂ as a starting material for chemical synthesis is one of the biggest scientific challenges of our time. The development of the reductive coupling of CO₂ with olefins could serve the dual purpose of reducing CO₂ emissions and producing value-added chemical building blocks, hence helping the environment while creating new opportunities for the chemical industry. The reductive coupling of CO₂ with alkenes is a highly desirable reaction, leading to the formation of acrylic acids and acrylates. Since ethylene and CO₂ 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.

Reductive Coupling of CO₂ with Ethylene



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 CO₂ 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.

Coach Dr. César A. Urbina Blanco	Supervisor(s) Prof. Mark Saeys Dr. Vladimir Galvita	Funding CATCO2RE
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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 and 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.**

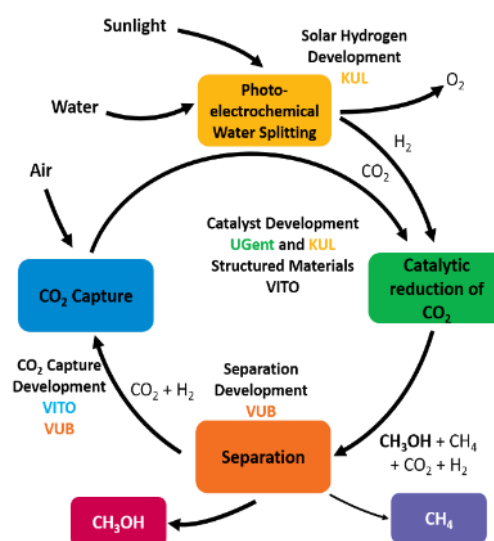


Figure 1: Schematic representation of integrated production of solar fuel as proposed in CATCO2RE.

Program

1. Literature survey on the hydrogenation of CO₂ to methanol using heterogeneous catalysts.
2. Benchmark the catalytic activity of the commercial Cu-Zn catalysts.
3. Synthesis and characterization of new heterogeneous catalysts based on Cu-Zn and Pd-Zn
4. Screening of reaction conditions using the high-throughput setup.

Coaches	Supervisors	Funding
ir. Lies De Keer, ir. E. Loccufier	prof. dr. ir. Dagmar D'hooge, prof. dr. ir. Karen De Clerck	-

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.

Coaches	Supervisors	Funding
Dr. Hilde Poelman	Prof. Vladimir Galvita, Dr. Hilde Poelman	

Tri-reforming of hydrocarbon mixtures for the production of syngas

Aim

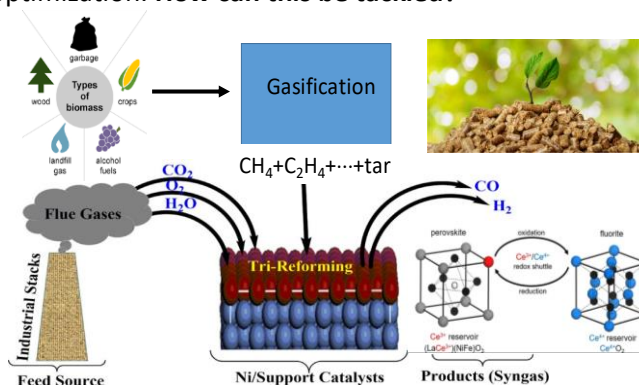
Tri-reforming of a hydrocarbons mixture utilizing CO_2 , H_2O and O_2 is an emerging technique for the production of synthesis gas and CO_2 abatement. Nevertheless, formulation and design of a low-cost, active and stable catalyst is a major challenge due to the complex reaction network and rapid catalyst 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 ($\text{CO}+\text{H}_2$) 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 prospective, because it is a CO_2 neutral resource, which is distributed extensively in the world. However, after the biomass gasification process, next to CO and H_2 there is a mixture of unreformed hydrocarbons ($\text{CH}_4 + \text{C}_2\text{H}_4 + \dots + \text{tar}$), 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 C_xH_y and H_2O 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, CO_2 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, CO_2 is utilized, the desired ratio H_2/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 ABO_3 , 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 H_2/CO molar ratio for the Fischer–Tropsch process and methanol production;
- Synthesis of perovskite materials (LaCeO_3 , LaFeO_3 , FeCeO_3 , $\text{LaNi}_{0.8}\text{Fe}_{0.2}\text{O}_3$, $\text{La}_{0.9}\text{Ca}_{0.1}\text{Ni}_{0.5}\text{Fe}_{0.5}\text{O}_3$, $\text{La}_{1-x}\text{Ce}_x\text{Ni}_{0.5}\text{Fe}_{0.5}\text{O}_3$);
- Catalyst characterization by BET, H_2 -TPR, O_2 -TPO, CO_2 -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.

