

General information

<http://www.lct.ugent.be/lct/vacancies>

The challenge for Chemical Engineering science is more than ever to bridge the gap between molecule and chemical plant. Increasing environmental constraints impose a “molecular” control of any, either existing or new, production process. The Laboratory for Chemical Technology is one of the few in the world who can claim to cover the wide spectrum of competences required to be successful in this respect. The research is focused on the design of new and the optimization of existing industrial processes in the field of transport fuels, energy carriers and functional materials. New feedstocks, e.g. renewables, new processes, e.g. controlled radical polymerization, and new functional materials, e.g. nanostructured polymers are aimed at. A common theme of the research projects is the development of multi-scale models of the relevant reactions and reactors with emphasis on the interaction between complex chemical kinetics and complex transport phenomena. A first principles approach is combined with experimental validation whenever possible.

Kinetic studies are not limited to the determination of empirical correlations between the reaction rate and the reaction conditions but are based on the fundamental knowledge of the involved elementary steps. When possible, ab initio calculations of rate coefficients are performed. A better understanding of the reaction mechanism is implemented in the kinetic models and is providing guide lines for product, catalyst and process optimization. The kinetic modeling of reactions involving several hundreds of types of molecules belongs to the specific expertise of the laboratory.

For the design and the simulation of industrial reactors, the Computational Fluid Dynamics (CFD) approach is followed. The hydrodynamics of multiphase flow are investigated separately i.e. in the absence of reaction. Transport of energy, mass and momentum is described with commercial and in-house developed codes. The latter can handle both gas and gas-solid flow. Heat and mass transport are described in both reactors and furnaces by CFD codes developed in house. Not only single phase but also gas-solid streams can be simulated.

The LCT consists of four tenured and one tenure track faculty members, two senior scientists and eight post-doc researchers, some 20 PhD students and an administrative and technical staff of 10 people. The communication language is Dutch or English. In total twenty lab-scale setups and two pilot plant units mainly aiming at kinetic experiments are available. One fifth of the funding is originating from industrial collaborations. The LCT is a founding member of EUROKIN, a consortium of ten companies and five universities. It coordinates and participates in European research programs.

PhD Fellowships are typically offered in the following domains:

- Biomass Conversion
- Transient Kinetics
- Metal catalyzed reactions
- Radical Polymerization
- Pyrolysis and Steam cracking

- Computational Fluid Dynamics coupled with kinetics

Unsolicited applications are always welcome

Typical activities during a 4 year PhD project:

- Experimental acquisition of intrinsic reaction rate data.
- Model construction based on reaction mechanisms and estimation of kinetic parameters by data regression and/or quantum chemical calculations.
- Scale-up of lab data and simulation of industrial processes by developing and implementing reactor models accounting for transport next to reaction. Development and application of Computational Fluid Dynamics models in that context.
- Normal duties will apply, including the preparation of scientific reports and publications and assisting in supervising of MSc students.

Requirements

Applicants must possess a MSc in Chemical Engineering or related subject and a TOEFL certificate with a minimum score of 95(iBT) or equivalent. Relevant experience in the area of reactor engineering, kinetics, and/or computational chemistry is strongly recommended. Candidates must have a strong mathematical background and be willing to focus on obtaining quantitative rather than qualitative results.

Inquiries/Application

Any additional information can be obtained by contacting Guy B. Marin. **Any application should enclose a C.V., a one page justification of your interest and the e-mail addresses of at least two references.**

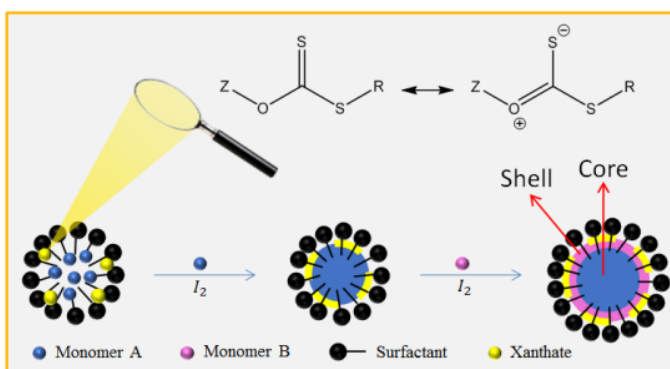
Design of dispersed phase polymerization reactors for the synthesis of functional nanoparticles

Aim

A multi-scale model will be developed, allowing the design of the industrial synthesis of functional nanoparticles in dispersed media (e.g. emulsion). Attention will be focused on the simultaneous control of the (co)polymer microstructure and the particle growth. Model validation will be performed with respect to experimental data, including a variation of the reactor size.

Justification

An important part of the polymer market relates to the synthesis of polymeric nanoparticles in a dispersed medium (e.g. emulsion or dispersion polymerization). These nanoparticles are used for applications such as automotive coatings, drug delivery, and paints. Typically radical polymerizations are considered in which a distinction can be made between conventional free radical polymerization (FRP) and reversible deactivation radical polymerization (RDRP). In FRP, a polymer with a rather broad chain length distribution (CLD) is obtained, whereas in RDRP the CLD is more narrow and ideally one functionality is present per chain, allowing further chemical modification (e.g. the synthesis of block copolymers). This improved microstructural design is obtained via the addition of RDRP agent (see figure; top part), allowing the temporary deactivation of macroradicals and the limited impact of conventional termination reactions. Next to the CLD, the particle size distribution (PSD) needs to be properly tuned in polymerizations in dispersed media, since the latter distribution has a direct impact on the polymer processability. By changing the initial conditions (e.g. surfactant type and concentration), a different nucleation behavior is obtained so that both nanoparticles with a low and large average diameter ($d = 20\text{-}300\text{ nm}$) can be targeted.



A research challenge remains the fundamental understanding of the interplay of micro- and meso-scale phenomena, in particular at industrial scale at which temperature and concentration gradients can be easily encountered. Notably this interplay is even more complex when targeting advanced nanoparticles such as core-shell nanoparticles (figure; bottom part) and nanocapsules. Small deviations from the targeted properties can already lead to a failure of the high-tech application, implying the necessity of a robust experimental protocol.

Program

The development of a software tool that allows the design, optimization and the control of radical polymerization processes in dispersed media, according to predefined quality requirements (e.g. given degree of functionality and average particle diameter) and process constraints (e.g. process time). Validation with an in-house set-up (see figure) will be performed. Attention will be focused on both FRP and RDRP processes, aiming at the full nanoparticle range and including a regulation of the feeding rates and temperature profile.



Advisors: Dagmar D'hooge en Guy B. Marin

Funding: Multi-scale Modeling and design of chemical Reactions and Reactors (M2dcR2)

Impact of the Use of Mixtures on Ideal Bifunctional Behavior in Hydroisomerisation and Cracking

Aim

Validation of the Single-Event MicroKinetic (SEMK) methodology against hydroisomerization and cracking data acquired using (model) mixtures. Evaluating the impact of the mixture composition, particularly aromatics containing ones, on the ideal bifunctional behavior.

Justification

Hydroconversion processes in general and hydroisomerization and cracking in particular are still gaining popularity because of the high quality products obtained. Whereas high total pressures and the use of hydrogen used to be driving forces for preferring carbon rejection, i.e., FCC, rather than hydrogen addition, i.e., hydrocracking, nowadays present fuel quality specifications lead to increased investments in the latter. Hence, related modeling and simulation capabilities strategies have become increasingly important.

The Laboratory for Chemical Technology at Ghent University has a long and versatile history in the fundamental kinetic modeling of complex reactions. Particularly with respect to hydrocracking a more than 20-year long experience involving more than a dozen of top qualified researchers has resulted in a Single-Event MicroKinetic (SEMK) model that is capable to simulate the conversion of model compounds over a wide range of catalysts, including extremely shape-selective ones as well as catalysts exhibiting intracrystalline diffusion effects. The applicability of the model at gas and liquid phase conditions has been demonstrated and a version for the simulation of the processing of complex feeds at industrially relevant conditions has been constructed. Of course, opportunities for further model enhancement and acquiring a closer match between experimentation and SEMK model simulations remain, particularly in the area of (aromatics containing) mixtures conversion as well as of accounting for non-ideal bifunctional behavior in terms of elementary steps.

Program

- Inventarisation of available data and decision on necessity of additional data acquisition. Historical data are available at the Laboratory for Chemical Technology at Ghent University. Data sets of course comprise pure model compound behavior of various types of molecules such as alkanes, cycloalkanes and aromatics but also of mixtures of these (types of) model compounds. Additional data can be acquired in the high throughput kinetics set-ups at LCT.
- Experimental data analysis with respect to mixture effects. Determination whether simple, additive behavior is concerned or whether synergetic or inhibiting effects are occurring. Verification whether the available model can qualitatively and/or quantitatively account for the observed mixture effects.
- Model enhancement with respect to mixture effects. It is anticipated that, particularly, the impact of alkane – aromatics mixtures will require intervention in the definition of the presently used model equations, because the ideal bifunctional behavior seems not to be preserved when adding aromatics above a certain threshold value. More explicitly accounting for the occupancy of the metal sites and the potentially rate-determining character of the metal catalyzed reactions will have to be incorporated.
- Extrapolations from laboratory-scale (mixture) model compound behavior to industrially relevant feeds, operating conditions and reactor configurations using the SEMK model. Validation of these extrapolations against true data would be a major asset.