Coaches Varun Singh and Marian Flores Granobles	Supervisors Prof. Mark Saeys and Prof. Vladimir Galvita	Funding EU Horizon 2020
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Reactor design for a gas-solid reaction to produce H₂

Aim

Develop a **large-scale reactor** model for the **gas-solid iron looping** process to **produce H₂**

Justification

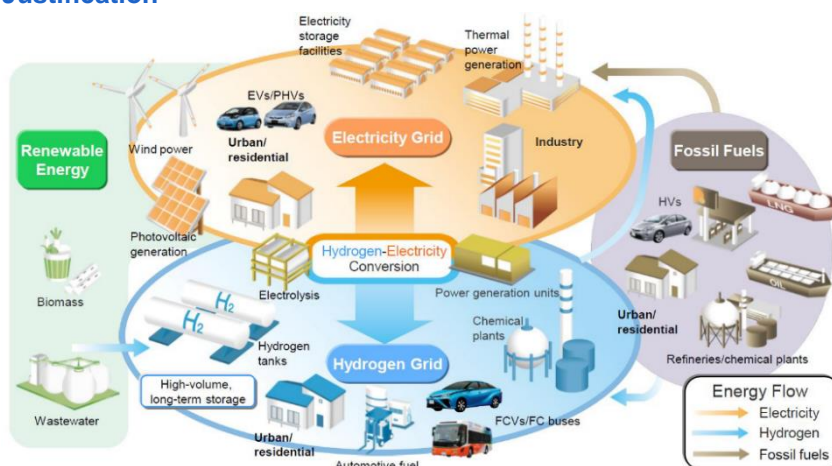


Figure 1. A schematic showing the move towards an H₂-based sustainable society¹

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 H₂ from H₂O is chemical looping, a two-steps process, with abundantly available iron oxide. Chemical

looping offers not only the production of a high purity H₂ stream² (ppm level impurities), but also the advantage of inherent separation of CO₂, 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 H₂ while simultaneously separating the CO₂ and other impurities (a schematic is displayed in Figure 2). Chemical looping as a means to produce high purity H₂ had been first developed on an industrial scale more than a century ago³ but modern reactors may prove to be more efficient for the envisioned approach mentioned herein.

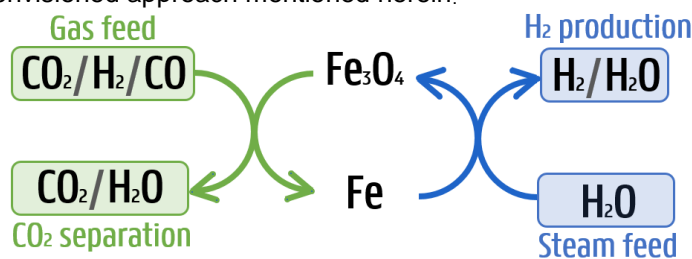


Figure 2 Iron looping for H₂ production with inherent CO₂ and impurities separation

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.

¹ K. O'M. Bockris, *Science* **176**, pp. 1323 (1972). DOI: 10.1126/science.176.4041.1323

² V. Galvita et al., *Int. J. Hydrogen Energy* **33**, pp. 1354. DOI: 10.1016/j.ijhydene.2007.12.022

³ A. Messerschmitt, 1910, Process of producing hydrogen, US971206A (US patent)

Coaches	Supervisors	Funding
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Selective oxidation of bio-methane to formaldehyde: core-shell catalyst approach