Advisors: Prof. Joris Thybaut, Prof. Guy B. Marin

Funding: Sabic

Process Analysis for Oxidative Coupling of Methane based on Microkinetic Modeling: Impact of Catalyst Properties and Reactor Configurations

Aim

A quantified understanding of the dominant factors in oxidative coupling of methane, ranging from catalyst properties as determined by the catalyst descriptors to alternative reactor configurations.

Justification

Oxidative Coupling of Methane (OCM) remains intriguing as an alternative reaction for natural gas valorisation. Despite decades of research into this reaction, today only a single commercial implementation has been claimed, i.e., the one by Siluria. Key features of that implementation are (i) adiabatic reactor technology, (ii) low light-off temperature and (iii) catalyst stability rather than elevated C₂ yields or selectivities (per pass).

Total has interest in exploring and evaluating alternative technologies, such as OCM, for chemicals and fuels production. Ghent University has a proven track record in quantifying elementary phenomena in large-scale chemical reactions, among others for OCM. The corresponding microkinetic model for OCM developed at Ghent University has been embedded in a reactor model accounting for the most essential phenomena as they occur in an isothermal, laboratory scale reactor. Among others, these include the simultaneous occurrence of catalytic and gas phase reactions, transport phenomena in the catalyst pores as well as in the interstitial phase between the catalyst pellets, etc... Total and Ghent University are teaming up now to reach a better understanding of how OCM and economic viability go hand in hand by exploring industrially relevant reactor configurations and evaluating how optimal catalyst properties may depend on the selected reactor configuration.

Program

The planned activities for the PhD program have been logically combined into 3 work packages (WP) focusing on the reactor model, the kinetics and the 'process' integrating the kinetics and the reactor. These 3 WPs will potentially be complemented by a 4th WP on measuring low temperature OCM activity

1. WP1: reactor model construction/enhancement
 - a. Adiabatic reactor model
 - b. Heat transport phenomena
 - c. Fluidized bed reactor model
2. WP2: (catalytic) kinetics model assessment
 - a. Principal component analysis for the model simulations with respect to the catalyst descriptors
 - b. Reaction network assessment in view of light-off temperature and interplay between exothermic (OCM) and endothermic reactions (reforming reactions, CO and/or CO₂ as oxidant)
 - c. Determination of the C₂ yield/selectivity at the relevant catalyst descriptor values
3. WP3: process configuration optimization
 - a. Comparison of the simulations results obtained within an isothermal, laboratory-scale reactor with an adiabatic reactor and a fluidized bed reactor
 - b. Feed composition effects/Alternative process configurations (recycle/added components)
 - c. Catalyst bed composition optimization

Advisors: Prof. Joris Thybaut, Prof. Guy B. Marin

Funding: Total

First principles based kinetic modeling of hetero atomic systems

Aim

The aim of this work is to develop a program that can automatically generate kinetic models for the pyrolysis hetero atomic systems using a 3D representation of species.

Justification

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, including combustion, pyrolysis, and partial oxidation of hetero atomic mixtures, constructing a reliable and sizable kinetic model remains to be very difficult and time consuming. Such models contain typically thousands of reactions involving hundreds of intermediates with only a small fraction of the reaction rate coefficients known experimentally. Moreover, it is usually impossible to measure the concentrations of all the kinetically significant chemical species.

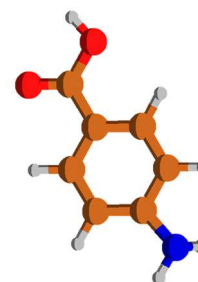
Automatic network generation technology is a branch of chemical engineering involving many cross disciplinary concepts from other engineering domains, such as chemo-informatics, Boolean algebra, graph and network theory, algorithms, software architecture and design etc. In most cases chemical species are represented as graphs consisting of nodes (atoms) and edges (bonds) allowing the use of many powerful graph algorithms. Genesys is a recently developed automatic network generation code build on advanced open-source chemo-informatics libraries. Genesys is not constrained to specific chemical elements or to specific chemistries. Genesys makes use of an efficient way of calculating on-the-fly species properties and reaction kinetics is by implementing fast estimation methods such as group additivity, Evans-Polanyi and Blowers-Masel correlations. These methods typically generate reasonable good results for a certain subspace of molecules, and only if accurate values are available, which is often troublesome. Therefore, all possible databases containing useful values for network generation need to be implemented to cover a wide applicability range. Furthermore, Genesys needs to be extended with new quantum chemically derived group additive values to construct more accurate kinetic models. These computationally intensive methods will only be used when necessary, i.e. when accurate thermodynamics and kinetic data is lacking.

Program

- Implementing existing group additivity values from literature and collaborators in Genesys.
- Critical evaluation of GAV values and identification of the missing groups for modeling heteroatomic systems
- Determination of new kinetic and thermodynamic group additivity values and implementing them in Genesys.
- Assembling of a database of well-defined and reliable experimental data suitable for validation.
- Assessment of the predictive capability of kinetic models and using network reduction techniques to enable the implementation of the models in CFD.

Advisor: Prof. Kevin. M. Van Geem

Funding: Bilateral with company



Prediction of Turbulent Reactive Flows by means of Numerical Simulations (PRETREF)

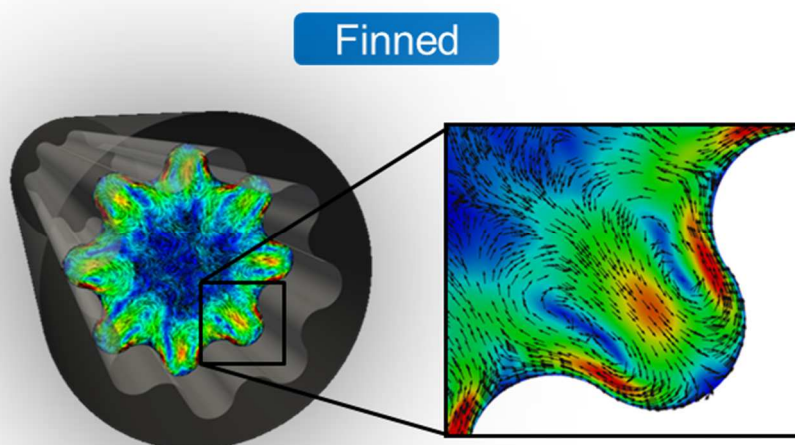
Aim

The goal of this PhD is coupling detailed kinetic models for free radical and surface processes with Computational Fluids Dynamics (CFD) accounting properly for turbulence.

Justification

The 20th century has proven to be a fruitful century in modeling chemical reactors using simplified reactor models and simplified kinetic models. Hence, there's a good reason to believe that many of those systems are actually far from optimal. Indeed, the supercomputer capabilities in the 21st century make that on a computational level new innovations are possible that 5 years ago one could not even dream

of. The current state of the art in CFD makes use almost exclusively of traditional Reynolds-Averaged Navier-Stokes (RANS). The main limitation of RANS modeling is that RANS variables do not depend on time and only averaged flow fields are obtained of which the accuracy can be debated. It must be clear that an instantaneous and averaged turbulent flow field have not much in common. Also intuitively it seems obvious that certain phenomena can simply not be averaged like ignition, quenching, flow instabilities, acoustic waves and thermoacoustics. Note that implementation of detailed chemistry in CFD is at present almost not done, not even when simple turbulence models are used.



Program

Coupling detailed kinetic models with OpenFOAM accounting properly for turbulence. The approach will be validated using a unique set of newly acquired experimental data on the flow field in well-defined reactor geometries using 2D/3D Particle Image Velocimetry (PIV) and liquid crystal thermography.

Implementation of kinetic models with more than 50 species In OpenFOAM using LES. Therefore a dynamic kinetic model reduction method will be developed for the OpenFoam platform in order to drastically decrease the required CPU time. This will be combinend with the classical tools for obtaining reduced chemistry, i.e.: quasi steady state approximation, rate of production and sensitivity analysis.

Evaluate the developed OpenFOAM LES code for low NO_x burners, pyrolysis and selected surface reactions

Advisor: Prof. Kevin. M. Van Geem

Funding: Geconcerteerde Onderzoeksacties (Bijzonder Onderzoeksfonds (BOF))

Unraveling coke formation on high temperature Alloys

Aim

The aim of this work is to gain fundamental understanding of coke formation under typical industrial reactor conditions.

Justification

Light olefins such as ethylene and propylene are the most important basic chemicals for the petro-chemical industry. The dominant process to manufacture them is the thermal cracking in the presence of steam. Coke deposition on the inner wall of the tubular cracking reactors is the main drawback of this process. The resulting coke layer reduces the cross-sectional area of the tubular reactors, causing a continuous increasing pressure drop. Thus, bimolecular reactions gain ground, leading to lower olefin selectivity. In addition, the resistance to heat transfer from the furnace to the feed is increased. All the above lead to higher tube metal temperatures and eventually, to process shutdown in order to decoke the reactors. This negatively affects the desirable production and the economics of the process.