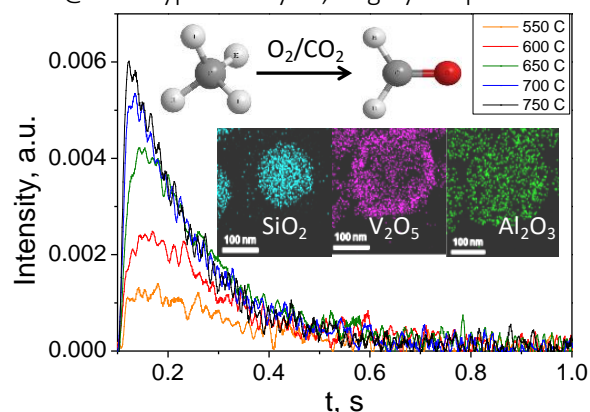
Aim

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 $\text{SiO}_2@V_2O_5@Al_2O_3$ 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_3OH), and ethylene (C_2H_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_2O_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_2O_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_2O_5 nanocatalysts supported on SiO_2 spheres with Al_2O_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_2O_5 , prepared by impregnation. The effect of the presence of CO_2 as well as using CO_2 as soft oxidant will be investigated.

Coach Yu Zhang	Supervisor(s) Kevin Van Geem	Funding UGent
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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 NO_x emission in steam cracking furnaces. As the conventional flame burners almost reached their limits in NO_x 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 NO_x 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 applications¹.

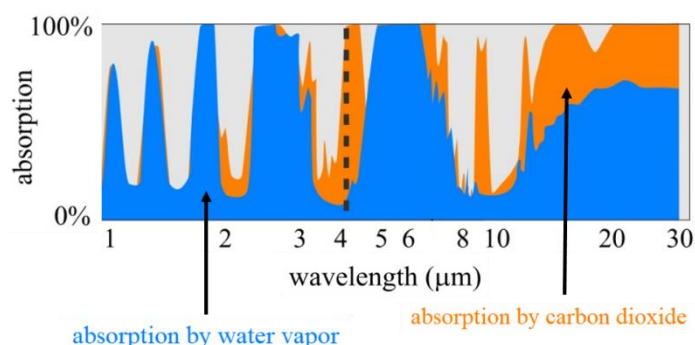


Figure 1: Atmospheric absorption bands of the most important radiative transfer participating media of flue gas (H₂O and CO₂).

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 inaccuracy². 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.

1. Tan, Y.; Douglas, M. A.; Thambimuthu, K. V., CO₂ capture using oxygen enhanced combustion strategies for natural gas power plants. *Fuel* **2002**, 81, (8), 1007-1016.

2. Guo, J.; Li, X.; Huang, X.; Liu, Z.; Zheng, C., A full spectrum k-distribution based weighted-sum-of-gray-gases model for oxy-fuel combustion. *International Journal of Heat and Mass Transfer* **2015**, 90, 218-226.

Coach Ir. Jia Zhang	Supervisor(s) Prof. Dr. Ir. Kevin M. Van Geem Prof. Dr. Ir. Reyniers M.F.	Funding China Scholarship Council
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Coke formation simulation during steam cracking

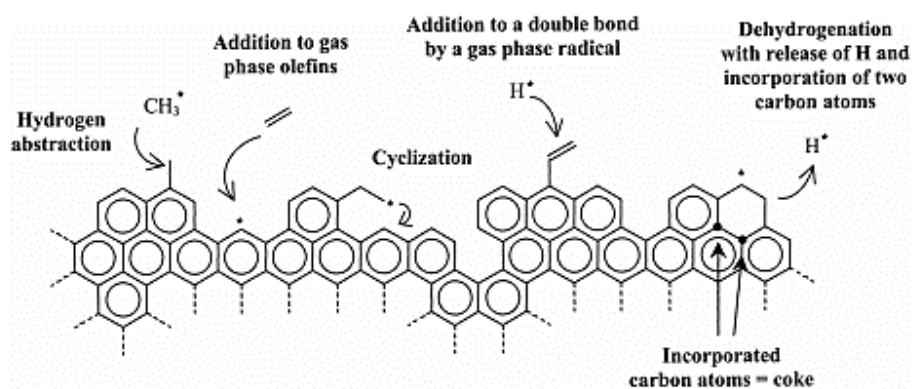
Aim

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 decoke 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

- 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.
- 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.
- Developing a general understanding of the Genesys code and Chemkin simulation.