The reactor material is one of the most important factors affecting the deposition of coke. However, only a limited number of studies have been carried out evaluating the effect of metal surface technologies, including the use of low-coking alloys and coatings. For feedstocks heavier than ethane fundamental understanding of the relation between the materials composition/state and coke formation on is limited to non-existing. Ideally a model could be developed that predicts the coking rates (initial and asymptotic coking rate) for different materials and coatings, taking into account feedstock composition of the used, as well as the operating conditions and the surface composition. This will help to optimize the runlength of steam crackers, determine optimal pretreatment conditions, and maximize its profit.

Program

Experimental thermogravimetric investigation of coke formation on desired samples of coated/ uncoated metal to evaluate:

- The influence of temperature (up to 886 °C)
- The desired material composition, coating and surface morphology (roughness)
- Difference in feed composition (naphtha versus ethane, naphtha composition) using surrogate feedstocks

The coated or uncoated metals will be examined using:

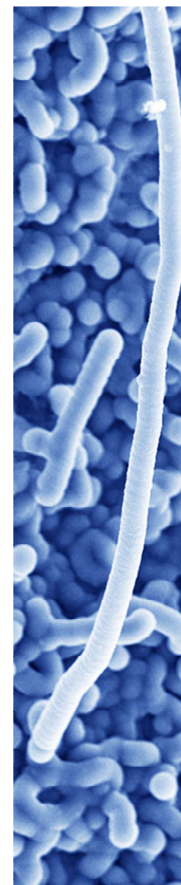
- Physical analysis of the coke (SEM) to understand the structure of the coke
 - Chemical analysis of the coke (EDX) and gas phase composition of feed and effluent
- Chemical composition and structural analysis of the reactor material surface after coking

With the above information a model will be developed that describes the coking rate taking into account process conditions, reactor material composition, and reactor material surface/ coating morphology for different feed compositions

Scale-up to a real industrial plant by modeling and experimental tests on pilot plant and bench scale

Advisor: Prof. Kevin. M. Van Geem

Funding: Bilateral with company



First principles based design of radical (co)polymerization

Aim

Explore the use of quantum chemical calculations to obtain reliable rate coefficients for propagation and side reactions involved in (controlled) radical (co)polymerization processes. The calculated rate coefficients are to be implemented in available microkinetic models and validated by comparison of simulation results with experimental data from pulsed laser polymerization (PLP) and (co)polymerization. A user-friendly database with validated rate coefficients will be established.

Justification

The fundamental understanding and in-silico guided design of controlled and free radical polymerization processes and the development of new functional polymer materials remains a tremendous challenge. At the molecular level, the outcome of a radical polymerization process is determined by the interplay of a multitude of discrete elementary reactions. The relation between the resulting polymer microstructure and the polymerization conditions is obscured due to the inherent complex nature of this interplay between these reactions. Knowledge of the underlying reaction mechanism and the intrinsic chemical rate coefficients of the elementary reactions involved is thus critical to optimize polymerization processes and to design new functional polymer materials.

In general, the experimental study of an elementary reaction in a radical polymerization process in isolation is almost impossible. Moreover, the experimental determination of intrinsic rate coefficients is not always straightforward and requires dedicated experimental studies. One of the most established experimental techniques to measure propagation rate coefficients is pulsed laser polymerization (PLP). However, the occurrence of side reactions can complicate or even prevent the accurate determination of the propagation rate coefficient. Alternatively, reliable parameter fitting by regression to experimental polymerization data is possible but this can become very tedious for more complex polymerization systems.

Instead of applying the aforementioned experimental techniques, intrinsic rate coefficients can also be obtained from quantum chemical calculations in combination with textbook statistical thermodynamic formulae and conventional transition state theory. The last decades there has been a fast-paced development of quantum chemical methods and the application of computational chemistry as a complement to experiment opens up the possibility to accelerate the optimization of polymerization processes and the in-silico design of functional polymer material.

Program

First, an appropriate computational method is to be selected to calculate reliable propagation rate coefficients for a limited range of well-established vinylmonomers (e.g. styrene, MMA).

In a second step, this method will be applied to calculate rate coefficients for propagation and side reactions (e.g. transfer to monomer, thermal initiation, etc.) involved in the (controlled) radical (co)polymerization of a broad range of vinylmonomers. Attention will be focussed on vinylmonomers relevant for the synthesis of polymers with high-tech and biomedical applications. Next to that, an evaluation of the effect of the chain length and the solvent on the intrinsic rate coefficient is to be performed.

Validation of the calculated rate coefficients will be performed in close collaboration with the ongoing experimental and model development work in the group. In a first stage, the calculated rate coefficients will be implemented in available microkinetic models to compare model predictions with experimental data. In a second stage, the rate coefficients will be used to design experimental recipes for (controlled) (co)polymerization of a selected set of (co)monomers that are to be validated by experiment.

Advisors: Prof. Dr. Marie-Françoise Reyniers; Prof. Dr. ir Maarten Sabbe

Funding: Multi-scale Modeling and design of chemical Reactions and Reactors (M2dcR2)

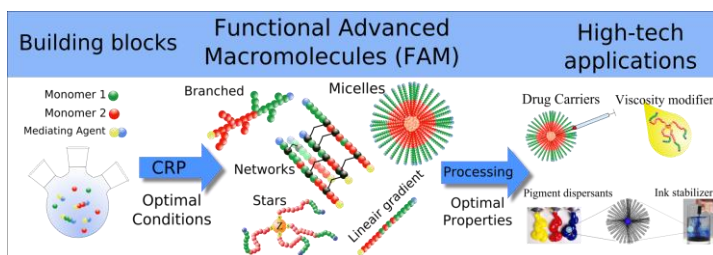
First principles design of mediating agents for controlled radical (co)polymerization

Aim

Explore the use of quantum chemical calculations to obtain reliable rate coefficients for RAFT and NMP specific reactions involved in controlled radical (co)polymerization. The influence of the chemical structure on the performance of a range of RAFT and NMP mediating agents will be assessed. Optimal combinations of mediating agent and polymerization conditions to synthesize a range of targeted functional (co)polymers will be specified. A user-friendly database with validated rate coefficients will be established.

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 controlled radical polymerization (CRP) techniques that do not require industrially unattractive stringent oxygen or water free environments or highly purified reagents. In CRP, a mediating agent is added to reversibly capture macroradicals in a dormant state preventing the uncontrolled growth that is typical for conventional free radical polymerization (FRP). Despite intense research efforts, however, industrial application has remained elusive, since a commercially viable CRP product must possess the unique pre-defined properties dictated by the targeted application.



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. This rate control pertains not only to initiation, propagation and termination reactions but more importantly also includes activation/deactivation reactions involving the mediating agent. Possible side reactions leading to structural defects in the polymer chain have also to be accounted for.

To elucidate and quantify the effect of the molecular structure of the monomer and the mediating agent 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 controlled polymerization processes and the in-silico design of functional polymer material.

Program

First, an appropriate computational method is to be selected to calculate reliable activation/deactivation rate coefficients for a limited range of well-established vinylmonomers (e.g. styrene, MMA). In a second step, this method will be applied to evaluate rate coefficients for activation/deactivation and possible side reactions for a broad range of potential RAFT and NMP mediating agents and vinylmonomers. Attention will be focussed on vinylmonomers relevant for the synthesis of polymers with high-tech and biomedical applications. Evaluation of the performance of the candidate RAFT and NMP mediating agents will be performed by implementing the calculated rate coefficients in available microkinetic models to simulate conversion and (co)polymer microstructural characteristics. In a second stage, the rate coefficients will be used to design optimal combinations of promising mediating agent, monomer and polymerization conditions to synthesize targeted functional (co)polymers that are to be validated by experiment.

Advisors: Prof. Marie-Françoise Reyniers, Prof. Maarten Sabbe

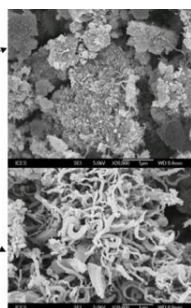
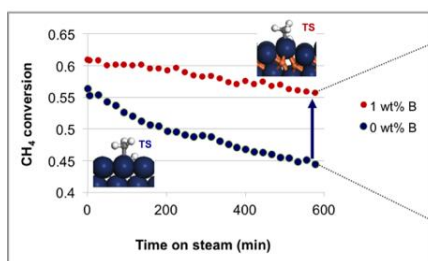
Funding: Multi-scale Modeling and design of chemical Reactions and Reactors (M2dcR2)

Combining molecular modelling and experimental kinetics to unravel the role of Boron, a versatile promoter in catalysis

Aim

Boron has been found to dramatically enhance the stability of Ni and Co catalysts. However, the exact role and location of the boron promoter remains unknown. The aim of this project is to gain an in depth understanding of the role of boron, and to extent its applicability.