Coach Farhan Siddiqui	Supervisor(s) Maarten Sabbe Marie Françoise Reyniers	Funding
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First principles prediction of transfer and secondary reactions kinetics in free radical polymerization of industrially viable monomers

Aim

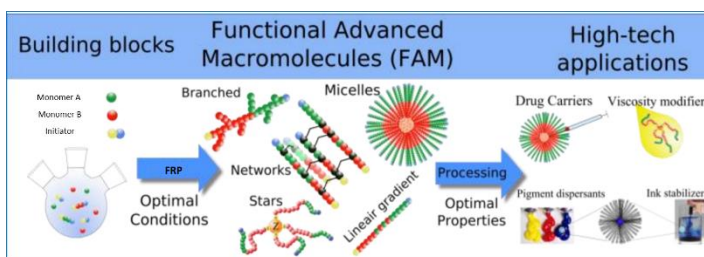
Implementation of micro-kinetic modelling to obtain reliable kinetics of the occurrence of rare events and side reactions to assess the influence of the chemical structure on properties of the polymer.

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.

Coach Francisco Arraez, Pieter Cools	Supervisor(s) Dagmar D'hooge, Rino Morent	
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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.

Coaches ir. Yoshi Marien	Supervisors prof. dr. ir. Dagmar D'hooge dr. ir. Paul Van Steenberghe	Funding -
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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 ν (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).

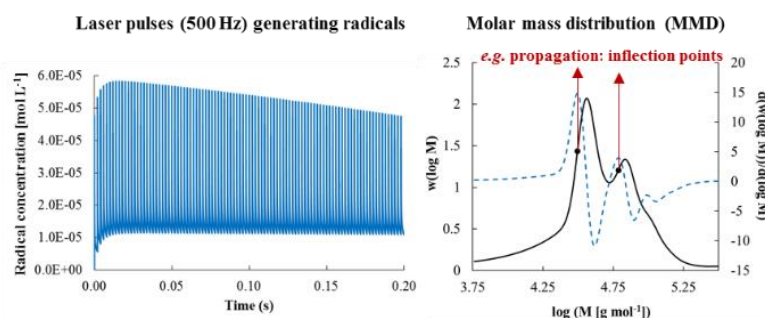


Figure 1. Radical concentration profile (left) and molar mass distribution (full black line; right) allowing the determination of the propagation rate coefficient via the inflection points, which correspond to maxima of the derivative (dotted blue line).

In this thesis, PLP is used for the determination of backbiting, β -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.

Coach ir. Sri Bala Gorugantu	Supervisor(s) Prof. dr. ir. Kevin Van Geem	Funding
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Unravelling lignin pyrolysis chemistry using phenolic model compounds

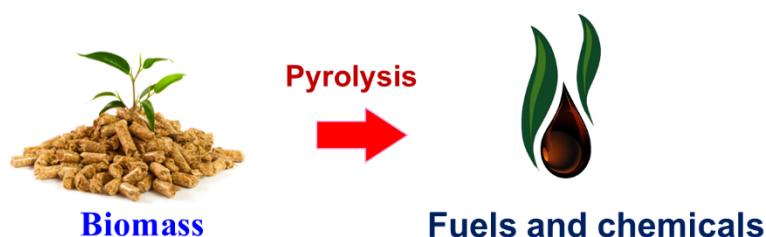
Aim

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.

Coach Dr. César A. Urbina Blanco Dr. Andrés R. León Garzón Ir. Mostafa Ali	Supervisor(s) Prof. Mark Saeys Dr. Vladimir Galvita	Funding CATCO2RE
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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 $M^{II}_{1-x}M^{III}_x(OH)_2(A^{n-})_{x/n} \cdot yH_2O$, where M^{II} is a divalent metallic cation (Mg²⁺, Ca²⁺, Ni²⁺, ...), M^{III} a trivalent metallic cation (Al³⁺, Ga³⁺, Fe³⁺, ...), Aⁿ⁻ 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.