Justification



Catalysis plays a critical role in chemical transformations. The production of clean transportation fuels, of bulk and fine chemicals, and the prevention and abatement of pollution would be impossible without catalytic processes. Promoters often play an important role for enhancing activity, selectivity and/or stability of catalysts but frequently their exact role is not fully understood.

Boron promotion of a Ni/ γ -Al₂O₃ catalyst reduces deactivation and increases conversion

The addition of small amounts of boron has recently been found to dramatically enhance the stability of Ni/Al₂O₃ and Co/Al₂O₃ catalysts during methane steam reforming and Fischer-Tropsch synthesis of

clean fuels. For methane steam reforming, boron also enhances activity, making boron the first promoter to enhance *both* activity and stability. Expanding on these ideas, the addition of small amounts of boron was experimentally found dramatically enhance the selectivity of Pd-based catalysts in the hydrogenation of alkynes. Theoretical calculations for a series of transition metal borides reveal a unique sigma-aromatic bonding pattern, and predict several unprecedented 2-dimensional transition boride structures containing square-planar boron. Experimental verification of these structures is, however, lacking and will be a main aim of this research project. These recently proposed structures are radically different from the original ideas about the catalyst structure and are likely responsible for the unique role of boron as a versatile promoter in transition metal catalysis.

References

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 Chan, Mahadi, Li, Corbos, Tang, Jones, Kuo, Cookson, Brown, Bishop, Tsang, *Nature Commun.*, 2014, 5
 Xu, Chen, Tan, Borgna, Saeys, *J. Catal.*, 261, 158, 2009
 Tan, Chang, Borgna, Saeys, *J. Catal.*, 280, 50, 2011

Program

We will combine catalyst synthesis, experimental testing and characterization with computational catalysis to elucidate the location and the electronic and structural role of the boron promoter. We will first fully study the role of boron for the well-established Ni- and Co-based catalysts verifying location, chemical state and the electronic and/or geometric effect on the metal catalyst. This insight will constitute the basis to extent the project to the study of B-promoted Pd- and Pt-based catalysts in (de)hydrogenation reactions. Again we aim at clarifying and understanding the state and role of B and its influence on the Pd/Pt by combining in situ characterization, kinetics and molecular modelling.

Advisor: Prof. Dr. ir. Mark Saeys

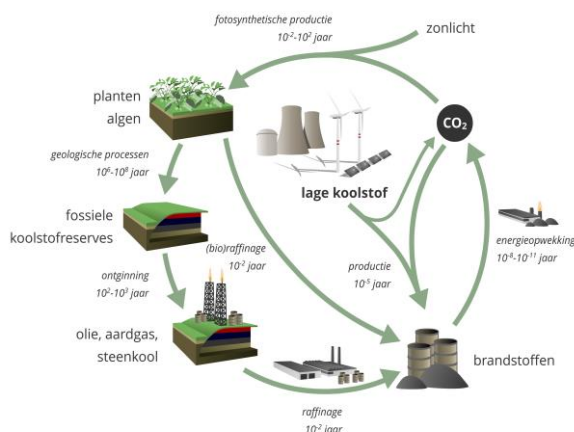
Funding: Modelling-guided Design of Selective Catalytic Processes (Odysseus)

Modeling guided design of selective catalysts for catalytic CO₂ reduction

Aim

Develop catalytic processes to activate CO₂ and introduce CO₂ as an extension block to add value to base chemicals.

Justification



Closing the carbon cycle through catalysis.

The necessary transition to **CO₂-neutral** human activity introduces immense scientific and technological challenges. Our high standard of living relies heavily on carbon-based materials and high-density energy carriers. A drastic move away from a carbon-based society is not expected. The accumulation of CO₂ in the atmosphere is a **timing problem** – CO₂ is produced at a much faster rate than natural processes consume it. In this project we develop catalytic materials to re-activate CO₂ with a productivity (kg CO₂/m³_{reactor} s) and an efficiency commensurate with the tremendous rate of CO₂ production in order to close the carbon cycle. Such a productivity can only be achieved by catalytic processes. The reductive power to activate CO₂ will be supplied by H₂ produced from low-CO₂ energy sources such as solar energy. Catalyst design and kinetic modeling often start from molecular-scale hypotheses about the reaction mechanism, the structure of the active catalyst and the

nature of the rate and selectivity determining steps. Computational catalysis has become a crucial tool to analyze molecular-scale concepts and elucidate their electronic origin. In combination with characterization and experimental kinetic validation, insights gained from computational catalysis can be translated all the way to the industrial scale. This pas-de-deux between experiment and theory is becoming the new paradigm in catalyst design and kinetic modeling, both in academia and in industry.