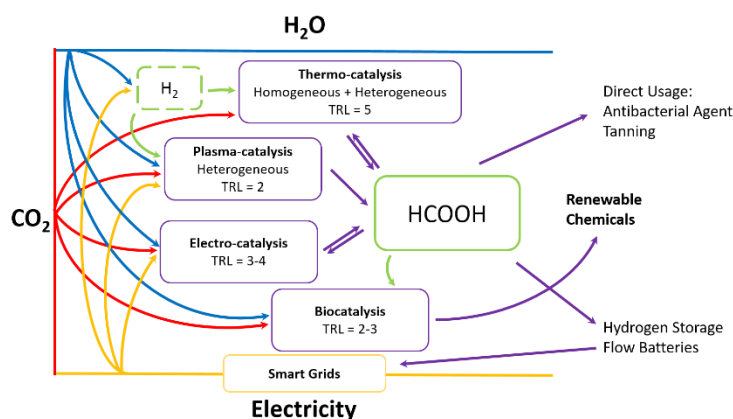


Figure 2: Schematic representation of the CO2PERATE project

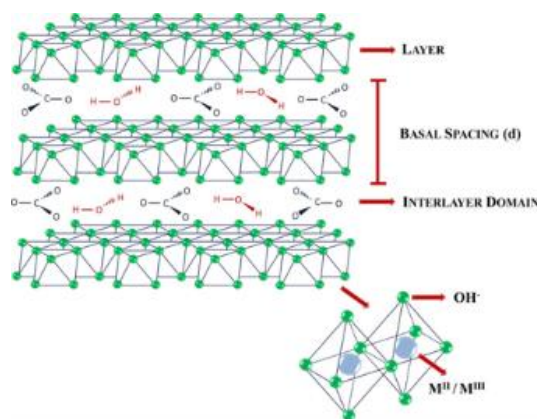


Figure 1: Layered Double Hydroxide (LDH)

Program

1. Literature survey on the hydrogenation of CO₂ to 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.

Coach Jenoff De Vrieze, Andrès Ricardo León Garzón	Supervisors Mark Saeys	Funding CATCO2RE
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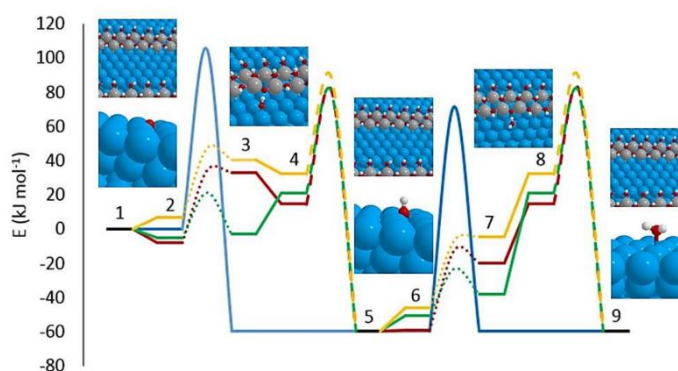
Design of bimetallic catalysts for CO₂ hydrogenation

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 these reactions 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.

Coach ir. Yoshi Marien	Supervisor(s) Dr. ir. Paul Van Steenberge, Prof. dr. Marie-Françoise Reyniers	Funding -
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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 ($A\beta$) 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 $A\beta$ polymerization process, which involves two competing nucleation mechanisms (Figure 1). The fibril length distribution (FLD) was characterized using fluorescence correlation spectroscopy (FCS) and fibrillar 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.

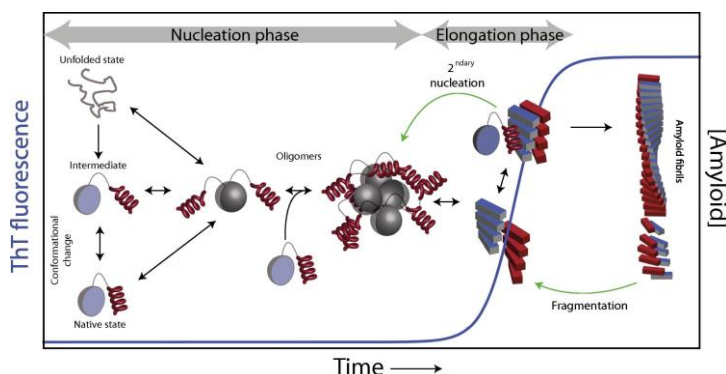


Figure 1: Polymerization of peptides toward fibrils, involving competing nucleation mechanisms. The schematic represents some of the possible routes of amyloid formation through primary (black arrows) or secondary pathways (green arrows). Assembly commences from a monomeric precursor that could be unfolded, 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.

Program

- Concise literature study of experimental and modeling techniques for $A\beta$ peptide polymerization.
- Adjusting and benchmarking an existing kMC polymerization code toward reactions of $A\beta$ 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.

Coach Florian Wéry	Supervisor(s) Prof. dr. ir. Kevin M. Van Geem	Funding FWO Flanders
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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 C_2 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 C_2 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 several 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

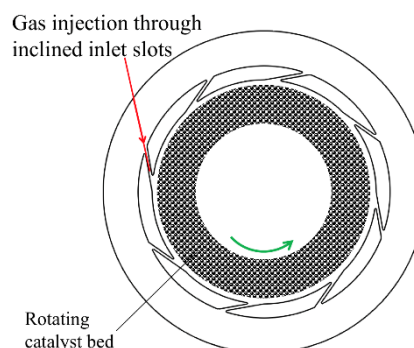


Figure 1: Schematic representation of a GSVR.

Coach Pedro Mendes	Supervisor Joris Thybaut Pedro Mendes	Funding UGent (BOF)
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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.

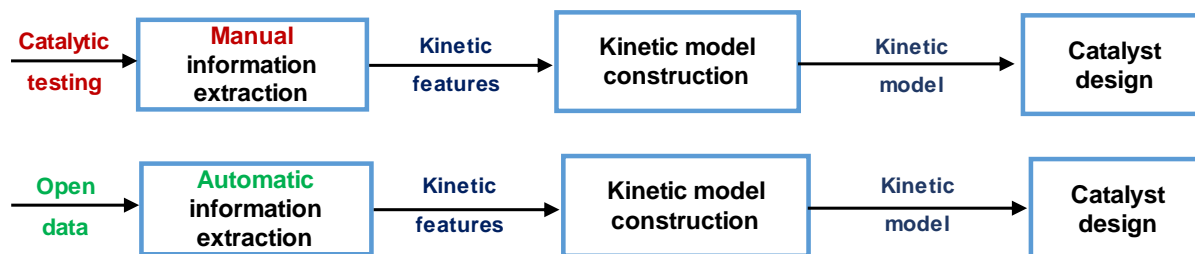


Figure 1: Simplified flowchart for kinetic modelling. Top: current status (bottleneck in red). Bottom: future (innovations by master thesis in green).

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.

[1] K. Van der Borght, K. Toch, V. Galvita, J. Thybaut and G. Marin, *Catalysts*, 2015, **5**, 1948.

[2] <https://www.openaire.eu/>

[3] J. M. Caruthers *et al.*, *J. Catal.*, 2003, **216**, 98-109.

Coach Pedro Mendes, Jeroen Lauwaert	Supervisor Joris Thybaut, Jeriffa De Clercq	Funding EU Commission FWO
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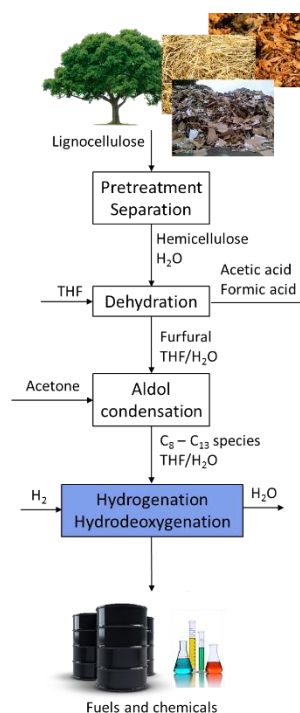
Upgrading of a bio-refinery stream via hydrodeoxygenation: a kinetic study

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.



Scheme 1. Conversion of lignocellulose into fuels and chemicals

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.