References

Banerjee, van Bavel, Kuipers, Saeys, ACS catal. **2015**
Zhuo, Borgna, Saeys, *J. Catal.* **297**, 217, **2013**
Tan, Chang, Borgna, Saeys, *J. Catal.*, **280**, 50, **2011**

Program

The project extends our experimental and modeling experience with CO hydrogenation (Fischer Tropsch synthesis) to CO₂ hydrogenation. We will start by studying the hydrogenation of CO₂ to methane and methanol, but expect to expand the scope by studying reactions related to hydroformylation and carboxylation which use CO₂ as an extension unit to add value to base chemicals.

Advisor: Prof. Dr. ir. Mark Saeys

Funding: Modelling-guided Design of Selective Catalytic Processes (Odysseus)

Catalytic Conversion of Bio-Ethanol to Hydrocarbons

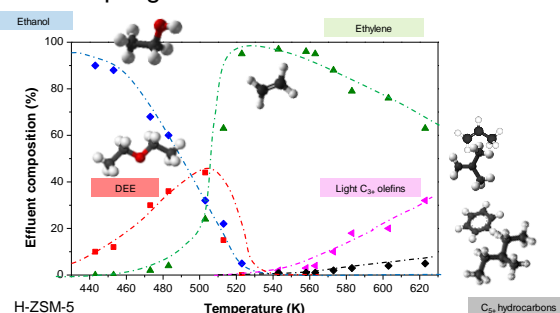
Aim

Understanding the conversion of ethanol to valuable chemicals and fuels by combining steady state and non-steady state experimentation with detailed kinetic characterization of the catalyst.

Justification

Ethanol can be considered to be one of the most promising alternatives for fuel applications to overcome the decreasing availability of fossil resources. However, recovering pure ethanol from aqueous bio-ethanol requires energy intensive distillation and/or membrane techniques which can be avoided by the catalytic upgrading of bio-ethanol towards chemicals. Zeolites are known to be hydrothermal stable catalysts at elevated temperatures and selective for the production of these hydrocarbons from alcohols. However, future catalyst and process improvements can be hampered by the lack of insight in the reaction mechanism governing the conversion of ethanol to hydrocarbons.

Three rivaling mechanisms have been proposed for the conversion of ethanol to C_{3+} hydrocarbons on H-ZSM-5: an acid catalyzed reaction mechanism with ethene as primary product of the fast dehydration reaction and the subsequent production of higher hydrocarbons requiring the direct coupling of ethene as crucial reaction step, a radical assisted mechanism and a dual cycle mechanism analogous to the one proposed for the Methanol-To-Olefins (MTO) process. The latter comprises an aromatic hydrocarbon pool assisted mechanism for the production of ethene and propene, and a methylation/cracking cycle for the production of higher olefins and was confirmed from both experimental and theoretical studies.



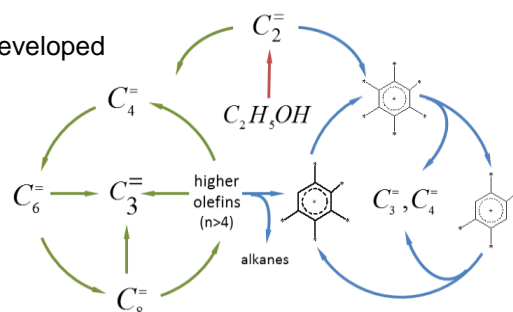
Program

This work will result in a detailed understanding in the reaction mechanism for the conversion of ethanol to hydrocarbons and will be elucidated by combining steady state and non-steady state experimentation and catalyst characterization using UV-VIS spectroscopy and HRTEM.

- ✓ Transient experiments on fresh catalyst:
 - Investigation of mechanistic differences of ethene transformation to higher hydrocarbons over H-ZSM-5 and H-ZSM-22.
 - Cofeed experiments of higher olefins (propene, butene, hexene) and aromatics (benzene, alkyl benzene) with ethene by single pulse and pump-probe experiments to assess the role of higher hydrocarbons in the reaction mechanism
 - Role of adsorbed surface species will be investigated by isotopic labelled ethylene experiments over catalyst bed pretreated with olefins and/or aromatics.

Pressure-Vacuum experiments

- A combination of continuous flow experiments until a fully developed bed followed by transient pulse experiments with isotopic labelled species will provide insight in the performance and behavior of the catalyst at working conditions.
- ✓ Spent catalyst characterization at different stages of the reaction by UV-VIS, XPS and TEM to investigate the nature of surface species



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