[1] J. Lauwaert, E.G. Moschetta, P. Van Der Voort, J.W. Thybaut, C.W. Jones, G.B. Marin, *J. Catal.* 325 (2015) 19.

[2] A. Galadima, O. Muraza, *J. Ind. Eng. Chem.* 29 (2015) 12.

[3] A. Daudin et al., in: P. Raybaud et al. (eds.) *Catalysis by Transition Metal Sulphides*, Ed. Technip, 2013, 739.

Coaches	Supervisors	Funding
ir. Onur Dogu, ir. Liang Li	Prof. dr. ir. Kevin Van Geem, Dr. ir. Paul Van Steenberge	-

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.

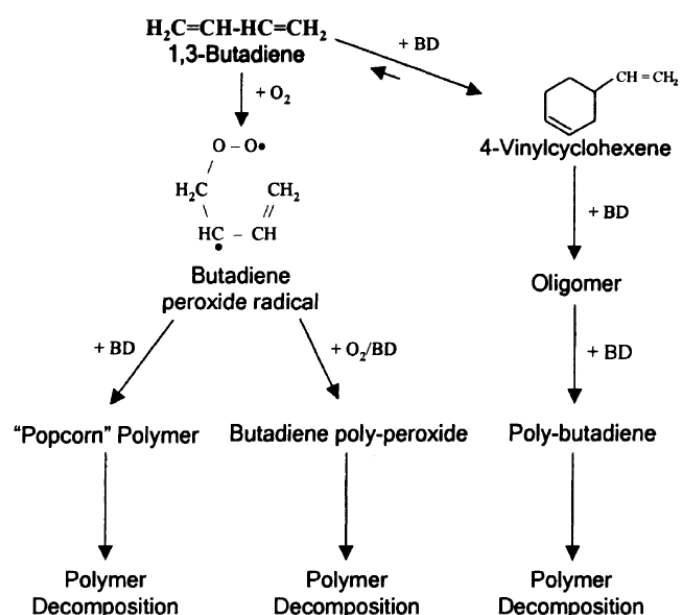


Figure 1: Reaction mechanism for 1,3-butadiene. Adopted from Levin et al. *Journal of Hazardous Materials* **2004**, 115, 71–90.

Program

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

Coach Nebojsa Korica	Supervisors Joris Thybaut Pedro Mendes	Funding
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The impact of hydrocarbon chain length on mixture effects in alkanes and cycloalkanes hydrocracking

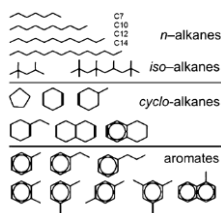
Aim

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

Thybaut, J.W., Marin, G.B., Baron, G.V., Jacobs, P.A., Martens, J.A., Alkene Protonation Enthalpy Determination from Fundamental Kinetic Modeling of Alkane Hydroconversion on Pt/H-(US)Y-Zeolite, *J.Catal.* 2001, 202, 324-339
Weitkamp, J., *Catalytic Hydrocracking – Mechanisms and Versatility of the Process*, *ChemCatChem* 2012, 4, 292-306

Coach Ir. Manjunath Patil	Supervisor(s) Prof. dr. Kevin Van Geem Prof. dr. Kim Verbeken
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Reducing Coking During Steam Cracking Of Hydrocarbons

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.

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Experimental study on the influence of reactor alloys on coke formation on a newly developed setup

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.

Coach Ana Rita Costa da Cruz	Supervisor(s) Joris Thybaut Jeroen Poissonnier	Funding ERC- PoC SERENiTi
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Transient kinetics: development of a general non-steady state solver for plug flow reactors

Aim

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

Justification

The μ KE, 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, μ KE 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 μ KE for other processes.

Program

Firstly, a literature survey on solvers for systems of partial differential equations into the μ KE 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 μ KE. 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.

[1] K. Metaxas et al., 2010, Top. Catal. 53, 64–76.

[2] N. Kageyama et al., 2017, Ind. Eng. Chem. Res. 56, 1148–58.

[3] C. Sprung et al., 2015, Appl. Catal. A: Gen. 492, 231–42

[4] J. Van Belleghem et al, 2016. Comp. Chem. Eng., in press.